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Adsorption Phenomena on Platinum Group Metal Electrodes

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Certain fundamental concepts and definitions in the thermodynamic theory of the platinum electrode are examined and the concepts of the zero total charge and zero free charge potentials and methods for determination of these quantities are discussed. Data indicating charge transfer in chemisorption processes are analysed and a thermodynamic approach to the analysis of this phenomenon is considered. The influence of the pH of the solution on the structure of the platinum metal-electrolyte solution interface is examined.
The bibliography includes 186 references.

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I. INTRODUCTION

The study of the structure of the platinum metal–electrolyte solution interface was begun by Frumkin and coworkers at the end of the 1920s and the beginning of the 1930s.[1-8] They developed methods for the measurement of charging and adsorption curves, laid the foundations of the thermodynamic theory of surface phenomena on platinum metals, and formulated the fundamental idea of a close relation between the adsorption of ions in solution and the adsorption of hydrogen and oxygen atoms. Subsequently the Soviet electrochemical school made a significant contribution to the study of the above interface, which has been reflected in a number of reviews[9-13]. Some of the main results obtained in the last 10–15 years are discussed in the present review. The considerable attention devoted to the adsorption properties of platinum metals during this period is due to attempts at devising fuel cells and the extensive development of research on liquid-phase catalytic hydrogenation and oxidation reactions and electrosynthetic processes.

One of the characteristic features of the development of such studies in recent years is the increased number of systems investigated. Together with a further deepening of the investigation of the adsorption properties of the platinum electrode, measurements have also been made on other platinum metals and their alloys (on smooth polycrystalline and single-crystal electrodes, on electrolytic deposits of platinum metals, on metal blacks, and on deposited catalysts).

A second noteworthy characteristic feature is the wide range of experimental techniques which have been used in the investigation of adsorption phenomena on platinum group metals. Thus the method of radioactive tracers[14-16] has been significantly improved, which made it possible to increase the accuracy and reliability of the results obtained by this method and extended its scope, particularly in the study of the kinetics of adsorption and of the exchange of adsorbed ions with ions in the solution. The potentiodynamic method and potentiostatic pulse methods for the investigation of adsorption have been appreciably expanded and developed[17-23]. A series of adsorption studies has been carried out by the two-electrode thin-layer method[24-48]. New information about the state of the surface layer on platinum metals has been provided by the method involving the measurement of estance[49-66]. The method of the rotating disc electrode with a ring has been used to investigate the adsorption and anodic elimination of adsorbed species[67-78]. Attempts have been made at a detailed study of the surface properties of platinum metals with the aid of optical methods (ellipsometry, electroreflectance)[79-86] and by measuring the electrical resistance of thin metallic films sputtered *in vacuo* on to a non-conducting base[87-95].

II. SOME CONCEPTS AND RELATIONS OF THE THERMODYNAMIC THEORY OF THE PLATINUM ELECTRODE

The third characteristic feature of the period under consideration is the application of the thermodynamic theory of the reversible electrode in the interpretation of the behaviour of platinum metals in electrolyte solutions. This theory was outlined by Frumkin and coworkers[7-9], was applied by them for the first time in a later study[96], and was subsequently developed further[97-124]. The last series of studies was stimulated directly by the derivation[97] of an equation which made it possible to carry out a comparatively simple experiment test of the applicability of the Gibbs adsorption equation to platinum metals. Such a test for 30 different systems comprising platinum[98,99,101,105,109,110,112,125], palladium[126], rhodium[100,101,104,111], iridium[108,111,115], ruthenium, and platinum–ruthenium[101,103] electrodes showed that the thermodynamic theory is applicable not only at potentials in the hydrogen and "double layer" regions, but also in the initial section of the region corresponding to the adsorption of oxygen on the electrodes. The pronounced phenomena associated with the chemisorption of ions from solution result in a narrowing of the region of practical applicability of the theory.

