WORK FUNCTION, ELECTRONEGATIVITY, AND ELECTROCHEMICAL BEHAVIOUR OF METALS

II. POTENTIALS OF ZERO CHARGE AND "ELECTROCHEMICAL" WORK FUNCTIONS

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INTRODUCTION

It is known[1] that the rate and mechanism of an electrochemical reaction is closely related to the nature of the electrode material[2-5]. This aspect of electrochemistry has been defined as *electrocatalysis*[6], and some comprehensive reviews have been recently published on this subject[7-10]. The problem may be viewed from two different stand points. On one hand, the nature of the electrode may be changed in searching after the best performance of a cell, and in this case the term *electrocatalysis* suits well the essentially technological application of electrochemistry in fuel cells[11]. On the other hand, the opposite (though only conceptually) point of view is in the study of the electronic structure of solids by close examination of a simple electrochemical reaction largely known as to mechanism and kinetics. This latter point of view becomes particularly relevant as we have to deal with new electrode materials of difficult classification (oxides, for instance), where it would be extremely useful to be able from some simple electrochemical measurements to go back to the principal electric and electronic properties. In this respect, where electrochemistry approaches the field of catalysis and surface science[5,7,8,12] or, even farther, the field of solid state chemistry[13], the situation is as yet rather obscure. The electrochemical quantities which, on the whole, have been more often taken as parameters for correlation with the electronic structure of metals (this work will not be concerned with semiconductors) are the potential of zero charge[14-17], the rate (or overpotential) of cathodic evolution of hydrogen[2,3,18-20], and the rate of simple electron exchange reaction[5,21,22]. In no case, however, has a correlation between electrochemical and electronic properties, which could enable reliable predictions to be made in the case of unknown materials, been found with a sufficient degree of certainty and accuracy.

The physical quantity of metals which best expresses the electronic characteristics of the solid from a practical point of view is the work function, and it is this that has so far been used to develop correlations of the type described above[3,14-21]. The lack of a practically useful correlation between electrochemical and electronic properties is due, in the opinion of the writer, to poor accuracy in the experimental measurement of the work function. There are, on the contrary, many electrochemical quantities which can be measured with greater accuracy than that of the work function, and the author is considering if it would not be possible to utilise some electrochemical

measurements to obtain better approximations to the work functions to be used, in turn, for further correlations. In other words, it seems reasonable that these correlations should unavoidably exhibit a certain degree of internal consistency to which due attention has perhaps not so far been paid.

Modern electrochemistry certainly possesses an interdisciplinary character, which is at the present further emphasised by the rapid progress achieved in neighbouring fields such as materials science, and particularly the chemistry and physics of surfaces. Electrochemistry now possesses suitable tools to go beyond the direct interest in the electrodic event in itself and pay due attention to the fact that the electrochemical reaction is an expression of the nature of the electrode material and must therefore reveal to a close examination the intimate structure of the solid. This is the sort of cooperation between electrochemistry and catalysis which the present author considers[12] to be desirable.

The essential purpose of this series of papers is to analyse critically experimental data of potentials of zero charge (E_z), exchange currents for the hydrogen evolution reaction ($i_{0,H}$) and Fe^{2+}/Fe^{3+} redox couple ($i_{0,Fe}$), and work functions (Φ) to investigate the existence of simple and general correlations which could be used to characterise unknown materials on the one hand, and to elucidate better the intimate structure of the electrode/solution interface on the other hand.

RELATIONSHIPS BETWEEN E_z AND Φ

It was pointed out some time ago[23] that the difference in E_z for two metals is approximately equal to their contact potential difference, and that any deviation from this rule must be attributed to different orientation of solvent molecules at the interface. Since then, no substantial progress has been made in this direction, in the sense that the role of the solvent has not yet been rationalised. Frumkin[14] has shown that analysis of some experimental data of E_z and Φ might suggest a linear relationship to exist between these two quantities:

$$E_z = \Phi - 4.72 \tag{1}$$

where the value of the constant results from the data of mercury considered as the most certain. The role of solvent is in eqn. (1) again underestimated, or alternatively, the deviations due to the solvent behaviour are simply obscured by a dispersion in experimental data.

A different relationship in which the role of the solvent is in some way accounted for was proposed by Vasenin[16]:

$$E_z = 0.86\Phi - 4.25 \tag{2}$$

where the slope less than unity would arise from the fact that the orientation of water would vary with a change in Φ.

A third relationship was derived by Argade and Gileadi[17] on the basis of calculations made using physicochemical constants of metals. The result, average of nine metals (Ga and Tl fall far from the average) is:

$$E_z = \Phi - 4.78 \tag{3}$$

which is close to eqn. (1). No explanation is given for the deviations in the case of Ga and Tl.

Finally, Khomutov[24] attempted to correlate Φ and ΔG_2^0, and found that:

$$\Phi = 0.305 \Delta G_2^0 \tag{4}$$

where ΔG_2^0 is the sum of the standard free energy of sublimation and the energy of ionisation of metals to bivalent ions. The following equation was derived from eqns. (1) and (4):

$$E_z = 0.305 \Delta G_2^0 - 4.72 \tag{5}$$

Equations (1), (2), (3) and (5) suggest that a linear relationship may substantially exist between E_z and Φ, but at the same time they do not exclude the possibility that the influence of water may be in some case determining. Practically, all the equations given above cannot possess a general validity. In the opinion of the writer, the main reason for so large scatter of data within each relationship and for the different forms of eqns. (1) and (2) is to be found in the low accuracy in the experimental determination of Φ, so that discrepant values may be used by different authors for the same metal. This fact obscures, on one hand, the possible effect of the orientation of solvent molecules, and on the other hand misleads to the search for a *unique* correlation comprehending *all* metals, since simple scatter of data and actual meaningful deviations are lumped together and regarded as experimental inaccuracies.

The values of E_z for metals in molten electrolytes should not be affected by any factor such as water dipoles in aqueous solutions, and the difference in E_z between two metals is in fact very close to the contact potential difference[14]. Apart from the fact that no definite experimental confirmation of that exists in any case because of the strong effect of temperature on E_z[25], any attempt to derive E_z for metals in aqueous solutions from E_z values in molten salts[26] is to be regarded, *in principle*, as meaningless, even though it may happen for some metals that measured and calculated values are very close.

WORK FUNCTIONS

In the previous paper[27], a list has been compiled of the most probable value of Φ for 32 metals. For any detail regarding the criteria adopted for selection the reader is referred to that paper. The values selected are here summarised in Table 1 for comparison with Michaelson's values [28], used by Kita[19] for his correlations with $i_{0,H}$, the list reported by Parsons[29] in his Handbook, and the values adopted by Matthews[18], Argade[30], Frumkin[14], and Conway and Bockris[3] for their correlations with electrochemical quantities.

We will examine, at this point, the real meaning which a correlation between Φ and E_z may possess. As already pointed out by Frumkin[14], the experimental measurement of Φ takes place under experimental conditions at first sight quite different from those in an electrochemical cell. The metal is well outgassed, kept in vacuum, and often undergoes special treatment to clean up its surface[31] (ion bombardments, flashing to high temperatures, etc.). Moreover, a film rather than bulk metal is used as a sample. The last fact does not seem to have any particular effect, since the Φ values coincide in the two cases[31], and some experimental measurements also suggest that the electrochemical behaviour of films differs from that of bulk metal only if the thickness of the film is below some critical values[32].

If the surface of the metal is clean, in other words if no surface compound is present, there is no reason not to assume *a priori* that the mechanism of extraction of an electron from the metal may be the same in vacuum and in solution. It is necessary to consider two additional factors: the probable modification of the double layer in the surface region of the metal due to asymmetric distribution of electrons across the

