A theory for amalgam forming electrode reactions

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Abstract

A theory for amalgam forming electrode reactions is formulated, based on a recently suggested extension of the Anderson model that allows a unified treatment of electron and ion transfer reactions. The predictions and classifications suggested by the model for both one- and two-electron reactions are compared with earlier phenomenological theories and with experimental data. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the study of the mechanistic aspects of simple electrode reactions, the reduction of metal ions at the mercury|solution interface still plays a key role. For example, modern theories of outer-sphere electrochemical electron transfer reactions have been tested by employing mercury electrodes [1]. However, it has been pointed out repeatedly that quite a few electrode reactions at mercury are not simple outersphere reactions, but are likely to involve several steps [2,3]. This is especially true for electrode reactions in which more than one electron is transferred, and/or in which the reduced species must dissolve into the mercury phase, thereby forming an amalgam.

Several authors have suggested mechanistic schemes to describe such multistep electrode reactions. Experimental kinetic data are then compared with the predictions of these schemes in order to deduce the most likely mechanism. Especially the groups of Sluyters and Fawcett have embraced this approach. Sluyters-Rehbach and Sluyters [4,5] have considered schemes consisting of potential-dependent electron transfer (ET) steps and potential-independent chemical steps, whereas Fawcett [6–8] has, in addition, called attention to the importance of considering potential-dependent ion transfer (IT) steps. Although these approaches may lead to a versatile interpretation of experimental data, they have as an inherent limitation that the kinetic data are not confronted with a microscopic theory, nor are the mechanistic schemes screened by ‘first-principles’ considerations.

In this paper, we propose a theory for amalgam forming electrode reactions involving the discharge of both uni- and divalent cations. To this end, we use a theory recently suggested by Schmickler [9,10] which allows the description of electrochemical electron and ion transfer on a unified quantum-mechanical basis. This model illustrates some of the basic similarities and differences between electrochemical electron and ion transfer reactions. From the potential energy surfaces calculated in this model, the various reaction rate theories allow one to estimate rate constants [11,12]. The amalgamation process proper is not treated in our model, as its physics are very poorly understood, but we believe that from the appropriate Born-Haber cycle at the equilibrium potential, we can still say something meaningful about the likelihood of the amalgamation
The model to amalgam forming electrode reactions. and it is for this reason that we restrict our discussion perfect single crystal. Such complications are essentially inhomogeneity of the electrode surface, even of an almost cations, such as surface diffusion and the energetic processes at solid electrodes involve additional consider-
ations such as univalent cations, such as zinc, lead, or cadmium, is treated. Here,
we treat the reduction of univalent cations such as the alkali ions or thallium by a spinless Anderson-Newns Hamiltonian, extended to the electrochemical interface [13]. We compare the predictions of our theory with the phenomenological approach for such reactions suggested by Fawcett. In the second part, the reduction of divalent cations, such as zinc, lead, or cadmium, is treated. Here, we have to introduce spin into the model. The multi-step nature suggested by the potential energy surface and the possible role of electron-and ion-transfer steps in the overall mechanism are analyzed in some detail. Quite a few of our conclusions will be of a more general validity in electrodeposition processes. However, processes at solid electrodes involve additional considerations such as surface diffusion and the energetic inhomogeneity of the electrode surface, even of an almost perfect single crystal. Such complications are essentially absent in electrodeposition reactions at liquid mercury, and it is for this reason that we restrict our discussion to amalgam forming electrode reactions.

2. Reduction of univalent cations

2.1. The model

In this section we consider a reaction of the type

\[ \text{M}^+ + e^- \rightarrow \text{M(Hg)} \]  \hspace{1cm} (2.1)

On the solution side of the mercury/solution interface, the system is characterized by the following model Hamiltonian:

\[ H = H_e + H_{\text{sol}} + H_{\text{int}} \]  \hspace{1cm} (2.2)

where the three terms are the electronic, solvent, and interaction parts of the Hamiltonian. Since only one electron is involved in the reduction of the univalent cation, we assume the electron to be spinless. This is a good enough approximation for the qualitative purposes of this section. The ion is characterized by a single electronic state of energy \( e_{\alpha} \), whose value will be specified below; the occupation number of this state is \( n_{\alpha} \) with \( c_{\alpha}^\dagger \) and \( c_{\alpha} \) the corresponding creation and annihilation operators. The electronic states on the metal are labelled by the quantum number \( k \); \( n_k \), \( c_k^\dagger \) and \( c_k \) denote the corresponding number, creation and annihilation operators. So \( H_e \) is:

\[ H_e = e_{\alpha} n_{\alpha} + \sum_k e_k n_k \]  \hspace{1cm} (2.3)

The interaction part \( H_{\text{int}} \) is

\[ H_{\text{int}} = \sum_k \left[ V_k(x)c_k^\dagger c_{\alpha} + V_k^*(x)c_{\alpha}^\dagger c_k \right] \]  \hspace{1cm} (2.4)

which accounts for the electron exchange between the ion and the metal. The \( V_k(x) \) are the corresponding matrix elements which depend on the distance \( x \) from the metal surface.

In considering the solvent and its interaction with the ion, we follow ideas familiar from electron transfer theory [14] and distinguish between fast (electronic) and slow solvent modes. The former are assumed to be instantaneous and incorporated in the electronic energy \( e_{\alpha} \). The slow solvent modes are represented as a collection of harmonic oscillators; their interaction with the reactant is assumed to be linear and proportional to the charge. Thus \( H_{\text{sol}} \) reads:

\[ H_{\text{sol}} = \frac{1}{2} \sum_v \hbar \omega_v (p_v^2 + q_v^2) + (z - n_{\alpha}) \sum_v \hbar \omega_v g_v(x)q_v \]  \hspace{1cm} (2.5)

The first term denotes the unperturbed solvent; \( q_v \) and \( p_v \) are the dimensionless coordinates and momenta, \( \omega_v \) the frequencies and \( v \) labels the solvent modes. The second term accounts for the interaction; \( z \) is the charge number of the ion (i.e. \( z = 1 \) for univalent metal cations) and the \( g_v(x) \) are the coupling constants. They depend on the distance \( x \) to account for a change in solvation as the ion approaches the surface (see below).