The thermodynamic theory led to the development of the method of isoelectric potential shifts[98,99] (the first measurements of the shifts of the potential of an isolated

electrode following the alteration of the pH of the solution were undertaken in early investigations[7,8]). A potentiometric titration procedure for a constant total surface charge, which made it possible to investigate the adsorption properties of platinum and rhodium in the range of intermediate pH value which had been previously inaccessible to experimental study[128-131], was developed recently[127].

In the experimental test of the thermodynamic theory in solutions of acids HA with an excess of the neutral salt CA $\{[HA] \ll [CA]\}$ the following relation was used:

$$(\partial\varphi_r/\partial\mu_{H^+})_{\Gamma_H,\mu_{CA}} = (\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+},\mu_{CA}}/(\partial\Gamma_H/\partial\varphi_r)_{\mu_{H^+},\mu_{CA}}, \quad (1)$$

where φ_r is the potential relative to the reversible hydrogen electrode in the same solution, μ_{H^+} and μ_{CA} are the chemical potentials of hydrogen ions and the salt, and Γ_H and Γ_{H^+} are the Gibbs adsorptions of hydrogen atoms and ions respectively. All the quantities in Eqn. (1) are expressed in electrical units. This equation is valid also for solutions of neutral salts which have been made alkaline. The term "isoelectric potential shift" (introduced for the first time by Ponomarenko et al.[132]) was proposed for the quantity $(\partial\varphi_r/\partial\mu_{H^+})_{\Gamma_H,\Gamma_{CA}}$. The Gibbs adsorptions Γ_H and Γ_{H^+} represent the amounts of the corresponding components which must be introduced into the system for their chemical potentials to remain unchanged without the supply of electricity from the outside when the surface area of the electrode is increased by 1 cm^2. Evidently the electrode potential also remains constant under these conditions. The Gibbs adsorptions must be distinguished from the excess surface amounts, which are designated by A_H and A_{H^+} respectively. The relations between Γ_H and A_H and between Γ_{H^+} and A_{H^+} are

$$\Gamma_H = A_H - \varepsilon, \quad (2)$$

and

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

where ϵ is the charge of the metallic component of the electrical double layer.

Whereas both Γ_H and Γ_{H^+} are thermodynamic quantities susceptible in principle to direct experimental determination, the introduction of the quantities A_H, A_{H^+}, and ϵ is associated with definite model assumptions. In particular, in the determination of A and ϵ no account is taken of the partial charge transfer via the Lorenz mechanism[133] for all the ions in the double layer. For strongly chemisorbed ions, it is almost impossible to determine ϵ unambiguously. In the presence of an excess of the salt in solution, hydrogen ions are displaced from the diffuse part of the double layer by the salt cation[113,134,135], so that $A_{H^+} = 0$ and $\Gamma_{H^+} = \epsilon$.

It has been shown[117-119] that $\Gamma = -Q'$ and $\Gamma_{H^+} = Q''$, where Q' and Q'' are the total surface charges, i.e. the amounts of electricity which must be introduced at μ_{H^+} = const. or μ_H = const. respectively in order to prevent a change in the composition of the bulk phase following an increase of the surface area of the electrode by 1 cm^2 when the loss of material is compensated by the introduction of an amount of substance $\Gamma_H + \Gamma_{H^+} = A_H + A_{H^+}$ (H in the former case and H^+ in the latter case). Henceforth the symbol Q will be used for Q' and this quantity will be called the total charge (the condition μ_{H^+} = const. is omitted for brevity). Instead of Q'', the symbol Γ_{H^+} will be empoyed; in order to distinguish this total charge from Q, we shall adopt the term free charge for Γ_{H^+}.

