THERMODYNAMICS OF SURFACE PHENOMENA ON PLATINUM-GROUP METALS AT OXYGEN ADSORPTION POTENTIALS IN BASIC SOLUTIONS

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The thermodynamics of surface phenomena on electrodes made of metals of the platinum group were examined in [1-6]. The relations in these papers, and their verification, referred in general to acidic solutions and to potentials of hydrogen adsorption on the electrode surface. In this paper, the thermodynamic relations for basic solutions and for oxygen adsorption potentials are considered, and an experimental confirmation of these relations for the case of the rhodium electrode is reported.

We consider a solution containing a neutral salt CA and a base COH. We denote by μ_{CA} and μ_{COH} the chemical potentials of CA and COH, and by Γ_{CA} and Γ_{COH} the surface densities of these components in the Gibbs sense ($\Gamma_{H_2O} = 0$). We denote by μ_H and Γ_H respectively the chemical potential and the surface density of hydrogen; φ_r is the electrode potential, measured relative to the reversible hydrogen electrode in the same solution, in equilibrium with H_2 at atmospheric pressure, and σ is the surface free-energy density. We assume that the effects of dissolved H_2 on μ_{COH} and μ_{CA} can be neglected. The quantities Γ and μ are given in electrical units. It is evident that in basic solutions

$$\Gamma_{COH} = \Gamma_{OH^-};\ \Gamma_{C^+} = \Gamma_{CA} + \Gamma_{COH};\ \Gamma_{A^-} = \Gamma_{CA};\ \Gamma_{OH^-} = \Gamma_{C^+} - \Gamma_{A^-}. \tag{1}$$

From the Gibbs equation,

$$d\sigma = -\Gamma_H d\mu_H - \Gamma_{COH} d\mu_{COH} - \Gamma_{CA} d\mu_{CA}; \tag{2}$$

using

$$d\mu_H = -d\varphi_r, \tag{3}$$

we obtain

$$\left(\frac{\partial \Gamma_{COH}}{\partial \varphi_r}\right)_{\mu_{COH},\,\mu_{CA}} = \left(\frac{\partial \Gamma_{OH^-}}{\partial \varphi_r}\right)_{\mu_{COH},\,\mu_{CA}} = \left(\frac{\partial \Gamma_H}{\partial \varphi_r}\right)_{\mu_{COH},\,\mu_{CA}} \left(\frac{\partial \varphi_r}{\partial \mu_{COH}}\right)_{\Gamma_H,\,\mu_{CA}}. \tag{4}$$

Since the relation [4]

$$\Delta \Gamma_H = -\Delta Q \tag{5}$$

holds between the change in the magnitude of Γ_H and the amount of charge Q brought to the electrode from outside, Eq. (4) can also be written in the following form:

$$\left(\frac{\partial \Gamma_{OH^-}}{\partial \varphi_r}\right)_{\mu_{COH},\,\mu_{CA}} = -\left(\frac{\partial Q}{\partial \varphi_r}\right)_{\mu_{COH},\,\mu_{CA}} \left(\frac{\partial \varphi_r}{\partial \mu_{COH}}\right)_{Q,\,\mu_{CA}}. \tag{6}$$

When there is an excess of an inert electrolyte ([CA] $\gg$ [COH]), μ_{C^+} remains practically constant with a change in [COH], if [CA] = const. Then

$$d\mu_{COH} = d\mu_{OH^-} + d\mu_{C^+} = d\mu_{OH^-}, \tag{7}$$

where the quantity $d\mu_{OH^-}$ can be found from the change in the potential of the hydrogen electrode with [CA] = const. In this case it follows from (6) that

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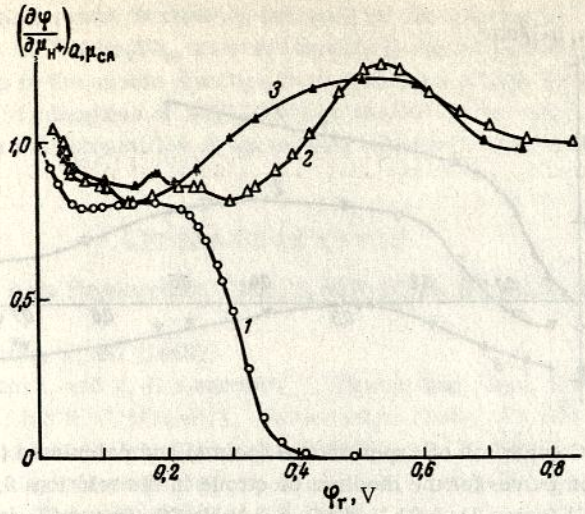

Fig. 1. Dependence of $(\partial\varphi/\partial\mu_{H^+})_{Q,\mu_{CA}}$ on φ_r for the rhodium electrode in the solutions 0.01 N H_2SO_4 + 1 N Na_2SO_4 (curve 3); 0.01 N KOH + 1 N KCl (curve 2); and 0.01 N HCl + 1 N KCl (curve 1).