It is possible to derive an expression for the ground-state potential energy surface from the above Hamiltonian. We refer the interested reader to the literature [12,13] and simply state the final result:
\[ V(q,x) = \tilde{e}_a(q,x)n_a(q,x) + \Delta(x) \ln \left( \frac{\tilde{e}_a^2(q,x) + \Delta^2(x)}{\tilde{e}_a(q,x) - U_x^2} + \lambda(x)q^2 \right) + 2\pi \lambda(x)q - V_{\text{int}}(x) - z\tilde{e}_a(x) - zF(x)\Delta\phi \]

In Eq. (2.6), the various symbols have the following meaning:

- \( \Delta(x) = 2\pi \sum_k |V_k(x)|^2 \delta(\omega - \varepsilon_k) \) is the broadening of the ion’s orbital energy, due to the electronic interaction with the metal states \( k \). It is assumed to be independent of the energy \( \omega \). Quantum-chemical calculations indicate that this interaction falls off approximately exponentially with the distance \( x \) from the electrode [9], so that we have taken \( \Delta(x) = \Delta_0 \exp(-x/l) \), with \( l = 1 \) Å.

- \( q = q_r/g_s \) where \( q \) is equal to the (fractional) charge on the reactant.

- \( n_\text{c}(q,x) = (1/\pi) \arccot(\varepsilon_0(q,x)/\Delta(x)) \) is the occupation probability of the reactant orbital.

- \( U_x \) is the energy of the bottom of the conduction band. Its exact value is immaterial; in all that follows we have taken it to be -12 eV.

- \( \lambda(x) = \sum_s \hbar \omega_s g_s^2(x)/2 \) is the distance-dependent solvent reorganization energy. Its bulk value is estimated as the slow part of the ion’s solvation energy, i.e. \( \lambda(x) = - (\varepsilon_\text{opt}^1 - \varepsilon_\text{opt}^-1)(1 - \varepsilon_\text{opt}^-1)\Delta G_\text{solv}(M^+) \). \( \varepsilon_\text{opt}^1 \) and \( \varepsilon_\text{opt}^-1 \) are the optical and static dielectric constants of the solvent, and for practically all solvents the quantity \( (\varepsilon_\text{opt}^1 - \varepsilon_\text{opt}^-1) \approx 0.5 \): \( \Delta G_\text{solv}(M^+) \) is the real Gibbs solvation energy of the ion, values for which were taken from Ref. [15]. Molecular dynamics simulations show that the solvent’s potential of mean force depends on the distance from the electrode surface; the ion has to overcome a solvent barrier in order to adsorb onto the metal [16,17]. One can take this important effect into account by introducing a distance-dependent solvation energy [9]. In previous work, we based the parametrization of the distance dependence on molecular dynamics simulations for an iodide ion adsorbing onto Pt and Hg electrodes, for which it was found that the interaction energy of the adsorbed iodide ion with water is about half the bulk value [16–18]. However, this factor of one half is not universal; for smaller ions, one generally finds that the solvation energy barrier for adsorption onto the mercury is smaller, presumably because smaller ions can displace more easily adsorbed water molecules [18,19]. We have therefore chosen the following form for the distance dependence:

\[ \lambda(x) = \lambda(\infty)(\xi + (1 - \xi)p(x/L)) \]

where \( \xi \) is the fraction of the bulk solvation energy that the ion experiences in the adsorbed state (so \( \xi = 0.5 \) for iodide), and \( p(x) \) is an interpolating function given by

\[ p(x) = \begin{cases} (3 - 2x)x^2 & \text{for } 0 \leq x \leq 1 \\ 1 & \text{for } x > 1 \end{cases} \]

\( L \) is the distance at which \( \lambda \) reaches its bulk value, taken to be 4 Å.

- \( \lambda(x) \) is the fast part of the distance-dependent solvation energy. Its bulk value is estimated as \( \lambda_\text{b}(\infty) = - (1 - \varepsilon_\text{opt}^1)/\varepsilon_\text{opt}^1\Delta G_\text{solv}(M^+) \), its distance dependence has the same form as Eq. (2.7).

- \( V_{\text{int}}(x) \) is the image interaction of the core of the reactant with the electrode. We have used the classical form of the image law with a distance-dependent dielectric constant as specified in Ref. [9].

- \( F(x)\Delta\phi \) is the electrostatic potential in the electric double layer. \( \Delta\phi = (E - E_{\text{pzc}}) \) is the electrode potential with respect to the potential of zero charge. In most of our calculations, \( E = E_{\text{eq}} = E^0 \). \( F(x) \) models the distribution of the potential in the double layer region. As a rough estimate we have assumed a linear drop of the potential between the metal surface and the outer Helmholtz plane which is at \( x = L \).

