

POTENTIALS OF ZERO TOTAL AND ZERO FREE CHARGE OF PLATINUM GROUP METALS

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Abstract—Some fundamental definitions and relations of the thermodynamic theory of the platinum electrode are considered. The notions of the potential of zero total charge (*pztc*) of the first and second kind are discussed. It is shown that in the presence of excess of surface-inactive ions, the potential of zero total charge of the second kind can be regarded as the potential of zero free charge (*pzfc*). The *pzfc* is an analogue of the *pzc* of metals not adsorbing hydrogen and oxygen. The methods of determination of the *pztc* and the *pzfc* of platinum metals, of their dependence on solution pH and salt concentration are considered, as well as the dependence of the *pzfc* on surface coverage with adsorbed hydrogen. Tables listing the *pztc* and the *pzfc* of platinum metals are given. The conditional nature of the notions *pzfc* and the charge of the double layer in the presence of strong chemisorption of ions is demonstrated and the difference between the formal and the true coefficients of charge transfer is emphasized. The notion of the charging curves and electrocapillary curves of the first and second kind is introduced and the methods of their finding are discussed. The electrocapillary curves of the first and second kind are given for platinum in solutions of different composition.

The thermodynamic theory of surface phenomena at platinum metals was outlined in [1, 2], set out in [3] and developed further in [4-27]. In this theory the electrode is assumed to be reversible with respect to the hydrogen (or oxygen) discharge-ionization and ions adsorption processes and therefore its state can be described by means of the Gibbs adsorption equation. The theory was experimentally verified for thirty systems with electrodes from Pt [5, 6, 8, 12, 15, 16, 18, 28], Pd [29], Rh [7, 8, 11, 17], Ir [14, 17, 21], Ru and Pt-Ru [8, 10]. The verification has shown that the theory developed is applicable not only at the potentials of the hydrogen and "double layer" regions, but also in the initial section of the region of oxygen adsorption. Strongly pronounced chemisorption of solution ions limits the practical applicability of the theory.

Both in the first stage of development (see discussion in [3]) and later (eg, [30]) some questions were posed and critical remarks made, pointing primarily to the difficulty of understanding the physical meaning of the quantities contained in the thermodynamic relations (in Parsons's preface to the book [31] it is stated that the theory in question is a "controversial" one). The discrepancies in the terminology and designations of the same quantities were one of the reasons of the difference between the conclusions formulated in [32] and [23] (see also [30] and [33]*). So far only in [35] the thermodynamic theory of surface phenomena on reversible electrodes was used and extended to new systems. Therefore, before passing to the analysis of some new results, it is necessary to dwell once more on some relations of this theory.

1. FUNDAMENTAL RELATIONS OF THE THERMODYNAMIC THEORY OF THE PLATINUM ELECTRODE

In the experimental verification of the theory in solutions of acids with neutral salt excess ($\text{HA} + \text{CA}$, $[\text{HA}] \ll [\text{CA}]$) use was made of the relation

$$\left(\frac{\partial \varphi_r}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}}, \mu_{\text{CA}}} = \left(\frac{\partial \Gamma_{\text{H}^+}}{\partial \varphi_r} \right)_{\mu_{\text{H}}, \mu_{\text{CA}}} : \left(\frac{\partial \Gamma_{\text{H}}}{\partial \varphi_r} \right)_{\mu_{\text{H}}, \mu_{\text{CA}}} \quad (1)$$

where φ_r is the potential with respect to the reversible hydrogen electrode in the same solution, μ_{H^+} and μ_{CA} the chemical potentials of the H^+ ions and of the salt CA, Γ_{H} and Γ_{H^+} the Gibbs adsorptions of hydrogen atoms and ions, respectively. All quantities in relation (1) are expressed in electrical units. This equation is valid also for alkalinized solutions of neutral salts. The name "isoelectric shift of potential" was proposed for the quantity $(\partial \varphi_r / \partial \mu_{\text{H}^+})_{\Gamma_{\text{H}}, \mu_{\text{CA}}}$ †.

The Gibbs adsorptions Γ_{H} and Γ_{H^+} are understood to be the amounts of the respective components to be introduced into the system in order that with the electrode surface increase by 1 cm^2 without electricity supply from outside, the chemical potentials of these components in the bulk phase remain unchanged. Evidently, in this case the electrode potential also keeps its constant value.

As the surface increase is carried out without supply of electricity from a foreign source, the fundamental Gibbs equation can be applied without the introduction of the electrode potential. It is convenient to write it in the form

$$d\sigma = -\Gamma_{\text{H}} d\mu_{\text{H}} - \Gamma_{\text{H}^+} d\mu_{\text{H}^+} - \sum_i \Gamma_i d\mu_i \quad (1a)$$

* In the last mentioned case as the result of the discussion, the points of view drew somewhat closer to one another.

† This term was first used in [36].

where σ is the reversible work of unit surface formation, μ_H the chemical potential of hydrogen in the atomic form. The summation $\sum_i \Gamma_i d\mu_i$ extends on all components of the solution except the H^+ ion and the H atom, the position of the interface is defined by the condition $\Gamma_{H,O} = 0$. From equation (1a) the relation (1) can be easily derived.*

Equation (1a) can be applied to our system irrespective of what happens to the hydrogen atoms and ions introduced into the system after surface increase. However, taking into account the possibility of an exchange between ions and atoms, we must distinguish between the Gibbs adsorptions and the actual surface excesses designated by us as A_H and A_{H^+} . Within the limits of the applicability of the classical concept of the electrode charge ϵ , the relation between Γ_H and A_H and between Γ_{H^+} and A_{H^+} can be expressed by the formulas

$$\Gamma_H = A_H - \epsilon \quad (2)$$

$$\Gamma_{H^+} = A_{H^+} + \epsilon \quad (3)$$

The distinction between Γ and A is a characteristic feature of the system of designations used by us. It should be once more emphasized that while Γ_H and Γ_{H^+} are thermodynamic quantities, which in principle can be directly determined experimentally, the introduced quantities A_H , A_{H^+} and ϵ are associated with certain models. For this reason, it appears to us inadmissible to call the quantities A Gibbs adsorptions, as it is often done.

Introducing the quantities A and ϵ , we do not take into account for all ions present in the double layer what Lorenz[37] calls partial charge transfer. The relationship between our terminology and that of Schultze and Vetter[30] is discussed in detail in [33]. As will be shown later, in the case of ions strongly chemisorbed on platinum metals, it is practically impossible to determine the value of ϵ and hence to divide the quantities Γ into A and ϵ .

In the presence of a salt excess in solution, hydrogen ions are displaced from the diffuse part of the double layer by salt cations†, so that $A_{H^+} = 0$ and $\Gamma_{H^+} = \epsilon$. Practically complete displacement of hydrogen ions from the double layer is reached, as shown in [19, 38, 39] at a 5-10-fold excess of alkali metals salts in solution. Under these conditions equation (1) can be rewritten as:

$$\begin{aligned} \left(\frac{\partial \varphi_r}{\partial \mu_{H^+}} \right)_{(A_H - \epsilon), \mu_{C_A}} &= \left(\frac{\partial \epsilon}{\partial \varphi_r} \right)_{\mu_{H^+}, \mu_{C_A}} \left/ \left(\frac{\partial (A_H - \epsilon)}{\partial \varphi_r} \right)_{\mu_{H^+}, \mu_{C_A}} \right. \\ &= \frac{1}{(\partial A_H / \partial \epsilon)_{\mu_{H^+}, \mu_{C_A}} - 1} \end{aligned} \quad (4)$$

Relation (4) is no longer a strictly thermodynamic one, but its correctness depends only on the possibility of

determining unambiguously ϵ and A_H and does not depend on the use of the terminology proposed by us.

As already mentioned, in the electrochemical literature the symbol Γ is often used instead of A for designation of surface excesses without due regard to the fact that this quantity cannot be given a thermodynamic definition. With the use of this designation, instead of (4), we should write

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}} \right)_{(\Gamma_H - \epsilon), \mu_{C_A}} = \frac{1}{(\partial \Gamma_H / \partial \epsilon)_{\mu_{H^+}, \mu_{C_A}} - 1} \quad (4a)$$

As is shown in [23], $\Gamma_H = -Q'$ and $\Gamma_{H^+} = Q''$, where Q' and Q'' are the total surface charges, i.e., the amounts of electricity to be introduced at $\mu_{H^+} = \text{constant}$ or $\mu_H = \text{constant}$, respectively, so that with the electrode surface increase by 1 cm², the bulk phase composition should not change if the loss of hydrogen through adsorption is compensated by introduction of an amount of hydrogen equal to $\Gamma_H + \Gamma_{H^+} = A_H + A_{H^+}$ in the form of H in the first case and of H^+ in the second. Therefore

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}} \right)_{Q', \mu_{C_A}} = - \left(\frac{\partial \epsilon}{\partial \varphi_r} \right)_{\mu_{H^+}, \mu_{C_A}} \left/ \left(\frac{\partial Q'}{\partial \varphi_r} \right)_{\mu_{H^+}, \mu_{C_A}} \right. = - \frac{C_{dl}}{C} \quad (5)$$

or

$$C_{dl} = - \left(\frac{\partial \varphi_r}{\partial \mu_{H^+}} \right)_{Q', \mu_{C_A}} C \quad (6)$$

where C_{dl} is the equilibrium capacity of the electric double layer, C the overall polarization capacity of the electrode. Thus, the isoelectric shift of potential characterizes the contribution of the double layer capacity to the overall polarization capacity of the electrode [40, 41].

