THERMIONIC EMISSION OF ELECTRONS AS AN INTERMEDIATE STEP IN THE CATHODIC EVOLUTION OF HYDROGEN FROM A BASIC SOLUTION

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From a study of the kinetics of hydrogen evolution from basic solutions on metals with high overvoltages and from a study of the decomposition of amalgams of alkali metals, it has been concluded that these processes can proceed by two mechanisms: an electrochemical one, i.e., by the attachment of an electron to an adsorbed water molecule; and a chemical one, i.e., by the interaction of the alkali metal, formed during the cathodic polarization of the amalgam, with water, without separation of the cathodic and anodic processes [1-5]. At pH > 10, the chemical mechanism is observed on mercury, and the electrochemical mechanism is observed on gallium [6]. Indium amalgams are an intermediate case: the electrochemical mechanism, observed at potentials which are not too negative, is replaced by a chemical mechanism when the polarization is increased [7]. Recently, in connection with the discovery of solvated electrons during the radiolysis of aqueous solutions, it has been suggested that the first process during the cathodic polarization is the thermionic emission of electrons into the solution [8, 10]. The solvated electrons thus formed then react with water, and hydrogen is evolved. The recently derived quantitative theory of the photoemission of electrons into electrolytic solutions, which has received experimental support [11-13], permit us to determine how well these ideas agree with experimental data, since the work function of a metal in contact with an aqueous solution can be determined from measurements of the photoeffect. At the zero charge potential of mercury, this work function is 3.2 ±0.1 V; at a potential of φ_0 with respect to the zero charge potential of mercury, this value is $(3.2 + \varphi_0)$ V. Significantly, this quantity does not depend on the nature of the metal [12-15] at a given potential with respect to a constant comparison electrode,* so it cannot change when an amalgam of an alkali metal is formed during cathodic polarization. It follows from this value of the work that the thermionic emission current for emission from a metal into an electrolyte is

$$i_e = k_e 10^{-(3.4 \pm 0.1 + \varphi)F/(2.3RT)}, \quad (1)$$

where the potential φ is reckoned from the zero charge potential. As an upper estimate of the constant k_e, expressed in current-density units, we can use the Sommerfeld emission constant (multiplied by the square of the absolute temperature), which gives, conditionally, the number of electron collisions with the wall in the metal-box model. The corresponding quantity should be increased by about an order of magnitude, however, because of the special behavior of electrons at a metal–electrolyte interface [11]. Accordingly, we obtain the value $(10^2\text{-}10^3)T^2$ A/cm^2.

The maximum value of the logarithm of the current density, for an electrochemical process in which thermionic emission of electrons into an aqueous solution is an intermediate step, is given by

$$\lg i_e < 3 + 2\lg T - (3.4 \pm 0.1 + \varphi)F / (2.3RT); \quad (2)$$

at 20°C (with φ in volts and i_e in amperes per square centimeter), we have

*We will not discuss here all the reservations which should be made for the case of dilute electrolytic solutions [13] and for the case of an essentially nonspherical Fermi surface.

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$$\lg i_e < -51 \mp 1 - \varphi / 0.058. \quad (2a)$$

It follows from Eq. (2a) that the currents i_e are many orders of magnitude below those observed experimentally. For the case of hydrogen evolution on mercury from a basic solution by the electrochemical mechanism, e.g., the constant a in the Tafel equation would be 1.7 V, so that

$$\varphi = -1.7 - 0.82 - 0.116 \lg i = -2.52 - 0.116 \lg i, \quad (3)$$

from which we find that $\varphi = -2.52$ V when $i = 1$ A/cm^2. According to Eq. (2a), we have $i_e < 10^{-8.5}$ at this potential, i.e., almost nine orders of magnitude lower. Because of the difference between the coefficients of log i and i_e (0.116 and 0.058 respectively), the discrepancy is even greater when a comparison is made at a less negative φ. The highest overvoltage for hydrogen evolution on mercury has been observed in a 0.1 N solution of $N(C_4H_9)_4OH$ [16]. The reaction occurs by an electrochemical mechanism, and the transfer coefficient is $\alpha \approx 0.43$; this contradicts the assumption of thermionic emission of electrons as an intermediate step. The value of a in this case is 2.27 V, from which we find a value of -3.03 V for φ at $i = 1$ A/cm^2. According to Eq. (2a), the thermionic-emission current at this value of φ could approach this value. In this case, however, the value obtained from Eq. (2a) for the thermionic-emission current should probably be reduced, because of the hydrocarbon film which forms on the surface in the presence of $N(C_4H_9)_4^+$ cations [17]. In any case, the thermionic-emission current, could, in principle, reach this observed value only for the reaction cited above (which is the limiting case in terms of overvoltage, in aqueous solutions).