TABLE 1

SELECTED VALUES OF WORK FUNCTION OF METALS, Φ/eV

Metal	(a)	(b)	(c)	(d)^a	(e)^a	(f)	(g)
Ag	4.30	4.70	4.28	4.6	4.00	4.5	4.50
Al	4.19	4.20	3.74	4.2	—	4.1	4.22
Au	4.78	4.71	4.58	4.45	4.82	4.7	4.71
Bi	4.29	4.34	4.28	—	—	4.2	4.29
Cd	3.97	4.04	3.92	3.6	4.10	3.6	3.96
Co	4.70	4.25	4.18	—	—	—	4.16
Cr	4.40	4.45	4.51	—	—	—	4.38
Cu	4.55	4.48	4.47	4.45	4.35	4.5	4.45
Fe	4.65	4.63	4.36	4.45	4.40	4.6	4.51
Ga	4.30	4.16	3.96	4.15	4.20	4.1	4.02
Hg	4.50	4.53	4.52	4.5	4.53	4.5	4.51
In	4.08	—	4.0	—	4.05	—	—
Ir	—	4.57	4.57	—	—	5.3	4.57
Mn	3.90	3.35	3.95	—	—	3.8	—
Mo	4.30	4.24	4.27	4.2	—	4.2	—
Nb	4.20	3.99	3.99	3.95	—	4.0	—
Ni	4.73	4.91	4.84	4.6	—	4.6	4.83
Os	4.83	4.55	4.55	—	—	—	—
Pb	4.01	4.04	4.02	4.0	4.12	4.0	3.98
Pd	5.00	4.98	4.82	5.1	—	5.1	4.73
Pt	5.40	5.36	5.29	5.2	5.30	5.2	5.32
Re	4.95	4.97	5.1	—	—	—	—
Rh	—	4.65	4.65	5.0	—	5.0	4.57
Ru	4.80	4.52	4.52	—	—	—	4.52
Sb	4.56	4.56	5.08	—	4.05	—	—
Sn	4.35	4.39	4.11	—	4.37	4.1	4.29
Ta	4.22	4.13	4.12	—	—	4.2	—
Ti	4.10	4.16	4.09	—	—	4.0	—
Tl	3.84	4.05	3.76	3.7	3.70	3.7	3.76
V	4.44	4.11	4.11	—	—	—	—
W	4.55	4.53	4.50	4.5	—	4.5	—
Zn	4.30	4.27	3.74	—	—	—	3.95

^{a} Estimated from Figures.
(a) Trasatti[27]; (b) Parsons' Handbook[29]; (c) Michaelson[28]; (d) Conway and Bockris[3]; (e) Frumkin[14]; (f) Matthews[18]; (g) Argade[20].

surface[15,33], and the additional double layer in the surface layer of the solution arising from oriented water dipoles[15,34,35]. Two surface potentials are associated with these two double layers. Let χ^M be the surface potential of a metal exposed to vacuum (χ is positive when the positive end of the dipole layer is toward the interior of the solid)[15] and g^M_{dipole} the surface potential when the metal is in contact with a solution. We may write, in principle:

$$g_{\text{dipole}}^{M} = \chi^{M} + \delta\chi^{M} \tag{6}$$

where $\delta\chi^{M}$ is due to modifications which occur in the surface layer of the metal upon contact with water.

On the solution side, let χ^{S} be the surface potential of water exposed to air, and g_{dipole}^{S} that developed after the contact with the metal. Accordingly:

$$g_{\text{dipole}}^{S} = \chi^{S} + \delta\chi^{S} \tag{7}$$

By definition[15], the work function (in eV) is given by:

$$\Phi = -\mu^{M}/F + \chi^{M} \tag{8}$$

where μ^{M} is the chemical potential of an electron in the metal. According to the definition of χ, eqn. (8) predicts that Φ increases as χ^{M} becomes more positive. Now, Φ is measured when there is the potential χ^{M} at the interface. On the contrary, g_{dipole}^{S} is actually operative as E_z is experimentally determined. Therefore, the separation expressed in eqn. (6) is really needed, but that in eqn. (7) is not. Thus, when a metal is in contact with an aqueous solution of not adsorbed electrolytes, the potential of zero charge may be written in the form:

$$E_z = \Phi + \delta\chi^{M} - g_{\text{dipole}}^{S} + K \tag{9}$$

where the minus sign arises from the fact that the double layer on water is opposite to that on the metal. K is a constant including the potential drop at the reference electrode/solution interface.

Introduction into eqn. (9) of experimentally determined work functions implies the assumption that the conditions of the metal surface, apart from the different nature of the phase in contact, are comparable in the two cases. There is no reason to suppose that a *clean* surface exposed to vacuum be different from a *clean* surface in contact with water. Capacity measurements in electrochemistry should always be carried out on smooth surfaces from which any residue coming from previous contacts with the atmosphere has been removed. This means that eqn. (9) can be considered as operative even from an experimental point of view, provided that the metal in question does not react with water forming a surface compound.

POTENTIALS OF ZERO CHARGE

Lists of potentials of zero charge can be found in the literature; those by Argade[30] and Perkins and Andersen[34] appear to be the most complete. A table has recently been compiled[36] reporting also values in non-aqueous solvents, but this list, besides being on the whole largely incomplete and without any comment, presents some uncorrected values and wrong notations. Generally, published lists merely report values for each metal obtained by different authors by different methods, without any indication as to preferred or more probable values. The thesis by Argade[30] appears to be the sole example of an attempt in this sense for a limited number of metals, even though selection is implied in the table compiled by Frumkin[14].

Many results have been obtained during the last few years especially by Russian workers, which now makes the picture more complete and some debated values more certain. This enables a selection to be made on a more realistic basis, but at the same

TABLE 2

SELECTION OF EXPERIMENTAL VALUES OF POTENTIAL OF ZERO CHARGE

Metal	E_z/V (NHE)	Refs.
Ag	−0.44	37, 72
Al	−0.52	58
Au	0.18	37, 38, 72
Bi	−0.39	39
Cd	−0.72	40
Co	−0.45	68, 69
Cr	−0.45	57
Cu	0.09	41
Fe	−0.35	78–81
Ga	−0.69	42, 82, 83
Hg	−0.19	43
In	−0.65	48, 70
Ir	−0.04	48
Nb	−0.79	59
Ni	−0.30	37, 65, 86–88
Pb	−0.62	44
Pd	0.00	48
Pt	0.02	48
Rh	−0.02	48
Sb	−0.14	45
Sn	−0.43	46, 48, 84
Ta	−0.85	59
Ti	−1.05	60
Tl	−0.75	47, 76
Zn	−0.63	62–65, 67, 85

time discussion is still necessary for some metals to justify the choice of preferred values. The value of E_z generally depends on the purity of the metal, the crystallographic orientation of the surface, the nature of the solution, and the treatment before the measurement. When these factors are standardised, values may still be influenced by the method of measurement which otherwise is of secondary importance.

The values of E_z (NHE) selected in this work are collected in Table 2. No other list of E_z is reported for comparison, since the values selected by different authors are on the whole in agreement with each other, except for one or two metals, which once again supports the view that the lack of a reliable correlation between Φ and E_z has so far been due to the low accuracy with which work functions are known. For the analysis of the experimental methods for the determination of E_z the reader is referred to the recent work by Perkins and Andersen[34].

Very simple criteria of selection were adopted. Where possible, preference has been given to the value obtained by the method of minimum capacity in very dilute solutions. This, therefore, has been done in all cases where capacity curves appear to be as reliable and to have the same peculiarities as in the case of mercury. In other cases, selection has relied on the basis of reproducibility with different methods. For some metals there exists only one experimental value of E_z.

E_z has been derived from the potential at minimum capacity in dilute solution in the case of Ag, Au, Bi, Cd, Cu, Ga, Hg, Pb, Sb, Sn, and Tl[37–47]. These values are

confirmed by experimental determinations with different methods, but reference is made in Table 2 only to the original paper whence the value chosen has actually been taken. For a more complete bibliography the reader is referred to reviews[30,34]. In the case of Fe and Ni, the selected value is the average of a group of results obtained with different experimental methods. The spread of data is in any case small, of the order of $\pm$ 0.03 V.

The values obtained in neutral solution with the method of open circuit scrape have been adopted for Ir, Rh, Pd, and Pt[48]. There exists a series of very well reproducible data obtained by Frumkin and his group with the adsorption and radiotracer methods[49-54], but these values include contributions from adsorbed hydrogen. Those adopted in this work refer, on the contrary, to surfaces free of chemisorbed hydrogen. On the other hand, the value for Pt $(0.02$ V$)$[48] is fairly close to that expected for neutral solutions from data by Frumkin and Petry[55] on the shift of E_z with pH. This seems to be confirmed also by calculations on the effect of the Pt–H dipoles[56]. Something similar is to be expected also in the case of Pd, whereas for Rh the value expected for neutral solutions from the data of Frumkin and Petry[55] is more negative than that obtained by the open circuit scrape method[48]. No explanation can be given at the moment for this. No comparison is possible in the case of Ir because of lack of data. On the other hand, the results obtained with the scrape method[56] appear to a close examination to be quite reasonable. Some problem may perhaps arise in the case of Rh and Ir from the fact that these metals exhibit a very narrow double layer region.

Only one experimental value of E_z is available in the case of Cr, Al, Nb, Ti, and Ta[57-60]. On the other hand, any value calculated on the basis of Φ/E_z relationships found in molten salts[26] cannot be taken into consideration in view of the meaning of eqn. (9).

In the case of Zn, some results[61] give $E_z \simeq -0.9$ V, whereas others[62-65] locate the potential of zero charge around -0.65 V. A close inspection of the C/E curves reveals that they are very close to those of Ga $(E_z = -0.69$ V$)$, especially on the cathodic side[66]. Very recent data[67] of capacity indicate that E_z is around -0.7 V, but the value cannot be derived from the minimum in the C/E curve because Zn dissolves as its surface is still negatively charged. The value of -0.63 V has been selected on the basis of the reproducibility with various experimental methods.

