

Determination of the entropy of formation of the Pt(111) | perchloric acid solution interface. Estimation of the entropy of adsorbed hydrogen and OH species

Nuria Garcia-Araez · Victor Climent · Juan M. Feliu

Received: 9 January 2007 / Accepted: 25 May 2007 / Published online: 19 September 2007
© Springer-Verlag 2007

Abstract The entropy of formation of the interface between a Pt(111) electrode and a 0.1-M HClO₄ solution is calculated here for the first time from the temperature dependence of total charge vs potential curves following a thermodynamic analysis based on the electrocapillary equation. From this quantity, the absolute entropies of specifically adsorbed species (hydrogen and OH) can be estimated. The present method is an alternative treatment of data that overcomes some of the limitations involved in the approach that uses a generalized isotherm. However, it requires additional experimental data: the temperature coefficient of the potential of zero total charge of the working electrode and the temperature coefficient of the reference electrode. Comparison of the results obtained by both approaches shows that, for hydrogen adsorption, the agreement is reasonable, but the differences are larger for OH adsorption, thus showing the limitations inherent in the treatment based on the generalized isotherm.

Keywords Pt(111) electrode · Entropy of formation of the interface · Gibbs thermodynamics · Hydrogen adsorption · Hydroxyle adsorption

Introduction

The temperature dependence of electrode processes provides unique information about the electrochemical interface. Furthermore, the knowledge of the temperature coefficient of interfacial properties (differential capacity, potential of zero charge) is of undoubted importance for testing the validity of metal|solution interface models because the temperature coefficients are more sensitive to structural details of the interface than the parameters themselves. In this respect, apart from the classical works with mercury electrodes [1–3], the high-quality work by Silva and coworkers on the gold single-crystal|solution interface should be mentioned [4–6].

Comparatively few studies deal with temperature effects in the platinum|solution interface. Apart from the problems derived from its higher reactivity, the occurrence of charge transfer adsorption phenomena (in the following, CTA) complicates the interpretation of the experimental results. Consequently, the temperature coefficient of the pure double-layer differential capacity or the potential of zero free charge are not thermodynamically available, while the study of the entropy changes associated to CTA processes is not straightforward.

Several studies have analyzed the temperature effect of CTA processes on platinum surfaces using a generalized adsorption isotherm. The work of Conway et al. [7] deserves special attention because the standard entropies of hydrogen adsorption in different states on platinum polycrystalline electrodes were evaluated in solutions of different composition and pH and compared with statistical mechanics calculations. A similar approach was used in Jerkiewicz and Zolfaghari [8, 9], Gomez et al. [10], and Climent et al. [11] with platinum single-crystal electrodes,

Dedicated to Professor Oleg Petrii on the occasion of his 70th birthday on August 24, 2007.

N. Garcia-Araez · V. Climent · J. M. Feliu (✉)
Instituto Universitario de Electroquímica,
Universidad de Alicante, Apartado 99,
03080 Alicante, Spain
e-mail: juan.feliu@ua.es

and the analysis was extended to the calculation of enthalpy changes, which were compared with energetic parameters in the platinum|gas interface. One limitation of this thermodynamic analysis is that a Langmuirian type of isotherm is implicitly assumed [12], and, therefore, this treatment might not be adequate in the presence of coadsorption phenomena or other kinds of isotherms [13]. In addition, the coverages are usually calculated from coulometric data obtained from the integration of voltammograms, assuming a constant double-layer capacity (corrected as a straight baseline) and a constant value of the electrosorption valency, considered equal to the charge of the adsorbing species in solution.

In this paper an alternative method that overcomes the above-mentioned limitations is proposed. The benefits of this new approach are analogous to those of the thermodynamic method to determine Gibbs excesses from the analysis of the dependency of voltammetric data on the chemical potential of the adsorbing species, which overcomes the method of integration of voltammograms with an arbitrary correction of double-layer contributions and the assumption of a given number for the electrosorption valency (see, for example, Herrero et al. [14]). The present analysis is based on the concept of entropy of formation of the interface, introduced by Harrison, Randles, and Schiffrin [1] as the difference in entropy of the components of the interface when they are forming part of it and when they are present in the bulk of their respective phases. This property can be calculated up to a constant of integration from the temperature coefficient of the electrode potential at a constant charge. These data can be obtained from experiments performed either in a nonisothermal cell (i.e., the reference electrode is maintained at a constant temperature) with a further correction for the thermodiffusion potential or in an isothermal cell (i.e., with the reference electrode at the same temperature as the working electrode) with a correction for the temperature coefficient of the potential of the reference electrode. In the present paper, experimental data corresponding to an isothermal cell will be used and the temperature coefficient of the reversible hydrogen electrode (RHE) will be taken from Debethune et al. [15].

The formalism of the entropy of formation of the interface was successfully applied to mercury electrodes [1]. The entropy of formation of the mercury–solution interface showed a maximum at potentials lower than the potential of zero charge, this fact being explained by a preferential orientation of water molecules with the oxygen towards the metal in the absence of the electric field. Thus, negative charge is needed to overcome this specific interaction and to achieve the maximum disorder in the water adlayer. The same methodology was later applied

to Au single-crystal electrodes, obtaining similar results [6, 16].

The application of the concept of the entropy of formation of the interface to platinum electrodes presents the complication of the occurrence of specific adsorption processes involving (partial) charge transfer (CTA). This contribution can be avoided with the use of nanosecond laser pulses, the effect of which is to increase the interfacial temperature in the submicrosecond time scale [16, 17]. Under particular selected conditions, CTA processes are too slow to contribute to the response of the electrode towards the laser heating, and hence, the measured response is only due to purely double-layer phenomena. Then, the temperature coefficient of the double-layer, $\left(\frac{\partial \Delta_S^M \phi}{\partial T}\right)_{\sigma, T}$, can be determined, and this property can be used to calculate the entropy of formation of the double-layer. Conversely, in the time scale of the acquisition of voltammograms, specific adsorption processes contribute to the measured charge and differential capacity. Then, if equilibrium conditions are attained in this time scale, the temperature coefficient of the potential drop at the interface at a constant total charge $\left(\frac{\partial \Delta_S^M \phi}{\partial T}\right)_Q$ can be determined from the integration of the temperature-dependent voltammograms, provided that the temperature coefficient of the potential of zero total charge (PZTC) is known. For this last quantity, the results of the CO displacement method may be used, further corrected for the residual charge density on the CO-covered electrode, as explained by Weaver [18]. Then, the entropy of formation of the interface, which includes double-layer contributions (coming from the metal, the water adlayer, or the diffuse double layer) and contributions of specific adsorption processes, can be determined from the integration of $\left(\frac{\partial \Delta_S^M \phi}{\partial T}\right)_Q$ with the total charge density, up to a constant of integration.

Finally, the entropy of formation of the interface can be used to estimate the absolute entropies of specifically adsorbed hydrogen and OH. However, it will be shown that the contribution of double layer changes taking place during the adsorption process cannot be separated from these quantities. For the calculation, Gibbs excess values of hydrogen and OH determined from a thermodynamic analysis of the dependency of voltammetric features on the bulk pH solution [19] and tabulated values of individual ionic entropies in solution [7] will be used. Comparison with entropy terms of hydrogen and OH adsorption obtained by the application of the generalized isotherm will be made.