The thermionic emission of electrons and the evolution of hydrogen by the electrochemical mechanism show significantly different behavior. In the first case, when the potential is shifted in the cathodic direction by $|\Delta\varphi|$, the activation energy is reduced by $F|\Delta\varphi|$; in the second case, it is reduced by $\alpha F|\Delta\varphi|$, where $\alpha \approx 1/2$. The rate of water-molecule discharge depends significantly on the nature of the metal; for liquid gallium, i.e., for which this value has been reliably determined [6], it is four orders of magnitude higher than the corresponding value calculated for mercury. Accordingly, thermionic emission of electrons is not an intermediate step in hydrogen evolution from a basic solution when this evolution occurs by an electrochemical mechanism.

Actually, as was mentioned above, hydrogen evolves from a basic solution at a mercury electrode not by an electrochemical mechanism, but by a chemical mechanism. Hydrogen evolution by the chemical mechanism appears at first glance to behave in a manner similar to that of thermionic emission. For example, the rate of this process at a given value of φ depends little on the nature of the metal, in several cases. The rate of hydrogen evolution at a ternary amalgam, containing indium and an alkali metal, does not depend on the indium concentration and is almost independent of the nature of the alkali metal [4]. The rate at which the amalgam of an alkali metal not containing indium decomposes at a given potential is also only slightly dependent on the nature of the alkali metal. When the potential is shifted in the cathodic direction by $|\Delta\varphi|$, and if this shift is caused by a change in the concentration of the alkali metal, the activation energy for this process, like that of thermionic emission of electrons, is reduced by an amount close to $F|\Delta\varphi|$. However, this similarity goes no further. If a potential change at the amalgam–solution interface occurs, not because of a change in the concentration of the alkali metal at the mercury, but because of the change in the concentration of Me^+ ions in the solution, this change will not affect the decomposition kinetics of the amalgam. In other words, the rate of hydrogen evolution during the chemical decomposition of amalgam, in contrast with the case of thermionic emission of electrons, is governed, not by the potential drop at the amalgam–solution interface, but by the activity of the metal dissolved in the mercury. The difference between the two mechanisms is observed most clearly in a comparison of the rates of the two reactions. The numerical data on the chemical mechanism have been obtained over the widest range of current densities from polarization measurements in solutions of LiOH, NaOH, and KOH on indium amalgams [4, 5]. These results can be described by

$$\varphi = a - b \lg i, \quad (4)$$

where $a \simeq -2.5$ V (s.c.e.), and b is equal to or slightly greater than 2.30 RT/F. For LiOH solutions, we have $a = -2.50$ V and $b = 0.059$ V. This relation also describes approximately data on the decomposition of lithium amalgam not containing indium. After a conversion to express potentials in terms of the zero charge potential, we find

$$\lg i = (-2.22 - \varphi) / 0.059, \quad (4a)$$

from which, at $\varphi = -2.252$ V, e.g., we find log i = 5.1. Thus the decomposition rate of amalgam by the chemical mechanism is roughly 15 orders of magnitude greater than the value which could be realized through an intermediate thermionic emission of electrons.

One can, in principle, imagine another mechanism for the transfer of an electron from the metal to the solution, during which a solvated electron would be formed directly; i.e., an electron would appear in a trap formed by oriented water molecules. No experimental data referring to this mechanism have been reported. A rough estimate, based on the value of the total hydration energy of an electron given by Baxendele, 1.75 V [18], leads to a work function of 2.5 V at the zero charge potential [14]. However, the increase in the rate due to the reduction of the work function is largely balanced by a reduction in the preexponential coefficient by a factor of 10^{3n}, where $10^3 \approx M/m_e$ (m_e/M is the ratio of the electron mass to that of the proton) is raised by a power of $n \geqslant 3$, corresponding to the degree of nonadiabaticity of the electronic transitions directly into the solvated state. In any case, a mechanism involving this direct formation of a solvated electron as an intermediate step cannot compete with a mechanism involving a direct electrochemical reaction, which would have a larger preexponential factor and a smaller energy barrier, unless some additional special assumptions are made.

This conclusion has been strengthened by the fact that such a direct formation of a solvated electron has not been observed during photoemission experiments [12]. Furthermore, since the rate of this process should increase more slowly as the potential is made more negative than follows from Eq. (1) (with a transfer coefficient of $\alpha \approx 1/2$), there is no basis for assuming that this process can compete with thermionic emission of electrons in this case, and there is even less basis for assuming it can compete with electrochemical or chemical reactions. We conclude that the formation of a solvated electron is not an intermediate step during hydrogen evolution from an aqueous basic solution. However, an extension of this conclusion to the case of nonaqueous solutions, particularly ammonia solutions, would not be justified without a corresponding comparison of the rate constants and parameter changes.

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