$$\left(\frac{\partial\Gamma_{OH^-}}{\partial\varphi_r}\right)_{\mu_{OH^-},\,\mu_{CA}} = -\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{OH^-},\,\mu_{CA}}\left(\frac{\partial\varphi_r}{\partial\mu_{OH^-}}\right)_{Q,\,\mu_{CA}} \tag{8}$$

Since $\Gamma_{OH^-} = -\Gamma_{H^+}$, and $d\mu_{OH^-} = -d\mu_{H^+}$, Eq. (8) can be rewritten in the form

$$\left(\frac{\partial\Gamma_{H^+}}{\partial\varphi_r}\right)_{\mu_{H^+},\,\mu_{CA}} = -\left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{H^+},\,\mu_{CA}}\left(\frac{\partial\varphi_r}{\partial\mu_{H^+}}\right)_{Q,\,\mu_{CA}}, \tag{9}$$

which is identical to the equation given in [2] for acid solutions, and is thus applicable for any pH values.

The region of applicability of Eq. (9) can be extended to potentials at which the hydrogen adsorbed on the electrode surface is replaced by adsorbed oxygen; i.e., in the oxygen region of the charging curve. Assuming that under these conditions the system can be treated as reversible, Eqs. (3), (2), and (5) must be replaced by the following:

$$d\mu_O = d\varphi_r, \tag{10}$$

$$d\sigma = \Gamma_O d\mu_O - \Gamma_{HA} d\mu_{HA} - \Gamma_{CA} d\mu_{CA}, \tag{11}$$

where HA is the acid, or

$$d\sigma = -\Gamma_O d\mu_O - \Gamma_{COH} d\mu_{COH} - \Gamma_{CA} d\mu_{CA}, \quad \Delta\Gamma_O = \Delta Q, \tag{12}$$

where μ_0 and Γ_0 are also expressed in electrical units. Since the changes in the signs preceding $d\varphi_r$ in (10) compared with (3) and preceding ΔQ in (12) compared with (5) compensate for each other, Eq. (9) and all those which follow from (9) retain their validity. If then only the assumption of the reversibility of the ionization of adsorbed oxygen is justified, the experimental results can be treated regardless of whether there is adsorbed hydrogen or oxygen on the surface. This result is understandable, for when $\Gamma_{H_2O} = O$, oxygen adsorption may be considered a negative adsorption of hydrogen. The case of a simultaneous presence of H_{ads} and O_{ads} does not require a separate consideration, for their presence in equivalent amounts does not differ thermodynamically from the chemisorption of water, and need not be taken into account under the condition $\Gamma_{H_2O} = O$. Only that part of Γ_H or Γ_O which exceeds the equivalent of the other need be considered in the calculation.

An experimental check of Eq. (9) was made for the following systems: 1 N KCl + 0.01 N KOH and 1 N Na_2SO_4 + 0.01 N H_2SO_4 on platinum covered with rhodium black. The preparation of the electrodes, the experimental procedure, and the treatment of the results are laid out in detail in [5, 6].

The dependence of $(\partial\varphi/\partial\mu_{H^+})_{Q,\mu_{CA}} = (\partial\varphi_r/\partial\mu_{H^+})_{Q,\mu_{CA}} + 1$ on φ_r for the systems studied is shown in Fig. 1, with a comparison of the data for the solution 1 N KCl + 0.01 N NCl obtained earlier [6]. The quantities $(\partial\varphi_r/\partial\mu_{H^+})_{Q,\mu_{CA}}$ were determined by substituting the solutions 0.001 N H_2SO_4 (or KOH) + 1.009 N Na_2SO_4 (or

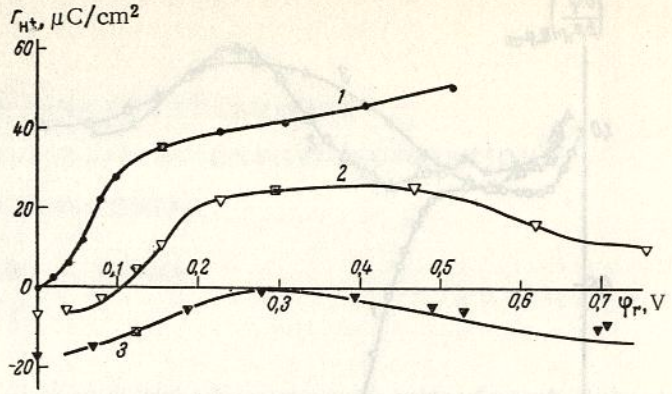

Fig. 2. Comparison of experimental (points) and calculated (solid lines) adsorption curves for the rhodium electrode in the solutions 0.01 N HCl + 1 N KCl (curve 1); 0.01 N H_2SO_4 + 1 N Na_2SO_4 (curve 2); and 0.01 N KOH + 1 N KCl (curve 3).

