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REAL FREE SOLVATION ENERGY OF AN ELECTRON IN A SOLUTION IN EQUILIBRIUM WITH THE ELECTRODE AND ITS DEPENDENCE ON THE SOLVENT NATURE

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ABSTRACT

The dependence of the real free solvation energy of an electron $\epsilon_K = \Delta_S^M\varphi - \mu_e^M/F + \chi^S$ on the nature of the solvent S is considered. It is shown that ϵ_K also expresses the work of a metal electron tranfer to infinity for an electrode in electrochemical equilibrium with a solution with an uncontaminated surface, the condition $\psi^S = 0$ being fulfilled. The electrochemical equilibrium between metal and solution can be established by any method, in particular, with the use of a dissolved redox system.

As was shown earlier (refs. 1 and 2), the quantity

$$\epsilon_K = \Delta_S^M\varphi - \mu_e^M/F + \chi^S \qquad (1)$$

where $\Delta_S^M\varphi$ is the Galvani potential at the metal/solution interface, μ_e^M the chemical potential of the electron in the metal and χ^S the surface potential of the solvent (Galvani potential at the solution/gas interface), expresses the real free solvation energy of the electron in a solution which is in electronic equilibrium with the metal. The quantity

$$\epsilon_T = \Delta_S^M\varphi - \mu_e^M/F \qquad (2)$$

is the corresponding chemical solvation energy. In Trasatti's terminology [3,4] ϵ_T is the absolute electrode potential *. The value of μ_e in eqns. (1) and (2) at infinity is equated to zero.

In the deduction given in refs. 1 and 2 use is made of the notion of the solvated electron in the solution, whose electrochemical potential is designated as $\tilde{\mu}_e^S$. The validity of this deduction was questioned in ref. 4 on account of the infinitesimal value of the electron concentration in the solution in equilibrium with the electrode at not very negative electrode potentials E. The infinitesimal value of this concentration results from the relatively small standard free hydration energy of the electron in its localized state, that is −36 kcal [5] **. Though

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* For the history of this question, see ref. 2.

** In the calculation given in ref. 5 account was taken for the first time of the difference in the standard free energies of atomic hydrogen in gaseous and dissolved states. However, in calculating on the basis of the found value of the standard free hydration energy 36 kcal = 1.56 eV the value of E_e^0 an arithmetical error was committed in ref. 5, which resulted in an erroneous value of $E = -2.5$ V. The correct result would be −2.86 V.

we do not consider this circumstance to affect the validity of using $\tilde{\mu}_e^S$ in the thermodynamic treatment, it seems worth while to show that the same result can be obtained without introducing the notion of the solvated electron as being one of the system components. In fact

$$\mu_e^M = \tilde{\mu}_e^M + \varphi^M F \tag{3}$$

where $\tilde{\mu}_e^M$ is the electrochemical potential of the electron in the metal and φ^M the inner potential of the metal. Let us assume the electrode to be covered by a solution layer with which it is in electrochemical equilibrium and whose surface does not carry any free charges, i.e. $\psi^S = 0$. The electrical potential φ at infinity is taken to be zero. Then

$$\varphi^M = \chi^S + \Delta_S^M \varphi \tag{4}$$

(in refs. 1 and 2 χ^S was designated as ${}_0\varphi_S$). It follows from (1), (3) and (4) that

$$\epsilon_K = -\tilde{\mu}_e^M/F \tag{5}$$

For the case $\chi^S = 0$, considered by Trasatti, in accordance with (2) and (4), ϵ_K in (5) should be substituted by ϵ_T.

It follows from (5) that ϵ_K is the electrochemical potential of the electron in the metal in equilibrium with the solution (at the Galvani potential $\Delta_S^M\varphi$ and the surface potential χ^S), or, in other words, the work function of the electron escape from the metal through an equilibrium solution with an uncharged surface. If the solution surface is charged, ϵ_K is the work of electron transfer from the metal (or from the solution from point C) to point B (Fig. 1), which lies at a distance from the solution surface exceeding the action radius of the molecular forces, but small compared with the geometrical dimensions of the system *.