- \( \tilde{e}_a = \varepsilon_a - 2\pi(x)q \) is the renormalized electronic energy of the ion’s orbital. \( \varepsilon_a = -I + \Phi + \Delta\psi_{\text{M,solv}} + \lambda(x) + \varepsilon_{\text{in}}(x) + F(x)\Delta\phi \), where \( I \) is the ionization energy of \( M \), \( \Phi \) is the work function of mercury (4.49 eV), \( \Delta\psi_{\text{M,solv}} \) is the change in the surface dipole potential at the mercury|solute interface, due to changes in both the metal and solvent surface dipole potentials as a consequence of the presence of the other phase. The quantity \( \Phi + \Delta\psi_{\text{M,solv}} \) may be viewed as the ‘electrochemical work function’, or as the potential of zero charge on the vacuum or absolute scale [20]. Since the experimental pzc for mercury|water is -0.273 V vs SHE, and we take the absolute standard potential of the SHE as 4.44 eV [21], one has \( \Delta\psi_{\text{Hg/H}_2\text{O}} \approx -0.34 \text{ V} \). \( \varepsilon_{\text{in}}(x) \) is the image interaction of the electron with the mercury electrode.

Using literature values for the various parameters, one can calculate the potential energy surface (PES) for the transfer of the univalent cation as a function of the solvent coordinate \( q \) and the distance from the electrode \( x \). From the shape of the PES one can make conclusions about the relative importance of electron and/or ion transfer in the electrode reaction under study. This application of the model has been illustrated in Refs. [9,10]. The only important unknowns are \( \Delta_0 \) and \( \tilde{e}_a \), two quantities that have to be obtained from quantum-chemical and molecular dynamics or Monte Carlo simulations, respectively. They have not yet been calculated for most systems, but from the available results for other ions one can make reasonable guesses. In the following two subsections, we discuss the PES for the thallium and potassium reduction (the latter as a representative of the alkalis), for which the model suggests different mechanisms, as explained below. The various parameter values are given in Table 1 and in the figure captions.
Table 1

<table>
<thead>
<tr>
<th>M</th>
<th>$-\Delta G_{\text{hyd}} (M^+)/eV$</th>
<th>$I_V/eV$</th>
<th>$E_{\text{M}^+/\text{M(Hg)}}^0/eV$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>3.557</td>
<td>6.108</td>
<td>-0.294</td>
</tr>
<tr>
<td>K</td>
<td>3.505</td>
<td>4.341</td>
<td>-1.975</td>
</tr>
</tbody>
</table>

We remark that all PES shown below (Figs. 1, 2 and 4–6) were calculated at the equilibrium potential of the overall reaction (M$^{n+}$ (aq)/M(Hg)). The figures, however, do not show the final state, i.e. the metal atom dissolved in the mercury, since our model does not treat the amalgamation step. This state has the same energy as the initial state M$^{n+}$ (aq), which is the energy of the M$^{n+}$ ion at infinite separation. The difference in energy between M in the mercury and M in the solution is therefore exactly the sublimation energy plus a correction for the different standard potentials for M$^{n+}$ (aq)/M(Hg) and M$^{n+}$ (aq)/M (see Eq. (3.5) below), as we are assuming that the solvation energy of M is negligible. Separate reaction steps, such as the transfer of the ion to the surface of the mercury electrode, are therefore not in their proper equilibrium at the equilibrium potential of the total reaction, but the combination of overall equilibrium and detailed balancing guarantees us that all the required equilibrium relationships between forward and back rate constants are satisfied.

2.2. Thallium reduction

The thallium reduction from aqueous solution has been studied extensively by the Sluyters group [24–26]. The reaction is found to be fast ($k = 1.2$ or even $\sim 10$ cm s$^{-1}$), the transfer coefficient is approximately 0.5, and it is found from the impedance data that weak reactant adsorption accompanies the reaction. From their data, the authors cannot decide whether the adsorbed species is an intermediate in the electron transfer process.

Fig. 1 shows the potential energy surface and the corresponding contour plot calculated with our model for the Tl$^{+}$ reduction at the equilibrium potential. This figure was calculated with the ‘iodide value’ of $\bar{\zeta} = 1/2$. Note that the reaction coordinate is mainly in the $x$-direction; electron transfer to form a Tl species, at whatever location in the double layer, is extremely unlikely. For this value of $\bar{\zeta}$, the activation energy for ion transfer is 0.68 eV, with a partial charge of 0.94 in the saddle point; for a larger value of $\bar{\zeta}$ (which, as mentioned, seems more appropriate for ions smaller
than iodide), say 0.75, the activation energy is reduced to 0.17 eV and the saddle point partial charge is 0.96.

From these calculations, we are led to propose the following mechanism:

\[ \text{Tl}^+ + \delta e^- \rightarrow \text{Tl}_{\text{ads}}^{(1-\delta)} + \]
\[ \text{Tl}_{\text{ads}}^{(1-\delta)} + (1 - \delta)e^- \rightarrow \text{Tl} \hspace{1pt} (\text{Hg}) \]  

(2.9)

i.e. an ion transfer (with partial charge transfer), followed by an amalgamation step through which the thallium dissolves as a completely discharged species.

We cannot decide which of the two is rate determining, as we have no model for the amalgamation process. However, from the mere fact that weak reactant adsorption is found in the experiments, we deduce that the amalgamation process is an activated process. It seems likely that the ion transfer is also an activated process, and if it is rate determining, then from the experimental rate constant we estimate from transition state theory [11] that the activation energy would be \( \sim 0.17 \text{ to } 0.23 \text{ eV} \), favouring the higher value of \( \xi \) mentioned in the previous paragraph. We do note, however, that a higher value of the electronic interaction \( \Delta_0 \) (2 eV in Fig. 1) would also lead to a lower activation energy.