III. CHARGING CURVES OF THE FIRST AND SECOND KINDS

According to the general concept of the electrode charge, there should exist two types of charging curve for platinum metals. The usual charging curve, characterising the relation between the total charge Q and the potential φ at a constant chemical potential of hydrogen ions (μ_{H^+} = const.) may be called the charging curves of the first kind. Since according to the literature[117,119]

$$(\partial\sigma/\partial\varphi_A)_{\mu_{HA},\mu_{CA}} = \Gamma_H = -Q, \quad (4)$$

where σ is the amount of reversible surface work and φ_A the potential referred to an electrode reversible with respect to the anion, integration of charging curves of the first kind makes it possible to determine the electrocapillary curves of the first kind (to within an integration constant). Accordingly, the derivative $(\partial Q/\partial\varphi)_{\mu_{H^+},\mu_{CA}} = -(\partial\Gamma_H/\partial\varphi)_{\mu_{H^+},\mu_{CA}} = C$ may be called the differential capacitance of the first kind. In the literature this quantity is usually referred to as the polarisation capacitance or the total capacitance of the electrode.

Charging curves of the second kind represent the relation between the total charge Γ_{H^+} and the electrical potential corresponding to a constant chemical potential of hydrogen μ_H = const. (φ_r = const.). Since

$$(\partial\sigma/\partial\varphi_A)_{\mu_H,\mu_{CA}} = -\Gamma_{H^+}, \quad (5)$$

integration of charging curves of the second kind leads to electrocapillary curves of the second kind. The quantity $(\partial\Gamma_{H^+}/\partial\varphi)_{\mu_H,\mu_{CA}}$ may be called the differential capacitance of the second kind. In a solution containing an excess of an extraneous inactive electrolyte, it can be set equal to the equilibrium capacitance of the electrical double layer.

The methods for the measurement of the usual charging curves are generally known[9]. In order to find the charging curves of the second kind corresponding to φ_r = 0, a potentiometric titration method with a large indicator electrode has been employed[7,8,136,137]. Charging curves of the second kind for anodic values of φ_r have been obtained by intersecting a family of Γ_{H^+}–φ_r curves, obtained by potentiometric titration under isoelectric conditions, by vertical φ_r = const. lines[130,138]. These curves have a simpler shape than the usual charging curves corresponding to the condition μ_{H^+} = const., since the changes in the amounts of adsorbed hydrogen and oxygen at φ_r = const. are relatively small. The decrease of the slope of the curves with increasing φ_r is due to the transition from the region of adsorption of the cations to that of the anions.

IV. THE ZERO TOTAL CHARGE AND ZERO FREE CHARGE POTENTIALS

It follows from the general concept of electrode charge that there should exist zero total charge and zero free charge potentials for platinum metals. The potential at which the quantity $-\Gamma_H = Q = \epsilon - A_H$ becomes zero is called the zero total charge potential $\varphi_{Q=0}$ (z.t.c.p.). The potential at which the total charge Γ_{H^+} becomes zero in a solution with an excess of a neutral salt is called the zero free charge potential $\varphi_{\Gamma_{H^+}=0}$ (z.f.c.p.).

A method for determination of z.t.c.p. on the basis of the non-thermodynamic equation $Q = \epsilon - A_H$ has been

described[7,8,116] and the results of the determination of $\varphi_{Q=0}$ for platinum metals by this procedure are presented in Table 1. The highest anodic values of $\varphi_{Q=0}$ correspond to palladium and platinum. The $\varphi_{Q=0}$ shift in the negative direction with increase of the adsorbability of the anions of the solution and in the positive direction with increase of the adsorbability of the cations. It has been shown[115,124] that the method in which the surface of the electrode is scraped off in solution[139-142] should lead in principle to $\varphi_{Q=0}$ if an equilibrium is established during the scraping process between the electrode and the solution and the pH of the latter remains constant.

Table 1. Zero total charge potentials of platinum metals.