In what follows we shall use the following designations and terminology. For Q' we shall retain the symbol Q and will call this quantity the total surface charge (Lorenz's thermodynamic surface charge), neglecting for brevity sometimes the condition $\mu_{H^+} = \text{constant}$. Instead of Q'' we shall use the symbol Γ_{H^+} and to distinguish this total charge from Q , we shall call Γ_{H^+} the free charge, bearing in mind, however, that this is admissible only in the presence of a supporting electrolyte excess and that this term overpasses the limits of the thermodynamic theory. In the general case Q'' stands for the total electrode charge at $\mu_H = \text{constant}$. The quantities Q and Γ_{H^+} can be also called total charges of the first and second kind respectively. In pure acid solution $\Gamma_{H^+} = \Gamma_{A^-}$.

In the verification of the thermodynamic theory in acid solutions, HA, without neutral salt addition the relation

$$\left(\frac{\partial \varphi_r}{\partial \mu_{+}} \right)_Q = 2 \left(\frac{\partial \Gamma_{H^+}}{\partial \Gamma_H} \right)_{\mu_{+}} \quad (7)$$

was used, where μ_{+} is the mean chemical potential of the ions of the acid. Since $\Gamma_{H^+} = \Gamma_{A^-}$ and $\Gamma_H = -Q$

$$\begin{aligned} \left(\frac{\partial \varphi_r}{\partial \mu_{+}} \right)_Q &= \left(\frac{\partial \varphi_r}{\partial \mu_{+}} \right)_{\epsilon - A_H} = -2 \left(\frac{\partial \Gamma_{A^-}}{\partial Q} \right)_{\mu_{+}} \\ &= -2 \left[\frac{\partial \Gamma_{A^-}}{\partial (\epsilon - A_H)} \right]_{\mu_{+}} \end{aligned} \quad (8)$$

* In order to give equation (1a) a symmetrical form use was made of the chemical potential of the H^+ ion instead of that of an acid molecule. This partly limits the applicability of equation (1a) to dilute solutions. It was shown in ref. [8] how this limitation can be eliminated.

† The hydrogen ions contained in the dense part of the double layer and not displaced by foreign surface inactive cations are indistinguishable from adsorbed hydrogen atoms and are numbered with these.

In many thermodynamic relations for a mercury electrode ϵ is used as the quantity remaining constant during differentiation, whereas in the relations for a platinum electrode considered above we have a more complex quantity $Q = \epsilon - A_H$. This is explained by the fact that in measurements on platinum metals the condition $Q = \text{constant}$ only can be fulfilled and not $\epsilon = \text{constant}$.

2. POTENTIALS OF ZERO TOTAL CHARGE

In accordance with the concept of the electrode charge and the terminology introduced above for platinum metals, we should distinguish between potentials of zero total charge and those of zero free charge.

The potential at which the quantity $Q = -\Gamma_H = \epsilon - A_H$ vanishes we call the potential of zero total charge $\varphi_{Q=0}$ (*pztc*) or potential of zero charge of the first kind.

* Such measurements were attempted with smooth platinum [42]. But the extent of evacuation was, probably, insufficient and the potentials set up were treated as the potentials of zero charge of the double layer. In the case of the Pt/Pt electrode, additional difficulties arise due to sintering and possible changes in the surface layer structure during heating, which is necessary for evacuation. Measurements with smooth Pt are continued.

Evidently, the potential $\varphi_{Q=0}$ should be set up when an electrode previously completely degassed under vacuo is immersed into solution [23]. Up to the present time, this direct method of determination of the *pztc* has not been properly realized*.

For determination of *pztc* was based on the nonthermodynamic equation $Q = \epsilon - A_H$. Experience shows that in a certain potential range, which became known as the double layer region, in HCl + KCl and HBr + KBr solutions ($[HCl] \ll [KCl]$ and $[HBr] \ll [KBr]$), the Q, φ_r and Γ_{H^+}, φ_r -curves for platinum electrodes are parallel. This leads to the assumption that in this potential range $A_H = 0$ and $Q = \epsilon$. Thus in the case of the solutions mentioned in the double layer region of potentials it is possible to determine the values of Q . Knowing Q at some potential, we can determine $\varphi_{Q=0}$. For this purpose it is convenient to use the graphical method described in [1, 22]. Since in fluoride [43], acidified sulphate and alkalinized solutions due to the overlapping of the hydrogen and oxygen regions, no real double layer region exists, for determination of $\varphi_{Q=0}$, the transition from these solutions to chloride solutions under isoelectric conditions was used. A similar method was used for rhodium and palladium. Owing to the absence of a clearly defined double layer region, even in the presence of bromine anions, $\varphi_{Q=0}$ for iridium could be determined only approximately [21]. For Ru $\varphi_{Q=0}$ could not be determined.

Table 1. Potentials of zero total charges of platinum metals

Solution	$\varphi_{Q=0}, V$ (<i>nhe</i>)	Reference	<i>pzc</i> according to [44]
Platinum			
0.3 M HF + 0.12 M KF (pH 2.4)	0.235	[43]	
0.5 M Na ₂ SO ₄ + 0.005 M H ₂ SO ₄ (pH 2.4)	0.20	[24]	
0.05 M K ₂ SO ₄ + H ₂ SO ₄ (pH 2.4)			0.14
1 M KCl + 0.01 M HCl	0.14	[6]	
0.1 M KCl + HCl (pH 2)			0.08
1 M KBr + 0.01 M HBr	0.06	[24]	
0.1 M KBr + H ₂ SO ₄ (pH 2)			0
0.5 M Na ₂ SO ₄ + 0.01 M NaOH	-0.25	[24]	
0.05 M K ₂ SO ₄ + NaOH (pH 12)			-0.33
1 M KCl + 0.01 M KOH	-0.30	[24]	
0.1 M KCl + NaOH (pH 12)			-0.33
1 M KBr + 0.01 M KOH	-0.33	[24]	
0.1 M KBr + NaOH (pH 12)			-0.33
1 M KJ + 0.01 M KOH	-0.48	[24]	
0.1 M KJ + NaOH (pH 12)			-0.51
0.005 M H ₂ SO ₄ + 0.05 M Na ₂ SO ₄ + 0.005 M ZnSO ₄	0.29	[48]	
Palladium			
0.05 M Na ₂ SO ₄ + 0.001 M H ₂ SO ₄	0.26	[29]	
Rhodium			
0.3 M HF + 0.12 M KF (pH 2.4)	0.085	[43]	
0.5 M Na ₂ SO ₄ + 0.005 M H ₂ SO ₄	0.03	[24]	
0.5 M K ₂ SO ₄ + H ₂ SO ₄ (pH 2.4)			0.07
1 M KCl + 0.01 M HCl	0.02	[24]	
0.5 M Na ₂ SO ₄ + 0.01 M NaOH	-0.40	[24]	
0.5 M K ₂ SO ₄ + NaOH (pH 12)			-0.47
Iridium			
0.5 M Na ₂ SO ₄ + 0.005 M H ₂ SO ₄	0.10	[21]	
0.5 M K ₂ SO ₄ + H ₂ SO ₄ (pH 2.4)			0.1
1 M KCl + 0.01 M HCl	0.06	[21]	
1 M KBr + 0.01 M HBr	-0.03	[21]	
1 M KBr + H ₂ SO ₄ (pH 2)			-0.08

The results of determination of $\varphi_{Q=0}$ on platinum metals are listed in Table 1. The most anodic values of $\varphi_{Q=0}$ correspond to palladium and platinum. The values of $\varphi_{Q=0}$ shift in the negative direction with increasing adsorbability of the solution anions and in the positive direction with increasing adsorbability of the cations.

Table 1 also gives the potentials set up on the electrodes when their surface is continuously scraped at open circuit, determined by Fyring *et al* [44]. This method of determination of the potentials of zero charge is similar to that of the streaming electrode used for mercury and other liquid electrodes [45]. If we assume an equilibrium between electrode and solution to be present during the renewing of the electrode surface, then on platinum metals we must obtain the values of $\varphi_{Q=0}$ [21] and not those of the potentials of zero charge of the double layer. The data compared in Table 1 confirm this assumption*.

The authors of [47] used a variety of the method suggested in [44]: the cleaning of the electrode surface was carried out at constant potential and the current arising in the circuit was measured. Evidently, the potential at which the current vanishes must be also equal to $\varphi_{Q=0}$.