Hence our model suggests that the thallium reduction involves a partially discharged adsorbed intermediate. In general, the experimental interpretation of data only very rarely takes into account the possibility of partially charged adsorbed intermediates. Although it adds another adjustable parameter to the interpretation of the data, it is a physical reality which would follow from any microscopic model which properly incorporates the basic quantum mechanics of the system (though it should be remarked that in a complete quantum-mechanical treatment the definition of partial charge is not as unambiguous as in our model). Finally, we note that a mechanism through which a short-lived thallium atom is formed in the solution, which then rapidly penetrates the double layer and amalgamates, is very unlikely on energetic grounds.

2.3. The reduction of alkali ions

The reduction of alkali ions is quite different from that of thallium because their equilibrium potentials lie far below the potential of zero charge (pzc) of mercury. This means that there is a strong field in the double layer, which will have an effect on the potential energy surface for the ion transfer process. This is illustrated in Fig. 2, which shows the potential energy surface for the potassium reduction both at the potential of zero charge and at the equilibrium potential. Although quantitatively these surfaces are caricatures of reality, they serve to illustrate one important point: that at the equilibrium potential the ion transfer solvation barrier is strongly reduced by the high electric field, which attracts the ion towards the surface. For an equilibrium potential of \( \sim -2.0 \text{ V} \) and a double layer thickness of \( \sim 4 \text{ Å} \), one estimates a field of \( \sim 4.109 \text{ V m}^{-1} \). Molecular dynamics simulations of iodide transfer at the Pt-water interface also indicate that at such high fields the barrier for ion transfer is significantly reduced [17].

Hence for alkali reduction reactions, we may propose a similar mechanism as for thallium,

\[ M^+ + \delta e^- \rightarrow M_{\text{ads}}^{(1-\delta)} + \text{ (fast)} \]
\[ M_{\text{ads}}^{(1-\delta)} + (1 - \delta)e^- \rightarrow M \hspace{1pt} (\text{Hg}) \text{ (rate determining)} \]  

(2.10)

but now with the explicitly mentioned expectation that the amalgamation process is rate-determining. The ion transfer step is expected to be fast because of the abovementioned field assistance. This mechanism is in contrast with the mechanisms proposed by Baranski and Fawcett [27,28]. They found that the rate of the amalgam forming reduction reactions of the alkali ions correlates with the solvation energy of the ion in a particular solvent. Hence they concluded that the ion transfer process must be rate determining. However, we believe it is quite likely that the rate of the second step would also show a correlation with the ion’s solvation energy, certainly if one considers that the intermediate in our mechanism is partially charged and therefore has a strong interaction with the solvent.

2.4. Further remarks

From the above, we are led to classify the reduction of univalent ions on mercury into two groups having different mechanisms: those occurring close to the mercury’s pzc (Tl\(^+\), Cu\(^+\)) for which we expect a mechanism in which both the ion transfer (with partial charge transfer) and the amalgamation can be rate determining, and those occurring far negative from the pzc (the alkalis) for which we expect the ion transfer to be strongly field-assisted, and hence fast.

It is very difficult to design unequivocal experimental kinetic criteria to decide between the two classes. As mentioned above, the solvent dependence of the reduction rate of the alkalis has been interpreted by Fawcett and coworkers [27,29] to be evidence for the ion transfer being rate determining, but it seems that such a statement remains unsettled as long as we have no model for the amalgamation reaction, a process which one can reasonably expect to depend on the nature of the solvent as well. We are not aware of an experimental study reporting the solvent dependence of the thallium reduction, although such a study would seem worthwhile. The Cu\(^+\) reduction has been studied only in acetonitrile [30], as in other solvents it tends to be unstable. We note that opposing trends have been observed in the influence of the size of cation of the
supporting electrolyte on the rate of Cu\(^{+}\) reduction and the alkali metal reductions. Fawcett and Foss suggest that the double-layer effects reverse when the electrode potential is made more negative. An alternative explanation could make use of our model’s suggestion that the nature of the rate-determining step changes as the electrode potential is made more negative. Of course, it then remains to be explained why the size of the base electrolyte cation has opposing effects, which themselves may involve an element of arbitrariness and are not always very reliable). As we pointed out before [11], this \(x\) is to be interpreted as the fraction of the double layer potential being passed by the ion as it moves from the reaction plane to the \(x\)-location of the saddle point of the PES (see Fig. 1), disregarding partial charge transfer to the saddle point. There is no reason why this formula is that we do not expect this quantity to be close to 0 or 1.

We believe that the only useful remark that can be made about this formula is that we do not expect this to be close to 0 or 1.

As a final remark about \(x\), we stress that in our model for ion transfer \(x\) cannot be related to the classical Marcus-Hush theory of electrochemical electron transfer reactions [32–34], as has been done by some authors. The key concept is that as the ion moves towards the metal surface, there is partial electron exchange with the electrode. There is no location in the double layer where the ion all of sudden takes up one entire electron. Our potential energy surfaces show that this would be very unfavourable energetically.

### 3. Reduction of divalent cations

#### 3.1. The model

When considering the transfer of two electrons to a divalent cation,

\[
M^{2+} + 2e^- \rightarrow M(Hg)
\] (3.1)

one has to consider the spin of the electrons [10]. The Hamiltonian now has to account for the spin states \(\sigma\) of the electron, and for the Coulombic repulsion \(U\) when two electrons of opposite spin occupy the reactant’s orbital:

\[
H_e + H_{\text{int}} = \sum_{a} \varepsilon_a n_{aa} + U n_{aa} n_{a\sigma} + \sum_{k,a} \varepsilon_k n_{ka} \\
+ \sum_{k,a} [V_k(x) c_k^a c_k^\sigma + V_k^* c_k^\sigma c_k^a] \tag{3.2}
\]

The solvent part of the Hamiltonian does not change; one only has to replace \((z - n_a)\) in Eq. (2.5) by \((z - \Sigma_{a} n_{aa})\).