Let us assume that the electrochemical equilibrium between metal and solution is established at a certain potential E (SHE) owing to the presence in the solution of a reversible redox system with a one-electron transition, which can occur with the participation of a metal electron

$$Ox + e^-(M) \rightleftharpoons Red$$

e.g.

$$Fe(CN)_6^{3-} + e^-(M) \rightleftharpoons Fe(CN)_6^{4-}$$

Then at the electrode potential E

$$\tilde{\mu}_{Ox}^S + \tilde{\mu}_e^M = \tilde{\mu}_{Red}^S \tag{6}$$

It follows from (5) and (6)

$$\epsilon_K = (\tilde{\mu}_{Ox}^S - \tilde{\mu}_{Red}^S)/F \tag{7}$$

$\tilde{\mu}_{Ox}^S$ and $\tilde{\mu}_{Red}^S$ refer to any concentrations of Ox and Red, if their ratio corresponds to the equilibrium condition at given E. It follows from (7) that ϵ_K is the real free solvation energy of the electron in the redox system which is in equi-

* Trasatti considers this location of e^- as being "physically an artifact" [4]. However, the electron location "near" the metal surface after its escape from the metal is always made use of in determining the work function.

librium with the electrode at given E since the electron solvation process under these conditions leads to the transition of an Ox particle into a Red particle (the localized electron state in the given system is its state in a Red particle).

It can be also envisaged that the Ox-Red transition occurs in the solution bulk with the participation of a solvated electron $e^-(S)$. In this case, from the equilibrium condition

$$\tilde{\mu}^S_{Ox} + \tilde{\mu}^S_e = \tilde{\mu}^S_{Red} \tag{8}$$

and from (7) we obtain

$$\epsilon_K = -\tilde{\mu}^S_e/F \tag{9}$$

which brings us back to the conclusion of refs. 1 and 2.

If we put $\chi^S = 0$, then in (7) and (9) ϵ_K should be substituted by ϵ_T, the corresponding "chemical" quantity according to the usual terminology.

It is clear from Fig. 1 that

$$\epsilon_K = W_e/F + \Delta^M_S\psi \tag{10}$$

where W_e is the work function for the electron emission into vacuum and $\Delta^M_S\psi$ the Volta potential metal/solution difference at the electrode potential E. Assuming $W_e^{Hg} = 4.51$ eV * and $(\Delta^{Hg}_S\psi)_{Q=0}$ according to Randles to be equal to —0.26 V [6], we find $(\epsilon_K)_{Q=0} = 4.25$ V. Since for Hg $E_{Q=0} = -0.19$ V (SHE) $\epsilon^0_K(H^+, H_2) = 4.25 + 0.19 = 4.44$ V. On the basis of a model, which we shall not discuss here, Trasatti [1] arrives at the conclusion that in the case of water $\chi^S = +0.13$ V. Hence, according to (1) and (2), we obtain for ϵ_T the value $4.44 - 0.13 = 4.31$ V, which Trasatti calculated following a somewhat different path. The values of $(\tilde{\mu}^S_{Ox} - \tilde{\mu}^S_{Red})$ or $\tilde{\mu}^S_e$ in equilibrium with the electrode depend on its potential. In a usual Galvanic circuit they are different in the immediate vicinity of the electrodes M_1 and M_2. In the general case

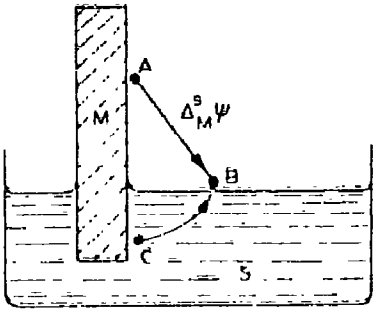
$$E_{MF} = (\epsilon_K)^{M1} - (\epsilon_K)^{M2} = (\epsilon_T)^{M1} - (\epsilon_T)^{M2} + \chi^{S1} - \chi^{S2} \tag{11}$$

where E_{MF} is the equilibrium potential difference at the ends of the circuit. The term $(\chi^{S1} - \chi^{S2})$ in (11) should be taken into account if the components of the redox system, or the solvated electron, influence the surface potential of the solvent. Such influence was observed in the case of solutions of electrons in hexamethylphosphortriamide [7,8]. If this term can be neglected, eqn. (11) turns into Trasatti's relation.

The difference of the electrochemical potentials corresponds to that of the concentrations of solvated electrons, or, at least, of one of the components of the redox system, which should lead to a certain charge leakage from the electrodes. However, if the concentration of solvated electrons, or of the redox system components, which can be formed in the solution, e.g. at the expense of traces of organic impurities inevitably present in solution, are small enough, this leakage can be ignored.