In the case of Co, E_z seems to depend on pH[68,69]. Preference has been given to the value obtained at pH 3–5 because in these solutions the minimum in the C/E curves is well developed. The value reported for pH = 1 is *in principle* less reliable because it has been obtained from the slope of the C/E plot.

The majority of the available experimental data[48,70,71] points to $E_z = -0.65$ V as a very probable value for In, but some results[71] suggest that the actual value might be somewhat more negative.

Finally, the case of Ag appears to be in some respect rather puzzling. A group of results[37,72] gives for E_z a value around -0.45 V, whereas capacity curves by Leikis *et al.*[73,74] suggest that E_z is located at -0.7 V. It has recently been suggested[34] that E_z may shift toward more negative values as the purity of the metal is increased. Something similar, but to much less extent, has been observed in the case of Ga[75]. The values around -0.7 V were in fact obtained with 99.9999 % Ag, whereas the other group of results refer to 99.99 % Ag, a *normal* purity. Some effect of surface irregularities

cannot be excluded[76]. It may be thought that data obtained with *normal* purity Ag be more relevant to the experimental conditions used in measuring the work function. At any rate, data of $i_{0,H}$ to be used for successive correlations with Φ refer again to *normal* Ag[77]. In other words, the value $E_z = -0.44$ V would correspond more closely to the actual state of Ag. For these reasons, the value of -0.44 V is selected here. No greater justification can be given for this choice at the moment, although many experimental data giving -0.7 V as E_z appear as reliable as those giving -0.44 V. A justification can be given only *a posteriori* in that, as the reader will see later, if the value of -0.7 V is used, Ag would be the sole metal behaving in an anomalous way, at least in the light of the present knowledge of the properties of this element. This point will be further discussed later.

DISCUSSION

The values of Φ and E_z reported in Table 1 and 2 are exclusively experimental data selected independently. The task is now to find a relationship between the two quantities. The experimental data will be examined and discussed, for the sake of clarity, through successive approximations, trying first of all to understand for what reasons certain metals do not follow expected relationships.

First approximation
      The values of E_z are plotted in Fig. 1 against work functions. A first examination of the graph reveals that the metals cannot be lumped all together, even though linear E_z/Φ relationships certainly exist for restricted groups of elements. The plot shows that the metals can be assembled at least into two groups, *i.e. transition metals*, for which the apparent relationship is:

$$E_z = \Phi - 5.01 \tag{10}$$

and *sp metals*, for which the more probable equation is:
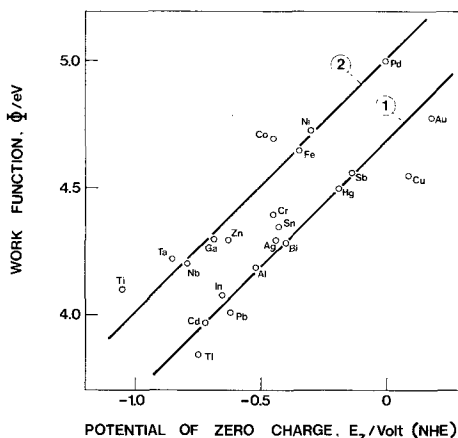
$$E_z = \Phi - 4.69 \tag{11}$$

Fig. 1. Potentials of zero charge plotted against values of work functions of metals selected from exptl. data.

Equation (11) is very close to that proposed by Frumkin[14]. The difference in the value of the constant is due to different values accepted for the work function of mercury. *Separately*, eqns. (10) and (11) seem to confirm the hypothesis previously made by some authors[14,15,17,24,34] of a linear E_z/Φ relationship with unity slope. However, whereas eqn. (10) can be applied to all transition metals (at least those for which E_z is known), eqn. (11) appears to be strictly applicable only to some of the *sp* metals.

(*i*) *Transition metals.* A few metals fall far from the straight line expressed by eqn. (10), but it is difficult to establish whether this is due to an erroneous value of Φ or E_z. In the case of transition metals, the potential of zero charge cannot be measured experimentally with the same accuracy as for *sp* metals. For Ti no data are available to distinguish between the two above possibilities, whereas for Co it is more probable that E_z is to be modified. In effect, the value of -0.31 V for E_z calculated from eqn. (10) using the experimental work function[27], is very close to that found experimentally[68,69] at pH $= 1$ and would place Co between Fe and Ni, as would appear to be quite reasonable.

The problem is more complicated for Cr in that this metal falls in Fig. 1 far from the expected straight line. E_z was in this case obtained by the method of contact angle[34,57] and it seems possible that values of E_z were affected by a thin film of undesired species on the surface of the sample. On the other hand, Φ for Cr has been derived[27] from data by Suhrmann and Wedler[89], who obtained with their method reliable results for quite a number of metals[27]. To a first approximation, and for lack of other data, we prefer to retain the experimental value of Φ and suggest, from eqn. (10), that the potential of zero charge of Cr could be around -0.61 V. The value of Φ for Cr will be checked by other electrochemical correlations in future papers of this series.

The values of Φ for Ru found by Rivière[31] may be considered as reliable, but no value of E_z can be found in the literature. $E_z = -0.21$ V is derived from eqn. (10), which seems quite reasonable in the light of data by Frumkin *et al.*[53] who place the potential of zero charge for this metal *certainly* below -0.12 V. In the case of Os, the only recent value of Φ available in the literature[27] seems reasonable also in the light of considerations regarding $i_{0,H}$. From eqn. (10), $E_z = -0.24$ V is derived for Os.

For the group Pt, Pd, Rh, and Ir, values of Φ for Pd fall consistently around 5.0 eV, while for Pt the experimental work function is much higher[27]. On the other hand, values of E_z, $i_{0,H}$[3,18,19], and $i_{0,Fe}$[21] clearly indicate that the behaviour of Pt is quite close to that of Pd, and even to those of Ir and Rh. If the available experimental values of Φ for the above four metals are examined[27,31], it can be noted that *certainly* Φ increases in the series Ir $<$ Rh $<$ Pd $<$ Pt, and the same sequence holds for E_z[48-56], and substantially also for the values of i_0[18,19,21]. There is no doubt, therefore, that a close relationship exists between Φ and the electrochemical quantities mentioned above, and one can reasonably conclude that, if E_z, $i_{0,H}$, and $i_{0,Fe}$ for the four metals under consideration are very close to each other, this must be the case also for the values of Φ, certainly from an electrochemical point of view, and more than may be apparent from experimental data. For these reasons, it seems to us reasonable to derive the actual values of Φ for Pt, Pd, Ir and Rh from eqn. (10), and utilise these values in successive correlations. Because of the way in which they are obtained, these Φ are here referred to as "*electrochemical work functions*".

While for Rh, Ir, and especially Pd, physical and electrochemical work

functions are rather close, for Pt, on the contrary, they differ markedly. Since the simple thermal treatment of Pt leads to more positive values of E_z[37,90,91], it is here suggested that the last traces of oxygen may be removed from the surface of platinum more easily and effectively with an electrochemical than another physical treatment. Alternatively, we may suppose that the state of the surface of Pt exposed to vacuum is different from that in solution. However, there is no reasonable explanation, besides the hypothesis made above, why this would occur only in the case of platinum. No definite experimental proof can be given at the moment, we can only take note of the evidence. On the other hand, Bockris et al.[37,90] found for thermally treated Pt a value for E_z of 0.56 V in acid solution. This value could satisfy eqn. (10) (or perhaps eqn. (11)) only if a value were accepted for Φ close to the experimental one, but this value would not be suitable for other correlations and platinum would be anomalous. Thus, from eqn. (10) we calculate the values of 4.97, 4.99, and 5.03 eV for Ir, Rh and Pt, respectively, and recalculate the value of 5.01 eV for Pd.

In the case of Mn, Mo, W and Re, for which the work functions are known with fairly good approximation[27], we suggest the following possible potentials of zero charge: -1.11 V for Mn, -0.71 V for Mo, -0.46 V for W and -0.06 V for Re. No experimental data of E_z are available for Mo and Mn. In the case of W, it can be noted that the scrape potential in neutral solution[48] is -0.47 V, but the authors do not identify this value with E_z. It can be recalled at this point that also for Co the scrape potential in acid solution $(-0.26$ V$)$[48] is close to the E_z given here, and again the authors do not recognise this value as E_z. No experimental data exist in the case of Re, but we may refer to the value of -0.2 V, close to that calculated from eqn. (10), suggested on the basis of adsorption data[92].

