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Experimental Verification of the Thermodynamic Theory of the Platinum Hydrogen Electrode Surface State

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SUMMARY

The dependence of the adsorption of hydrogen ions upon the electrode potential has been calculated by determining the dependence of the hydrogen electrode potential upon pH of the solution at a constant quantity of electricity stored on its surface In the case of a 1N KCl+0.01N HCl solution, the dependence obtained is in agreement with experiment, which proves the applicability of Gibbs thermodynamics of the surface phenomena to the platinum hydrogen electrode and at the same time provides a new method for the determination of the position of the point of zero charge.

Whereas the application of Gibbs thermodynamics of the surface phenomena to mercury and other liquid metal electrode has been experimentally substantiated and is at present in common use, the possibity of a similar approach to electrocapillary phenomena on the surface of the platinum hydrogen electrode has been scantily studied in the literature. The first attempt in this direction was made by Frumkin and Slygin[1], but the formula derived by them was in such a form that it could be hardly checked experimentally and therefore was verified only semiquantitatively. Some thermodynamic relations were considered by Frumkin, Balashova and Kazarinov[2].

By applying Gibbs thermodynamics to the platinum hydrogen electrode, in ref [3]., was obtained the following equation :

$$\left(\frac{\partial \psi_z}{\partial \mu_{H^+}}\right)_{\lceil H, \mu s} = \left(\frac{\partial \lceil H^+}{\partial \psi z}\right)_{\mu H^+, \mu s} \quad \ldots (1)$$

where $\lceil H$ and $\lceil H^+$ are the surface densities of hydrogen and hydrogen ions, ψz—the potential referred to a reversible hydrogen electrode in the same solution, μH^+ and μs—the chemical potentials of hydrogen ions and of the indifferent electrolyte ions. The quantities $\lceil$ and μ are expressed in electric units.

The present communication reports the results of an experimental verification of eq. (1).

The experiments were carried out with platinized platinum electrodes at room temperature 20 ± 1°C. The electrode pretreatment was described in detail in[4]. The visible surface of the electrodes was 20 and 80 cm², the quantity of platinum per 1 cm² of surface ~ 5-10 mg. The true surface of the electrodes was determined from the length of the hydrogen part of the charging

curve in a 1 N KCl + O,1 N HCl solution assuming the amount of adsorbed hydrogen at $\psi_z = O$ to be equal to 210 μcoul/cm^2 [5]. It was found to be 0,66 m^2 for the first electrode and 9,8−6,3 m^2 for the second. The solutions were freed of dissolved oxygen by means of specpure helium.

Eq (1) was verified for a 1 N KCl + 0,01 N KCl solution.

The values of $\left(\frac{\partial\ H}{\partial\psi_z}\right)_{\mu H^+,\mu s}$ were obtained from the slope of the charging curve of a Pt/Pt electrode in the above solution. The current density in the charging curve measurements was 50 μA/cm^2 of visible surface. The derivative

$$\left(\frac{\partial\psi_z}{\partial\mu H^+}\right)_{\Gamma H,\ \mu s}$$

was determined from the change in the electrode potential with changing $[H^+]$ under isoelectric conditions, i.e. at constant Γ_H[6,3]. The design of the cell used in these experiments made possible independent replacement of the electrolyte solution in the operating and reference electrodes compartments and in the connecting bridge. ψ_z was observed to change when a 0,001N HCl+1,009 N KCl solution was replaced by a 0,1 N HCl+0,91 NKCl one. In order to increase the accuracy of the determination of $\left(\frac{\partial\psi_z}{\partial\mu H^+}\right)_{\Gamma H,\mu s}$ at, $\psi_z > 300$ mv when $\triangle\gamma_z$ became large, the measurements were carried out with pH of the solution changing within a narrower range : a 0,005 N HCl +1,005 N KCl was replaced by a 0,02 N HCl+ 0,99 N KCl solution In dilute acid solutions the changes in pH upon contact with a large platinized electrode can be considerable due to ionization of adsorbed hydrogen or to the hydrogen ions discharge. Therefore before the measurements, after the potential became stabilized at a given value, the electrolyte solution in the operating electrode compartment was replaced five times, whereupon it was substituted by a more acid one. As had been shown by blank experiments, when a portion of electrolyte was replaced by an indentical one, the potential of the platinum electrode previously polarized to $\psi_z > 120-130$ mv shifted by no more than 0,2−0,3 mv. A similar solution replacement at lower ψ_z led to a more significant potential change, this change being the larger, the lower was ψz. This fact is due to the presence in the portion being replaced of considerable quantities of dissolved hydrogen which is in equilibrium with adsorbed hydrogen[x], as well as to the possible transition of hydrogen into the gas phase when the electrolyte is replaced. There-