In the Hartree-Fock approximation, the expression for the potential energy surface now becomes

\[
V(q,x) = \sum_{\sigma} \left\{ \varepsilon_{\text{int}}(q,x) n_{\sigma\sigma} (q,x) + \frac{\Delta(x)}{2\pi} \ln \left( \frac{\tilde{\varepsilon}_{\text{int}}(q,x) + \Delta(x)^2}{\tilde{\varepsilon}_{\text{int}}(q,x) - \Delta(x)^2} \right) \\
- Un_{\sigma\sigma} + \lambda(x)q^2 + 2z\lambda(x)q - V_{\text{int}}(x)q \\
- z^2\dot{\lambda}(x) - zF(x)\Delta \phi \right\}
\] (3.3)

where \(n_{\sigma\sigma}\) now denotes the occupation probability of the spin state \(\sigma\), given by \(n_{\sigma\sigma} = (1/\pi) \arccot [\tilde{\varepsilon}_{\text{int}}(q,x)/\Delta(x)]\). The expression for \(\tilde{\varepsilon}_{\text{int}}(q,x)\) is:

\[
\tilde{\varepsilon}_{\text{int}}(q,x) = -I_2 + \Phi + \Delta \psi_{M_{\text{solv}}} + 3(\dot{\lambda}(x) + \varepsilon_{\text{int}}(x)) - 2\lambda(x)q \\
+ Un_{\sigma\sigma} + F(x)\Delta \phi \tag{3.4}
\]

where \(U = I_2 - I_1 - 2\lambda(x) + \varepsilon_{\text{int}}(x)\), with \(I_1\) and \(I_2\) the first and second ionization energies of M, respectively.

Note that in contrast to the one-electron model of the previous section, this potential energy surface has to be calculated self-consistently.
The reorganization energies $\lambda$ and $\lambda_{e}$ are again estimated from the real solvation energies of the doubly-charged species $\Delta G_{\text{solv}}^{e}(M_{2}^{+})$, given in Table 2. The employed relations are

$$\lambda(\infty) = -\left(\epsilon_{\text{opt}}^{1} - \epsilon_{s}^{1}\right) + \frac{1}{(1 - \epsilon_{s}^{1})}\Delta G_{\text{solv}}^{e}(M_{2}^{+})/z_{2}^{2}$$

and

$$\lambda_{e}(\infty) = -\left(\epsilon_{\text{opt}}^{1} - \epsilon_{s}^{1}\right) + \frac{1}{(1 - \epsilon_{s}^{1})}\Delta G_{\text{solv}}^{e}(M_{2}^{+})/z_{2}^{2}.$$ 

Note that this means that we estimate the real solvation energy of the singly-charged species by $\Delta G_{\text{solv}}^{e}(M^{+}) = \Delta G_{\text{solv}}^{e}(M_{2}^{+})/4$. That this assumption presumably underestimates the real solvation energy of the singly-charged species can be illustrated by comparison to the solvation energies of the Cu$^{2+}$ and Cu$^{2+}$ ions, the only metal for which both values are available [15]: $\Delta G_{\text{solv}}^{e}(\text{Cu}^{2+}) = 0.2726 \Delta G_{\text{solv}}^{e}(\text{Cu}^{+}) = 0.25 \Delta G_{\text{solv}}^{e}(\text{Cu}^{2+}) - 0.489$ eV. Although 0.2726 is quite close to 0.25, the absolute energy difference still amounts to about half an electronvolt, which can be quite substantial, considering the subtracting and adding in the Born-Haber relationships.

### 3.2. Classification of two-electron transfer reactions

We suggest a first classification of two-electron transfer reactions based on their equilibrium PES along the $q$-coordinate far from the electrode surface at the standard equilibrium potential of the $M^{2+}/M$ couple. Our classification is based on the relative energy levels of the species with integer charge far from the electrode surface. In all cases given in Table 2, the energies of the $M^{+}$ and $M$ species (in solution) are higher than that of the $M^{2+}$ species. Since the energy of $M$(Hg) is equal to that of $M^{2+}$ in the solution, this also implies that $V_{M} - V_{M^{+}} > V_{M}(\text{Hg})$. For the energy differences, one derives that

\[ V_{M} - V_{M^{2+}} = \Delta G_{\text{solv}}^{e} + 2\left(E_{M^{2+}/M}^{0} - E_{V_{M^{2+}/M}}^{0}\right) \]

and

\[ V_{M} - V_{M^{2+}} = -I_{2} + \frac{3}{4}\Delta G_{\text{solv}}^{e}(M^{2+}) + \phi_{M^{2+}/M}^{0} + (E_{M^{2+}/M}^{0} - E_{V_{M^{2+}/M}}^{0}) \]

where

\[ \phi_{M^{2+}/M} = \frac{1}{2}\left[\Delta G_{\text{solv}}^{e}(M^{2+}) + \Delta G_{\text{solv}}^{e}(M) + I_{1} + I_{2}\right] \]

In our classification, class I is defined by $V_{M} < V_{M^{+}}$, class II by $V_{M} > V_{M^{+}}$ (see Fig. 3). According to our model, Zn, Cd, Mg and Hg belong to class I, all the others in Table 2 to class II.

![Fig. 3. Classification of two-electron transfer reactions at their standard equilibrium potentials.](image)
3.3. $\text{Zn}^{2+}/\text{Zn(Hg)}$ couple

The PES for this class I reaction is given in Fig. 4. On the basis of this PES, one may suggest two different mechanisms, in both of which the first step is a one-electron transfer to the $\text{Zn}^{2+}$ species.