It follows from Table 1 that $\varphi_{Q=0}$ depends on solution pH. Theoretically this dependence can be discussed on the basis of equation (4) written for $Q = 0$ [24]

$$\left(\frac{\partial \varphi_r}{\partial \mu_{H^+}} \right)_{Q=0, \mu_{CA}} = \frac{1}{(\partial A_H / \partial \epsilon)_{\mu_{H^+}, \mu_{CA}} - 1} \quad (9)$$

or, if we pass to the potentials φ measured against a constant reference electrode:

$$\left(\frac{\partial \varphi}{\partial \mu_{H^+}} \right)_{Q=0, \mu_{CA}} = \frac{1}{1 - (\partial \epsilon / \partial A_H)_{\mu_{H^+}, \mu_{CA}}} \quad (10)$$

According to equation (10) at $(\partial \epsilon / \partial A_H)_{\mu_{H^+}, \mu_{CA}} = 0$, i.e., at $(\partial \epsilon / \partial \varphi_r)_{\mu_{H^+}, \mu_{CA}} = 0$, $(\partial \varphi / \partial \mu_{H^+})_{Q=0, \mu_{CA}} = 1$ and *pztc* shifts with pH just as the potential of the reversible hydrogen electrode. If, however, at $Q = 0$, the value of $(\partial \epsilon / \partial A_H)_{\mu_{H^+}, \mu_{CA}} < 0$, which corresponds to increase of the positive charge of the double layer with the potential shifting in the anodic direction, then $(\partial \varphi / \partial \mu_{H^+})_{Q=0, \mu_{CA}} < 1$.

The dependence of $\varphi_{Q=0}$ on pH was plotted in [24] from the results of measurements of the isoelectric shifts of potential with change in pH for initial $Q = 0$. Both on platinum and on rhodium, in acid sulphate, chloride and bromide solutions the shift of $\varphi_{Q=0}$ with pH is somewhat less than that of the reversible hydrogen electrode potential. In agreement with the experimental data this points to the fact that $(\partial \epsilon / \partial A_H)_{\mu_{H^+}, \mu_{CA}} < 0$. In alkaline solutions $(\partial \varphi / \partial \mu_{H^+})_{Q=0, \mu_{CA}} \approx 1$. This result also agrees with the direct measurements of the Γ_{H^+}, φ -curves in alkaline solutions [23] since in these solutions at $\varphi_{Q=0}$ $\partial \epsilon / \partial \varphi_r)_{\mu_{H^+}, \mu_{CA}} \approx 0$. More detailed measurements of the dependence of $\varphi_{Q=0}$ on pH are possible if use is made of the method of potentiometric titration at constant total surface charge, that is under isoelectric condi-

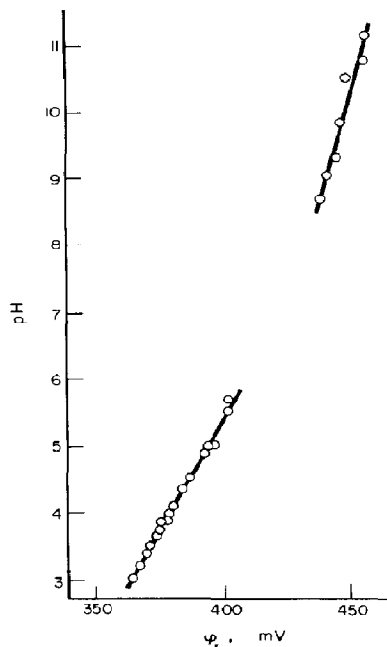


Fig. 1. Dependence of the potential of zero total charge on pH at Pt/Pt electrode in 0.05 M Na_2SO_4 obtained by potentiometric titration under isoelectric conditions (according to the data of T. Kolotyrykina).

tions, developed recently [49]. The method is essentially as follows: the solution surrounding an isolated Pt/Pt (platinized platinum) electrode, previously stabilized at a given potential value, is titrated in an inert gas atmosphere. Owing to introduction of a glass electrode into the cell, it is possible, along with the platinum electrode potential, to determine the solution pH and to obtain the dependence of the electrode potential on pH at constant total surface charge in integral form. Figure 1 shows the dependence of the potential corresponding to zero total surface charge, on solution pH, in 0.05 M Na_2SO_4 . On the basis of the results of potentiometric titration under isoelectric conditions, the conclusions made earlier for pH ranges 1.5–3 and 11–13 could be extended to pH 5.5 and 8.5, respectively. In pH range 5.5–8.5 without buffering additions it proved impossible to reach a completely reversible potential shift with changing pH, owing, probably to the difficulties of levelling the H^+ and OH^- ions concentrations near different areas of the electrode surface [49]. As will be shown in a forthcoming publication we succeeded recently in overcoming this difficulty and obtaining a continuous $(\partial \varphi / \partial \text{pH})_{Q=0, \mu_{CA}}$ relation.

The thermodynamic theory also gives a relation for the dependence of *pztc* on neutral salt concentration, at constant solution pH, or at constant acid concentration in solution [3]:

$$\left(\frac{\partial \varphi_r}{\partial \mu_{CA}} \right)_{Q, \mu_{HA}} = -2 \left(\frac{\partial \Gamma_{C^+}}{\partial Q} \right)_{\mu_{CA}, \mu_{HA}} \quad (11)$$

$$\left(\frac{\partial \varphi_r}{\partial \mu_{CA}} \right)_{Q, [\text{HA}]} = -2 \left(\frac{\partial \Gamma_{C^+}}{\partial \varphi} \right)_{\mu_{CA}, \mu_{HA}} - \left(\frac{\partial \Gamma_{H^+}}{\partial Q} \right)_{\mu_{CA}, \mu_{HA}} \times \left(\frac{\partial \mu_{HA}}{\partial \mu_{CA}} \right)_{[\text{HA}]} \quad (12)$$

* Unlike Trasatti [46], we borrowed from [44] the values obtained in acidified or alkalinized solutions. It seems to us that in neutral unbuffered solutions continuous surface renewing could lead to a change of solution pH.

where Γ_{C^+} is the Gibbs adsorption of cations, μ_{HA} is the chemical potential of acid and μ_{CA}^\pm the mean chemical potential of the salt ions. In diluted solutions with neutral salt excess

$$\left(\frac{\partial \varphi_i}{\partial \mu_{CA}^\pm}\right)_{Q, \mu_{H^+}} = -\left(\frac{\partial \Gamma_{C^+}}{\partial Q}\right)_{\mu_{H^+}, \mu_{CA}^\pm} - \left(\frac{\partial \Gamma_{A^-}}{\partial Q}\right)_{\mu_{H^+}, \mu_{CA}^\pm} \quad (13)$$

where Γ_{A^-} is the Gibbs adsorption of anions.

In accordance with the terminology used in earlier works [50–52], the quantity $(\partial \varphi_i / \partial \mu_{CA}^\pm)_{Q, \mu_{H^+}}$ was called the adsorption shift of potential.

By determining the adsorption shift of potential at the initial potential equal to $\varphi_{Q=0}$, it is possible to find the dependence of *pzt*c on salt concentration. This dependence was obtained for acidified KBr [18] and KCl [53] solutions. The increase of KBr concentration by an order of magnitude shifts the *pzt*c in the negative direction by ~ 20 mv. When a 2×10^{-3} M HCl + 10^{-2} M KCl solution is substituted by a 2×10^{-3} M HCl + 2.5×10^{-1} M KCl solution, the shift of *pzt*c in the negative direction is ~ 15 mv. A more negative value of $\varphi_{Q=0}$ than in the initial solution, established with increasing concentration of specifically adsorbed ions, is due to the fact that the potential difference arising between the layer of superequivalently adsorbed anions and the cations attracted to them, is subtracted from the potential difference in the 'Pt A' layer. This problem is considered at length in [18].

3. POTENTIALS OF ZERO FREE CHARGE

The potential $\varphi_{\Gamma_{H^+}=0}$ at which, in a solution with neutral salt excess, the total charge Γ_{H^+} vanishes we call the *pzt*c of the second kind or (with the restrictions mentioned above) the potential of zero free charge (*pzfc*). This potential can be found from direct measurements of the dependence of Γ_{H^+} on φ or from those of the dependence of the anions (Γ_{A^-}) and cations (Γ_{C^+}) adsorptions on φ in solutions with salt excess. In the second method, first used by Balashova [54], the *pzfc* is the potential at which $\Gamma_{A^-} = \Gamma_{C^+}$, because according to the condition of electroneutrality $\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+}$.

In solutions with excess of surface-inactive electrolyte, the quantity defined by us as *pzfc* is the potential of zero charge of the double layer and an analogue of the *pzc* of metals not adsorbing hydrogen. As a rule, the surface activity of ions on platinum group metals is more pronounced than on mercury. This is clear, for example, from the large difference in the adsorbability of sodium and cesium [55] or fluorine and sulphate [43] ions on platinum. The Li^+ and Na^+ cations and F^- anions show the lowest adsorbability on platinum. It is in the presence of these ions that *pzfc* can be regarded as the characteristic *pzc* of the platinum group metals at a given A_H value.