It is of significant interest to note again the closeness of scrape potentials[48] to E_z values calculated from eqn. (10). For V, $E_z = -0.57$ V is obtained, and the scrape potential is -0.59 V. The experimental value[59] of E_z for Ta is -0.85 V and the scrape potential in neutral solution is -0.78 V. Moreover, the scrape potential of Ti is -0.93 V in acid solution and may be compared to -1.05 V for E_z from experiments[60], or to -0.91 V calculated from eqn. (10) using for Φ the accepted value of 4.1 eV[27]. Further, the scrape potential of Co is -0.26 V in acid solution, but -0.42 V in neutral solution, -0.31 V for Fe in acid solution, and for Ni -0.10 V in acid solution and -0.34 V in neutral solution.

This surprising closeness of E_z calculated from eqn. (10) and scrape potentials in various solutions[48] is puzzling. At first sight, since the authors who used the open circuit scrape method do not identify the scrape potentials of these metals with the corresponding potentials of zero charge, one may be led to suspect that eqn. (10) might be misleading. Caution is still needed about this point. According to the above authors[48], the scrape potentials of most transition metals would be a mixed potential determined by the reduction of water and the oxidation of the metal. Now, the experimental value of E_z for Pd can be accepted, and the potentials of zero charge for Fe and Ni can be considered as fairly reliable because they have been obtained with more than one experimental method. If we take into consideration only Pd, Fe and Ni, we already obtain the relationship expressed by eqn. (10), so that it seems more surprising that the scrape potentials fit eqn. (10) than that they do not.

This aspect of the problem is very interesting because it can cause either scrape potentials or the values of E_z given by eqn. (10) to be viewed in a completely new

light. It must be noted however that for metals liable to really rapid anodic dissolution such as Al, Cd, Pb, Tl and Zn, the scrape potentials[48] are in fact far from the values expected for the potentials of zero charge. No deeper comparison can be made at this point between the two sets of data, and the state of the art does not allow a definite conclusion to be reached at this stage. However, it will be shown in the following that the E_z values derived from eqn. (10) are reasonably consistent with a general picture of the structure of the double layer, and can be obtained from a general equation valid for all metals.

(ii) *sp Metals*. It can be seen in Fig. 1 that the *sp* metals can be grouped by a straight line expressed by eqn. (11). Significant deviations are however observable. One of these is certainly represented by Ga, for which both Φ^{27} and $E_z^{42,82,83}$ are known with high accuracy. On the other hand, E_z is very well known for the majority of the *sp* metals, and any deviation from eqn. (11) must be due either to Φ or other factors to be taken into consideration.

Second approximation. The role of water molecules.

It becomes apparent from eqn. (9) that two factors can cause deviations from the simple eqn. (11): $\delta\chi^M$ and g_{dipole}^S. The term $\delta\chi^M$ can be thought of to a reasonable extent as independent of the nature of the metal. This can be supported by the experimental observation that in quite a number of cases, within the limits of reproducibility and accuracy of measurement, the difference in E_z between two metals in molten salts equals the difference in work function[25,26,34]. Since any problem due to solvent reorientation is absent with molten electrolytes, the above finding indicates that the variation in the surface potential of metals, *if any*, upon contact with the molten bath is the same for all metals.

Some change in χ^M is to be expected, on the other hand. The amount of spilling of electrons over the edge of the surface of metals is determined by the equilibrium between the lowering in kinetic energy and the increase in potential energy which such spreading out of the electron distribution produces[93,94]. It can be thought that the potential energy for electrons constituting the negative end of the surface dipoles depends on the apparent dielectric constant but not on the discrete nature of the particles forming the phase in contact with the metal. If this is the case, the term $\delta\chi^M$ should then be the same for all metals and depend only on the nature of the bordering phase. Equation (9) can thus be rewritten in the form:

$$E_z = \Phi - g_{dipole}^S + K'\tag{12}$$

Equation (12) may be an oversimplification, but certainly makes easier, at a first stage, the discussion of the experimental results. Equation (12) establishes that any deviation from a linear E_z/Φ relationship of unity slope must be attributed to g_{dipole}^S, *i.e.* to a different orientation of water dipoles at the interface.

Let us examine first the case of Ga, for which a great deal of relevant experimental data is available. All experimental results[42,82,83] lead to the conclusion that water must be more strongly adsorbed and oriented on the Ga surface than on Hg. This signifies that g_{dipole}^S introduces a negative contribution not predicted or considered by eqn. (11). To arrive at a quantitative conclusion, it is necessary to know with high accuracy each term of eqn. (12). This is possible in the case of Ga, if we compare the charge/potential curves with those of Hg[75]. It is possible to see that the q^M/E curves

differ around E_z, but for sufficiently negative charges they become parallel. This may signify that as the charge on the metal is strongly negative the orientation of water molecules is the same for both metals, i.e. g^S_{dipole} is the same in both cases; hence, one can assume that the difference in potential at constant surface charge equals the difference in work function[95]. Now, in the case of Ga, with $E_z = -0.62$ V (corresponding to 99.996% purity) it has been found that $\Delta E = -0.17$ V with respect to mercury at the same strongly negative charge[75]. If 99.9998% Ga is used[42], $E_z = -0.69$ V. For this type of Ga, q^M/E curves have not been reported, but a similar shift can also be expected in the potential at constant charge, and examination of capacity curves for very pure Ga shows that this is the case[82]. Thus, we have $\Delta E = -0.25$ V. Since 4.50 eV is the work function of mercury, that of Ga must be 4.25 eV. Now, if the orientation of water on Ga were the same as on Hg, from eqn. (11) we would obtain $\Phi = 4.00$ eV. Since the work function of Ga covered with adsorbed water molecules has been found[96] to be 3.92 eV, one can calculate that the contribution of water dipoles on Hg is $g^S_{dipole} = 80$ mV, and this result is in excellent agreement with what has been derived from the adsorption of neutral organic substances on this metal[97]. Water is therefore oriented with the negative end of its dipole toward mercury. This fact, previously suggested by other authors[98-102], is here corroborated through a combination of physical and electrochemical data. It can be further noted that for a monolayer of ethylene glycol which on replacing water molecules introduces a negligible residual dipole with the positive end toward the metal[103], it has been found that $\Delta E_z = 86$ mV, which compares very well to the value obtained in this work. The orientation of water on Ga is therefore such that the surface potential on the solution side is 0.33 V. These values can be considered as quite accurate for they are derived from very precise electrochemical measurements.

The above arguments may also apply to those metals for which q^M/E curves are available. In the case of Cd[40], the difference in E_z with respect to Hg is -0.53 V, but ΔE at strongly negative charges (parallel curves have been found also in this case) is only -0.38 V. This therefore equals the difference in work function, which for Cd is thus 4.12 eV. This value is closer to the experimental value for films on tantalum (4.22 eV)[31] than that estimated (3.97 eV)[27], and is very similar to that used by Frumkin[14]. In practice, also Cd does not follow eqn. (11), because water is more oriented on its surface than on mercury, but the contribution of water dipoles is in this case less than on Ga, and the surface potential g^S_{dipole} is 0.23 V.

A further possibility is offered by lead[104]. In this case the calculation of Φ cannot be as accurate as above because the q^M/E curves in NaF solutions do not display a region where they parallel the curves for mercury, although the general qualitative behaviour is similar to that of Ga and Cd. No satisfactory explanation is available for this at the moment. However, ΔE_z between Pb and Hg at strongly negative charges $(-15\,\mu C\,cm^{-2})$ is -0.32 V. One may thus derive a work function for lead of 4.18 eV, and a surface potential due to water dipoles of 0.19 V.

The above calculations show that g^S_{dipole} increases in the sequence Hg < Pb < Cd < Ga, and this must be attributed to increasing orientation of water molecules at the interface. In effect, a great deal of experimental results[44,105,106] does indicate that the extent of adsorption of organic substances decreases in the same sequence, which suggests that water is more and more strongly held at the surface from Hg to Ga. Further, the specific adsorption of ions also decreases in the same series, and this

can be seen experimentally from the shift of E_z due to anions[40,75,95,107,108].

The fact that the points representing Pb, Ga and Cd fall further from the straight line expressed by eqn. (11) and nearer to that of eqn. (10) the greater the orientation of water suggests that eqn. (10) may represent a group of elements on which the orientation of solvent molecules is maximum. This could be quite possible for transition metals where water molecules can be chemisorbed through the oxygen atom. Hence, g_{dipole}^S may be reasonably thought to be the same for all transition metals, which explains the form of eqn. (10), and supports at the same time the view that this equation would represent a particular aspect of a more general relationship including sp metals.

Many experimental observations corroborate the above views. Capacity curves for Sb[45] show that this metal behaves like mercury, which makes understandable the fact that it lies in group 1 (Fig. 1). Adsorption data[109,110] on Bi indicate that this metal should adsorb water more strongly than mercury, but the q^M/E curves[111] show that the difference is very small. The fact that Bi lies on curve 1 can be accepted as a satisfactory approximation for the moment. No exact data are available for Ag, but from a qualitative point of view the capacity curves in dilute solutions[37,73,74,112] look very close to those of mercury around E_z.