Mechanism 1:

\[ \begin{align*}
\text{Zn}^{2+} + e^- &\rightarrow \text{Zn}^+ \\
\text{Zn}^+ + \delta e^- &\rightarrow \text{Zn}^{(1-\delta)+} \\
\text{Zn}^{(1-\delta)+} + (1-\delta)e^- &\rightarrow \text{Zn}^{(Hg)}
\end{align*} \tag{M-1} \]

Mechanism 2:

\[ \begin{align*}
\text{Zn}^{2+} + e^- &\rightarrow \text{Zn}^+ \\
\text{Zn}^+ + e^- &\rightarrow \text{Zn}
\end{align*} \tag{M-2} \]

(ET = electron transfer, IT = ion transfer, AC = amalgamation of a charged species, AN = amalgamation of a neutral species). Clearly our model does not allow us to decide which of the two mechanisms would be the most probable.

It follows from the phenomenological theory of multistep reactions [35] that the rate-determining step in a mechanism is not the reaction with the highest Gibbs activation energy, but rather that step in which the highest point of the potential curve is passed. On the basis of the PES shown in Fig. 4, we therefore expect that in both mechanism 1 and 2 (Eqs. (M-1) and (M-2)) the first two steps have comparable rates at equilibrium. Application of a cathodic overpotential $\eta$ would shift the $\text{Zn}^+$-channel upward by $\eta$, and the $\text{Zn}^{2+}$-channel by $2\eta$, so that at sufficiently high overpotential one expects the first electron transfer step to become rate determining.

Qualitatively, these conclusions are in excellent agreement with the mechanism suggested by Andreu et al. [36] for the $\text{Zn}^{2+}$ reduction from aqueous solutions. From their measurements they find a Tafel plot which can be fitted very well to the above two-step electron-transfer mechanism 2 (Eq. (M-2)) with the transfer coefficients for the separate steps being ca. 0.4–0.5 [36,37]. Of course, mechanism 1 (Eq. (M-1)) can give the same fit, but with a reinterpretation of the nature of second step. At high overpotentials, the data suggest that the first step becomes rate determining.

Quantitatively, however, there are dismaying differences that cannot be swept under the carpet. If the first step is electron transfer, then in our model it would follow that the transfer coefficient must be larger than 0.5 (experimentally, one usually works with the quantity $x_e = (RT/nF)\ln k/dE$, which must then be larger than 0.25). This is because the $\text{Zn}^+$ species is a metastable intermediate of high energy, making the first ET step an almost barrierless process. Barrierless ET has a transfer coefficient of 1. For the PES in Fig. 4, we calculate $x_1 = 0.76$. The second ET step tends towards an activationless process, therefore $x_2 < 0.5$; the PES in Fig. 4 gives $x_3 = 0.41$. Secondly, the activation energy for the first ET step is very high in our model, ca. 1.56 eV. This would imply an adiabatic transition-state theory (TST) rate constant of ca. $10^{-21}$ cm s$^{-1}$ [12], very much smaller than the experimental rate constant of $10^{-3}$ cm s$^{-1}$. Unfortunately, we can only speculate about the origin of this large difference. For one thing, the difference is too large to be explained by inaccuracies in the Born-Haber cycle, or by inaccuracies in our assumption about the solvation energy of the $\text{M}^+$ species. If we assume that $\Delta G_{solv}^r(\text{Zn}^+)$ = 0.2726 $\Delta G_{solv}^r(\text{Zn}^{2+})$, as for copper, the activation energy becomes 1.22 eV and the rate constant $10^{-15}$ cm s$^{-1}$. We do note that our estimate for the reorganization energy for the $\text{Zn}^{2+} + e^- \rightarrow \text{Zn}^+$ reaction is 2.6 eV, implying a TST rate constant of ca. $10^{-5}$ cm s$^{-1}$ at the equilibrium potential of the $\text{Zn}^{2+}/\text{Zn}^+$ couple. This would agree considerably better with experiment if the equilibrium potentials of the $\text{Zn}^{2+}/\text{Zn}^+$ and $\text{Zn}^{2+}/\text{Zn}^{(Hg)}$ couples were close, which would require a solvation energy of $\text{Zn}^+$ of −6.88 eV, an unreasonably low value for a singly-charged ion. The explicit inclusion of inner-sphere modes, quantum effects and/or a non-symmetric shape of the PES would be able to account for only a small part of the difference. It is to be noted, however, that our estimate for the activation energy is based on bulk properties. Quantum-chemical calculations and molecular dynamics simulations of multiply charged species near electrode surfaces, preferably in the presence of a base electrolyte, are very rare, but clearly desirable in order to resolve this point. Furthermore, one cannot exclude the possibility of more specific chemical steps, possibly associated with ion pairing or complex formation. Andreu et al. [36] have postulated the presence of a chemical step prior to the first ET step, based on their finding that the rate depends on the water activity, which is changed experimentally by the concentration of the $\text{NaClO}_4$ base.
electrolyte. They were led to the conclusion that the species directly participating in the reaction is less hydrated than the primary reactant, and therefore ascribe this chemical step to a 'partial dehydration step'. That the concentration of the base electrolyte might affect the reaction rate beyond the usual double layer corrections, was not considered. Recent MD simulations, however, have reported an effect of the counter-ion on the potential energy surface [38] of an electrochemical electron-transfer reaction. A further alternative involves the assumption that the first step in the zinc reduction involves ion transfer. This can be achieved in our model by a higher value of $\zeta$ or $\Delta_0$. A specific example will be worked out in the next section on the lead couple.