Theory

In the following, the derivation given by Harrison et al. [1] will be extended to a situation with CTA processes. The

starting point of the thermodynamic analysis is the Gibbs equation for an interface:

$$-d\gamma = \sum_i \Gamma_i d\bar{\mu}_i + \Gamma_S dT \tag{1}$$

where γ is the interfacial tension, Γ_i and $\bar{\mu}_i$ are the Gibbs excess and electrochemical potential of species i , Γ_S is the entropy of the real system minus that of the ideal Gibbs system per unit surface, and T is the temperature. For the interface between a platinum electrode and a perchloric acid solution, one has to consider the equilibrium of adsorption of hydrogen and OH species and water dissociation:

$$\bar{\mu}_{H^+} + \bar{\mu}_{e^-} = \mu_H \tag{2}$$

$$\bar{\mu}_{OH^-} = \mu_{OH} + \bar{\mu}_{e^-} \tag{3}$$

$$\bar{\mu}_{H^+} + \bar{\mu}_{OH^-} = \mu_{H_2O} \tag{4}$$

Taking into account the above relationships, the Gibbs equation can be rewritten as:

$$\begin{aligned} -d\gamma = & -\left(\frac{\sigma_M}{F} - \Gamma_H + \Gamma_{OH}\right) d\bar{\mu}_{e^-} \\ & + (\Gamma_H + \Gamma_{H^+} - \Gamma_{OH} - \Gamma_{OH^-}) d\bar{\mu}_{H^+} \\ & + \Gamma_{ClO_4^-} d\bar{\mu}_{ClO_4^-} + \Gamma_S dT \\ & + (\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-}) d\mu_{H_2O} + \Gamma_M d\mu_M \end{aligned} \tag{5}$$

where σ_M is the actual charge density on the metal: $\sigma_M = -F\Gamma_{e^-}$. At this point, we will separate the chemical and the electrical contributions from the electrochemical potentials and introduce the electroneutrality condition:

$$\begin{aligned} -d\gamma = & Qd\Delta_S^M\phi - \frac{Q}{F}d\mu_{e^-} \\ & + (\Gamma_H + \Gamma_{H^+} - \Gamma_{OH} - \Gamma_{OH^-})d\mu_{H^+} \\ & + \Gamma_{ClO_4^-}d\mu_{ClO_4^-} + \Gamma_S dT \\ & + (\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-})d\mu_{H_2O} + \Gamma_M d\mu_M \end{aligned} \tag{6}$$

where $\Delta_S^M\phi$ is the potential difference through the interface and $Q = \sigma_M - F\Gamma_H + F\Gamma_{OH}$ is the total charge density. Next, the two remaining dependent variables can be eliminated through the Gibbs–Duhem equations for the solution and metal phases:

$$d\mu_M = -\bar{S}_M dT + \bar{V}_M dP \tag{7}$$

$$d\mu_{H_2O} = -\frac{\bar{S}_{sol}}{\chi_{H_2O}} dT + \frac{\bar{V}_{sol}}{\chi_{H_2O}} dP - \sum_{j \neq H_2O} \frac{\chi_j}{\chi_{H_2O}} d\mu_j \tag{8}$$

obtaining that:

$$\begin{aligned} -d\gamma = & Qd\Delta_S^M\phi - \frac{Q}{F}d\mu_{e^-} + \Gamma_{H,H_2O}d\mu_{H^+} \\ & + \Gamma_{ClO_4^-,H_2O}d\mu_{ClO_4^-} + \Gamma_{S,H_2O,M}dT \\ & - \Gamma_{V,H_2O,M}dP \end{aligned} \tag{9}$$

where:

$$\Gamma_{S,H_2O,M} = \Gamma_S - (\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-}) \frac{\bar{S}_{sol}}{\chi_{H_2O} + \chi_{OH^-}} - \Gamma_M \bar{S}_M \tag{10}$$

$$\Gamma_{V,H_2O,M} = -(\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-}) \frac{\bar{V}_{sol}}{\chi_{H_2O} + \chi_{OH^-}} - \Gamma_M \bar{V}_M \tag{11}$$

$$\Gamma_{ClO_4^-,H_2O} = \Gamma_{ClO_4^-} - (\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-}) \frac{\chi_{ClO_4^-}}{\chi_{H_2O} + \chi_{OH^-}} \tag{12}$$

$$\begin{aligned} \Gamma_{H,H_2O} = & \Gamma_H + \Gamma_{H^+} - \Gamma_{OH} - \Gamma_{OH^-} \\ & - (\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-}) \frac{\chi_{H^+} - \chi_{OH^-}}{\chi_{H_2O} + \chi_{OH^-}} \\ = & \Gamma_H + \Gamma_{H^+} - (\Gamma_{OH} + \Gamma_{OH^-}) \frac{\chi_{H_2O} + \chi_{H^+}}{\chi_{H_2O} + \chi_{OH^-}} \\ & - \Gamma_{H_2O} \frac{\chi_{H^+} - \chi_{OH^-}}{\chi_{H_2O} + \chi_{OH^-}} \end{aligned} \tag{13}$$

At a constant solution composition and pressure, taking into account that $d\mu_i = -\bar{S}_i dT$, the Gibbs equation can be rewritten as:

$$-d\gamma = Qd\Delta_S^M\phi + \left(\frac{Q}{F}\bar{S}_{e^-} - \Gamma_{H,H_2O}\bar{S}_{H^+} - \Gamma_{ClO_4^-,H_2O}\bar{S}_{ClO_4^-} + \Gamma_{S,H_2O,M}\right) dT \tag{14}$$

Using Parsons function to change the independent variable, and after cross-differentiation, one obtains:

$$\begin{aligned} & \left[\frac{\partial \left(\Gamma_{S,H_2O,M} - \Gamma_{ClO_4^-,H_2O}\bar{S}_{ClO_4^-} - \Gamma_{H,H_2O}\bar{S}_{H^+} \right)}{\partial Q} \right]_{T,P,a_{HClO_4}} \\ & + \frac{1}{F}\bar{S}_{e^-} = - \left(\frac{\partial \Delta_S^M\phi}{\partial T} \right)_{Q,P,a_{HClO_4}} \end{aligned} \tag{15}$$

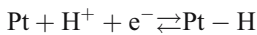
The entropy of formation of the interface is defined as the difference in the entropy of the elements when they are forming part of it and when they are present in the bulk of

their respective phases. Consequently, in the absence of CTA processes:

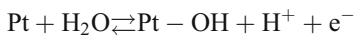
$$\Delta S_{dl} = \Gamma_S - \Gamma_{e^-} \bar{S}_{e^-} - \sum_i \Gamma_i \bar{S}_i - \Gamma_{H_2O} \bar{S}_{H_2O} - \Gamma_M \bar{S}_M \quad (16)$$

The term corresponding to the entropy of electrons was explicitly neglected in Harrison et al. [1] for the mercury|solution interface. However, the definition given in Eq. 16 is more appropriate because electrons are involved in the formation of the interface, and therefore, Γ_S will include the corresponding contribution [20].

In the presence of CTA processes, the above definition of the entropy of formation of the interface is inappropriate. To properly include the contributions of these processes to ΔS , one has to take into account that the CTA of hydrogen involves the consumption of protons from the solution and electrons from the metal:



Hence, the corresponding term in the definition of the entropy of formation of the interface is $\Gamma_H (\bar{S}_{H^+} + \bar{S}_{e^-})$. Analogously, the CTA of OH involves the water and proton species in solution and electrons in the metal:



Hence, the corresponding term is $\Gamma_{OH} (\bar{S}_{H_2O} - \bar{S}_{H^+} - \bar{S}_{e^-})$. Consequently, a more adequate definition of the entropy of formation of the platinum|perchloric acid solution interface is:

$$\begin{aligned} \Delta S = & \Gamma_S + \frac{Q}{F} \bar{S}_{e^-} - (\Gamma_H + \Gamma_{H^+}) \bar{S}_{H^+} \\ & - (\Gamma_{OH} + \Gamma_{OH^-}) (\bar{S}_{H_2O} - \bar{S}_{H^+}) - \Gamma_{ClO_4^-} \bar{S}_{ClO_4^-} \\ & - \Gamma_{H_2O} \bar{S}_{H_2O} - \Gamma_M \bar{S}_M \end{aligned} \quad (17)$$

The above definition reflects the well-known fact that it is not possible to thermodynamically distinguish the specific adsorption of hydrogen (OH) from the nonspecific adsorption of proton (hydroxide) species [21]. As a result, the terms involved in the definition of ΔS are the total charge density and sum of the Gibbs excesses of proton and hydrogen (hydroxide and OH), while the microscopic magnitudes (the actual Gibbs excess of electrons, protons, hydrogen, hydroxide, and OH species) are beyond the thermodynamic framework.