In other cases there arise significant complications due to formation of strong chemisorption bonds between metal surface and adsorbed ions. The bonds between strongly adsorbed ions with platinum group metals proved to be mainly covalent. In some cases, for example, in adsorption of Cd^{2+} and Tl^+ ions, a surface alloy with platinum metals may be formed [56, 57] (results testifying to the formation of surface alloys during specific adsorption of cations have been obtained recently by means of the thin-layer two-electrode

technique [58] and by voltammetry at the rotating ring-disc electrode [59] as well). Therefore, as has been already pointed out, in considering the mechanism of ions chemisorption on platinum metals, it is necessary to take into account the partial transfer of the ions charge to the metal surface (using Lorenz's terminology [37]).

In what follows the problem of charge transfer is treated qualitatively just as in the case of the quantity λ used by Lorenz, which should be called "true (or microscopic) coefficient of charge transfer", because we have no quantitative method at our disposal for its determination. It should be noted that for the redox system H^+ , H_{ads} at platinum we determined another quantity $-n_2$, which we proposed to call "formal coefficient of charge transfer" during the transition of a dissolved hydrogen atom H_s into H_{ads} [33, 61]:

$$\begin{aligned} -n_2 &= -\left(\frac{\partial \epsilon}{\partial A_H}\right)_\varphi = -\left[\left(\frac{\partial \Gamma_{H^+}}{\partial \mu_H}\right)_{\mu_{H^+}} + \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\mu_{H^+}}\right] / \\ &\quad \left[\left(\frac{\partial \Gamma_H}{\partial \mu_H}\right)_{\mu_{H^+}} + 2\left(\frac{\partial \Gamma_{H^+}}{\partial \mu_H}\right)_{\mu_{H^+}} + \left(\frac{\partial \Gamma_{H^+}}{\partial \mu_{H^+}}\right)_{\mu_{H^+}}\right] \\ &= -\left(\frac{\partial A_H}{\partial \mu_{H^+}}\right)_{\mu_H} / \left[\left(\frac{\partial A_H}{\partial \mu_H}\right)_{\mu_{H^+}} + \left(\frac{\partial A_H}{\partial \mu_{H^+}}\right)_{\mu_{H^+}}\right] \end{aligned}$$

The right hand side of this equation represents the ratio of the contributions of the hydrogen atom X and the hydrogen ion Y (viz the corresponding free charge) to the establishment of the metal-solution potential difference

$$\begin{aligned} -\left(\frac{\partial \epsilon}{\partial A_H}\right)_\varphi &= \left(\frac{\partial \varphi}{\partial A_H}\right)_\epsilon / \left(\frac{\partial \varphi}{\partial \epsilon}\right)_{A_H} \\ &= \left(\frac{\partial \varphi}{\partial A_H}\right)_{\Gamma_{H^+}} / \left(\frac{\partial \varphi}{\partial \Gamma_{H^+}}\right)_{A_H} \end{aligned}$$

This was already shown in [1]. Grafov calls the quantity $-n_2$ "macroscopic charge transfer coefficient" [61]. Vetter and Schultze characterize the charge transfer on adsorption of a particle i in the simplest case of a foreign electrolyte excess introducing a quantity γ , which they call "electrosorption valency" and determine by the relation $\gamma = -(\partial \epsilon / \partial \Gamma_i)_\varphi$ [30]. The quantity Γ_i , which according to Schultze and Vetter designates the Gibbs adsorption, corresponds, as already noted, to our A. The identity between the definitions of our $-n_2$ and γ is therefore evident. Lorenz designates quantities which are equivalent to $-n_2$ and γ (cf [84]), that is to the formal coefficient of charge transfer, by the letters l and f . It should be kept in mind, that the formal coefficient of charge transfer, which depends not only on the distribution of the charge between the adsorbed ion and the electrode, but on the influence of the adsorbed particle on the double layer capacity as well [30, 33, 84], cannot be identified with the true coefficient of charge transfer.

Large extents of adsorption of some ions on platinum metals [57] are evidence in support of charge transfer, as in the absence of charge transfer such large extents would be hardly possible due to electrostatic mutual repulsion of adsorbed ions. This concept is supported by the data on the kinetics of adsorption and ion exchange [57, 60], analysis of the adsorption isotherms for anions [62] and measurements of the

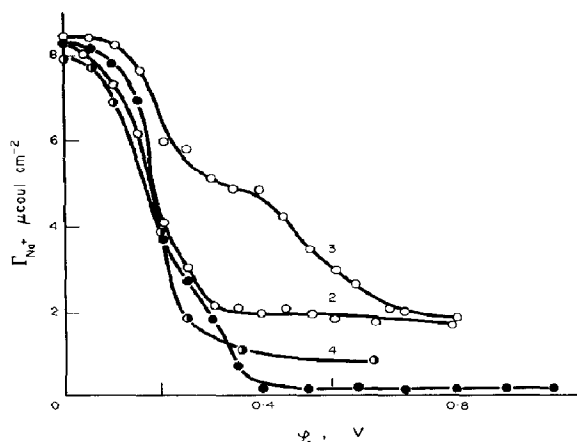


Fig. 2. Dependence of sodium cations adsorption on potential of Pt/Pt electrode in the solutions: 1- $5 \cdot 10^{-4}$ M H_2SO_4 + $15 \cdot 10^{-4}$ M Na_2SO_4 ; 2- 10^{-3} M HCl + $3 \cdot 10^{-3}$ M KCl ; 3- 10^{-3} M HBr + $3 \cdot 10^{-3}$ M NaBr ; 4- $5 \cdot 10^{-4}$ M H_2SO_4 + $3 \cdot 10^{-3}$ M NaI (according to the data of [63]).

superequivalent adsorption of anions, which were carried out on platinum and rhodium in acidified Na_2SO_4 , NaCl , NaBr and NaI solutions [63]. The results for a platinum electrode are shown in Fig. 2. In solutions of the same concentration in the region of positive surface charges at $\phi_r < 0.65$ V, the adsorption of sodium cations increases in the series $\text{Na}_2\text{SO}_4 < \text{NaCl} < \text{NaBr}$. In bromide solution the adsorption of Na^+ decreases with the shift of ϕ_r in anodic direction, and at $\phi_r \sim 0.7$ V is close to the value of Γ_{Na^+} in chloride solution. If we assume the adsorption of sodium cations at positive surface charges to be the result of the superequivalent adsorption of anions, then from the obtained data we can conclude that the superequivalent adsorption of anions on platinum increases in the series $\text{SO}_4^{2-} < \text{I}^- < \text{Cl}^- < \text{Br}^-$. At the same time, the adsorbability of anions on platinum metals increases in the series $\text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{I}^-$ [57]. The discrepancy between the series of increase of adsorbability and superequivalent adsorption can be explained qualitatively if we assume that with rising adsorbability, the state of adsorbed anions approaches more and more the atomic state or, in other words, the transfer of the anions charge to metal surface increases. With increasing adsorbability, the extents of superequivalent adsorption should increase, whereas as the result of charge transfer, the effective charge of superequivalently adsorbed anions, and, accordingly, the amount of cations attracted by them, decreases. The approximately constant value of Na^+ adsorption or its decrease with rising ϕ_r are probably due to increase in the degree of the anions charge transfer with the potential shifting in anodic direction. It follows from the comparison of the data for platinum and rhodium electrodes that the transfer of the anions charge to metal

surface increases when passing from platinum to rhodium.

Owing to partial charge transfer, the very definition of the quantity $pzfc$, as well as the validity of its equating with $\phi_{r_{\text{Na}^+}=0}$ becomes doubtful. Therefore, the quantity $\phi_{r_{\text{Na}^+}=0}$, whose physical sense does not depend on the solution nature, in solutions containing specifically adsorbable ions can be treated as $pzfc$ only conditionally.

The conditional character of the idea of the $pzfc$ in the presence of strong specific adsorption was illustrated for a Pt electrode covered by adsorbed iodine or thallium ions [64]. In these experiments the electrode had been previously kept in Ti_2SO_4 or KI solutions. Then the solution was washed off and the dependence of the adsorption of Na^+ and SO_4^{2-} ions on potential in acidified Na_2SO_4 solution was measured. The results are shown in Figs. 3 and 4. If the $pzfc$ is determined from the condition $\Gamma_{\text{Na}^+} = \Gamma_{\text{SO}_4^{2-}}$, i.e. the charge of chemisorbed thallium or iodine ions is included in that of the metal side of the double layer, the obtained results show that $pzfc$ shifts in the negative direction in the case of Ti^+ adsorption and in the positive direction for I^- adsorption. However, if we assume that $pzfc$ corresponds to the condition $\Gamma_{\text{Na}^+} + \Gamma_{\text{Ti}^+} = \Gamma_{\text{SO}_4^{2-}}$ or $\Gamma_{\text{Na}^+} = \Gamma_{\text{SO}_4^{2-}} + \Gamma_{\text{I}^-}$ respectively, then from the same data we can conclude that $pzfc$ shifts in the positive direction in the presence of Ti^+ and in the negative direction in the presence of I^- , as it is usually assumed. Since in this case only strongly adsorbed Ti^+ or I^- ions, not removed during its washing, are present on the electrode surface, then the $pzfc$ value corresponding to the condition $\Gamma_{\text{Na}^+} = \Gamma_{\text{SO}_4^{2-}}$ seems to fit better the real structure of the electrode-solution interface*.