In an open circuit the equilibrium conditions can be more rigorously satisfied, if it is rearranged as shown in Fig. 2 i.e. if we short-circuit metals M_1 and M_2

* According to ref. 3, $W_e^{Hg} = 4.50 \pm 0.02$. Randles takes $W_e^{Hg} = 4.53 \pm 0.02$ [6].



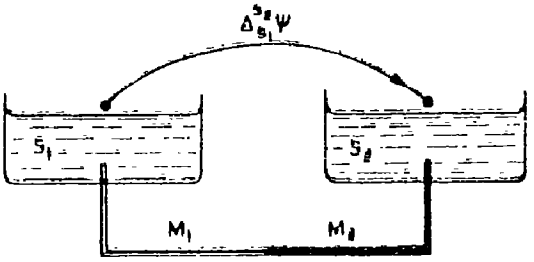


Fig. 1. Schematic diagram of the electrode M in the solution S.

Fig. 2. Schematic diagram of the equilibrium electrochemical circuit.

and break the connection between solutions S_1 and S_2, which are in electrochemical equilibrium with M_1 and M_2, respectively.

Evidently, the Volta potential between the points near the surface of S_1 and the surface of S_2 is

$$\Delta^{S_2}_{S_1}\psi = (\epsilon_K)^{M_1} - (\epsilon_K)^{M_2} = E_{MF} \tag{12}$$

It follows from the values 4.44 and 4.31, given above for the standard hydrogen electrode, that ϵ_K equal to $4.44 + E$ [1] at the potential $E = -4.44$ (SHE) is zero, and at $E = -4.31$, $\epsilon_T = 0$. Thus the values of ϵ_K and ϵ_T can be considered as electrode potentials measured against a reference electrode, whose potential in the hydrogen scale is -4.44 V, or -4.31 V, respectively. The value of $-\epsilon_K$ (but not of $-\epsilon_T$) can be decreased by changing χ^S, e.g. almost by a volt by depositing heptadecylamine on the surface of a dilute acidified aqueous solution [9]. The quantities ϵ_K and ϵ_T are not absolute, as in calculating ϵ_T, χ^S is conditionally taken to be equal to zero, whereas the value of ϵ_K can be varied over a wide range without affecting the bulk properties of the solution S, by depositing on its surface insoluble monolayers.

The introduction of the quantities ϵ_K or ϵ_T can be used for beaking the electrochemical process in a galvanic circuit into two parts, each depending only on one electrode and the solution surrounding it. In this respect, the interpretation of ϵ_K and ϵ_T as the values of the free solvation energy of the electron is particularly fitting. For illustration, let us take the classical example of Daniel's cell

$$Cu' \mid Zn \mid Zn^{2+}\,aq \,\|\, Cu^{2+}\,aq \mid Cu$$

The reaction

$$Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu \tag{a}$$

can be broken into two steps

$$Zn \rightarrow Zn^{2+}(aq) + 2\,e^{-}(aq) \tag{b}$$

$$Cu^{2+}(aq) + 2\,e^{-}(aq) \rightarrow Cu \tag{c}$$

For the reactions (b) and (c) to be reversible, it is necessary that the solution in

the left hand side of the circuit should be not only in ionic, but also in electronic equilibrium with Zn, and in the right hand side with Cu. Under these conditions, reactions (b) and (c) do not involve a change in the free energy of the system. However, the values of $\tilde{\mu}_e^s$ [or the equivalent values $(-\tilde{\mu}_{Ox}^s + \tilde{\mu}_{Red}^s)$] in the left hand $(\tilde{\mu}_e^s)_{Zn}$ and the right hand sides $(\tilde{\mu}_e^s)_{Cu}$ of the circuit are different. Therefore, if we transfer from the left hand side of the solution to the right hand side two moles of electrons through infinity, thus compensating for the gain in electrons as the result of reaction (b) in the left hand side of the solution and for their loss as the result of reaction (c) in the right hand side, we shall gain in the free energy $2(\tilde{\mu}_e^s)_{Zn} - 2(\tilde{\mu}_e^s)_{Cu}$ (at the surfaces of both solutions the outer potential $\psi^s = 0$). Hence we have for the emf of reaction (a) $E_{MF} = E_{Cu} - E_{Zn}$:

$$2FE_{MF} = 2(E_{Cu} - E_{Zn})F = 2(\tilde{\mu}_e^s)_{Zn} - 2(\tilde{\mu}_e^s)_{Cu} = -2(\epsilon_K)^{Zn}F + 2(\epsilon_K)^{Cu}F \qquad (13)$$

and

$$E_{MF} = (\epsilon_K)^{Cu} - (\epsilon_K)^{Zn} = (\epsilon_T)^{Cu} - (\epsilon_T)^{Zn} \qquad (14)$$