Taking into account Eqs. 10, 12, and 13 and the following expression for the entropy of the solution,

$$\bar{S}_{sol} = \chi_{H_2O} \bar{S}_{H_2O} + \chi_{OH^-} \bar{S}_{OH^-} + \chi_{H^+} \bar{S}_{H^+} + \chi_{ClO_4^-} \bar{S}_{ClO_4^-}, \quad (18)$$

the entropy of formation of the interface Eq. 17 can be rewritten as a function of the thermodynamic available magnitudes:

$$\begin{aligned} \Delta S = & \Gamma_{S,H_2O,M} + \frac{Q}{F} \bar{S}_{e^-} - \Gamma_{H+H^+,H_2O} \bar{S}_{H^+} \\ & - \Gamma_{ClO_4^-,H_2O} \bar{S}_{ClO_4^-} \end{aligned} \quad (19)$$

Furthermore, the combination of this result with Eq. 15 gives:

$$\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{a_{HClO_4}, P, Q} = - \left(\frac{\partial \Delta S}{\partial Q} \right)_{a_{HClO_4}, P, T} \quad (20)$$

Similar results can be obtained introducing into Eq. 14 the equilibrium condition for the RHE reference electrode:

$$\bar{\mu}_{H^+} + \bar{\mu}_{e^-}^R = \frac{1}{2} \mu_{H_2} \quad (21)$$

$$\Delta_S^M \phi^{RHE} = \frac{\mu_{H^+} + \mu_{e^-}^R - \frac{1}{2} \mu_{H_2}}{F} \quad (22)$$

Following a similar derivation as above one obtains:

$$\begin{aligned} \left(\frac{\partial \Delta S}{\partial Q} \right)_{a_{HClO_4}, P, T} - \frac{1}{F} \bar{S}_{e^-} - \frac{1}{F} \bar{S}_{H^+} + \frac{1}{2F} \bar{S}_{H_2} \\ = - \left(\frac{\partial E^{RHE}}{\partial T} \right)_{Q, P, a_{HClO_4}} \end{aligned} \quad (23)$$

where $E^{RHE} = \Delta_S^M \phi - \Delta_S^M \phi^{RHE}$. It should be noted that, in the above equation, the chemical potentials of the electrons in the working and the reference electrodes have been considered identical because both electrodes are made of the same material. It can be easily shown that Eqs. 15 and 23 become identical if the temperature coefficient of RHE is introduced. This quantity corresponds to the entropy change of the reaction of the reference electrode, which can be obtained by differentiation of Eq. 22 with the temperature:

$$\frac{d \Delta_S^M \phi^{RHE}}{dT} = \frac{1}{2F} \bar{S}_{H_2} - \frac{1}{F} \bar{S}_{H^+} - \frac{1}{F} \bar{S}_{e^-} = \frac{\Delta \bar{S}_{RHE}}{F}. \quad (24)$$

Experimental

The Pt(111) working electrode was prepared from a single crystal platinum bead oriented, cut, and polished down to 0.25 μm with diamond paste as described elsewhere [22]. Special care was taken to use a particular electrode with a small amount of surface defects that, in a 0.1-M HClO_4 solution, causes the appearance of peaks in the CV at ~ 0.11 and ~ 0.27 V (RHE). Before each experiment, the electrode was annealed and cooled down in hydrogen + argon

reductive atmosphere (N-50, Air Liquide) as described by Rodes et al. [23].

A two-compartment, all-Pyrex electrochemical cell was used. The electrochemical cell was immersed in a water bath whose temperature was controlled within ± 0.1 K by a thermostat (Haake FK). The temperature in the water bath was measured with a platinum resistance thermometer (± 0.1 K, Crison 638Pt). The experiments were carried out at six temperatures between 273 and 323 K at intervals of 10 K. All potentials were measured against a RHE immersed in the same working solution and at the same temperature as the working electrode (the so-called isothermal configuration). A coiled Pt wire was used as a counter electrode.

Aqueous solutions were prepared from concentrated HClO_4 (Merck Suprapur) and ultrapure water from a Millipore system (MilliQ plus 185). The electrochemical instrumentation consisted of an EG&G PAR Model 175 universal programmer, an AMEL 551 potentiostat, and a Philips PM 8133 X-Y recorder. After digitalization, the numerical treatment of the data was performed with the help of software packages Microcal Origin© 6.1 and Mathcad© Professional 2001.

Results

Evaluation of the absolute entropy terms of adsorbed hydrogen and OH species

Figure 1a shows the voltammetric profiles of a Pt(111) electrode in 0.1 M HClO_4 at six different temperatures between 273 and 323 K at intervals of 10 K. The reference electrode is a RHE maintained at the same temperature as the working electrode. Figure 1b plots the same experimental data in a potential scale where the reference electrode is a RHE at 298 K for all cases. To perform this correction, the temperature coefficient of the RHE must be known. From potential measurements of nonisothermal cells, Debethune et al. determined the temperature coefficient of the RHE in 0.1 M HCl ($+0.640$ mV/K) [15]. We will take this value for the RHE in 0.1 M HClO_4 , considering that the substitution of chloride by perchlorate anions does not significantly change the activity coefficients and that chloride is not specifically adsorbed at the RHE. Another way to estimate this thermal coefficient would be from values of individual ionic entropies. This

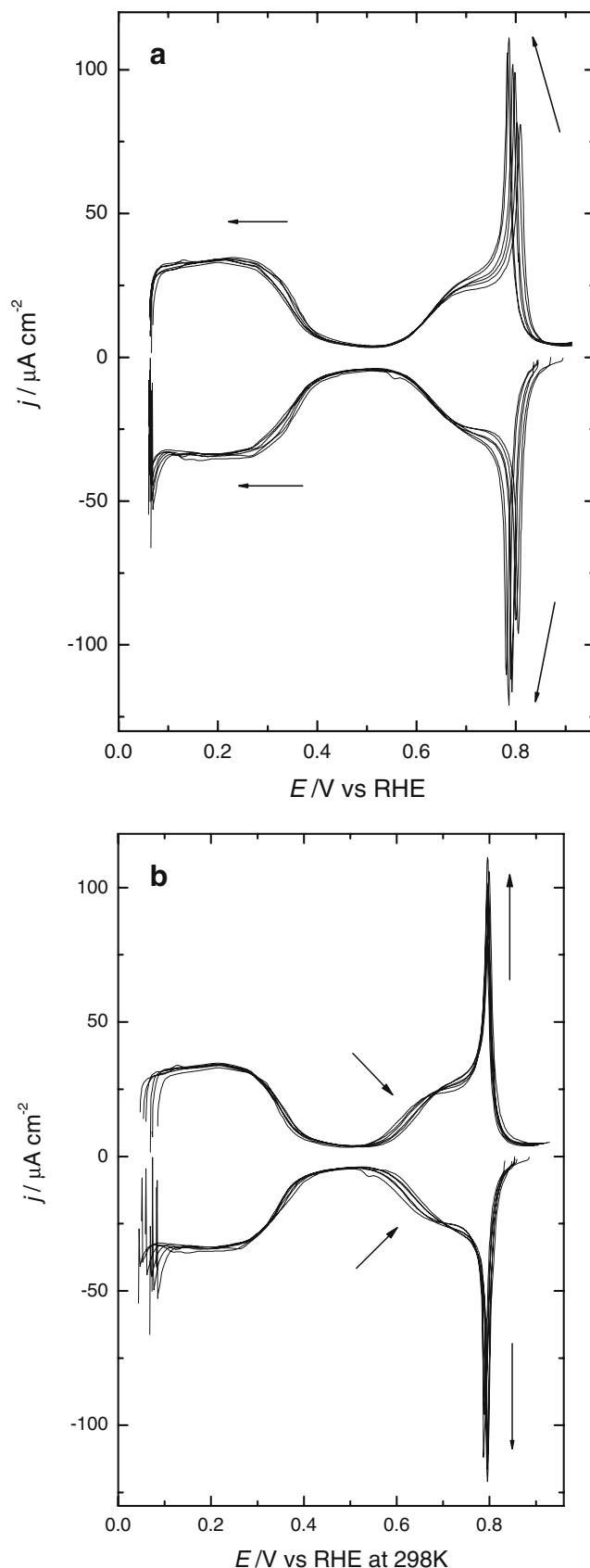


Fig. 1 Voltammograms of a Pt(111) electrode in 0.1 M HClO_4 at six different temperatures between 273 and 323: **a** in an isothermal cell, **b** after correction of the thermal coefficient of the reference electrode. Scan rate: 50 mV/s. The arrows indicate the effect of increasing the temperature

gives a temperature coefficient of the standard hydrogen electrode of +0.840 mV/K [7], a value very close to the extrapolation of the results in Debethune et al. [15] to unit activity of the proton ions (+0.871 mV/K), demonstrating that both values are reliable and that chloride adsorption at the RHE is negligible.