The concept of the conditioned nature of the notion of $pzfc$ in the presence of chemisorption was first advanced in the discussion of oxygen adsorption on platinum [65, 66]. If oxygen anions, e.g. OH^- anions,

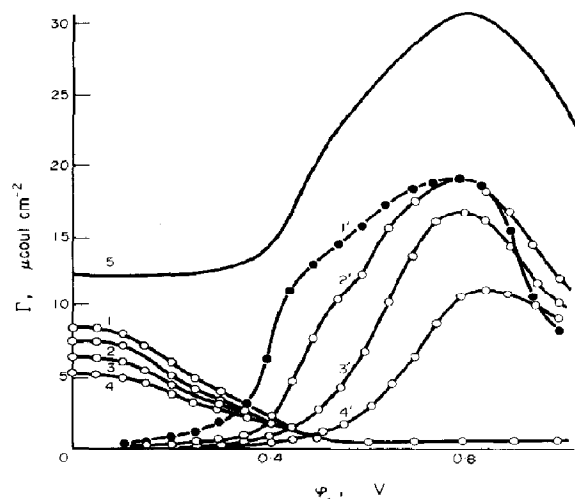


Fig. 3. Dependences of sodium (1-4) and sulphate (1'-4') ions adsorption on potential in $15 \cdot 10^{-4}$ M Na_2SO_4 + $5 \cdot 10^{-4}$ M H_2SO_4 solution at Pt/Pt electrode with iodine ions adsorption equal to: 0 (1,1'); 12 (2,2'); 26 (3,3'); 38 (4,4') $\mu\text{coul/cm}^2$. Curve 5 is the dependence of $\Gamma_{\text{I}^-} + \Gamma_{\text{SO}_4^{2-}}$ on ϕ_r at $\Gamma_{\text{I}^-} = 12 \mu\text{coul/cm}^2$ (according to the data of [64]).

* We could not, however, detect a differential capacity minimum caused by the diffuseness of the double layer on smooth platinum poisoned by I^- at $pzfc$ corresponding to the condition $\Gamma_{\text{Na}^+} = \Gamma_{\text{SO}_4^{2-}}$ at solution concentrations $\geq 10^{-3}$ M.

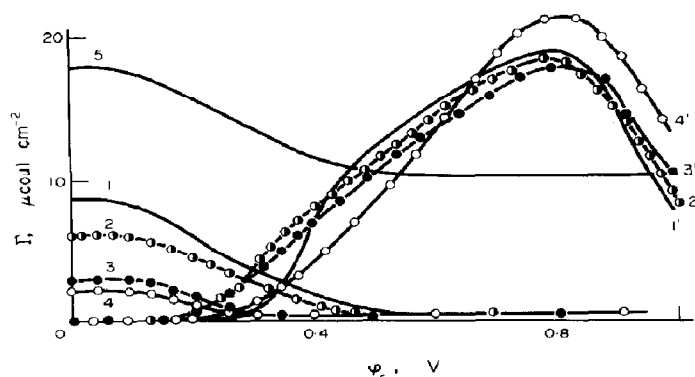


Fig. 4. Dependence of Na^+ (1-4) and SO_4^{2-} (1'-4') ions adsorption on potential in $15 \cdot 10^{-4} \text{ M Na}_2\text{SO}_4 + 5 \cdot 10^{-4} \text{ M H}_2\text{SO}_4$ solution at Pt/Pt electrode with thallium ions adsorption equal to: 0 (1,1'); 10 (2,2'); 26 (3,3'); 53 (4,4') $\mu\text{coul/cm}^2$. Curve 5 is the dependence of $\Gamma_{\text{Tl}^+} + \Gamma_{\text{Na}^+}$ on ϕ_r at $\Gamma_{\text{Tl}^+} = 10 \mu\text{coul/cm}^2$ (according to the data of [64]).

kept their charge during adsorption, their specific adsorption would lead to the shift of $pzfc$ in the negative direction. However, the adsorption and electrokinetic properties of the platinum electrode covered by a chemisorbed oxygen layer agree completely with the assumption that during oxygen chemisorption the $pzfc$ shifts in the positive direction. Hence it follows that the charge of oxygen atoms forming negative ends of the Pt-O dipoles turned towards solution should be included in the charge of the metal side of the double layer and not in that of the ionic side. This conclusion is in agreement with the increase of the work function of platinum when oxygen is chemisorbed on its surface.

The assumption of the $pzfc$ shift in the positive direction in the presence of chemisorbed halogen ions was used to explain the effect of the additions of various surfactants on the corrosion behaviour of an iron electrode [67, 68].

The $pzfc$ values determined by measurement or calculation of the dependence of Γ_{H^+} on potential and by the radioactive tracers technique from the condition of the equality $\Gamma_{\text{A}^-} = \Gamma_{\text{C}^+}$ are shown in Table 2. The potentials $\phi_{\Gamma_{\text{H}^+}=0}$ shift in the negative direction in the series $\text{Pt} > \text{Pd} > \text{Rh} > \text{Ir} > \text{Ru}$. In the case of unoxidized ruthenium, the $pzfc$ lies in the hydrogen overvoltage region. The addition of 10 per cent ruthenium to

Table 2. Potentials of zero free charges of platinum metals

Solution	$\phi_{\Gamma_{\text{H}^+}=0}$, V (nhe)	Reference
Platinum		
0.3 M HF + 0.12 M KF (pH 2.4)	0.185	[43]
0.15 M Li_2SO_4 + 0.005 M H_2SO_4	0.16	[19]
0.5 M Na_2SO_4 + 0.005 M H_2SO_4	0.16	[15]
0.005 M ZnSO_4 + 0.05 M Na_2SO_4 + 0.005 M H_2SO_4	0.27	[48]
1 M KCl + 0.01 M HCl	0.05	[6]
1 M KBr + 0.01 M HBr	-0.03	[15]
1 M KBr + 0.01 M KOH	-0.39	[12]
1 M KI + 0.01 M KOH	-0.52	[12]
$2 \cdot 10^{-3}$ M Na_2SO_4 pH 3-6	0.13 ± 0.02	[69]
Palladium		
0.05 M Na_2SO_4 + 0.001 M H_2SO_4 (pH 3)	0.10	[29]
Rhodium		
0.3 M HF + 0.12 M KF (pH 2.4)	-0.005	[43]
0.5 M Na_2SO_4 + 0.005 M H_2SO_4	-0.04	[11]
1 M KCl + 0.01 M HCl	-0.12	[7, 8]
Iridium		
0.3 M HF + 0.12 M KF (pH 2.4)	-0.01	[43]
0.5 M Na_2SO_4 + 0.005 M H_2SO_4	-0.06	[14]
1 M KCl + 0.01 M HCl	-0.13	[14]
1 M KI + 0.01 M KOH	-0.59	[21]
Ruthenium		
1 M HCl + 0.01 M HCl	0.50	[10]
Electrolytic mixed deposit Pt + Ru with 10 wt % Ru		
1 M KCl + 0.01 M HCl	-0.01	[10]

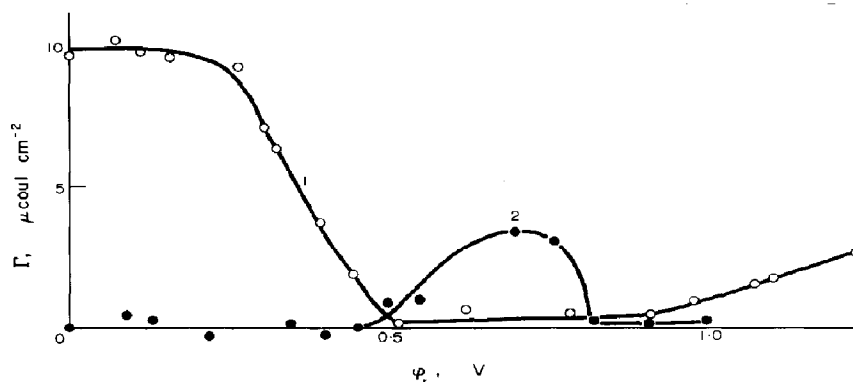


Fig. 5. Dependence of sodium (1) and sulphate (2) ions adsorption on potential in $2 \cdot 10^{-3}$ M Na_2SO_4 at pH = 6 (according to the data of [69]).

platinum causes the *pzfc* to shift in the negative direction by 60 mv. The potentials $\phi_{\Gamma_{\text{H}^+}=0}$ shift in the negative direction in the presence of specifically adsorbed anions and in the positive direction in the presence of specifically adsorbed cations. The potentials $\phi_{\Gamma_{\text{H}^+}=0}$ are less positive than $\phi_{Q=0}$. The most significant difference between $\phi_{\Gamma_{\text{H}^+}=0}$ and $\phi_{Q=0}$ is observed on palladium. For Ru in acidified KCl solution only the $\phi_{\Gamma_{\text{H}^+}=0}$ value, corresponding to the oxidized state of the surface could be determined. For iridium in, alkalized KI solution, two *pzfc* were detected corresponding to the reduced and oxidized states of the surface.