x) Ref.[7] deals with the effect of the hydrogen dissolved in solution and metal upon the results of measurements. The presence of dissolved hydrogen does not affect the results of the verification of eq (1), provided the equilibrium between the dissolved hydrogen does not affect the results of the verification of eq (1). provided the equilibrium between the dissolved and adsorbed hydrogen is maintained at all changes in the system state which, however, in some cases can be hardly realized in practice. In particular, it is shown by calculations that in our experiments at $\psi_z = 30$ mv, the amount of hydrogen dissolved in the electrolyte is ~10% of adsorbed hydrogen, so that it was necessary to take precautions to keep the system isoelectric at low ψ_z.

fore, to maintain isoelectric conditions in the experiments, at low ψ_z the change of $[H^+]$ was effected by adding a calculated amount of concentrated HCl + 1 N KCl solution to the solution in the operating electrode compartment. At the lowest value of ψ_z (~0,025 v), at which the measurements were performed, in blank experiments the above procedure resulted in the potential shift in the anodic direction by no more than 1—2 mv. This value was subtracted from $\triangle\psi_z$ observed with changing pH of the solution, which at close to 25 mv was ~7—9 mv. Already at ψ_z=40 mv the potential shift in the blank experiment resulting from the above procedure was practically close to zero.

From $\left(\frac{\partial\lceil H}{\partial\psi_z}\right)_{\mu H^+,\mu_S}$ and $\left(\frac{\partial\psi_z}{\partial\mu_{H^+}}\right)_{\lceil H,\mu_S}$ obtained by the above methods by means of eq (1) was calculated the dependence of $\left(\frac{\partial\lceil H^+}{\partial\psi_z}\right)_{\psi H^+,\mu S}$ upon ψ_z. Since it is difficult to determine with a high accuracy $\left(\frac{\partial\lceil H^+}{\partial\psi_z}\right)_{\mu H^+,\mu S}$ directly by experiment, the dependence of $\lceil H^+$ upon ψ_z was found by integrating the $\left(\frac{\partial\lceil H^+}{\partial\psi_z}\right)_{\mu H^+,\ \mu S}\ \psi_z$ curve and then compared with the experimental value. The theoretical value of $\lceil H^+$ at the reversible hydrogen potential was determined by linear extrapolation of the calcualted $\lceil H^+, \psi_z$ curve from ψ_z = 0,025 to ψ_z = 0. The value of $\lceil H^+$ corresponding to γ_z = 0, determined by direct adsorption measurements, was used as the integration constant. For this purpose, a Pt/Pt electrode carefully washed with bidistillate, dried in air and saturated with hydrogen was brought into contact with a 1 N KCl + 0,01 N HCl solution saturated with hydrogen under atmospheric pressure. The change in the solution composition caused by the formation of the electric double layer was recorded [8]. The experimental values of $\lceil H^+$ at other potentials were also determined from the change in the solution acidity by a somewhat modified procedure suggested earlier in [8], which is as follows. The elecrode (80 cm^2) was polarized to the desired potential in the solution being investigated. Since this involved a change in the solution composition due to the transport phenomena and a change in the surface charge it was necessary after the potential had been stabilized at open circuit to replace several times the solution in the operating compartment of the cell by a 1 N KCl + 0,01 N HCl solution. Then the electrode was saturated with hydrogen and change in the acidity of the solution due to the difference in the surface charges at the initial $\gamma\tau$ and at γ_z = O was estimated. The change in the acidity was determined by titrating the boiling solution with barium hydroxide using cresol red as an indicator. The values of $\lceil H^+$ were calucalted per unit of true electrode surface. Since in the course of operation, the electrode surface was somewhat reduced due to re-crystallization, in calulating $\lceil H^+$ the charging curve was measured at regular intervals, the change in $\lceil H^+$ being assumed to be proportional to the reduction of the hydrogen part of the charging curve. The accuracy in the estimation of $\lceil H^+$ was ~ ± 2 μcoul/cm^2.

