

SHORT COMMUNICATION

Physical meaning of the Gibbs adsorption Γ in the case of substances whose adsorption leads to surface charging

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As has been already pointed out (see refs. 1 and 2), there exist two different interpretations of the meaning of the quantity Γ in the case of adsorption of substances leading to surface charging*. One of these interpretations, which is quite common, treats the Gibbs adsorptions of the components of a redox system Γ_O and Γ_R as measures of the surface excesses of these components, actually present in the surface layer (see *e.g.* ref. 3). According to the second definition, which was used in a number of our works, Γ_O and Γ_R are the amounts of the oxidizing and reducing agents to be introduced into the bulk phase, along with the Γ_i of other solution components undergoing adsorption, in order that the solution composition and hence the electrode potential, should remain unchanged with surface increase by a unity without electricity supply [1,2] (see also ref. 9).

This difference can be best exemplified by an actual experiment [4], which will be described here somewhat simplifying the conditions of its realization.

As has been shown in refs. 5 and 6, if we deposit on the surface of ash-free activated carbon, previously outgassed under vacuum, a small amount of platinum, covering in the form of crystallites only a very small part of its surface, the carbon acquires the ability to assume a reversible hydrogen potential in a hydrogen saturated electrolyte solution and to adsorb alkali (this carbon models to some degree the platinum-promoted carbon electrodes of fuel cells).

Let us assume hydrogen chemisorption on carbon surface not covered by platinum to be negligible and the platinum surface per unit carbon surface to be so small, that the contribution of hydrogen adsorbed on platinum crystallites can be ignored as well. These conditions are very similar to those obtained in reality. Let us immerse this carbon in aqueous KOH solution and bring the system into equilibrium with hydrogen at atmospheric pressure.

* To facilitate comparison, some simplifying assumptions are made in this paper, viz. no account is taken of the partial charge transfer, and the concentration in the solution bulk of the substances undergoing adsorption is taken to be small enough, so that it is possible to ignore the difference between the amount of substance actually present in the surface layer and its excess content as compared to the case when adsorption is absent. The values of Γ are given in electrical units.

Hydrogen undergoes ionization on platinum sites to form water molecules with the OH^- ions of the solution. This gives rise to negative charges, spreading over the carbon surface, attracting K^+ cations and repelling OH^- ions. This process of surface charging stops when the carbon potential reaches the equilibrium value.

Under the above assumptions, the amount of adsorbed hydrogen present on the surface is insignificant. Then there arises the question: what is the value of Γ_{H} in the given system?

According to the prevailing interpretation of the meaning of Γ_{H} , the answer to this question is $\Gamma_{\text{H}} \approx 0$. According to the system of notation used in our works, $\Gamma_{\text{H}} = -Q'$, where Q' is the charge density of carbon surface, which in this particular case is equal to the free charge density ϵ . In making this statement, we proceed from the fact that at a reversible increase of carbon surface s by ds , it is necessary, in order to maintain constant the chemical potential of hydrogen dissolved in water μ_{H} , to introduce into the system the amount of hydrogen $\Gamma_{\text{H}}ds$. To increase s , it is necessary to spend the work equal to σds , where σ is the reversible work of formation of unit surface, the newly formed surface being identical with that existing earlier [7]. The reality of the quantity Γ_{H} becomes apparent if we decrease the value of $-Q'$, by decreasing the solution pH. In this case the decrease of Γ_{H} leads to hydrogen evolution, as was shown [4]*. The amount of evolved hydrogen is equal to $\Delta Q'$'s, where $\Delta Q'$ is the change of the charge of unit surface. The vital reasons which led us to choose a new interpretation of the quantities Γ in redox systems, unlike that generally used at present, were discussed in sufficient detail in refs. 1 and 2 and also in ref. 9 and we need not return to them now. Our present purpose is to find out what significance Gibbs himself ascribed to the quantity Γ in his treatment of electrocapillary phenomena [8].

Applying to a mercury electrode in H_2SO_4 solution his general adsorption equation (508), Gibbs arrives at the relation (690)

$$d\sigma' = (\Gamma'_a/a_a) d(V' - V'') \quad (1)$$

In deducing eqn. (690), Gibbs considers a circuit of two electrodes to which polarization is applied, V' and V'' being the potentials of these electrodes. It is assumed further that the area of one of these electrodes is small as compared to that of the second electrode, so that "the state of polarization of only one of the electrodes is affected". Thus, we can substitute the quantity $V' - V''$ by E , the potential of the first electrode measured against a constant reference electrode and drop the primes on all other quantities. The quantity a is the

* Actually in ref. 4 the alkaline solution was acidified, which led to visible evolution of hydrogen bubbles and to an increase in the gas phase volume. The basic quantitative measurements were carried out at increase of alkali concentration, accompanied by hydrogen adsorption, and not at a decrease of it. It should be noted that there are some inconsistencies in the treatment of alkali adsorption from concentrated solutions in ref. 4, which we shall consider elsewhere.