The appearance of a *pzfc* in the oxygen region under certain conditions can be expected for the platinum electrode as well, if we proceed from the dependences of the free charge of the surface on the potential in acid and alkaline solutions. Indeed, in acid solutions with rising ϕ , Γ_{H^+} at first increases and then begins to decrease [65, 28, 22]. In an alkaline solution of surface-inactive electrolytes over the whole range of ϕ , Γ_{H^+} is negative [65, 28]. Evidently, at a certain intermediate pH values we must have a Γ_{H^+} vs ϕ curve intersecting the abscissa axis twice. The existence of a *pzfc* for oxidized platinum was established by the measurements carried out in [65, 66]. In [66] the *pzfc* of oxidized platinum was determined by electrokinetic measurements in 5×10^{-6} M H_2SO_4 . In order to elucidate the conditions of the appearance of a *pzfc* for oxidized platinum, in [69] the dependences of the adsorption of sodium, cesium and sulphate ions on potential at pH close to pH = 7 were measured by means of the radioactive tracer technique. As is clear from Fig. 5, at the Pt/Pt electrode in 2×10^{-3} M Na_2SO_4 solution with pH = 6, two *pzfc* can be observed, lying at 0.13 ± 0.02 and 0.47 V (*nhe*) respectively. A similar phenomenon is encountered in 2×10^{-3} M Cs_2SO_4 solution. These results have been confirmed recently by the potentiometric titration method at constant total charge Q .

The existence of two *pzfc* for platinum metals seems to be a general phenomenon. It is necessary, however, in each particular case to establish the conditions under which both *pzfc* can be observed. At the same time, the *pzfc* has only one value, which is due to the fact that when determining the *pzfc* only the systems with μ_{H^+} = constant are considered. For systems with $\mu_{\text{H}} = \text{constant}$, the *pzfc* also has only one value. The possibility of plotting the curves of Γ_{H^+} vs electrode potential at $\mu_{\text{H}} = \text{constant}$ will be discussed below.

A fundamental characteristic of platinum metals is the dependence of the *pzfc* on solution pH, which was for the first time established in [65]. Later this problem attracted interest in connection with the works of Kheifets and Krasikov [70]. A complete solution of this problem can be achieved on the basis of the thermodynamic theory of platinum electrode [15, 22]. Without taking account of Lorenz's charge transfer during adsorption, we can write

$$\left(\frac{\partial \phi}{\partial \mu_{\text{H}^+}} \right)_{\epsilon=0, \mu_{\text{CA}}} = \frac{1}{1 - (\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}}} \quad (14)$$

It follows from equation (14) that at $(\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}} = 0$ the *pzfc* shifts with increasing pH in the negative direction just as the potential of the reversible hydrogen electrode. If $1 > (\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}} > 0$, then the *pzfc* also shifts with increasing pH in the negative direction, the dependence of the *pzfc* on pH being even greater than for the potential of the reversible hydrogen electrode. Such phenomenon was observed, for instance, for the *pzfc* of oxidized iridium in alkaline iodide solutions [21], where the shift of the *pzfc* per unit pH is ~ -110 mv. At $(\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}} > 1$, the *pzfc* should shift with increasing pH in the positive direction, the magnitude of the shift decreasing with increase of $(\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}}$. So far, no positive shifts of the *pzfc* have been observed experimentally. Finally, at $(\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}} < 0$, the *pzfc* shifts with increase of pH in the negative direction, this shift being less than that of the reversible hydrogen electrode potential and at $(\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}} \rightarrow -\infty$ it tends to zero.

The experimental investigation of the dependence of the *pzfc* on pH revealed that, for a *pzfc* lying in the hydrogen region, $(\partial \phi / \partial \mu_{\text{H}^+})_{\epsilon=0, \mu_{\text{CA}}} < 1$. The magnitude of the shift of the *pzfc* depends on the nature of the anion and increases with increase of its specific adsorbability. It follows from the experimental values of $(\partial \phi / \partial \mu_{\text{H}^+})_{\Gamma_{\text{H}^+}, \mu_{\text{CA}}}$ that the derivative $(\partial \epsilon / \partial A_{\text{H}})_{\phi, \mu_{\text{CA}}}$ for platinum and rhodium usually lies within $-0.4 \sim -2.5$. Practical absence of the dependence of the *pzfc* on pH at low Na_2SO_4 concentrations [71] is in qualitative agreement with this conclusion because in diluted solutions the specific adsorption of sulphate anion should be less pronounced than in 0.5 M Na_2SO_4 used in [15].

In [69] the conclusion about the practical independence of the *pzfc* on pH in 2×10^{-3} M Na_2SO_4 solution (pH = 3–6) was confirmed and it was suggested that this result can be accounted for, not only directly by decrease of the adsorption of SO_4^{2-} , but also by overlapping of the hydrogen and oxygen adsorption regions due to this decrease and the transition with increasing pH of the *pzfc* from the hydrogen region to that of mixed adsorption of hydrogen and oxygen.

More detailed investigations of the dependence of the *pzfc* on pH can be made on the basis of the method of potentiometric titration under isoelectric conditions [49]. By determining by means of this method the isoelectric shifts, at different initial φ_r and knowing the charging curve at any one pH value, it is possible to plot the charging curves for other pH values. From the slope of the charging curves and corresponding values of the isoelectric potential shifts, it is possible to calculate the dependences of Γ_{H^+} on φ_r in solutions with different pH by means of equation (1), using, as integration constants in calculating the Γ_{H^+} , φ_r curves, the values of Γ_{H^+} found by potentiometric titration with a large indicator electrode at $\varphi_r = 0$. Such measurements and calculations are being carried out presently.

The *pzfc* must also depend on the neutral salt concentration at constant solution pH. The theoretical formula describing this dependence was obtained in [27]:

$$\left(\frac{\partial \varphi_r}{\partial \mu_{\text{CA}}} \right)_{\Gamma_{\text{H}^+}=0, \mu_{\text{HA}}} = -2 \left(\frac{\partial \Gamma_{\text{C}^+}}{\partial \Gamma_{\text{H}^+}} \right)_{\mu_{\text{CA}}, \mu_{\text{HA}}} - 2 \left(\frac{\partial A_{\text{H}}}{\partial \mu_{\text{CA}}} \right)_{\varphi_r, \mu_{\text{HA}}} / \left(\frac{\partial \Gamma_{\text{H}^+}}{\partial \varphi_r} \right)_{\mu_{\text{CA}}, \mu_{\text{HA}}} \quad (15)$$

Formula (15) as well as (13), (11) and (12) can be considered as the expressions for the Esin–Markov coefficient in the case of platinum metals. Unlike the case of mercury, owing to the existence of two total charges Q and Γ_{H^+} , for platinum metals there exist two Esin–Markov coefficients. Evidently, when making comparison with a mercury electrode, it is necessary to use the quantity $(\partial \varphi_r / \partial \mu_{\text{CA}})_{\Gamma_{\text{H}^+}=0, \mu_{\text{HA}}}$. It can be readily seen that equations (13) and (15) coincide and become identical with the formula for the mercury electrode [72, 73]:

$$\left(\frac{\partial \varphi}{\partial \mu_{\text{CA}}} \right)_{\epsilon, \mu_{\text{HA}}} = - \left(\frac{\partial \Gamma_{\text{C}^+}}{\partial \epsilon} \right)_{\mu_{\text{HA}}, \mu_{\text{A}^-}} - \left(\frac{\partial \Gamma_{\text{A}^-}}{\partial \epsilon} \right)_{\mu_{\text{CA}}, \mu_{\text{HA}}} \quad (16)$$

when the electrode surface is free of adsorbed hydrogen or oxygen atoms (double layer region of potentials). The measurements of the Esin–Markov coefficients in the double layer region of potentials [8] led to the conclusion that they are equal to -1 , which is equivalent to the absence of the so-called Esin–Markov effect for platinum metals in the case of adsorption of Cl^- and Br^- anions. No measurements were carried out for the I^- anion in acid solutions because the adsorption of this anion in the double layer region of potentials is irreversible. The absence of Esin–Markov effect is accounted for by a significant transfer of the anion charge to the metal surface and considerable decrease of the distance between the electric charge centre of the adsorbed particle and the metal surface.

The *pzfc* lie in the regions of hydrogen or oxygen adsorption. Therefore, in considering their dependence on salt concentration, it is necessary to take into account the second term in the right hand side of equation (15). In particular, in the case of anions adsorption, $(\partial A_{\text{H}} / \partial \mu_{\text{CA}})_{\varphi_r, \mu_{\text{HA}}} < 0$ and so the shift of the *pzfc* proves to be less than might be expected in the absence of adsorbed hydrogen. No detailed study of the dependence of the *pzfc* on salt concentration has been made so far. According to the tentative data [74], in a solution with pH = 3 the increase in the concentration of NaBr from 10^{-3} to 10^{-1} M brings about a shift of the *pzfc* in the negative direction only by ~ 50 mv. At pH = 12, the increase of NaBr concentration by an order shifts the *pzfc* in the negative direction by ~ 60 mv.