Integration of voltammograms of Fig. 1a and b provides the total charge density curves corresponding to an isothermal and nonisothermal cell, respectively, as long as the temperature-dependent PZTC is determined by an independent method. For this, the results of the CO displacement method at different temperatures will be used. Therefore, the conclusions obtained in the present analysis will be affected by the uncertainty of the CO displacement technique in the determination of the PZTC, as discussed in Weaver [18]. To estimate the effect of this inaccuracy, we will compare the results obtained from the raw experimental data of potential of zero CO displaced charge, with those corrected for the remaining charge density on the CO-covered electrode as explained in Weaver [18]. For this correction, an approximate value of the potential of zero charge of the CO-covered electrode is estimated from measurements performed in Ultrahigh vacuum. This correction involves a small charge density ($\sim 10 \mu\text{C}/\text{cm}^2$), which produces a small displacement of the PZTC ($\sim 30 \text{ mV}$), and hence, it is expected to cause only small changes in the results of the analysis. On the other hand, we will assume that this correction remains constant in the temperature range from 273 to 323 K. Consequently, the effect of this correction in the charge density curves would be a constant displacement on the charge density scale of $\sim 10 \mu\text{C}/\text{cm}^2$. The results are plotted in Fig. 2. It is worth noting that, after the conversion to a constant reference electrode, the temperature dependence of the charge density curves is greatly diminished in the hydrogen adsorption region and in the completion of OH adlayer region (the so-called butterfly), while it is notably increased in the double-layer region and the onset of OH adsorption.

To calculate the temperature coefficient of the potential of the electrode, one should take horizontal sections in Fig. 2b and plot the potential at a constant charge as a function of the temperature. Figure 3 shows the results of this plot at selected charge densities, together with the fit to a first-order polynomial, for data corresponding to a constant-temperature reference electrode. The plots are fairly linear and the slopes give the temperature coefficient

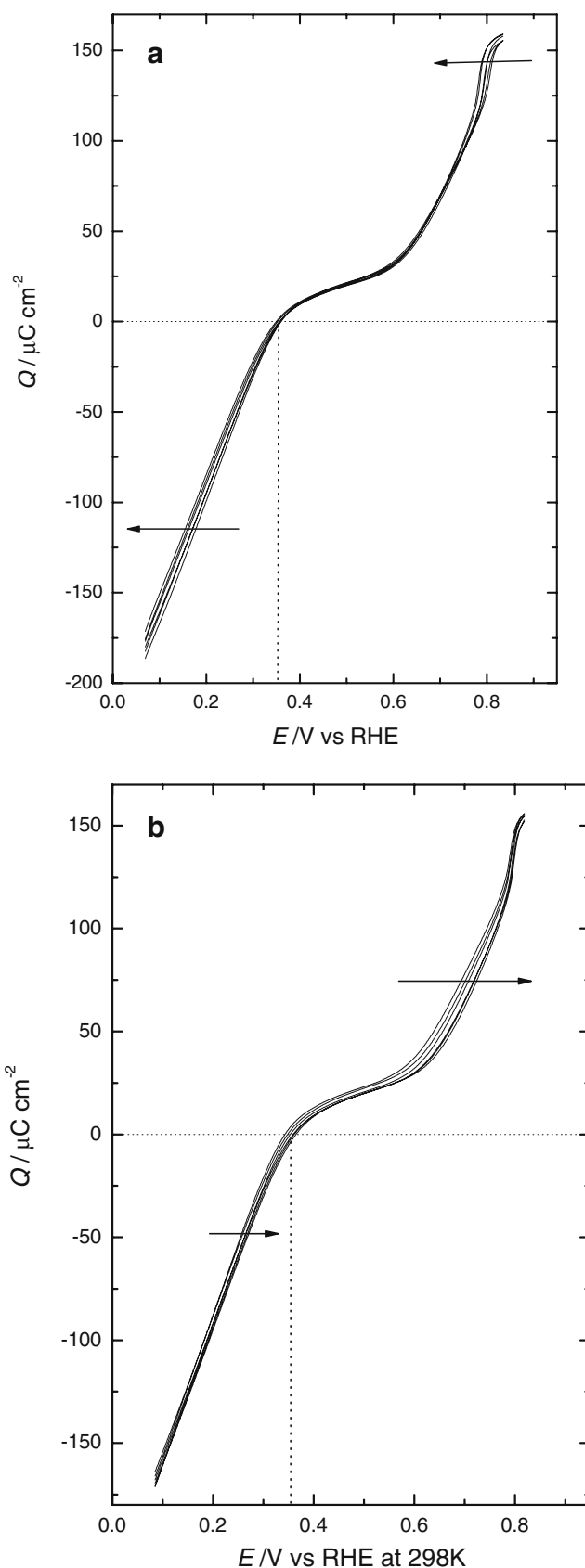


Fig. 2 Charge density plots as obtained from the integration of voltammograms of Fig. 1a (a) and b (b), using as the integration constant the PZTC obtained from CO displacement, corrected from the remaining charge on the CO covered electrode. The arrows indicate the effect of increasing the temperature

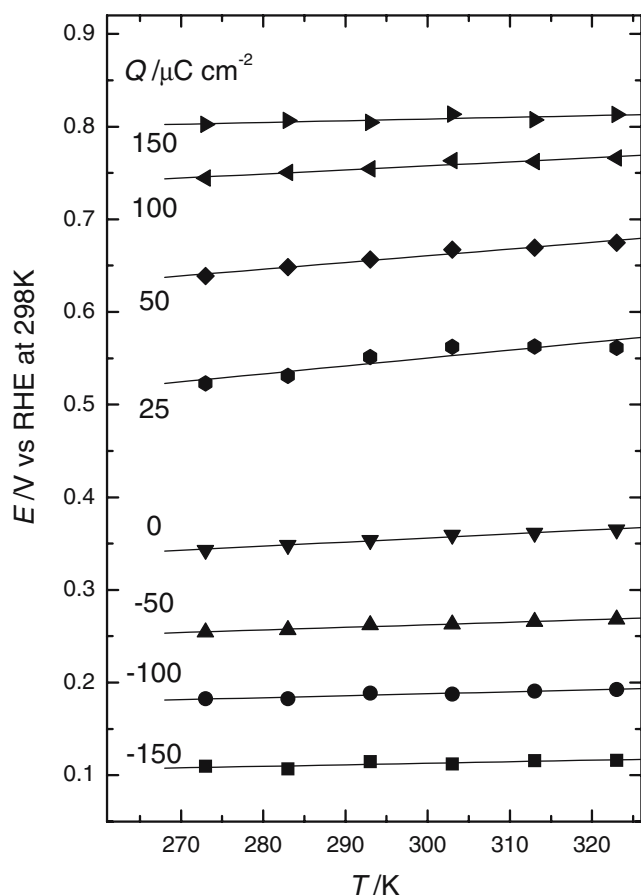


Fig. 3 Potential at constant charge plotted vs temperature, as obtained from the nonisothermal data in Fig. 2b, for selected charge densities, as labeled. Lines are the lineal fits of the experimental data

of the working electrode for potentials measured vs a reference electrode at 298 K. Following the same procedure for the data corresponding to an isothermal cell (Fig. 2a), the difference in the temperature coefficient of the working and the reference electrodes is obtained. Figure 4 compares both results. As expected, the above-mentioned quantities differ by a constant that is the temperature coefficient of the reference electrode (0.64 mV/K). In addition, it is shown that the introduction of the correction for the remaining charge density on the CO-covered electrode produces a small, constant displacement in the charge density scale.