KCl) for the solutions 0.1 N H_2SO_4 (or KOH) + 0.91 N Na_2SO_4 (or KCl). At small φ_r in all solutions, the rhodium electrode behaves approximately as the reversible hydrogen electrode, remaining in equilibrium with gaseous hydrogen at constant pressure. For more anodic potentials, however, the shape of the $(\partial\varphi / \partial\mu_{H^+})_{Q, \mu_{CA}}$, φ_r-curves depends strongly on the composition of the solution. If then the value of $(\partial\varphi / \partial\mu_{H^+})_{Q, \mu_{CA}}$ returns to zero with $\varphi_r \geqslant 0.4$ V in an acidified chloride solution, the values of $(\partial\varphi / \partial\mu_{H^+})_{Q, \mu_{CA}}$ in acidified sulfate and basic chloride solutions remain close to unity over the whole range of φ_r from 0 to 0.8 V. This means that the regions of hydrogen and oxygen adsorption overlap in the solutions named [2, 4, 5]. At $\varphi_r \geqslant 0.4$ V in the sulfate solution and at $\varphi_r \geqslant 0.3$ V in the basic chloride solution $(\partial\varphi / \partial\mu_{H^+})_{Q, \mu_{CA}}$ exceeds unity. This becomes possible, according to Eq. (9), because the quantity $(\partial\Gamma_{H^+} / \partial\varphi_r)_{\mu_{H^+}, \mu_{CA}}$ becomes negative; i.e., the dependence of Γ_{H^+} on φ_r passes through a maximum.

A comparison of the experimental and calculated (from Eq. (9)) Γ_{H^+}, φ_r curves is shown in Fig. 2. The values of $(\partial Q / \partial\varphi_r)_{\mu_{H^+}, \mu_{CA}}$ were found from the equilibrium charging curves for the rhodium electrode (for the method of measuring such curves, see [7]). The calculated and experimental curves agree quantitatively for acidic solutions. In basic solutions there is agreement only up to $\varphi_r \sim 0.3$ V. This may be connected with the difficulties of establishing an equilibrium in basic solutions at oxygen adsorption potentials. Even at the more anodic φ_r, however, the calculated curve approximately follows the path of the experimental one. The quantitative agreement of the theoretical and experimental curves shows the validity of treating the rhodium electrode surface in solutions of various compositions as an equilibrium system whose state at μ_{CA} = const is determined by the independent variables μ_H and μ_{H^+} or μ_{OH^-}. Especially interesting (and to a certain extent surprising) is that the assumption of reversibility is justified not only at hydrogen adsorption potentials, but at oxygen adsorption potentials also, within certain limits.

According to Fig. 2, the zero charge point of the rhodium electrode in the solution 1 N Na_2SO_4 + 0.01 N H_2SO_4 lies at $\varphi_r \simeq 0.10$ V, i.e., $\varphi_{z.ch.} \simeq -0.04$ V with respect to the N.H.E. The value of the zero charge point found for the sulfate solution agrees with that determined in [8] by a tracer atom method. In the basic solution, as was observed earlier on the Pt/Pt electrode [9, 10], there is no zero charge point in the usual sense on the rhodium electrode. Cation adsorption, passing through a minimum, begins to increase again. The change in cation adsorption in basic solutions is somewhat stronger, however, on rhodium that on platinum.

According to [8], the appearance of adsorbed oxygen on the surface of the rhodium electrode in acidic solution is caused by the drop in anion adsorption. Similar correlations apparently exist between the adsorption of cations and hydrogen.* Thus the values of $(\partial\varphi / \partial\mu_{H^+})_{Q, \mu_{CA}}$ on rhodium in 10^{-2} N H_2SO_4 + 1 N Na_2SO_4 at small values of φ_r exceed unity, implying a growth of Γ_{H^+} with a decrease of φ_r. A decrease in cation adsorption is not observed, however, during direct adsorption changes. The method of measuring the pH dependence of the potential at constant Q, yielding the slope of the adsorption curve directly, allows an apparently more accurate determination of the path of the Γ_{H^+}, φ_r curve near $\varphi_r = 0$. At low φ_r, however, difficulties in creating isoelectric experimental conditions arise; conclusions can be made after a refining of the experimental procedure for the case when dissolved H_2 is present in the solution in measurable concentrations according to the theory laid out in [4].

*It should be noted that a slight maximum in cation adsorption was obtained earlier in [1] in an approximate calculation of the platinum adsorption curve. The maximum was also described in [4, 5].

In comparison of the adsorption curves obtained in this work for the solution 10^{-2} N H_2SO_4 + 1 N Na_2SO_4 and in [8] for the solution 10^{-2} N H_2SO_4 + 10^{-2} N Na_2SO_4, a strong increase in the adsorption of SO_4^{2-} anions and a shift of the anion adsorption potential drop in the anodic direction in the presence of high Na_2SO_4 concentrations is evident. This apparently implies the specific adsorption of SO_4^{2-} anions on rhodium in the concentrated solutions, which provide more favorable conditions for the competition of anions with adsorbed hydrogen and oxygen for a place on the surface.

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