The breaking of E_{MF} into the terms $(\epsilon_K)^{Cu}$ and $-(\epsilon_K)^{Zn}$ corresponds to the division of the overall electrochemical process into two steps: the formation of the ion $Zn^{2+}(aq)$ from metal Zn with simultaneous transfer of two Zn electrons through the solution to infinity and a similar process for Cu, going in the reverse direction. The first step corresponds to the expenditure of the work $2F(\epsilon_K)^{Zn}$, the second to the gain in the work $2F(\epsilon_K)^{Cu}$ *.

The definition is very similar to that given by Trasatti [3]. In fact, according to Trasatti, the absolute zero of the thermodynamic potential is determined by the condition: "the work to extract an electron from the metal and to take it to infinity, passing through a surface layer equal to the electrode/solution double layer in the given solution, may be assumed as zero". However, Trasatti adds: "No practically realizable physical experiment can be devised to measure the above works". Substituting ϵ_T by ϵ_K and introducing the notion of the electron (or of the redox system equivalent to it) in solution, we make possible the experimental determination of the work sought for. It can be carried out combining two experiments: the measurement of the work function of the metal in vacuum and the determination of the Volta potential difference between the metal and the surface of the solution in equilibrium with the metal. It cannot be however carried out in a single experiment as the experimental determination of the electron work function gives the value of the work necessary to bring a metal electron to a point in the neighbourhood of the metal surface (point A in Fig. 1) and not to infinity.

The breaking up of E_{MF} into two terms $(\epsilon_K)^{Cu}$ and $-(\epsilon_K)^{Zn}$ proposed here offers the possibility to satisfy simultaneously two requirements, viz., that each of the two terms should depend only on one of the electrodes, and the process corresponding to each of the terms should be in principle physically realizable.

In carrying out the cyclic processes described above, it is possible to avoid the transfer of the metal electron through the solution. In fact, it follows from (10) that ϵ_K can be also considered as the work necessary to bring an electron

* Electrons may be transferred not only to infinity, but also to any conductor with preset ψ. In this case, the values of ϵ_K should be substituted by those of $(\epsilon_K - \psi)$.

to infinity from an electrode in equilibrium with the solution whose surface is uncontaminated, the condition $\psi^S = 0$ being fulfilled * since, under this condition $\psi^M = \Delta_S^M\psi$. In the case of such formulation, the choice of the reaction leading to the establishment of the metal/solution equilibrium is no longer of any importance for the determination of ϵ_K. This result can be also obtained without intermediate introduction of $\bar{\mu}_e^S$, as it follows from the deduction given above of eqn. (5). In this interpretation of ϵ_K the cyclic processes described above change as follows. The electrons formed during Zn ionization remain in the metal and are transferred to the vacuum through the metal/vacuum interface, which is charged to the potential $\Delta_S^M\psi$. A similar process occurs at the Cu electrode in the opposite direction. The overall electrochemical reaction is broken into two steps

$$Zn \rightarrow Zn^{2+}(aq) + 2(e^-)\ Zn$$

$$Cu \rightarrow Cu^{2+}(aq) + 2(e^-)\ Cu$$

The transitions of Zn into Zn^{2+} and of Cu^{2+} into Cu do not make any contribution to the balance of the free energy change, which is maintained due to the fact that the electrochemical potentials of e^- in Cu and Zn differ by $(-\epsilon_K)^{Zn} + (\epsilon_K)^{Cu}$. A similar interpretation of quantities equivalent to ϵ_K was given already by Kanevsky [10], who, however, sought to give these quantities the sense of absolute electrode potentials and did not correlate them with the electron free solvation energy.

Trasatti also breaks E_{MF} into two terms, each of which refers only to one particular electrode, but Trasatti is obliged to pass e^- through a potential difference equal to the Galvani potential $\Delta_S^M\varphi$, i.e. to introduce a non-thermodynamic quantity which in principle cannot be unambiguously determined.