Fawcett, Lasia and Bouderbala [39,40] have studied the zinc reduction at mercury from dimethylformamide and dimethylsulfoxide solutions. The rate is higher in DMF, which may be explained by the lower solvation energy in DMF. From the potential dependence of the rate, Fawcett and Lasia derive that the reaction involves two or more steps, but they emphasize that from their data alone it is difficult to decide between a mechanism involving only ET steps and a mechanism including IT step(s). Strong double layer effects, brought about by changing the size of the base electrolyte’s cation, are generally found, which are usually interpreted by Fawcett and coworkers in terms of the influence they have on the ion transfer rate.

Much of the story for zinc also applies to the other class I systems such as cadmium. Saakes et al. [41] have interpreted their kinetic data in aqueous solutions in terms of alternating chemical and electron-transfer steps, whereas Fawcett [42] and Lasia and Brisard [43], who carried out measurements in dimethylformamide and dimethylsulfoxide, also included the possibility of ion-transfer steps. As mentioned repeatedly, it is difficult to design unequivocal criteria to decide between the proposed mechanisms.

3.4. Pb$^{2+}$/Pb(Hg) couple

A typical example of a class II system in our model is lead reduction. A PES for the ‘iodide value’ $\zeta = 0.5$ is given in Fig. 5. Since in class II systems the M state lies higher in energy than the M$^+$ state, we derive that IT is a more likely second step than ET, so that our mechanism is ET-IT-AC:

$$\text{Pb}^{2+} + e^- \rightarrow \text{Pb}^+$$
$$\text{Pb}^+ + \delta e^- \rightarrow \text{Pb}_{\text{ads}}^{(\delta-\delta)}$$

$\text{Pb}_{\text{ads}}^{(\delta-\delta)} + (1 - \delta)e^- \rightarrow \text{Pb(Hg)}$

(M-3)

Again, this mechanism predicts that the transfer coefficient for the first step is larger than 0.5; for this particular example, one finds $\alpha_1 = 0.71$. Also, the TST rate for the first step is very low.

As was noted in Section 2.1, MD simulations indicate that for ions smaller than iodide, the ion transfer barrier is generally smaller [18,19], and hence the geometric factor $\zeta$ closer to 1. Also, as the solvation energy of Pb$^{2+}$ is about 5 eV smaller than that of, e.g. Zn$^{2+}$, a higher value of $\zeta$ will more readily give rise to a smaller ion transfer barrier. In Fig. 6, we show the PES for the Pb$^{2+}$/Pb(Hg) couple for $\zeta = 0.8$. An important change in the qualitative features of the PES is observed. The energetically most favourable path now involves ion transfer of the doubly-charged species:

$$\text{Pb}^{2+} + \delta e^- \rightarrow \text{Pb}_{\text{ads}}^{(\delta-\delta)}$$
$$\text{Pb}_{\text{ads}}^{(\delta-\delta)} + (2 - \delta)e^- \rightarrow \text{Pb(Hg)}$$

(M-4)

i.e. an IT-AC mechanism. The activation energy for the first step is 0.58 eV (TST rate constant $\sim 10^{-5}$ cm s$^{-1}$) for $\zeta = 0.8$, and 0.27 eV (TST rate constant $\sim 1$ cm s$^{-1}$) for $\zeta = 0.85$. This illustrates how sensitive the ion transfer rate is to our model parameter $\zeta$. We note that a stronger electronic coupling parameter $\Delta_0$ also leads to a lower activation energy. For $\zeta = 0.8$, the activation

Fig. 5. Potential energy surface of the Pb$^{2+}$/Pb(Hg) couple at the standard equilibrium potential. The ionic radius of Pb$^{2+}$ was taken 1.20 Å; $\zeta = 0.5$.

Fig. 6. Potential energy surface of the Pb$^{2+}$/Pb(Hg) couple at the standard equilibrium potential. The ionic radius of Pb$^{2+}$ was taken 1.20 Å; $\zeta = 0.8$. 
energy decreases from 0.58 to 0.48 eV by increasing $\Delta_0$ from 2 to 4 eV. It is to be remarked that the values for the ion transfer barrier are also quite sensitive to the models employed for the image interaction and the double-layer potential profile. Therefore the quantitative value of these numbers should not be taken too literally.

At this point, it is opportune to make a comment about the likelihood of the amalgamation step being fast or slow in a two-electron transfer reaction. As we showed in Section 3.3, the energies of the $M^+$ and $M$ species in solution are higher than that of the $M(Hg)$ by at least 0.5 eV (except for mercury) and in most cases by even more than 1 eV. This implies that the amalgamation of these species, or of absorbed intermediates related to these species, are likely to be (strongly) exothermic. The Brönsted-Polanyi relationship then suggests that these processes, as occurring in mechanisms M-1, M-2 and M-3 (Eqs. (M-1), (M-2) and (M-3)), are likely to be relatively fast. In contrast, our model does not predict the energy of the $Pb^{2+}$ species occurring in mechanism M-4 (Eq. (M-4)) to be much higher than that of the $Pb^{2+}$ species in solution, even if the extent of discharge is high. In fact, it rather predicts it to be lower. Therefore, the amalgamation step in mechanism M-4 (Eq. (M-4)) is predicted to be endothermic (or at least not strongly exothermic) in our model and therefore relatively slow.

In aqueous solutions, lead reduction is known to be a fast reaction [44], ca. 1 cm s$^{-1}$. In KNO$_3$, the experimental transfer coefficient is close to 1 [45], suggesting that a final potential-independent step is rate determining. At lower overpotentials, there are also indications for a slow preceding chemical step. However, in KNO$_3$ solutions stable PbNO$_3^{2-}$ species exist, so that our model calculations cannot be directly applied to this experimental situation.