Once the temperature coefficient of the potential drop at the interface is evaluated, following Eq. 20, the entropy of formation of the interface can be calculated from integration over the total charge density, up to a constant of integration:

$$\Delta S(Q) - \Delta S(Q = 0) = - \int_0^Q \left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{a_{HClO_4}, P, Q} dQ \quad (25)$$

If the integration is performed over the temperature coefficient determined in an isothermal cell, Eq. 23 gives the difference in the entropy of formation of the interface in the working and the reference electrodes:

$$- \int_0^Q \left(\frac{dE^{RHE}}{dT} \right)_{a_{HClO_4}, P, Q} dQ = \Delta S(Q) - \Delta S(Q = 0) + \frac{Q}{F} \Delta \bar{S}_{RHE} \quad (26)$$

Figure 5 shows the results of the two above-mentioned integrations. As stated in the Introduction, the entropy of formation of the Pt|solution interface contains contributions from adsorbed hydrogen and OH, water and metal species (Eq. 17). One can subtract the contribution of the entropy of proton and hydroxide species in solution using the tabulated values of individual ionic entropies in solution [7] jointly with the Gibbs excess values. The latter are obtained from the application of a thermodynamic analysis to the voltammetric data obtained in solutions of

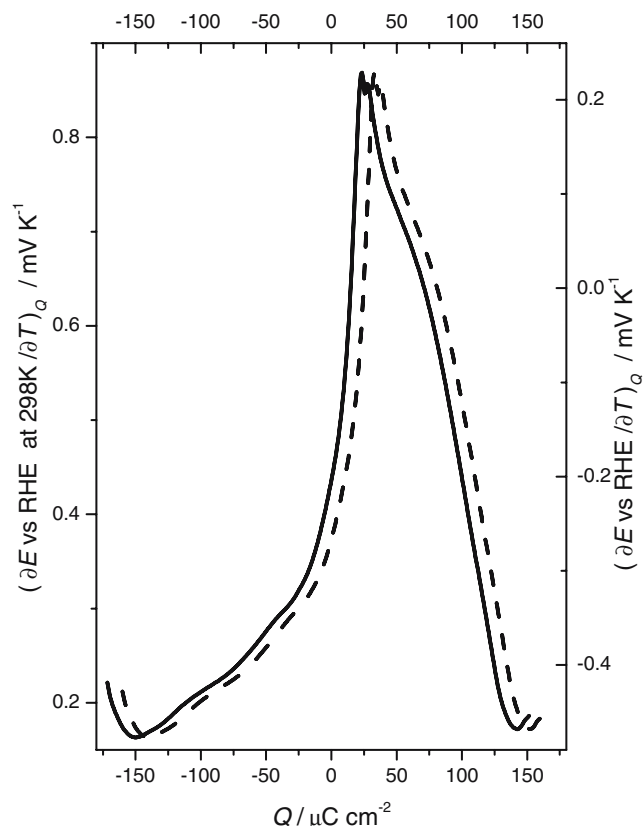


Fig. 4 Temperature coefficient of the Pt(111) electrode, as obtained from data in Fig. 2 (solid line). The results corresponding to the raw experimental data, without correction of the remaining charge on the CO covered electrode, are included for the sake of comparison (dashed line)

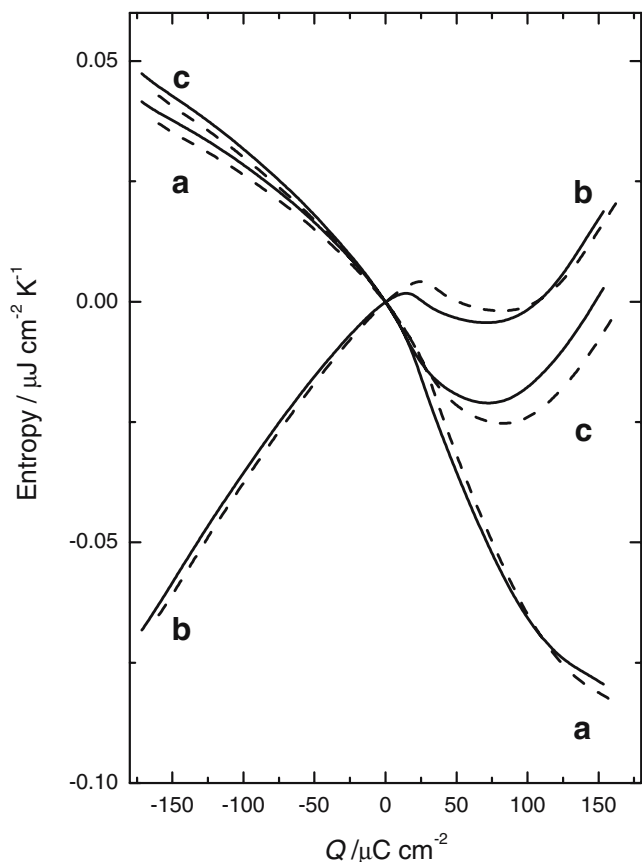


Fig. 5 Different entropy changes involved in the formation of the interface: *a* $\Delta S(Q) - \Delta S(Q = 0)$, Eq. 25; *b* $\Delta S(Q) - \Delta S(Q = 0) + \frac{Q}{F} \Delta \bar{S}_{RHE}$, Eq. 26; *c* $\Delta S_{H+OH+dl}$, Eq. 27; calculated from CO displacement experimental data corrected (*solid lines*) and uncorrected (*dashed lines*) from the remaining charge on the CO covered electrode

constant ionic strength and variable pH, as done in Mostany et al. [19]. By doing so, the following quantity is obtained:

$$\begin{aligned} \Delta S_{H+OH+dl} &= \Delta S(Q) - \Delta S(Q = 0) + \Gamma_H \bar{S}_{H^+} \\ &+ \Gamma_{OH} (\bar{S}_{H_2O} - \bar{S}_{H^+}) \\ &= \Gamma_S + \frac{Q}{F} \bar{S}_{e^-} - \sum_{i \neq H, OH} \Gamma_i \bar{S}_i - \Gamma_{H_2O} \bar{S}_{H_2O} \\ &- \Gamma_M \bar{S}_M - \Delta S(Q = 0) \end{aligned} \tag{27}$$

which contains the absolute entropy terms of adsorbed hydrogen and OH and the entropy change associated with the displacement of water and metal species from their respective bulk phases to form part of the interface. These results are also included in Fig. 5. To test the uncertainty introduced by the CO-determined PZTC values, the results obtained with charge density curves corrected and uncorrected by the CO remaining charge are compared in this figure. It can be seen that the introduction of the correction accounting for the remaining charge on the CO-covered electrode produces very little effect on the results.

The molar entropy of water in solution is very close to the standard value: $69.8 \text{ J mol}^{-1} \text{ K}^{-1}$ [7]. To calculate the molar entropy of proton species in solution, we used:

$$\bar{S}_i = \bar{S}_i^0 - \frac{d(RT \ln a_i)}{dT} = \bar{S}_i^0 - R \ln a_i - RT \frac{d(\ln \gamma_i)}{dT} \tag{28}$$

The activity coefficient and its temperature dependency were taken from Debethune et al. [15] in 0.1 M HCl: $\gamma_{H^+} = 0.7967$ and $\frac{d(\log \gamma_{H^+})}{dT} \approx -0.0002181 \text{ K}^{-1}$. Putting all these numbers together:

$$\begin{aligned} \bar{S}_{H^+} &= \bar{S}_{H^+}^0 - R \ln a_i - RT \frac{d(\ln \gamma_i)}{dT} \\ &\approx -18.8 + 21.02 + 1.24 = 3.5 \frac{\text{J}}{\text{molK}} \end{aligned} \tag{29}$$

At this point, it is convenient to define a molar entropy of adsorbed hydrogen and OH species that involves the absolute entropy of these CTA species and the entropy change involved in pure double-layer processes taking place during the adsorption process:

$$\begin{aligned} \bar{S}_{H+dl} &\equiv \frac{\Delta S_{H+OH+dl}}{\Gamma_H} \\ &= \frac{\Gamma_S + \frac{Q}{F} \bar{S}_{e^-} - \sum_{i \neq H, OH} \Gamma_i \bar{S}_i - \Gamma_{H_2O} \bar{S}_{H_2O} - \Gamma_M \bar{S}_M - \Delta S(Q = 0)}{\Gamma_H} \end{aligned} \tag{30}$$

(in the hydrogen adsorption region)

$$\begin{aligned} \bar{S}_{OH+dl} &\equiv \frac{\Delta S_{H+OH+dl}}{\Gamma_{OH}} \\ &= \frac{\Gamma_S + \frac{Q}{F} \bar{S}_{e^-} - \sum_{i \neq H, OH} \Gamma_i \bar{S}_i - \Gamma_{H_2O} \bar{S}_{H_2O} - \Gamma_M \bar{S}_M - \Delta S(Q = 0)}{\Gamma_{OH}} \end{aligned} \tag{31}$$

(in the OH adsorption region).