The problem is more complicated in the case of Au and Cu. The points of both metals lie below curve 1 and this does not seem to be attributable simply to inaccurate values of Φ (E_z is known with fair accuracy in both cases). If for other metals the fact that the shift of E_z due to adsorption of anions is lower than on mercury may be assumed as indicating a stronger adsorption of water, in the case of Cu and Au we should expect a lower orientation of water inasmuch as the experimental values[113,114] of ΔE_z are higher than on Hg. The real situation is probably not so simple; however, since a spontaneous orientation of water with hydrogen toward the metal does not seem to be likely, the hypothesis that the dipole of water would lie parallel to the metal surface (no preferential orientation) may be more reasonable. In other words, E_z for Au and Cu would be 80 mV more positive than expected from eqn. (11), and this can be readily accepted in the case of gold for which both E_z and Φ are fairly accurate, whereas in the case of Cu the known[41] value of E_z would require a value for the work function somewhat higher than that of 4.55 eV as estimated from some experimental results[27].

If the fact is now examined that the orientation of water increases in the series Au, Cu < Hg, Ag, Sb, Bi < Pb < Cd < Ga, one can realise that the situation may be rationalised in terms of a well known chemical quantity, the electronegativity (x_M) in the scale given by Pauling[115]. It becomes apparent that the more electropositive the metal, the greater is the preferential adsorption of the negative end of the water dipole. Inspection of the positions of Ga, Cd, Pb, Hg and Au, which should be very close to the actual positions, reveals that it is possible to write linear E_z/Φ relationships with unity slope only for groups of elements having *constant electronegativity* (Fig.2). To a first approximation, straight lines as in Fig. 2 may be drawn 80 mV apart per 0.1 unit of electronegativity. Hence, curve 2 in Fig. 1, expressed by eqn. (10), would correspond to a constant x_M of 1.5, while the line on which Au lies, to $x_M = 2.0$. Curve 1, as expressed by eqn. (11), would thus correspond to $x_M = 1.9$, which is not surprising inasmuch as Hg, Ag, Sb and Bi which fall on this line actually exhibit a Pauling electronegativity of 1.9.

Equations (10) and (11) can now be combined, and the relationship between Φ and E_z can be written in the form:

$$E_z = \Phi - 4.61 - 0.40\alpha \tag{13}$$

where $\alpha = (2.0 - x_M)/0.5 = (4.0 - 2x_M)$ can be defined as the *degree of orientation of water* at the interface. As explained above, x_M is taken as 1.5 for all transition metals, and 2.0 for Au and Cu. For all other metals the value of x_M coincides with that given by Pauling[115]; α thus changes from 0 (not oriented water) to 1 (fully oriented water).
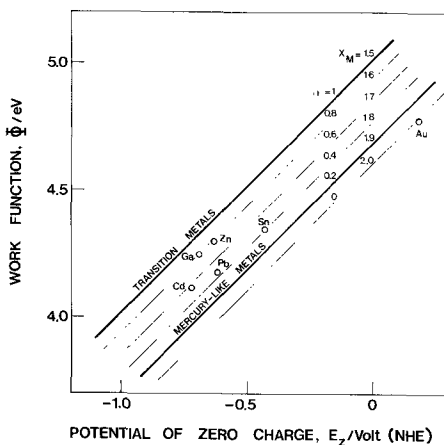

Fig. 2. Plots of potentials of zero charge against work functions of metals. x_M is the Pauling electronegativity. α is the degree of orientation of water molecules at the interface. Φ for Ga, Cd and Pb are *electrochemical* work functions (see text).

The fact that for Au and Cu x_M does not coincide with Pauling's value may depend firstly on the approximation to the first figure given by Pauling, and secondly on the fact that x_M is actually a chemical property of isolated atoms and not of bulk material. On the other hand, a correlation undoubtedly exists between Φ and x_M, even though a unique relationship[3,116,117] may be too great an oversimplification (see later). Thus, in the case of gold, the value of 5.3 eV for the work function, as given by many workers[27], could correspond to a state where $x_M = 2.4$ (Pauling's value), whereas the value of 4.78 eV accepted in this work would correspond to a surface condition for which $x_M = 2.0$.

In Fig. 2, zinc can be seen to lie exactly on the straight line for $x_M = 1.6$, as expected from its Pauling electronegativity. Consistently, tin belongs to the line with $x_M = 1.8$. Aluminium falls between $x_M = 1.8$ and 1.9, whereas it would be expected to lie on the line of the transition metals, the accepted value of its electronegativity being 1.5. Work function measurements[118] actually show that the decrease of Φ due to water adsorption may be of the order of 0.5 eV. It can be suggested therefore that the value of $E_z = -0.52$ V, as found by the immersion method[58], may in fact refer to an oxidised surface, which appears likely in view of the nature of the experimental method[34]. If this is the case, E_z for an oxide-free surface of Al should be -0.82 V, as results from eqn. (13).

Copper falls below the line corresponding to $x_M = 2.0$. However, if the experimental value of E_z is assumed to be highly accurate, as appears likely from an examination of experimental results[41,113], the estimated work function[27] of Cu must

be thought to be somewhat lower than the actual value. From eqn. (13), $\Phi = 4.70$ eV is readily calculated, and the validity of this value is supported by very recent measurements by Suhrmann et al.[119] (not reported by Rivière[31]) who consistently obtained values around 4.65 eV.

Two more metals are left for discussion, indium and thallium. For neither of these elements are there data as accurate as in the case of Cd, Pb and Ga. From a qualitative point of view, capacity data on In[120] and Tl[121] amalgams suggest that the orientation of water on these metals should be higher than on mercury. However, with $x_M = 1.7$ for In, $E_z = -0.77$ V is obtained from eqn. (13). The more probable value estimated from available experimental data[48,70] appears to be -0.65 V, but from the examination of inflection in the Tafel line for hydrogen evolution some authors[71] suggest that the potential of zero charge may be -0.80 V for metallurgical In and -0.65 V for electrolytic In. Further, experiments on In amalgams[120] show that E_z shifts toward more negative values as the In content increase, and is -0.635 V for 40% In amalgams; hence, it may be thought that E_z for bulk In may be somewhat more negative than this value. Finally, In–Ga amalgams behave as though the two metals possess very close values for E_z[122]. Since for Ga, $E_z = -0.69$ V[42,82,83], a very close value for In may be, in principle, either -0.65 V or -0.75 V. On the other hand, if E_z for In is placed at -0.65 V, from eqn. (13) with $x_M = 1.7$ the work function of 4.20 eV is derived, a value at the present time hardly justifiable by either experimental values of Φ[27], and measurements of E_z in molten salts[25,26,34]. However, the work function of In is expected to be lower than that of Pb. In conclusion, a more exact location of In in Fig. 2 would require a more certain knowledge of either Φ and E_z.

The situation of Tl is different. E_z is in this case fairly well known[47,76], whereas the work function is uncertain[27]. The fact that the point for Tl lies largely below curve 1 in Fig. 1 is therefore to be attributed to an incorrect value for the work function. From eqn. (13) the *electrochemical* work function of 4.02 is thus calculated for Tl. This value is 0.06 eV lower than that selected[25] for In. It is significant that E_z for Tl in molten electrolytes is 0.05 V more negative than the value found[25] for In. This result may support the procedure proposed here.

Third approximation. Effective electronegativity scale

Equation (13) may be corrected to give more accurate value of E_z by using the effective value of electronegativity. No doubt, the concept of electronegativity can be associated in solids to the concept of work function[123]. In fact, both quantities measure how strongly electrons are held in the highest occupied energy level. A correlation certainly exists between Φ and x_M; Sargood et al.[124] have very recently shown that surface potentials arising upon adsorption of electronegative elements on single crystal faces of tungsten can be correctly calculated in terms of difference in electronegativity, which for the solid increases with increasing work function. Relationships between work functions and electronegativities can be found in the literature[3,116,117], but they are unsatisfactory first of all because they assemble all elements into a single group although this is not clearly brought out. Further, the above proposed relationships were obtained using many unreliable values of work function.