Fawcett and Yee [46,47] have studied the lead reduction at mercury from dimethylformamide solutions. The reaction is considerably slower than from aqueous solutions, with a standard rate constant of ca. $10^{-4}$ cm s$^{-1}$. This rate constant is still too high to be explained by a Marcus-type ET reaction. Fawcett and Yee come to the same conclusion on the basis of their temperature-dependent measurements, from which they estimate the activation enthalpy. The experimental transfer coefficient decreases quite significantly with potential. Fawcett and Yee come to the conclusion that lead reduction in DMF involves ion transfer steps.

Finally, a few words about other class II systems. The Sn$^{2+}$ reduction is a very fast reaction in aqueous solutions (ca. 1 cm s$^{-1}$) [48], which seems to imply the involvement of ion transfer. In contrast, the Co$^{3+}$, Ni$^{2+}$ and Fe$^{2+}$ reductions are very slow, rate constants ranging from $10^{-8}$ to $10^{-2}$ cm s$^{-1}$ [44]. It is interesting to note that it is exactly these three metals which show a poor solubility in mercury [52]. In terms of our model, it is tempting to suggest that these ions have a high ion transfer barrier and that electron transfer is rate determining.

4. Discussion and conclusion

In this paper, we have attempted to formulate a microscopic model for the amalgam forming reduction reactions of uni- and divalent cations. The main advantage of our model over previous phenomenological models is that on the basis of thermodynamic, quantum-chemical and molecular dynamics data, one can calculate, in principle, the potential energy surface of the reaction and predict the mechanism of the reaction. By applying reaction rate theories, one can calculate reaction rate constants. The model also accounts for the quantum-mechanical nature of the transferred electron(s), that is, it allows for the sharing of the electron between the reduct species and the metal, a feature which is missing in most of the previous treatments.

Another advantage of our model is that it suggests a classification of amalgam forming electrode reactions. For univalent cations, our model suggests different mechanisms for couples having their standard equilibrium potential close to the pzc, and couples having their standard equilibrium potentials far below the pzc. In the case of the latter class (the alkalis), we deduced that the rate-determining step is most likely the amalgamation of a partially charged adsorbed intermediate, whereas for the former class, the preceding ion transfer may also be rate determining. As for the alkalis, it is fair to note that this conclusion is in contradiction with the existing interpretation of the experimental data. For the divalent cations, we also suggested a classification which is based on the relative energy levels of the species with integer charge. This classification is probably less useful, since it has nothing to say about the ion-transfer characteristics of the system, whereas a comparison of the theoretical and experimental data seems to indicate the importance of considering ion transfer steps.

Our model also points out certain problems or inconsistencies in previous phenomenological treatments. It is often assumed in multistep schemes with several electron-transfer steps that the transfer coefficients of the individual ET steps are equal to 0.5, with a reference to the Marcus theory as a justification [5]. However, such schemes often involve metastable species of high energy, and the Marcus theory predicts that an ET step giving rise to such a metastable species involves a transfer coefficient close to 1 (barrierless ET), whereas ET to such a species has a transfer coefficient close to 0 (activationless ET). This crucial result of the Marcus-Levich-Dogonadse theory is hardly ever incorporated
in the interpretation of kinetic data of two-electron transfer reactions (for other references on the theory of two-electron transfer reactions (see Refs. [49–51]).

Many previous workers have attempted to relate the rate of amalgam forming electrode reactions with certain physicochemical properties of the ion, solvent or ion-solvent system. For instance, Tamamushi [52] found a (weak) correlation between the reduction rate of the ion and the solubility of their metal atoms in mercury. In his plot, both uni-, di- and trivalent species are included. Tamamushi found no significant correlation when plotting the rate constant against the Gibbs energy of hydration or the exchange rate of water of the metal ion. By comparing rates in various different solvents, Broda and Galus [53] and Fawcett [29] have searched for correlations in the solvent dependence of ion transfer rates. It is generally found that the logarithm of the rate follows an approximately linear relationship with the ion’s solvation energy. Fawcett [29], applying results from stochastic reaction rate theories [1,12], postulated that the longitudinal dielectric relaxation time may have an influence on the pre-exponential factor of the ion transfer rate. Unfortunately, there are too few data points for the correlation to be convincing. Although there is experimental and theoretical evidence that the longitudinal dielectric relaxation time influences electron-transfer rates [1], it is unclear whether the longitudinal dielectric relaxation time is really the quantity determining the friction that the ion experiences during its movement through the double layer. Theories of bulk ion transfer suggest that for large ions, it is rather the solvent’s viscosity, whereas for smaller ions, it is the solvent’s Debye dielectric relaxation time [54]. Partial charge transfer during the ion transfer may further complicate the relationship between solvent properties and ion transfer rate [1,12].

If there is one main conclusion to be drawn from this paper, it is unfortunately a rather negative one, namely that amalgam forming electrode reactions are still poorly understood on the microscopic level. Our model can be only a modest first step towards a more realistic picture. Especially our inability to reconcile the experimental reduction rates of two-electron transfer reactions involving amalgam formation with the Marcus TST theory seems to be a major lack in understanding. A combination of Born-Haber cycles and Marcus theory predicts that the \( \text{M}^{2+} + \text{e}^- \rightarrow \text{M}^+ \) reaction at the equilibrium potential of the overall \( \text{M}^{2+} | \text{M} | \text{Hg} \) reaction must be extremely slow, and have a transfer coefficient substantially larger than 0.5. Experimentally, the (overall) reduction rate is measurable, and often even very fast. One way out is to assume that ion transfer is involved. It is clear that more elaborate and detailed computer simulations, which can also take into account the more strongly bound first solvation sphere of divalent transition-metal ions, are needed in order to gain further insight on this point.

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References