It is important to note that if double-layer effects are neglected (that is, the terms associated to water, metal, and not-adsorbing species), the above quantities correspond to

$$\begin{aligned} \bar{S}_{H+dl} &= \frac{\left[\Gamma_S + \frac{Q}{F} \bar{S}_{e^-} - \sum_{i \neq H, OH} \Gamma_i \bar{S}_i - \Gamma_{H_2O} \bar{S}_{H_2O} - \Gamma_M \bar{S}_M - \Delta S(Q = 0) \right]}{\Gamma_H} \\ &\approx \frac{\Gamma_S - \Gamma_H \bar{S}_{e^-} - \Gamma_S(Q = 0) - \Gamma_H \bar{S}_{e^-}(Q = 0)}{\Gamma_H} \approx \bar{S}_H - \bar{S}_{e^-} \end{aligned} \tag{32}$$

$$\begin{aligned} \bar{S}_{OH+dl} &= \frac{\left[\Gamma_S + \frac{Q}{F} \bar{S}_{e^-} - \sum_{i \neq H, OH} \Gamma_i \bar{S}_i - \Gamma_{H_2O} \bar{S}_{H_2O} - \Gamma_M \bar{S}_M - \Delta S(Q = 0) \right]}{\Gamma_{OH}} \\ &\approx \frac{\Gamma_S + \Gamma_{OH} \bar{S}_{e^-}}{\Gamma_{OH}} \approx \bar{S}_{OH} + \bar{S}_{e^-} \end{aligned} \tag{33}$$

where it has been considered that $Q \approx -FT_H$ in the hydrogen adsorption region, $Q \approx -FL_{OH}$ in the OH adsorption region, and $\Delta S(Q=0) \approx 0$. $\bar{S}_e = 0$ for the Fermi–Dirac electron gas [7].

The results of the calculation of \bar{S}_{H+dl} and \bar{S}_{OH+dl} are shown in Fig. 6. The values of hydrogen and OH Gibbs excesses are included in the upper part of the graph for the sake of comparison. It should be noted that values of \bar{S}_{H+dl} and \bar{S}_{OH+dl} calculated at small coverages are not meaningful as a result of the large error involved in the division by a very small number. Once a significant coverage is achieved, the entropy of adsorbed hydrogen attains a fairly constant value of $\sim 30 \text{ J mol}^{-1} \text{ K}^{-1}$. This value is very close to the $29.7 \text{ J mol}^{-1} \text{ K}^{-1}$ derived from statistic calculations for a fully mobile hydrogen adlayer, and it is significantly higher than that obtained for a totally immobile one ($4.7 \text{ J mol}^{-1} \text{ K}^{-1}$)

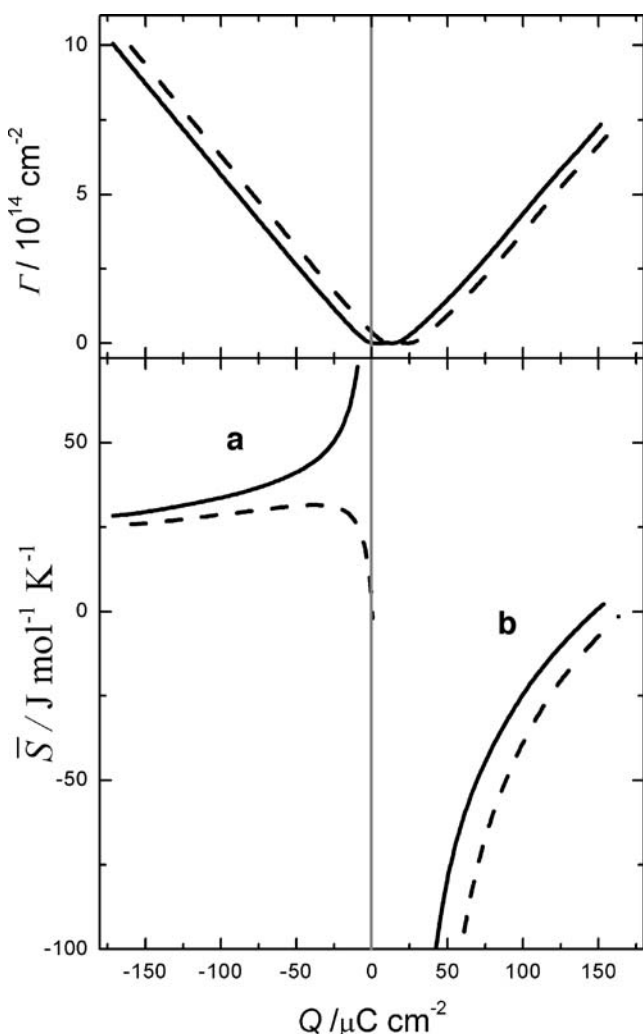
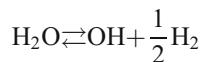
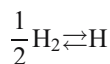


Fig. 6 Absolute molar entropies of adsorbed hydrogen (a) and OH (b) (Eqs. 30 and 31) as obtained from CO displacement data corrected (solid lines) and uncorrected (dashed lines) from the remaining charge on the CO covered electrode. Values of the Gibbs excesses are included for the sake of comparison

[10, 24, 25]. This fact suggests that hydrogen adsorption involves minor double-layer effects and can be reasonably described as an essentially mobile state. On the other hand, the entropy of adsorbed OH has negative values and markedly increases with coverage. Furthermore, values of \bar{S}_{OH+dl} are very different from the tabulated value of the entropy of OH in the gas phase: $183.74 \text{ J mol}^{-1} \text{ K}^{-1}$ [11]. This behavior indicates that, in the electrochemical media, the OH adsorption process involves significant double-layer contributions, associated to important ordering effects on the water structure.

Evaluation of the entropy changes associated to the global reactions of the cell

If the reaction on the reference electrode is included in the adsorption process under study, the global reactions for hydrogen and OH adsorption are obtained:



Consequently, the corresponding entropy changes would be given by:

$$\Delta \bar{S}_H = \bar{S}_H - \frac{1}{2} \bar{S}_{H_2} \tag{34}$$

$$\Delta \bar{S}_{OH} = \bar{S}_{OH} + \frac{1}{2} \bar{S}_{H_2} - \bar{S}_{H_2O} \tag{35}$$

It is interesting to calculate the entropy changes associated to the global reactions of hydrogen and OH adsorption because these results will be comparable with previous studies based on the application of a generalized isotherm. For doing so, we will employ the absolute entropies of adsorbed hydrogen and OH calculated in the present study, defined by Eqs. 30 and 31, and the entropies of H_2 and H_2O species in solution. For the latter, we will take the standard tabulated entropy values given in Conway et al. [7] ($129.6 \text{ J mol}^{-1} \text{ K}^{-1}$ for H_2 and $69.8 \text{ J mol}^{-1} \text{ K}^{-1}$ for H_2O).

The results are shown in Fig. 7. The entropy of the global reaction of hydrogen adsorption is $\sim -35 \text{ J mol}^{-1} \text{ K}^{-1}$ and has a small dependence with the hydrogen coverage. The entropy of reaction of OH adsorption has a much larger dependency with the OH coverage.