It is of interest to plot the $\varphi_{\Gamma_{\text{H}^+}=0}$, A_{H} curve, i.e. the dependence of the *pzfc* on the amount of hydrogen adsorbed on the electrode. Extrapolation of this dependence to $A_{\text{H}} = 0$ would give the *pzfc* of an electrode whose surface is free of adsorbed hydrogen and oxygen. Apparently, it will be possible to solve this problem after the determination of the *pzfc* at different pH, and hence at different A_{H} by means of a potentiometric titration at constant total charge. A very rough estimate of the *pzfc* at $A_{\text{H}} = 0$ can be obtained as follows. In [15] the contribution of adsorbed atoms to the establishment of the potential $X = (\partial \varphi / \partial A_{\text{H}})_{\Gamma_{\text{H}^+}}$ was determined for different solutions. Using the value of A_{H} at $\varphi_{\Gamma_{\text{H}^+}=0}$ and assuming the *pzfc* to be linearly dependent at small A_{H} on A_{H} with the slope $(\partial \varphi / \partial A_{\text{H}})_{\Gamma_{\text{H}^+}=0}$, we can find $\varphi_{\Gamma_{\text{H}^+}=0}$ at $A_{\text{H}} = 0$. Calculations show that according to the data for 0.5 M Na_2SO_4 solution for platinum $\varphi_{\Gamma_{\text{H}^+}=0}$ at $A_{\text{H}} = 0$ is ~ 0.05 V, and according to the data for 1 M KCl it is -0.05 V (*nhe*). For rhodium with a *pzfc* at relatively large A_{H} , such a calculation is unreliable.

Thus, the *pzfc* of platinum with a surface free of adsorbed hydrogen and oxygen, is more positive than the *pzc* of mercury by approximately 0.2–0.3 V. This value of the difference $\varphi_{\epsilon=0, \text{Pt}} - \varphi_{\epsilon=0, \text{Hg}}$ is at variance with the wellknown relation between the difference of the *pzc* of two metals and the difference of the work functions W_{Me} [75–77] since the value of $W_{\text{Pt}} - W_{\text{Hg}}$ is equal to about 0.9 V*. The discrepancies between these two values pointed out so far, as *eg* in the case of the system mercury–gallium, were explained by different degrees of orientation of adsorbed water molecules at the interface between uncharged metal and electrolyte solution [77, 78, 46]. The orientation of water particles so far observed was with the negative (oxygen) end of dipole turned towards metal [79]. In the case of platinum, the discrepancy should be thus associated with strong chemisorption of water particles on platinum with the positive (hydrogen) end of the dipole. Unfortunately, at present our knowledge of water adsorption on platinum is very limited [80]. It is possible, however, that the discrepancy observed is not associated with the structure of the adsorbed water layer, but rather with the difference in the structure of the surface layer of the crystallites of platinized platinum, grown in contact with water, or platinum subjected to anodic–cathodic activation, on one hand, and of platinum subjected to high-temperature treatment in ultravacuum prior to determination of W_{Pt} , on the other. This essential question requires further investigation.

* $W_{\text{Hg}} = 4.50$ V; $W_{\text{Pt}} = 5.40$ V (according to [46]).

So far, no reliable data have been obtained on the influence on *pzfc* of hydrogen-dissolution in metal causing changes in the lattice parameters. This problem can be most conveniently studied on palladium or its alloys. It should be noted that the effects caused by hydrogen dissolution in metal and by changes of pH can superimpose.

4. CHARGING CURVES AND ELECTROCAPILLARY CURVES OF THE FIRST AND SECOND KIND

In accordance with the generalized notion of the electrode charge for platinum metals, there should exist two types of the charging curves. The usual charging curves characterizing the relationship between the total charge Q and the potential ϕ at constant chemical potential of hydrogen ions ($\mu_{H^+} = \text{constant}$) can be called the charging curves of the first kind. Since according to [23]

$$\left(\frac{\partial \sigma}{\partial \phi_A}\right)_{\mu_{H^+}, \mu_{CA}} = I_H = -Q \quad (17)$$

where σ is the reversible surface work [81], ϕ_A the potential referred to an electrode reversible with respect to the anion, then by integration of the charging curves of the first kind, we can find the electrocapillary curves of the first kind (accurate to the integration constant)*. Accordingly, the derivative $(\partial Q / \partial \phi)_{\mu_{H^+}, \mu_{CA}} = -(\partial I_H / \partial \phi)_{\mu_{H^+}, \mu_{CA}} = C$ can be called the differential capacity of the first kind. In literature this quantity is usually called the polarization, or total, capacity of the electrode. The charging curves of the second kind represent the relationship between the total charge I_H and potential at constant chemical potential of hydro-

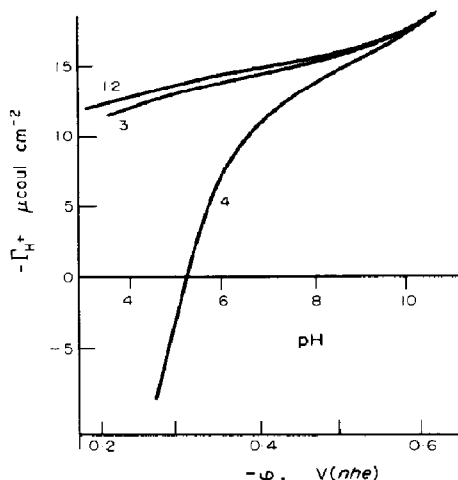


Fig. 6. Charging curves of the second kind of Pt/Pt electrode in 0.05 M Na₂SO₄ (1), 0.1 M NaCl (2), 0.1 M NaBr (3) and 0.1 M NaI (4) at $\phi_r = 0$ (according to the data of [82]).

gen in the system ($\mu_{H^+} = \text{constant}$). Since

$$\left(\frac{\partial \sigma}{\partial \phi_A}\right)_{\mu_{H^+}, \mu_{CA}} = -I_H \quad (18)$$

integration of the charging curves of the second kind leads to the electrocapillary curves of the second kind. The quantity $(\partial I_H / \partial \phi)_{\mu_{H^+}, \mu_{CA}} = C_{d1}$ can be called the differential capacity of the second kind. In solution with excess of foreign surface-inactive electrolyte it can be equated to the equilibrium capacity of the electrical double layer with the restrictions discussed above.

The methods of obtaining the charging curves of the first kind are generally known (see *eg.* [2]). To obtain the charging curves of the second kind, it is possible to use the method of potentiometric titration with a large indicator platinum or rhodium electrodes [82, 83]. Up to now this method has been used only at a hydrogen pressure equal to atmospheric ($p_{H_2} = 1$), *ie.* at $\phi_r = 0$. The charging curves of the second kind for $\phi_r > 0$ were plotted in [26] from the I_{H^+}, ϕ_r -curves for acid (pH =

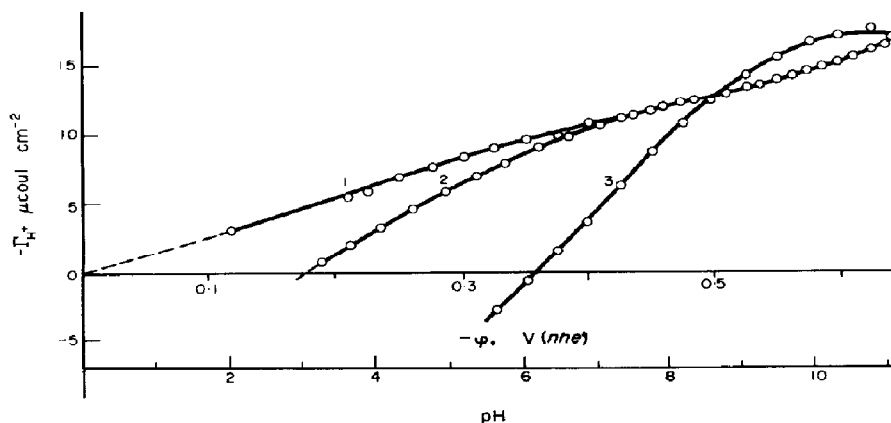


Fig. 7. Charging curves of the second kind of Rh electrode in 0.05 M Na₂SO₄ (1), 0.1 M NaCl (2) and 0.1 M NaBr (3) at $\phi_r = 0$ (according to the data of [83]).

* The quantity on the ordinate axes of Fig. 8 and Fig. 9 that is the reversible work spent in forming a unit of the surface σ in the case of a solid electrode should not be identified with the interfacial tension γ [81]. The dependence of the interfacial tension, representing the work of stretching the surface on ϕ for the case of a platinum electrode has been recently investigated by Gokhstein [85]. We thought it expedient to call the electrocapillary curve the σ, ϕ dependence as its shape is similar to that of an electrocapillary curve of mercury. The γ, ϕ dependencies in the case of Pt are quite different.