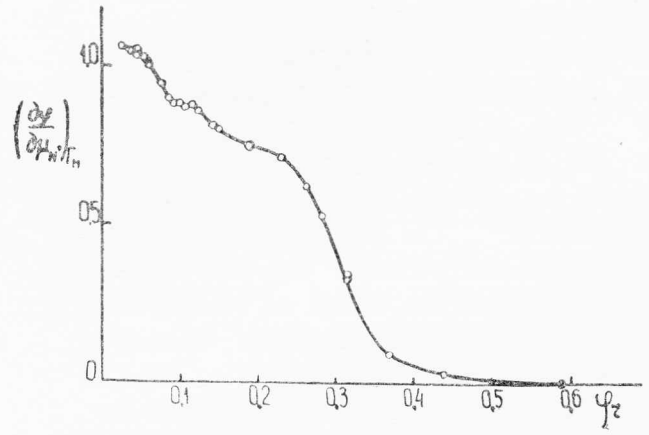


Fig. 1. Dependence of $\left(\frac{\partial\psi}{\partial\psi_{H^+}}\right)_{\Gamma_{H^+},\mu_S}$ upon ψz for a platinized platinum electrode.

Fig. 1 shows the dependence of $\left(\frac{\partial\psi}{\partial\mu_{H^+}}\right)_{\Gamma_{H},\mu_S}$ upon ψ_z. The quantity $\left(\frac{\partial\psi}{\partial\mu_{H^+}}\right)_{\Gamma_{H},\mu_S}$ is related to ..... $\left(\frac{\partial\psi_z}{\partial\mu_{H^+}}\right)_{\Gamma_{H},\mu_S}$ determined in the experiment by eq (2):

$$\left(\frac{\partial\psi}{\partial\mu_{H^+}}\right)_{\Gamma_{H},\mu_S} = \left(\frac{\partial\psi_z}{\partial\mu_{H^+}}\right)_{\Gamma_{H},\mu_S} + 1 \quad \ldots(2)$$

where ψ is the potential referred to normal hydrogen electrode.

The dependence of $\left(\frac{\partial\Gamma_{H^+}}{\partial\psi_z}\right)_{\mu_{H^+},\mu_S}$ upon ψ_z calculated by means of eq (1) is shown in Fig. 2. In Fig. 3 the calculated Γ_{H^+},ψ_z curve is compared with the experimental one.

As is clear from Fig. 1, at small $\left(\frac{\partial\psi}{\partial\mu_{H^+}}\right)_{\Gamma_{H},\mu_S}$ is close to unity. In other words, the dependence of the potential upon pH is similar to that observed in the case of an electrode being in equili-

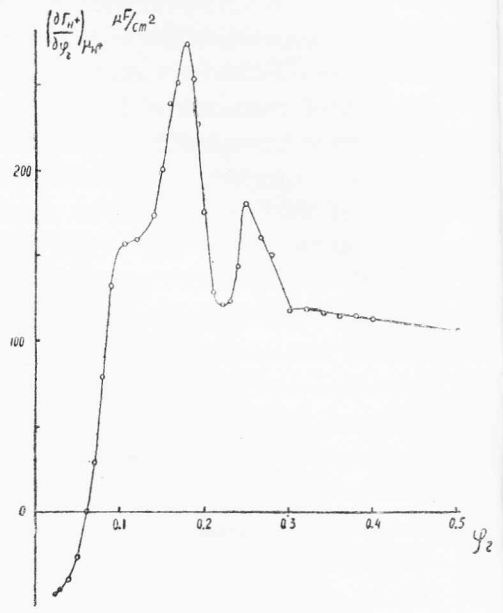


Fig. 2. Dependence of $\left(\frac{\partial\Gamma_{H^+}}{\partial\psi z}\right)_{\mu_S,\mu_{H^+}}$ upon ψz calculated by means of eq(1).