Comparison with results based on the application of the generalized isotherm

In the analysis of the temperature-dependent voltammograms by application of the generalized isotherm [10, 11],

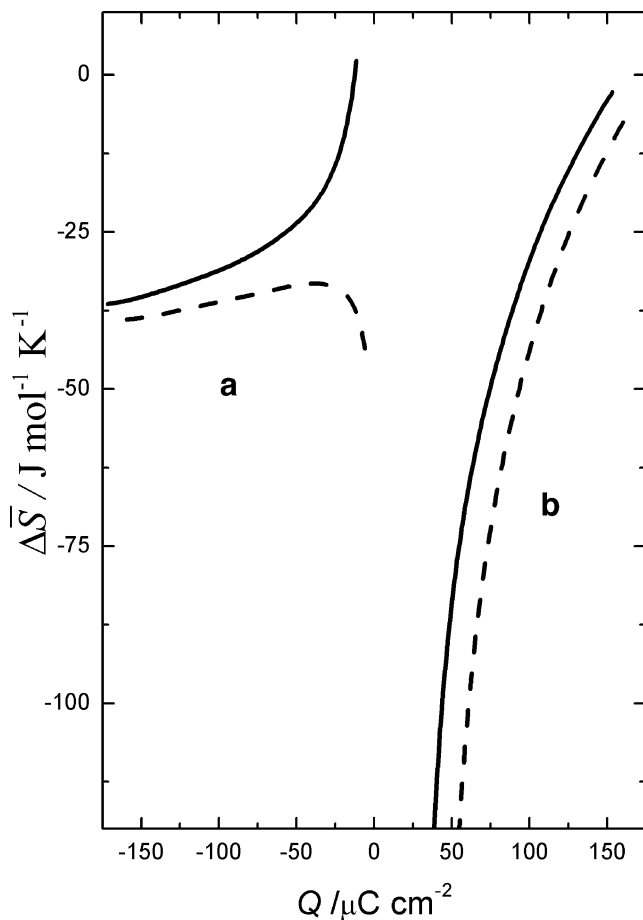


Fig. 7 Entropies of the global reaction of the cell in the adsorption of hydrogen (a) and OH (b) (Eqs. 34 and 35), as obtained from CO displacements data corrected (solid line) and uncorrected (dashed line) from the remaining charge on the CO-covered electrode

the formal or apparent entropy of hydrogen adsorption is calculated as:

$$\Delta\bar{S}_H^{formal} = -\frac{\partial}{\partial T} \left[-FE^{RHE} - RT \ln \left(\frac{\theta_H}{1 - \theta_H} \right) \right]_{\theta_H} \quad (36)$$

$$\Delta\bar{S}_{OH}^{formal} = -\frac{\partial}{\partial T} \left[FE^{RHE} - RT \ln \left(\frac{\theta_{OH}}{1 - \theta_{OH}} \right) \right]_{\theta_{OH}} \quad (37)$$

where the coverages θ are obtained from the integration of the (arbitrarily) double-layer corrected voltammogram, considering that the electroadsorption valency of hydrogen and OH are 1 and -1 , respectively. Please note that, in the above definition, the configurational entropy terms are explicitly excluded from the entropy change of reactions of hydrogen and OH adsorption. Consequently, this correction will be also performed in the entropy values calculated in the present study for the sake of comparison, using the Gibbs excess data determined from the thermodynamic

analysis in Mostany et al. [19]. For this, the following terms are defined:

$$\begin{aligned} \bar{S}_H^{config} &= -\frac{\partial}{\partial T} \left(RT \ln \left(\frac{\theta_H}{1 - \theta_H} \right) \right)_{\theta_H} \\ &= -R \ln \left(\frac{\theta_H}{1 - \theta_H} \right) \end{aligned} \quad (38)$$

$$\begin{aligned} \bar{S}_{OH}^{config} &= -\frac{\partial}{\partial T} \left(RT \ln \left(\frac{\theta_{OH}}{1 - \theta_{OH}} \right) \right)_{\theta_{OH}} \\ &= -R \ln \left(\frac{\theta_{OH}}{1 - \theta_{OH}} \right) \end{aligned} \quad (39)$$

We can then calculate the following quantities:

$$\begin{aligned} \Delta\bar{S}_H - \bar{S}_H^{config} &= \frac{\Delta S(Q) - \Delta S(Q=0) + \Gamma_H \bar{S}_{H^+} + \Gamma_{OH} (\bar{S}_{H_2O} - \bar{S}_{H^+})}{\Gamma_H} \\ &\quad - \frac{1}{2} \bar{S}_{H_2} + R \ln \left(\frac{\theta_H}{1 - \theta_H} \right) \end{aligned} \quad (40)$$

(in the hydrogen adsorption region)

$$\begin{aligned} \Delta\bar{S}_{OH} - \bar{S}_{OH}^{config} &= \frac{\Delta S(Q) - \Delta S(Q=0) + \Gamma_H \bar{S}_{H^+} + \Gamma_{OH} (\bar{S}_{H_2O} - \bar{S}_{H^+})}{\Gamma_{OH}} \\ &\quad + \frac{1}{2} \bar{S}_{H_2} - \bar{S}_{H_2O} + R \ln \left(\frac{\theta_{OH}}{1 - \theta_{OH}} \right) \end{aligned} \quad (41)$$

(in the OH adsorption region).

The relationship between the entropy changes of hydrogen and OH adsorption given by Eqs. 36, 37, 40, and 41 can be better understood by calculating the following quantities:

$$\begin{aligned} \Delta\bar{S}_H - \bar{S}_H^{config} &= \frac{-\int_0^Q \left(\frac{dE^{RHE}}{dT} \right) dQ}{\Gamma_H} - \bar{S}_H^{config} \\ &= \frac{\Delta S(Q) - \Delta S(Q=0) + \frac{Q}{F} \Delta\bar{S}_{RHE}}{\Gamma_H} - \bar{S}_H^{config} \end{aligned} \quad (42)$$

(in the hydrogen adsorption region)

$$\begin{aligned} \Delta\bar{S}_{OH} - \bar{S}_{OH}^{config} &= \frac{-\int_0^Q \left(\frac{dE^{RHE}}{dT} \right) dQ}{\Gamma_{OH}} - \bar{S}_{OH}^{config} \\ &= \frac{\Delta S(Q) - \Delta S(Q=0) + \frac{Q}{F} \Delta\bar{S}_{RHE}}{\Gamma_{OH}} - \bar{S}_{OH}^{config} \end{aligned} \quad (43)$$

(in the OH adsorption region).

It can be shown that $\Delta\bar{S}'_H$ and $\Delta\bar{S}'_{OH}$ are equal to $\Delta\bar{S}_H$ and $\Delta\bar{S}_{OH}$, respectively, provided that $Q \approx -F\Gamma_H$ in the hydrogen adsorption region and $Q \approx -F\Gamma_{OH}$ in the OH adsorption region. Moreover, the former quantities correspond to the formal entropy terms calculated from the application of the generalized isotherm when the coefficient $\left(\frac{dE^{RHE}}{dT}\right)$ is independent on the charge density and the conditions $Q \approx -F\Gamma_H$ and $Q \approx -F\Gamma_{OH}$ are fulfilled in the hydrogen and OH adsorption regions, respectively.