Solution	$\varphi_{Q=0}$, V (w.r.t. normal H e-de)	References
Platinum		
0.3 *N* HF+0.12 *N* KF (pH 2.4)	0.235	149
1 *N* Na_2SO_4+0,01 *N* H_2SO_4(pH 2.4)	0.20	120
1 *N* KCl+0.01 *N* HCl	0.14	99
1 *N* KBr+0.01 *N* HBr	0.06	120
1 *N* Na_2SO_4+0.01 *N* NaOH	−0.25	120
1 *N* KCl+0.01 *N* KOH	−0.30	120
1 *N* KBr+0.01 *N* KOH	−0.33	120
1 *N* KI+0.01 *N* KOH	−0.48	120
0.01 *N* H_2SO_4+0.1 *N* Na_2SO_4+0.01 *N* $ZnSO_4$	0.29	166
Palladium		
0.1 *N* Na_2SO_4+0.002 *N* H_2SO_4	0.26	126
Rhodium		
0.3 *N* HF+0.12 *N* KF(pH 2,4)	0.085	149
1 *N* Na_2SO_4+0.01 *N* H_2SO_4	0.05	120
1 *N* KCl+0.01 *N* HCl	0.02	120
1 *N* Na_2SO_4+0.01 *N* NaOH	−0.40	120
Iridium		
1 *N* Na_2SO_4+0.01 *N* H_2SO_4	0.10	115
1 *N* KCl+0.01 *N* HCl	0,06	115
1 *N* KBr+0.01 *N* HBr	−0.03	115

The most reliable values of z.f.c.p. were obtained from direct measurements of the relation between Γ_{H^+} and φ_r or from measurements of the dependence of the adsorption of anions Γ_{A^-} and cations Γ_{C^+} on φ_r in solutions with an excess of the salt. In the second method, employed for the first time by Balashova and Merkulova[143], z.f.c.p. represents the potential at which $\Gamma_{A^-} = \Gamma_{C^+}$, since, by virtue of the electroneutrality condition, $\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+}$. The values of z.f.c.p. found by the above method are listed in Table 2. The z.f.c.p. shift in the negative direction along the series Pt > Pd > Rh > Ir > Ru and are less positive than the z.t.c.p. Both z.t.c.p. and z.f.c.p. shift in the negative direction in the presence of specifically adsorbably anions and in the positive direction in the presence of specifically adsorbable cations.

In solutions of a surface-inactive electrolyte, z.f.c.p. is the zero-charge potential of the double layer (z.c.p.) and is analogous to z.c.p. of metals which do not adsorb hydrogen and oxygen. The Li^+ and Na^+ cations and F^- anions are least adsorbable on platinum metals[144-149]. In the presence of these ions z.f.c.p. may be regarded as z.c.p. In other cases chemisorption bonds arise between the surface of the metal and the adsorbed ions, whose strength depends on the nature of the ion and the electrode and also on the potential and pH of the solution. As a result, there is a possibility of partial or even total transfer of the charge of the ion being adsorbed to the surface of the metal. The transition of ions undergoing adsorption to the atomic adsorbed state under the conditions of an "insufficient potential", i.e. up to potentials corresponding to equilibrium values, for example in metal–metal ion systems, has been recently investigated by a wide variety of methods[24-48,67-78,83,95,150,151]. Measurements of the superequivalent adsorption of anions on platinum (Fig. 1) and rhodium are instructive in this respect[152]. These measurements indicate an increase of the superequivalent adsorption of anions on platinum in the series $SO_4^{2-} < I^- < Cl^- < Br^-$ and on rhodium in the series $SO_4^{2-} < Br^- < Cl^-$. The anomalous positions of I^- and Br^- in these series and also the nature of the variation of the degree of adsorption of cations with potential for positive surface charges (Fig. 1) can be interpreted, provided it is assumed that the degree of charge transfer from the anions to the surface of the metal increases with increasing adsorbability of the anions and when the potential shifts towards anodic values.

Table 2. Zero free charge potentials of platinum metals.