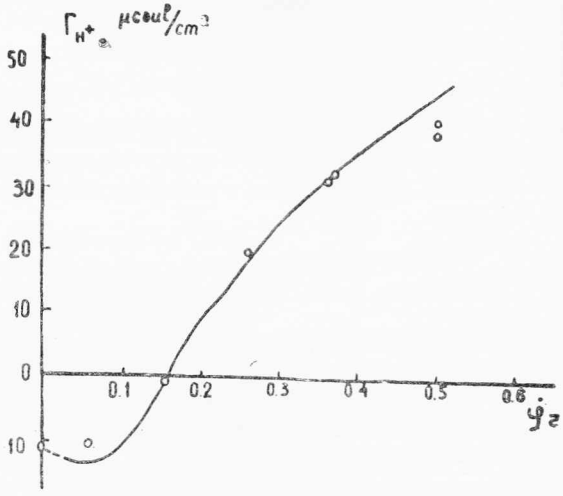
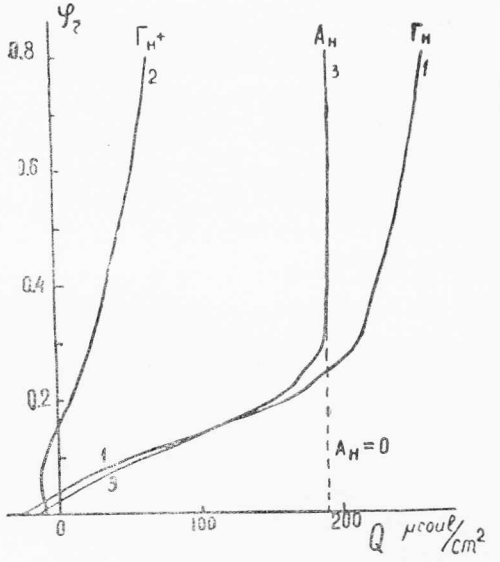


Fig. 3. Comparison of the theoretically calculated dependence of Γ_{H^+} upon ψz (full drawn curve) and the experimental values of Γ_{H^+} (circles) for 1N HCl+ 0,01N HCl solution.

brium with hydrogen gas at constant pressure. As it follows from eq (1) and a similar equation (8) in ref. [3], this is due to Γ_{H^+} but slightly changing with ψz at small ψz, rather than to the nature of the dependence of A_{H^-} the amount of hydrogen adsorbed on the electrode — upon ψz, e.g. to a considerable coverage of the surface with H_{ads} at small ψz. With increasing ψz $\left(\frac{\partial \psi}{\partial \mu_{H^+}}\right)_{\Gamma_H, \mu_S}$ dimirishes and at $\psi z \sim 0{,}5$ v becomes zero, i.e. the electrode ceases to operate as a hydrogen one, which is a natural consequence of the disappearance of A_H. According to Fig. 1, the coverage of the platinum surface with adsorbed hydrogen in a 1 N KCl + 0,01 N HCl solution is close to zero at $\psi z \sim 450$-500 mv.

As is evident from Fig. 3, the calculated values of Γ_{H^+} coincide with the experimental ones at ψ_z not in excess of 0,4 v within the accuracy of the measurements of Γ_{H^+} and which is especially important, the calculated curve intersects the abcissa at the same ψ_z as the experimental one. This supports the validity of treating the surface of the Pt/Pt electrode as an equilibrium system whose state at constant μ_s is determined by independent variables μ_H and μ_{H^+}, as well as the reliability of the experimental determination of the point of zero charges $\psi_{\varepsilon=0}$ [1, 8]. In the case of the system studied by us the latter lies at $\psi_z = 0{,}16$ v, i.e. $\psi_{\varepsilon=0} = 0{,}04$ v. The potential at which in the solution under investigation $\Gamma_H = 0$ can be determind from the intersection of the charging curve with the vertical line $A_H = 0$ (see ref. [1]. Such construction is shown in Fig. 4. Γ_H is seen to vanish at $\psi_z \sim 0{,}25$v, i e, $y \sim 0{,}14$v.

It is of interest to note that at $\psi_z < 0{,}06$ v, $\left(\frac{\partial \psi}{\partial \mu_{H^+}}\right)_{\Gamma_H \mu_S}$ is greater than unity i.e. $\left(\frac{\partial \psi_z}{\partial \psi_{H^+}}\right)_{\Gamma_H, \mu_S}$ is positive. According to eq (1), this is possible only at



Eig. 4. Charging curve (1), adsorption curve (2) and A_H ψz dependence (3) for 1 N KCl+0.01 N HCl solution.

$\left(\frac{\partial \Gamma_{H^+}}{\partial \psi^z}\right)_{\mu_{H^+}, \mu_S < 0}$. In other words, there should be a minimum on the Γ_{H^+}, ψ_z curve. This possibility was not envisaged in[1]. The acccuracy of the experimental determination of in the present investigation does not permit us to solve the problem of the reality of this effect. At $\psi_z = 0{,}5$ v there is certain discrepancy between the experimental and calculated values of Γ_{H^+}. It is possible that at this ψ_z the assumption of reversibility is not completely justified. This problem, however, requires furter investigation.

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