Thus we arrive at the conclusion that ϵ_K can be considered not only as the real solvation energy of the electron in the solution in equilibrium with the electrode, but also as a thermodynamic constant characterizing the electrode in equilibrium with the solvent with an uncontaminated ** surface under the condition $\psi^S = 0$.

In principle, the values of ϵ_K can be determined for any solvent. The main difficulty is to avoid an error in using simultaneously values of W_e and of $\Delta_S^M\psi$, due to the possible influence on W_e of the adsorption of solvent vapors on the metal surface. Taking into account that the presence of water vapors in a wide pressure range apparently does not affect W_e^{Hg} [11], we can assume that in Randles' measurements this error was avoided and that the use of the value −0.26 V found by him for $(\Delta_{H_2O}^{Hg}\psi)_{Q\to 0}$ along with that of W_e^{Hg}, determined for the metal/vacuum interface, is valid ***. In the transition from water (S_1) to a different solvent (S_2), there is no need to carry out measurements similar to those of Randles. Instead, it is sufficient to use the determination of the potential

* Physically this condition means that on the surface of the solution there are no free charges in excess of those necessary for the existence of the Volta potential difference $\Delta_S^M\psi$.

** "Uncontaminated" means that processes leading to a change of the value of χ^S, characterizing the pure solvent, are excluded.

*** It still seems to us desirable to determine this quantity once more, taking account of all possible sources of error.

TABLE 1

Real free solvation energy of electrons in the solution in equilibrium with the electrode at p.z.c./eV

Solvent	Hg	Bi	Ga	Ga + In (16 at. % In)
Water	4.25	4.06	3.75	3.77
Methyl alcohol	4.00	3.82	—	—
Ethyl alcohol	4.07	3.88	—	—
Dimethylformamide	3.84	3.66	—	—
Dimethylsulfoxide	3.83	3.64	3.12	3.20
Acetone	3.90	—	—	—

difference at the end of the circuit

$M_1|S_1|$vacuum or air$|S_2|M_1'$

equal to $(\epsilon_K)^{S_2}_{M_1'} - (\epsilon_K)^{S_1}_{M_1'}$ if the surfaces of both solutions are uncharged, as is done in using Kenrick's method. Such measurements were performed in refs. 12—14. The values of ϵ_K in different solvents can be compared for any standard potentials if a corresponding reversible reaction can be realized on the electrode. Thus, e.g., using the values of the free solvation energies of the proton in different solvents, found by Case and Parsons [13], we can show that the standard values of $\epsilon^0_K(H_2/H^+)$ in methanol, ethanol, formamide and acetonitrile are: 4.69, 4.67, 4.59 and 4.32 V, respectively. At the present time, however, it is practically more convenient to use electrodes at the p.z.c. of the solvent in the absence of specific absorption. We have now at our disposal in addition the values of $(E_{Q=0})_{M_1} - (E_{Q=0})_{M_2}$ for the combinations Hg—Bi, Hg—Ga and Hg—(In + Ga) in several solvents [15,16]. Using these values, the Volta potential measurements and the value of $(\epsilon_K)^{Hg,H_2O}_{Q=0} = 4.25$ V, obtained from Trasatti's data [3], we can calculate the values of $(\epsilon_K)^{M,S}_{Q=0}$ listed in Table 1. The physical meaning of these more easily measurable quantities is somewhat complicated by the introduction of the p.z.c. They are of interest, however, since in the literature [17,18] it was suggested more than once that the value of $(\Delta^M_S\psi)_{Q=0}$ is equal to zero. In this case, the values of $(\epsilon_K)^{M,S}_{Q=0}$ would be independent of the solvent nature (and equal to W^M_c), which is at variance with the data of Table 1. The question of the value of $(\Delta^M_S\psi)_{Q=0}$ is considered in more detail in refs. 19 and 20.

If we wanted to obtain similar data for ϵ_T, we would encounter the difficulty associated with the absence of information on the values of χ^S for non-aqueous solvents. Another possibility would be to use relations between the standard potentials of metals in different solvents, however, as we well know, these could not be reliably determined in spite of numerous attempts made in this direction.

In conclusion, we would like to emphasize once more that, though we see no reasons to call ϵ_K or ϵ_T absolute electrode potentials, it seems to us that a new consideration of these quantities has been helpful in clarifying certain, even if elementary, but conceptually important, problems of electrochemistry. Thus the initiative taken by Trasatti proved to be valuable

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