Pauling's electronegativities[115] are plotted in Fig. 3 against work functions including the *electrochemical* values found above. Alkali and alkaline earth metals are also reported[31] in the Figure. It can be seen that the metals are undoubtedly divided
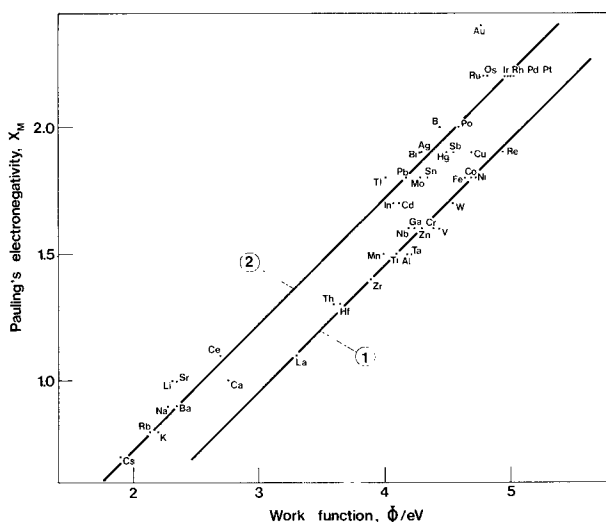
Fig. 3. Relationship between Pauling's electronegativity of metals and work function.

into *two* groups. Transition metals (with the exception of Pt and Pd groups) *plus Zn, Al, and Ga* belong to group 1 for which the relationship is the following:

$$x_M = 0.5\Phi - 0.55 \tag{14}$$

whereas alkali, alkaline earth and *sp* metals and Pt and Pd groups (plus Mo which seems anomalous from this point of view) belong to group 2 for which:

$$x_M = 0.5\Phi - 0.29 \tag{15}$$

Gold seems to fall far from group 2, but it is of interest to note that this metal belongs clearly to the group if $\Phi = 5.3$ eV is used as its work function[27]. When gold is in a state for which $\Phi = 4.78$ eV, an electronegativity of 2.1 must then be accepted for this metal, which is in accordance with arguments offered above. It is further possible to observe that in group 2 copper is very near gold, as should be reasonable in view of the closeness of their E_z and observed shifts of E_z due to anions.

In Fig. 4, the potentials of zero charge of all the metals examined are replotted against the work functions. Filled circles are used for Cu, Tl and Al because the work function for the first two metals and E_z for the last metal have been derived from considerations regarding Fig. 2. Theoretical straight lines for both cases of no preferential and maximum orientation of water molecules are also indicated; *sp* metals can be grouped around a straight line of equation:

$$E_z = 1.33\Phi - 6.18 \tag{16}$$

with *the exception of Ga, Zn and Al* which fit the equation:

$$E_z = 1.33\Phi - 6.35 \tag{17}$$

The results presented in this way clearly show that no linear relationship with unity slope is in fact possible for *sp* metals. Correlations of this sort reported in the literature[14,17] are incorrect and this appears to be due to inaccuracy of Φ rather than of E_z.
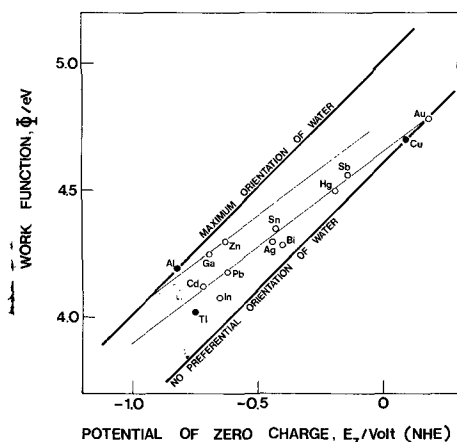
Fig. 4. Final plot of potentials of zero charge of metals against the work function. Φ for Tl and Cu are *electrochemical* values (see text). E_z for Al has been estimated from Fig. 2.

The results given by eqns. (16) and (17) can be expressed by a unique equation in terms of electronegativity:

$$E_z = \Phi - 4.61 - 0.666(2.10 - x_M) \tag{18}$$

where x_M is given by eqns. (14) or (15) for sp metals, and is 1.5 for transition metals. Equation (18) may be rewritten in the form:

$$E_z = \Phi - 4.61 - 0.40\alpha \tag{19}$$

where $\alpha = (2.10 - x_M)/0.6$ is the *degree of orientation of water* on the metal surface, and is zero for Au ($x_M = 2.10$) and unity for transition metals ($x_M = 1.5$). Equation (19) is formally identical to eqn. (13), in respect to which it must be considered as being an improvement, in that it has been obtained from the experimental dependence of x_M on the work function. Further, the range of electronegativity is from 1.5 to 2.1, whereas in the case of eqn. (13) x_M changes from 1.5 to 2.0 only. In other words, the actual contribution to the surface potential given by oriented water dipoles is 66.6 mV per 0.1 unit of electronegativity rather than 80 mV as obtained in the second approximation from Pauling's electronegativity.

Table 3 reports values of electronegativity as obtained from eqns. (14) and (15); Pauling's values are also shown for comparison. It can be noted that the effective electronegativities of metals are to within ± 0.1 the values given by Pauling, and usually less. Only gold, and perhaps copper too, show greater deviation. Since Pauling's values are approximate to ± 0.1, the effective electronegativities found here may be considered as a refinement of the original values. In this respect, the value of $x_M = 1.5$ to be used in eqn. (19) in the case of transition metals is to be regarded as a particular *interaction parameter* between water and metal surface. The fact that it is constant for all transition metals indicates that the effect of the electronegativity is obscured and smoothed out by the additional phenomena of chemisorption. Finally, it must be stressed the fact that x_M in eqn. (19) is not the electronegativity in Pauling's scale of the surface of metals, but is the electronegativity precisely in Pauling's sense[115], *i.e.* "*the power of an atom in a molecule to attract electrons to itself*". In this respect, eqn. (19)

TABLE 3

ELECTRONEGATIVITY OF METALS, x_M

(a) From work function (eqns. (9) and (10)); (b) Pauling's values[115].

Metal	(a)	(b)
Ag	1.86	1.9
Al	1.55	1.5
Au	(2.10)	2.4
Bi	1.86	1.9
Cd	1.77	1.7
Co	1.80	1.8
Cr	1.65	1.6
Cu	(2.06)	1.9
Fe	1.77	1.8
Ga	1.58	1.6
Hg	1.96	1.9
In	1.76	1.7
Ir	2.19	2.2
Mn	1.45	1.5
Mo	1.86	1.8
Nb	1.55	1.6
Ni	1.82	1.8
Os	2.13	2.2
Pb	1.80	1.8
Pd	2.21	2.2
Pt	2.22	2.2
Re	1.92	1.9
Rh	2.20	2.2
Ru	2.11	2.2
Sb	1.99	1.9
Sn	1.89	1.8
Ta	1.56	1.5
Ti	1.50	1.5
Tl	1.73	1.8
V	1.67	1.6
W	1.72	1.7
Zn	1.60	1.6

represents a striking example of how the behaviour of electrons can bridge the fields of electrochemistry, physics and chemistry, and focusing the attention upon the electronic structure may reveal the underlying unity of many apparently diverse subjects.

A few aspects of Fig. 4 are still to be discussed. Au, Cu, Sb, Hg, Sn, Ag, Pb, Cd on one side, and Al, Ga, Zn on the other side, are fairly well aligned, so that no further correction to Φ is needed. This could at most be only 0.01 to 0.02 eV. In the case of Bi, on the contrary, E_z is known with high accuracy[39] and the fact that the point for this metal falls far away from the line of eqn. (19) suggests that the actual work function may be somewhat higher. From eqn. (19), 4.36 eV is obtained for Bi, which is to be considered as an *electrochemical* work function. This value is the same as that accepted[27] for Sn, and the closeness of E_z in molten salts[25,34,125] for these two metals supports the validity of the above interpolation.

In the case of Tl, if the value of E_z at -0.75 V[47,76] is accepted, Fig. 4 and eqn.

TABLE 4

WORK FUNCTIONS OF SOME METALS, Φ/eV

(a) First approximation (selected exptl. values, from Table 1); (b) second approximation (*electrochemical* values); (c) third approximation (*electrochemical* values).

Metal	(a)	(b)^a	(c)
Bi	4.29	—	4.36^a
Cd	3.97	4.12	—
Cu	4.55	4.70	—
In	4.08^a	—	4.16
Ir	—	4.97	—
Pb	4.01	4.18	—
Pd	5.00	5.01	—
Pt	5.40	5.03	—
Rh	—	4.99	—
Tl	3.84	4.02	4.08

^{a} Recommended values.

TABLE 5

POTENTIALS OF ZERO CHARGE OF SOME METALS, E_z/V (NHE)

(a) Values calcd. from eqn. (14); (b) exptl. values (where available).

Metal	(a)	(b)
Al	-0.78	-0.52
Co	-0.31	-0.32 (pH = 1)
Cr	-0.61	-0.45
Fe	-0.36	-0.35
Mn	-1.11	—
Mo	-0.71	—
Nb	-0.81	-0.79
Ni	-0.28	-0.30
Os	-0.24	—
Re	-0.06	-0.20 (?)
Ru	-0.21	< -0.12
Ta	-0.79	-0.85
V	-0.57	—
W	-0.46	—

(19) show that the *electrochemical* work function should be 4.08 eV. Accordingly, with E_z at -0.65 V[48,70] the work function for In should be 4.16 eV. If the series Tl, Cd, In, Pb is now examined, it can be observed that the *electrochemical* work function increases in the sequence Tl < Cd < In < Pb. In spite of a certain scatter of data, there is strong evidence for E_z in molten salts to increase in the same order[26,126]. Further, $\Delta\Phi$ between Tl and Pb would be 0.1 eV, which agrees with $\Delta E_z = 0.11$ V as reported for the same metals in molten salts[25]. These results appear to support strongly the validity of the assumption made in this work. However, since also for Tl there exists some discrepancy in the exact location of E_z (Borisova and Ershler[127] found -0.82 V), we accept the *electrochemical* work function derived from the third stage of this work

only in the case of Bi. Thus, $\Phi = 4.36$ eV is suggested for this metal and, consequently, $x_M = 1.89$ in the place of 1.86 as reported in Table 3. On the contrary, for Tl and In we suggest here the values of 4.02 (*electrochemical*) and 4.08 eV, respectively, and defer the values of 4.08 and 4.16 eV, respectively, to other correlations to verify which values are actually to be preferred.