The comparison with results obtained from the application of the generalized isotherm should not be done in a charge density scale because, in this approach, the charge density is corrected from double-layer contributions, while in the present work, the total charge density is employed. Consequently, the comparison has been done using potential as the independent variable. Figure 8 plots the results obtained with data corrected from the remaining charge density on the CO-covered electrode. However, if this correction is not considered, the effect on the final results is

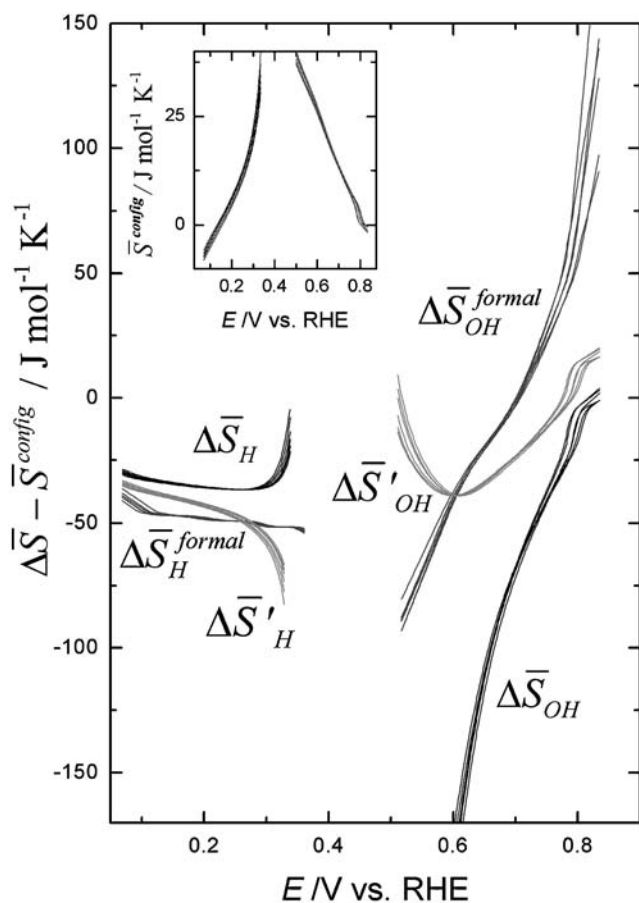


Fig. 8 Comparison of the entropies of reaction of adsorption of hydrogen and OH, determined with the use of the entropy of formation of the interface, with results obtained from the application of the generalized isotherm. The configurational terms are showed in the inset. See text for details

small, and it is not shown in Fig. 8 for the sake of clarity. It can be seen that the agreement between these three methods of analysis is reasonable for hydrogen adsorption. However, for OH adsorption, the differences are significant. This fact may be explained because more severe double-layer effects take place during OH adsorption. Hydrogen electroadsorption valency is very close to unity, and hence, the approximation $Q \approx -F\Gamma_H$ is adequate, but the electroadsorption valency of OH differs somewhat from -1 [19], and hence, the validity of the approximation $Q \approx -F\Gamma_{OH}$ in the OH adsorption region is more dubious. In addition, hydrogen adsorption is satisfactorily described by using a Frumkin isotherm, while for the study of the OH adsorption, the application of the generalized isotherm may not be adequate. The fact that the maximum OH coverage is lower than unity, and the characteristic sharp voltammetric spike associated to the completion of the OH adlayer, indicates the presence of strong repulsive interactions between adsorbed particles on neighboring positions [26, 27].

Conclusions

The entropy of formation of the interface formed by a Pt(111) electrode in 0.1 M HClO₄ solution has been evaluated here for the first time using voltammetric and CO displacement data as a function of the temperature and the experimental temperature coefficient of the RHE electrode given in Debethune et al. [15]. The results have been used for the estimation of the absolute entropies of adsorbed hydrogen and OH species. However, these quantities cannot be separated by thermodynamic means from contributions of entropy changes of double-layer phenomena taking place during the adsorption process. For the calculation, the thermodynamic Gibbs excesses of hydrogen and OH species were taken from Mostany et al. [19], and the ionic entropies of proton and hydroxide species in solution from Conway et al. [7] and Debethune et al. [15] were used.

It is found that the entropy of adsorbed hydrogen depends weakly on the coverage and it is about $\sim 30 \text{ J mol}^{-1} \text{K}^{-1}$, a value very similar to that calculated for a totally mobile hydrogen adlayer [10]. This fact indicates that double-layer contributions on the hydrogen adsorption process have minor importance, and the state of adsorbed hydrogen can be reasonably described as a totally mobile one.

On the other hand, the entropy of adsorbed OH has negative values and it is hence markedly different from the tabulated value of the entropy of OH in the gas phase: $183.74 \text{ J mol}^{-1} \text{K}^{-1}$ [11]. This fact indicates that mayor double-layer contributions are involved in the OH adsorption

process, associated to important ordering effects on the water structure.

The entropy changes of the global reactions of hydrogen and OH adsorption (which include the reaction on the reference electrode) are also evaluated and compared with results obtained with a generalized isotherm. Reasonable agreement is found for hydrogen adsorption, while significant differences are obtained for OH adsorption. This fact may be explained because more important contributions of double-layer effects take place within the OH adsorption, as evidenced from the higher deviation of the OH electro-sorption valency from unity, as compared with hydrogen adsorption [19]. In addition, the possible inapplicability of the generalized isotherm is suggested by the presence of strong interactions between neighboring OH particles, as evidenced from the saturation coverage lower than unity and the presence of the sharp voltammetric spike in the completion of the OH adlayer [26, 27].

Finally, it should be pointed out that the quantities calculated here have a clear physical meaning even when important double-layer contributions or severe deviations from the Langmuirian behavior are involved in the adsorption process. From the presently available experimental data, the entropy terms related to specific adsorbed species cannot be separated from double-layer contributions. Consequently, it seems more convenient to deal with thermodynamically determinable quantities rather than quantities whose determination relies on a number of uncertain assumptions. In conclusion, the validity of interfacial models would be better tested using experimentally determinable quantities like the entropy of formation of the interface.

Acknowledgements B. Álvarez-Ruiz is gratefully acknowledged for providing the experimental data. Financial support from the *Ministerio de Educación y Ciencia* (MEC) (Spain) through project CTQ 2006-04071/BQU is gratefully acknowledged. NG thanks the MEC (Spain) for the award of a *Formación de Personal Universitario* grant. VC acknowledges financial support from the MEC and the Generalitat Valenciana under the Ramon y Cajal program.

References

- Harrison JA, Randles JEB, Schiffrin DJ (1973) *J Electroanal Chem* 48:359
- Hills GJ, Hsieh S (1975) *J Electroanal Chem* 58:289
- Hills GJ, Payne R (1965) *Trans Faraday Soc* 61:326
- Hamelin A, Stoicoviciu L, Silva F (1987) *J Electroanal Chem* 229:107
- Silva F, Sottomayor MJ, Hamelin A (1990) *J Electroanal Chem* 294:239
- Silva F, Sottomayor MJ, Martins A (1996) *J Chem Soc Faraday Trans* 92:3693
- Conway BE, Angerstein-Kozłowska H, Sharp WB (1978) *J Chem Soc Faraday Trans* 74:1373
- Jerkiewicz G, Zolfaghari A (1996) *J Phys Chem* 100:8454
- Zolfaghari A, Jerkiewicz G (1997) *J Electroanal Chem* 422:1
- Gomez R, Orts JM, Alvarez-Ruiz B, Feliu JM (2004) *J Phys Chem B* 108:228
- Climent V, Gomez R, Orts JM, Feliu JM (2006) *J Phys Chem B* 110:11344
- Conway BE, Angerstein-Kozłowska H, Dhar HP (1974) *Electrochim Acta* 19:455
- Garcia-Araez N, Lukkien JJ, Koper MTM, Feliu JM (2006) *J Electroanal Chem* 588:1
- Herrero E, Mostany J, Feliu JM, Lipkowski J (2002) *J Electroanal Chem* 534:79
- Debethune AJ, Licht TS, Swendeman N (1959) *J Electrochem Soc* 106:616
- Climent V, Coles BA, Compton RG (2002) *J Phys Chem B* 106:5258
- Climent V, Coles BA, Compton RG (2002) *J Phys Chem B* 106:5988
- Weaver MJ (1998) *Langmuir* 14:3932
- Mostany J, Herrero E, Feliu JM, Lipkowski J (2003) *J Electroanal Chem* 558:19
- Guidelli R, Aloisi G, Leiva E, Schmickler W (1988) *J Phys Chem B* 92:6671
- Frumkin AN, Petrii OA (1975) *Electrochim Acta* 20:347
- Clavilier J, Armand D, Sun S-G, Petit M (1986) *J Electroanal Chem* 205:267
- Rodes A, El Achi K, Zamakhchari MA, Clavilier J (1990) *J Electroanal Chem* 284:245
- Adamson AW, Gast AP (1997) *Physical chemistry of surfaces*. Wiley, New York
- Hill TL (1986) *An introduction to statistical thermodynamics*. Dover, New York
- Koper MTM (1998) *J Electroanal Chem* 450:189
- Koper MTM, Lukkien JJ (2000) *J Electroanal Chem* 485:161