ZERO-CHARGE POTENTIALS AND ELECTRON WORK FUNCTIONS

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There has recently been a reawakening of interest in the relationship between the zero-charge potentials (zcp) of metals ε_Z and the corresponding electron work functions W^e (see, for example, [1,2]). In this connection, it is best to deal with its experimental basis.

Table 1 compares three series of zcp potentials: 1) those selected by Trasatti [1] as the most probable experimental values; 2) those calculated by the present author in 1953 [3]; 3) those corresponding to the results of electrocapillary and capacitance measurements in molten alkali metal chlorides at 700° [4-9].

The criteria for selection of the experimental values of ε_Z (the second column of Table 1) were discussed in detail by Trasatti [1]. The values of ε_Z in the third column were calculated from the equation [3,10-12]

$$_{H_2O}\varepsilon_z = \frac{W^e}{F} - 4.7 \qquad (1)$$

The figures in the fourth column were found by comparing Eq. (1) with the equations

$$_{s}\varepsilon_z = \frac{W^e}{F} - 4.8, \qquad (2)$$

$$_{s}\varepsilon_z = \frac{W^e}{F} - 5.3, \qquad (3)$$

which are valid for two different comparison electrodes used in chloride melts ($Pb/PbCl_2$ (2.5%) and Ag /AgCl (10%) respectively).

The last two columns of the table give the electron work functions used in the aforementioned studies [1,3].*

The discrepancy between the experimental (second column) and calculated (third column) zcp did not exceed ±0.05 V, the only exceptions being Co, Cu, Ni, Pt, and Ti. The electron work functions in the fifth and sixth columns agreed with the same precision (±0.05 eV) and with the same exceptions. The data for melts (fourth column) and solutions (second column) also differed insignificantly,† although the former were usually somewhat closer to the calculated values (third column).

One thus gets the impression that the experimental values of ε_Z and W^e have now been determined with rather high accuracy and that the relationship described by Eq. (1) exists between them.

However, this conclusion must be approached with some caution, since we are dealing not with definite, frequently reproduced, wholly reliable experimental values but with values selected from a broad spectrum of ε_Z [14] and W^e [15]. Although this selection is made on the basis of more or less logically

* The principles for selection of W^e are described in various publications [2,3,13],

† Comparison of the values of ε_Z in solutions and melts therefore has definite meaning, something denied by Trasatti [1]; it must be noted that the difference in the zcp for given metals is virtually independent of the nature of the solvent (water or molten salts).

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grounded assumptions, it does not enable us to be fully certain that the "most reliable" values thus obtained are the true ones. Other "reliability" criteria can be formulated and new, correlated values of ε_z and W^e obtained. In other words, if we assume some value of ε_z to be the most reliable, we can find the value of W^e (or vice versa) corresponding to a definite type of relationship between them. This can be illustrated with the example of silver, for which Frumkin [12] selected $\varepsilon_z = -0.7$ V and $W^e = 4.00$ eV, while Trasatti [1] selected −0.43 V and 4.30 eV respectively. Both these sets of values for ε_z and W^e roughly conform to Eq. (1). On the other hand, the differences between them (0.27 V and 0.30 eV) are in sharp contrast with the apparent accuracy of the figures in the second and fifth columns of Table 1 (to the second decimal place).

Further development of the zero-charge point theory is possible only if there is a material increase in the reproducibility and accuracy of determinations of ε_z and W^e under conditions where they are characteristic constants of a metal in contact with a vacuum or a solvent. In the overly broad sense in which the term zcp is used in the current electrochemical literature, it does not satisfy this requirement. It includes the potentials of the electrocapillary-curve maxima or the differential capacitance minima, regardless of the composition of the solution in which they are measured. It is therefore natural that a multiplicity of values of ε_z can be obtained for a single metal—solvent system (e.g., mercury—water), each value corresponding to an uncharged boundary but not being a constant typical of the given metal—solvent system, so that it cannot be compared with the electron work function in a vacuum. These values of ε_z, which depend on the solution composition, are best termed uncharged surface potentials (usp) and designated as $\varepsilon_{q=0}$ [16]. Extrapolation of the quantity $\varepsilon_{q=0}$ to zero solute concentration for surface-active particles can yield a specific value of ε_z that depends (at a given temperature) only on the nature of the metal and solvent. It can be defined (according to A. N. Frumkin's two initial publications in this area) as the zero point (zp) and designated as ε_N [16]. For the mercury—water system, such extrapolation of $\varepsilon_{q=0}$ obtained in the presence of various surface-active agents yields the same value of −0.190 ± 0.03 V [17, 18]. It is precisely this value that must be compared with the electron work function of mercury in a vacuum. In the case of solid metals, the quantities ε_N and W^e are functions of the face index and their effective values for polycrystalline specimens depend on the percentage ratio of the exit of different faces to the exposed surface, i.e., on the specimen history and fabrication method. For a number of reasons, this dependence is stronger in the case of "rigid" materials and weaker in the case of "soft" (mercury-like) materials [16]. The values of ε_N and W^e used for the comparison should therefore be for the same crystallographic face of the solid metal. However, there are almost no data of this type.

Tables of experimental values of ε_z are thus nonuniform and include the physically different quantities $\varepsilon_{q=0}$ and ε_N. Tables of experimental values of W^e contain primarily values for polycrystalline metal specimens with an indeterminate percentage exit of different faces to the exposed surface.

TABLE 1

Metal	Experimental ε_z in aqueous media [1], V	Calculated ε_z in aqueous media [3], V	Experimental ε_z in melts [4-9], recalculated for aqueous media, V	Experimental W^e [1], eV	Experimental W^e [3], eV
1	2	3	4	5	6
Ag	−0,44	−0,4	−0,3 to −0,4	4,30	4,3
Al	−0,52	−0,5	−0,4 to −1,0	4,19	4,2
Cd	−0,72	−0,7	−0,7 to −0,73	3,97	4,0
Co	−0,45	−0,3	−0,3	4,70	4,4
Cu	+0,09	−0,2	−0,4	4,55	4,5
Fe	−0,35	−0,4	−0,4	4,65	4,3
Fe	—	±0,0	—	—	4,7
Ga	−0,69	−0,6	−0,5 to −0,55	4,30	4,1
Hg	−0,19	−0,18	−0,20	4,50	4,5
In	−0,65	−0,7	−0,6 ÷ −0,7	4,08	4,0
Ni	−0,30	−0,2	−0,12	4,73	4,5
Pb	−0,62	−0,7	−0,45 to −0,55	4,01	4,0
Pt	+0,02	+0,2	−0,1 to +0,2	5,40	4,9
Sb	−0,14	−0,1	±0,0 to −0,1	4,56	4,6
Sn	−0,43	−0,4	−0,2 to −0,4	4,36	4,3
Ti	−1,05	−0,7	−0,75	4,10	4,0
Tl	−0,75	−0,8	−0,8	3,84	3,9
Zn	−0,63	−0,5	−0,65	4,3	4,2

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