1.5–3) and alkaline (pH = 11–13) solutions. The values of Γ_{H^+} in the pH range 3–11 were obtained by interpolation. Therefore, it was of interest to develop the methods of measuring the charging curves of the second kind for the whole pH range in the region of positive φ_r values.

The simplest method of measuring these curves would be to use mixtures of hydrogen with inert gases. By lowering the partial pressure of hydrogen in the mixture, it is possible to carry out potentiometric titration with a large indicator electrode at $\varphi_r > 0$. In this case, further processing of the results is the same as in [82, 83]. The disadvantage of this method is that its applicability is practically limited to $p_{H_2} \sim 10^{-4}$ atm., i.e., $\varphi_r \sim 0.12$ V.

A practicable method of obtaining the charging curves of the second kind at different φ_r consists in carrying out potentiometric titration under isoelectric conditions, in which case it is possible to calculate the set of the Γ_{H^+}, φ_r -curves in solution with different pH. Sections through this set of curves, corresponding to the condition $\varphi_r = \text{constant}$, are the charging curves of the second kind.

The charging curves of the second kind obtained by potentiometric titration at $\varphi_r = 0$ are shown in Figs. 6 and 7. Unlike the Γ_{H^+}, φ_r -curves at constant μ_{H^+} , these plots are relatively simple, especially in solutions without strongly surface-active ions. Apparently this is due to the smallness of the changes in the surface coverage with adsorbed hydrogen when pH changes at $\varphi_r = 0$. In solutions of sulphates, chlorides and bromides in the pH range studied, the surface of the Pt/Pt electrode is negatively charged and the *pzfc* can be found only by rough extrapolation of the Γ_{H^+}, φ_r -curve to its inter-

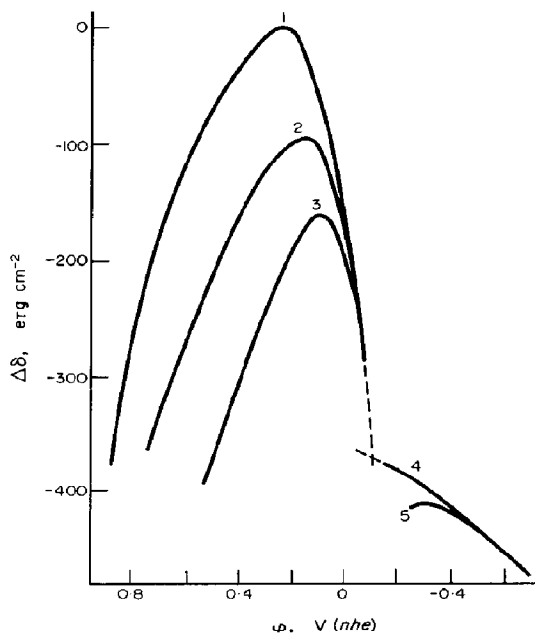


Fig. 8. Electrocapillary curves of the first kind (1–3) and of the second kind (4,5) of Pt/Pt electrode in the solutions: 1–0.005 M $H_2SO_4 + 0.5$ M Na_2SO_4 ; 2– 10^{-2} M $HCl + 1$ M KCl ; 3– 10^{-2} M $HBr + 1$ M KBr ; 4–0.5 M Na_2SO_4 ; 0.1 M KCl ($\varphi_r = 0$); 5–0.1 M KI ($\varphi_r = 0$) (according to the data of [26, 82]).

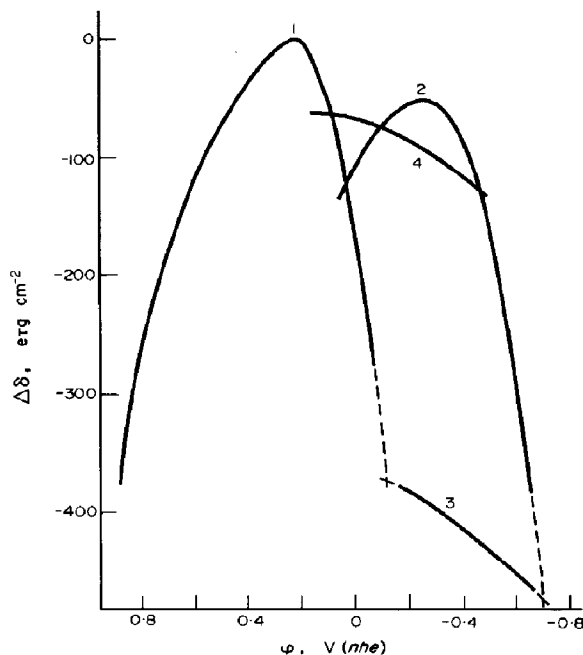


Fig. 9. Electrocapillary curves of the first kind (1,2) and of the second kind (3,4) of Pt/Pt electrode in the solutions: 1–0.005 M $H_2SO_4 + 0.5$ M Na_2SO_4 ; 2– 10^{-2} M $NaOH + 0.5$ M Na_2SO_4 ; 3–0.5 M Na_2SO_4 , $\varphi_r = 0$; 4–0.5 M Na_2SO_4 , $\varphi_r = 0.24$ (according to the data of [26]).

section with the abscissa axis in the range of potentials which cannot be reached experimentally by decreasing pH. This extrapolation shows that in 0.05 M Li_2SO_4 solution the *pzfc* of the electrode completely covered with H_{ads} is ~ 0.3 V (nhe). It follows from the comparison with *pzfc* at $A_H = 0$ given above that the monolayer of H_{ads} gives rise to the potential drop 0.2–0.3 V. In iodide solution the *pzfc* of platinum at $\varphi_r = 0$ is -0.31 V. Owing to stronger anions adsorption on rhodium the *pzfc* can be obtained at $\varphi_r = 0$ already in 0.1 M $NaBr$ solutions (-0.36 V). The values of the *pzfc* of rhodium at $\varphi_r = 0$, found by extrapolation for 0.1 M $NaCl$ and 0.05 M Na_2SO_4 solutions are -0.18 and ~ 0 V, respectively. These values differ relatively little from those listed in Table 2 since in 0.01 M $HCl + 1$ M KCl and 0.005 M $H_2SO_4 + 0.5$ M Na_2SO_4 solutions the *pzfc* correspond to rather large coverages of rhodium surface with adsorbed hydrogen.

Figures 8 and 9 show the electrocapillary curves of the platinum electrode in solutions of different composition, calculated by means of equations (17) and (18). Dashed lines show the sections of the curves obtained by extrapolation. The integration constants being unknown, the value of σ at the maximum of the curve of the first kind in 0.5 M $Na_2SO_4 + 0.05$ M H_2SO_4 solution is conditionally taken to be zero.

In spite of the fact that the absolute values of the reversible surface work cannot be determined from the calculations carried out, the relative position of the curves of the first and second kind for solutions of the same salt can be determined unambiguously. To determine the point of intersection of the curves of the first and second kind, use is made of the fact that the reversible surface work is a single-valued function of poten-

tial and solution composition. Taking this into consideration and plotting first the curve of the second kind for any value of μ_H , we can then determine the relative position of the $\Delta\sigma, \varphi$ -curves of the first kind in acid and alkaline solutions of the same salt. In comparing the $\Delta\sigma, \varphi$ -curves of the first kind in solutions of different composition but the same pH, the curves were shifted in the vertical direction until their descending branches merged at the negative potentials, at which the solution anions are not adsorbed on platinum but the surface is practically completely covered with adsorbed hydrogen (small differences in the adsorbability of Na^+ and K^+ ions were neglected in the first approximation). Therefore, the values of σ in solutions of different composition at the potentials considered should be the same. Practical merging of the $\Gamma_{H^+, \varphi}$ -curves at $\varphi_r = 0$ in solutions of sulphates, chlorides and bromides on platinum supports this assumption. In [43] it was shown that in the presence of F^- the values of σ are higher than in the presence of SO_4^{2-} .

As is clear from Figs. 8 and 9, the $\Delta\sigma, \varphi$ -curves of the first kind resemble, both in their shape and in the type of the dependence of σ on the salt anion nature, the electrocapillary curves of the mercury electrode. However, at $\mu_H = \text{constant}$ the reversible surface work of the platinum electrode changes much more than σ of the mercury electrode. This is primarily due to the adsorption on Pt surface of hydrogen and oxygen atoms. At $\mu_H = \text{constant}$ (the $\Delta\sigma, \varphi$ -curves of the second kind) the changes of σ are much less, as they are due mainly to the change of the double layer charge. The position of the σ, φ -curve of the second kind depends strongly on φ_r . Thus, at $\varphi_r = 0.24$ V, the curve lies much higher than the curve at $\varphi_r = 0$. This is accounted for by the significant surface coverage with H_{ads} in the latter case.

The position of the maxima of the electrocapillary curves of the first kind corresponds to the *pzc* and that of the curves of the second time (with the above reservations) to the *pzc*.

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