Table 4 summarises the *electrochemical* work functions estimated in this work, as compared to selected experimental values[27]. For metals not included in Table 4 the recommended work functions are those reported in Table 1. Moreover, Table 5 reports values of E_z calculated or estimated in this work essentially for those metals for which the experimental value of E_z is uncertain or even unknown. It appears from Table 5 that the experimental E_z for Al may refer to an oxidised surface. This is possible also in the case of Cr, although the experimental value of the work function of this metal still leaves some doubt[27]. No value of E_z has been calculated for Ti from eqn. (19), because the work function for this metal is somewhat uncertain. Finally, as to electronegativity, Mo falls in the group of *sp* metals, but if this metal chemisorbs water like any other transition metal, and this should be the case, then $x_M = 1.5$ is to be used, and the E_z predicted by eqn. (19) is thus -0.71 V.

Orientation of water molecules at the interface

The results, as expressed by eqn. (19), have so far been discussed in terms of varying orientation of water. Let us now examine if this model is consistent with a molecular point of view. First of all, let us consider the meaning of the term K' in eqn. (12). According to eqn. (9), $K' = K + \delta\chi^M$, where K depends exclusively on the reference electrode. In the case of an hydrogen electrode, Bockris and Argade[35] have calculated by using a thermodynamic cycle that $K = -4.78$ eV. However, if the more probable value of -263 kcal mol^{-1} is used for the standard chemical free energy of hydration of the proton[131], a value of -4.28 eV is obtained for K. Since in eqn. (19) $K' = -4.61$, it results that $\delta\chi^M = -0.33$ eV. At first sight, this term would represent the variation in the surface potential of the metal when it is brought into contact with the aqueous solution. This change is in the direction of a decrease in work function, and would imply a smaller spreading out of electrons. In view of the factors giving rise to the surface potential of metals[93,94], the above result would seem conceivable. As a limiting case, the surface potential of a metal should vanish if the bordering phase were the metal itself. In other words, the unbalanced forces acting at the surface of a solid should be at a maximum as the solid is exposed to a vacuum. Nothing definite can be said about the real meaning of $\delta\chi^M$ and additional evidence is needed to confirm this result. However, it can be readily realized that the value of $\delta\chi^M$ found here is consistent with a number of other considerations.

From Volta potential measurements by Randles[128] for mercury/solution contacts, and the knowledge of the potential of zero charge of mercury in the absence of specific adsorption[129], it has been derived[130] that the contact potential difference between mercury (uncharged) and water, *i.e.* the potential difference across the hypothetical cell:

$$\text{Hg} \,|\, \text{N}_2 \,|\, \text{H}_2\text{O} \,|\, \text{Hg} \tag{I}$$

is -0.26 V. One may thus write according to Frumkin[130].

$$-0.26 = \chi^S + \delta\chi^M - g^S_{dipole} \tag{20}$$

where the surface potential is positive when the dipole points the positive end towards the interior of the phase. Since $g^S_{dipole} = 0.08$ V, and $\delta\chi^M = -0.33$ V, one obtains from eqn. (20) $\chi^S = 0.15$ V. This value implies an orientation of water at the free surface with the oxygen atom pointing to the gas phase. The value found here is within the estimate by Frumkin et al.[100], and is very close to the value (0.11 V) preferred by Case and and Parsons[131] on the basis of other considerations. Furthermore, Randles and Schiffrin[132] indicate as 0.13 V the possible maximum value of χ^S from considerations regarding the temperature coefficient of the surface potential.

Bockris and Argade[35] found $\chi^S = 0.20$ V with a very similar but not identical procedure, but this result appears somewhat fortuitous, since the authors wrote eqn. (20) the wrong way as to the sign of the surface potentials. It appears that the incorrect value for K used by the above authors balanced more or less the error made in eqn. (20). The value for χ^S found by Bockris and Argade[35] would disagree with that obtainable by considerations involving the value of the hydration free energy used by themselves[131], so that their calculations would show at any rate some internal inconsistency. Finally, it should be noted that Frumkin[130] from eqn. (20) estimated to 0.36 V the value of g^S_{dipole}, but he neglected in his calculation the term $\delta\chi^M$. The present work shows that *in principle* this may not be justified, though the assumption that $\delta\chi^M$ is the same for all metals, *i.e.* depends only on the nature of the bordering phase, may be again a simplification.

The preferential orientation of water at the free surface with oxygen toward the gas phase is strongly evidenced by the negative temperature coefficient[132] of χ^S. Randles and Schriffin[132] have tentatively suggested that the orientation of water in contact with mercury may be higher than that at the free surface of solutions, inasmuch as the value of $d\chi/dT$ is more negative in the former case[99]. The values found in this work would indicate quite the contrary. An attempt will now be made to explain this apparent contradiction in terms of a contribution given by the work function to $d(\Delta\phi)/dT$ at the metal/solution interface. The work function of a metal tends[93] to increase with T. Recalling eqn. (19), an increase in Φ would correspond to a shift of E_z to the positive direction. Thus, Φ and g^S_{dipole} *separately* have opposite temperature coefficients, but at the metal/solution interface the two terms sum because g^S_{dipole} is opposite to the surface of the metal. This brings about an additive contribution to $d(\Delta\phi)/dt$ which thus would appear higher than the sole term dg^S_{dipole}/dT would be in reality. Many data indicate that the work function of metals increases with temperature[27], but some difficulty arises when a definite value is to be assigned to the temperature coefficient of Φ. In Riviere's review[31], only two data appear to be useful for a rough calculation of $d\Phi/dT$. Garron and Testard[133] measured 2.177 eV at 206 K and 2.217 eV at 300 K for the work function of potassium. Garron et al.[134] found for the same metal that the work function drops to 2.137 eV at 82 K. Assuming to a first approximation a linear variation in Φ with T, the temperature coefficient should be 0.4 mV K^{-1}, to be compared with -0.4 mV K^{-1} for χ^S and -0.57 mV K^{-1} for $\Delta\varphi$ at the solution/mercury interface given by Randles and Schiffrin[132]. If now the first value is subtracted from the last, one obtains -0.17 mV K^{-1} for the temperature coefficient of the surface potential of the solution surface region alone at the solution/mercury boundary. This calculation obviously implies independency of $d\Phi/dT$ of

the nature of the metal. Analysis of this point[31,93] indicates that this may be a fair approximation, and in any case the value for Hg may be somewhat higher because the thermal expansion coefficient of this metal is about twice as high as that of potassium. Now, if dg^S_{dipole}/dT is supposed to be constant up to a critical temperature at which it vanishes, the values reported above suggest the orientation of water at the free surface to be about twice as strong as that at the solution/mercury boundary, as seems in fact to be the case.

According to eqn. (19), the difference in surface potential between Au and transition metals due to water dipoles is 0.40 V. If this result is explained in terms of orientation of water, which would be zero on gold and maximum on transition metals, one must conclude that the maximum orientation should be far from corresponding to perpendicular dipoles. In effect, if χ_{H_2O} is calculated with the following equation[15,135]:

$$\chi_{H_2O} = 4\,\pi\mu n/\varepsilon \tag{21}$$

where the dipole moment of water is $\mu = 1.84\,D$, $n = 0.813\,10^{15}$ dipole cm^{-2} (assuming for water a projected area[136] of 12.3 $Å^2$) and the dielectric constant of water is $\varepsilon \simeq 7.5$ (being water in a position of dielectric saturation)[137,138], a surface potential of about 0.75 V would correspond to perpendicular dipoles. If the maximum surface potential must be 0.4 V, eqn. (21) shows that the dipole of water must form an angle of about 32° with the metal surface.