reciprocal of the charge of an electrochemically active particle (presently designated as $1/nF$). According to Gibbs this is hydrogen: "In applying equations (689) and (690) to dilute sulphuric acid between electrodes of mercury, as in Lippmann's electrometer, we may suppose that the suffix refers to hydrogen". It is of no account for further consideration whether it is hydrogen in atomic or in molecular form which is in question. In order to simplify as much as possible the writing of the equation, let us choose the atomic form. Then, considering that we express Γ in electrical units, we can substitute α_a in (1) by unity and rewrite eqn. (690) in the form

$$d\sigma = \Gamma_H dE \quad (2)$$

The fact that according to Gibbs in the case of mercury in the H_2SO_4 solution "in its natural state" hydrogen is the electrochemically active particle should not be surprising, since this assumption was in current use at that time. Thus, in his first paper [10] Lippmann says that as the result of contact with a sulphuric acid solution, mercury "polarisiert sich dieselbe dadurch mit Wasserstoff". According to Varley [11], who was the first to carry out a quantitative study of the electric double layer structure, the polarization of a mercury electrode depends on the "nascent hydrogen". It should be remembered that Warburg's paper [12], in which he showed that upon contact of H_2SO_4 solution with mercury in the presence of air, mercury salt is formed and adsorbed on the surface of mercury, appeared much later.

Let us follow Gibbs' reasoning: "It will be most convenient to suppose the dividing surface to be so placed as to make the surface density of mercury zero. The matter which exists in excess or deficiency at the surface may then be expressed by the surface densities of sulfuric acid, of water, and of hydrogen. The value of the last may be determined from equation (690). According to M. Lippmann's determinations, it is negative, when the surface is in its natural state (i.e. the state to which it tends when no external force is applied), since σ increases with $V'' - V'$ " (in our notation $V'' - V'$ is $-E$, thus the increase of $V'' - V'$ means cathodic polarization). It should be also pointed out that, as it follows from what Gibbs says further, he was quite certain about the positive sign of the charge of the mercury surface "in its natural state".

In the usual understanding of the word "adsorption" a significant negative adsorption of hydrogen on mercury surface seems to be difficult to understand. This was pointed out by Rice [13] in his well-known commentary to the works of Gibbs. To get out of this difficulty Rice suggested that it was not hydrogen that Gibbs meant but a hydrogen ion, whose negative adsorption was caused by repulsion by the positive charges of the mercury surface. However, Gibbs' formulation does not warrant this unexpected interpretation, as Gibbs did not consider (and could not do this) the structure of the ionic side of the electric double layer. Moreover, in the simplest picture of the double layer the positive charge of a positively charged metal surface is com-

pensated by the attraction of anions and not by the repulsion of cations*. The difficulties of the interpretation of the negative value of Γ_H are eliminated if we assume that Gibbs understood the sense of Γ_H as it is understood in ref. 1. In fact, according to Gibbs, the charging of mercury surface s_{Hg} follows the mechanism which can be written in the form**



i.e. it is accompanied by hydrogen evolution. This hydrogen does not remain on the mercury surface, but passes into the solution bulk, which corresponds to a negative adsorption in our understanding of this term. The sulphate ion remains adsorbed on the positively charged surface.

The above picture is quite similar to that suggested by us for the case of platinized carbon electrode in alkaline solutions at which a reaction similar to reaction (3) occurs, though in the opposite direction, which leads to hydrogen adsorption and negative surface charging. If weak sulphuric acid solutions are added to "hydrogen carbon" without preliminary adsorption of alkali, no hydrogen evolution occurs [4]. This is to be expected because the SO_4^{2-} anion is not adsorbed on an uncharged, the more so on a negatively charged carbon surface from diluted solutions [14]. However, when 2 M and 5 M concentrations of H_2SO_4 were reached in ref. 4 a significant hydrogen evolution was observed. Apparently, the sign of the charge on carbon changed with increase of the sulphuric acid concentration and the reaction on its surface proceeded in accordance with scheme (3). This conclusion, however, needs verification because the studies carried out in ref. 4 were concerned mainly with the phenomena observed in alkaline solutions.

If we use the notation adopted in ref. 1, the scheme of the interpretation of mercury charging according to Gibbs can be written as follows

$$Q' = -\Gamma_H = \epsilon; A_H = 0 \quad (4)$$

Though Gibb's scheme is not realized on mercury owing to the slowness of reaction (3) (and a more negative value of the p.z.c. as compared to carbon), nevertheless, if we assume its validity, all further conclusions made by Gibbs are quite justified in terms of the unique rigorously thermodynamic interpretation of the formation of the electric double layer at non-ideal polarized electrodes [1,2,9,15].

* In actual fact, due to the superequivalent adsorption of the SO_4^{2-} ions, the adsorption of H^+ at a positive charge of mercury is positive and not negative.

** Gibbs says nothing about the fate of the rest of the H_2SO_4 particle after hydrogen evolution.

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