Figure 5 shows a scale drawing of a water molecule. It is possible to note that a molecule lying on the surface such as that in Fig. 5a forms with its dipole an angle of about 34° with the plane of contact. Any other position appears to be less favourable. It can be seen that the molecule can still form a hydrogen bond towards the bulk of the solution, and even in the surface layer. This possibility results in a poor depolarisation of dipoles and therefore a stabilisation from an energy point of view. Any rotation of the molecule would occur around an axis lying on the surface, as shown in Fig. 5b. Since the centre of gravity of the negative charges is very close to the centre of the oxygen atom [139], the effect of rotation is practically restricted to approach of the centre of the positive charges (hydrogen atoms) to the surface.
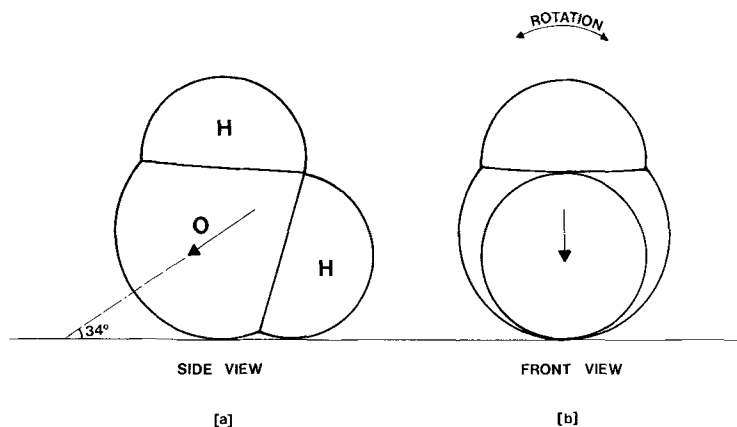

Fig. 5. Scale drawing of a water molecule in the suggested position of maximum orientation on a plane surface.

At the potential of zero charge the position of water on different metals is not determined by electrostatic attraction or repulsion, but the forces in play should arise from difference in electronegativity between the metal and the atoms forming the molecule of water, *i.e.* different energy levels for electrons in the metal and in water. On the other hand, metals with low work function possess electrons with low kinetic energy in the Fermi level[123], which should therefore give rise to small spreading out of electron distribution and hence to a small surface potential. This could favour a large interaction with the oxygen atom of water, whereas a large electron density in the surface layer as implied by a high work function would favour a strong interaction with the hydrogen atoms, resulting in a molecule of water lying flat on the metal as in the case of gold.

It is very difficult at this point to go beyond a simple qualitative picture, but it must be stressed that the closeness of the calculated value of the dipole moment of water perpendicular to the surface to the value resulting from the model proposed in Fig. 5 is too striking to be meaningless. On the other hand, an alternative model may be proposed on the basis of partial charge transfer between metal and oxygen atom due to difference in electronegativity. This model is much more complicated and prevents the giving of a simple physical picture of the double layer. Acceptance of this model, proposed however also in the case of adsorption of ions[140], would perhaps approach more closely the actual situation, but would imply a radical change in the way of interpreting double layer phenomena, as already pointed out by Parsons[141]. However, the oxidation of the surface of metals is more rapid and easy the more electropositive the element, *i.e.* the lower the work function. This signifies that charge transfer processes from metal to water are easier the lower the metal electronegativity. Thus, from a chemical point of view the results in Fig. 4 are readily understood, even though the physical picture given in Fig. 5 may be an oversimplification.

The situation for transition metals is more complicated. Following the proposed model, the results can be explained in terms of maximum orientation of water irrespective of the nature of the metal. This may be conceivable in view of possible chemisorption phenomena which would force water molecules to the orientation characteristic of low work function *sp* metals. The conceptual problem may arise whether a chemisorbed molecule retains its own structure. Water it has been suggested adsorbs on transition metals through a dissociation reaction[119,142]. The resulting OH groups would still lower the work function of the metal, but this lowering in the case of iron[119] would result to be of the order of 1 V, much more than expected even for perpendicular dipoles of water. It may be suggested that similar adsorption hardly occurs without charge transfer processes, so that the metal cannot be considered to remain at the potential of zero charge. This possibility may make any comparison with the present situation meaningless. Apart from any reserve about the real situation, the fact may be emphasised that the case of transition metals can be discussed in terms of the same model proposed for *sp* metals with the sole difference that water is not free to rotate. Dielectric saturation and restricted possibility of rotation are in fact suggested first of all by the absence in the capacity curves of transition metals[88,143-145] of any anodic hump of the type observed on mercury[141]. Secondly, in the potential region where the preferential adsorption of either hydrogen or oxygen is minimum, the capacity of platinum, freed from adsorption pseudocapacitance, shows a value of about 17 μF cm^{-2} [146], which corresponds to the capacity of mercury

at the cathodic minimum[102]. On the other hand, this value could indicate that water, while chemisorbed, behaves dielectrically and structurally as though it retained the properties pertaining to the isolated molecule. The conclusions reached above cannot be regarded as definitive inasmuch as the experimental results for transition metals are not so certain as to be clearcut, but the picture appears quite attractive and reasonable from a speculative point of view.

CONCLUSIONS

This work has shown that the linear relationships with unity slope between work functions and potentials of zero charge previously reported in the literature[34] are to be considered as essentially incorrect owing to the use of inaccurate values of work function. Similar relationships can in fact exist only in the case of constancy in the orientation of water molecules at the interface. This occurs with transition metals where water is forced to the position of maximum orientation by additional force arising from chemisorption phenomena.

In the case of sp metals no true chemisorption of solvent molecules is to be expected, and water is more or less strongly adsorbed (hence, more or less strongly oriented) with the negative end of the dipole toward the metal, depending on the electronegativity, or, alternatively, the work function of the metal, being Φ and x_M linearly related. Vasenin[16] suggested a similar model, but his relationship actually predicts a stronger adsorption the higher the work function, quite the contrary of the present findings. The more electropositive the metal, the stronger is the adsorption of water. From this point of view, Al represents the extreme limit of sp metals and behaves similarly to the group of transition metals.

It has been proposed in this work that successive approximations may be used to estimate work function values with more accuracy. The results show that this procedure may be considered as valid for two reasons. First of all, for every metal the value of Φ arrived at can be reasonably justified from an experimental point of view. Secondly, the approach has started from exclusively experimental data obtained with independent methods. However, in consideration of the fact that in some particular case the work functions proposed here differ significantly from the values usually accepted for metals in vacuum[27], these Φ have been defined as *electrochemical* work functions. In the opinion of the writer, the use of these values for works in the field of catalysis or surface science may prove to be surprisingly favourable, as can be seen from some correlation or application of Sabatier's principle to heterogeneous catalytic reactions[147]. Tests in this direction may be useful for two reasons: firstly, they should prove whether *electrochemical* work functions may be also considered as *physical*, *i.e.* as having a general validity. Secondly, if this is the case, such tests should clearly demonstrate that electrochemical measurements can lead to the attainment of more accurate values of quantities not directly related to electrochemistry.

Other data are however needed to verify the correctness of the conclusions reached in this work. The potentials of zero charge of many transition metals need to be confirmed. No data are even available for Ru, Os and Re. The value of Cr seems doubtful, and even more that for Al. q^M/E curves for some more sp metals would be very useful to verify the method of derivation of *electrochemical* work functions. The value of E_z should be checked in the case of In. Some confirmation would be wel-

come for the q^M/E curves of Pb. In the case of Ag, the problem of the actual value of E_z is still unsolved. The value of -0.7 V, as recommended by Leikis et al.[73][74], does not appear to agree with the most probable value of the work function. From the foregoing, it is also obvious that any value of E_z for aqueous solutions calculated by making use of previous relationships, those found for molten salts included, is to be considered as meaningless. In spite of some uncertainty, however, the fact that a great number of E_z and Φ are already known with fairly good accuracy gives a greater degree of reliability to the model proposed here with respect to previous suggestions.

ACKNOWLEDGEMENT

SUMMARY

Preferred values of Φ, work function, and E_z, potential of zero charge, for metals have been collected through a critical examination of much experimental data. It is shown, through three successive approximations, that the best relationship between the two above quantities is expressed by the equation: $E_z = \Phi - 4.61 - 0.40\ \alpha$, where $\alpha = (2.10 - x_M)/0.6$ is defined as the degree of orientation of water at the interface. x_M is the effective electronegativity derived from plots of Φ against the chemical electronegativity given by Pauling. $x_M = 0.50\ \Phi - 0.29$ is the experimental relationship for sp metals (including alkali and alkaline earth metals, with the exception of Ga, Zn and Al). For the last three metals the relationship is $x_M = 0.50\Phi - 0.55$. x_M is to be taken as 1.5 for all transition metals. $\alpha = 1$ for transition metals, and $\alpha = 0$ for gold, on whose surface water molecules do not present any preferential orientation. The value of x_M for transition metals must be regarded as a particular interaction parameter between surface and water arising from additional phenomena of chemisorption. The problem of the orientation of water at the free surface of solutions and at the interface with metals is discussed in detail.

Complete lists of effective electronegativities, electrochemical work functions (derived from electrochemical considerations), and potentials of zero charge calculated for those metals for which no experimental data are available have been compiled.

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