Solution	$\varphi_{\Gamma_{H^+}=0}$, V (w.r.t. normal H e-de)	References
Platinum		
0.3 *N* HF+0.12 *N* KF(pH 2.4)	0.185	149
0.3 *N* Li_2SO_4+0.01 *N* H_2SO_4	0.16	113
1 *N* Na_2SO_4+0.01 *N* H_2SO_4	0.16	109
0,01 *N* $ZnSO_4$+0.1 *N* Na_2SO_4+0.01 *N* H_2SO_4	0.27	166
1 *N* KCl+0.01 *N* HCl	0.05	99
1 *N* KBr+0.01 *N* HBr	−0.03	109
1 *N* KBr+0.01 *N* KOH	−0.39	105
1 *N* KI+0,01 *N* KOH	−0.52	105
$4 \cdot 10^{-3}$ *N* +Na_2SO_4 pH 3÷6	0.13±0.02	168
Palladium		
0.1 *N* Na_2SO_4+0.002 *N* H_2SO_4(pH 3)	0.10	126
Rhodium		
0.3 *N* HF+0.12 *N* KF(pH 2.4)	−0.005	149
1 *N* Na_2SO_4+0.01 *N* H_2SO_4	−0.04	104
1 *N* KCl+0.01 *N* HCl	−0.12	100, 101
Iridium		
0.3 *N* HF+0.12 *N* KF (pH 2.4)	−0.01	149
1 *N* Na_2SO_4+0.01 *N* H_2SO_4	−0.06	108
1 *N* KCl+0.01 *N* HCl	−0.13	108
1 *N* KI+0,01 *N* KOH	−0.59	
	0.06	115
Ruthenium		
1 *N* KCl+0.01 *N* HCl	0.50	103
Electrolytically mixed Pt-Ru deposit with 10 wt.% Ru		
1 *N* KCl+0.01 *N* HCl	−0.01	103

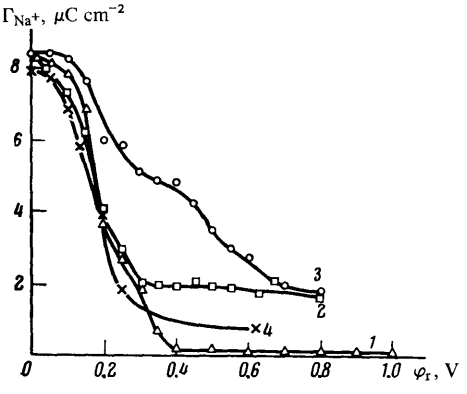


Figure 1. Variation of the degree of adsorption of sodium cations with the potential of a platinised platinum electrode in different solutions: 1) 0.003 *N* H_2SO_4 + 0.003 *N* Na_2SO_4; 2) 0.001 *N* HCl + 0.001 *N* KCl; 3) 0.001 *N* HBr + 0.003 *N* NaBr; 4) 0.001 *N* H_2SO_4 + 0.003 *N* NaI (according to the data of Kazarinov et al.[152]).

Owing to charge transfer, the definition of ϵ and the assumption that $\varphi_{\Gamma_{H^+}=0}$ is equal to z.c.p. become arbitrary. For this reason, the quantity $\varphi_{\Gamma_{H^+}=0}$, the physical significance of which is independent of the nature of the solution, may be regarded as equal to z.c.p. merely as a matter of convention in systems containing specifically adsorbable ions. The conventional nature of the concept of z.c.p. in the presence of strong specific adsorption can be clearly demonstrated[153] for a platinum electrode coated by adsorbed iodide and thallium ions. It has been shown that the position of z.c.p. depends on whether the adsorbed iodide and thallium ions become attached to the metallic or ionic components of the double layer.

V. FORMAL CHARGE TRANSFER COEFFICIENTS IN CHEMISORPTION PROCESSES

The problem of charge transfer in chemisorption processes has been recently discussed in detail[154-165]. It is noteworthy that the thermodynamic approach to charge transfer in the adsorption of hydrogen atoms on the surface of platinum was outlined in early investigations[7,8] in terms of the contributions of the hydrogen atom (X) and the double layer ion (Y), with the corresponding charge on the metal, to the potential jump at the electrode/solution interface. It has been shown[158,163] that chemisorption processes can be usefully characterised by formal charge transfer coefficients, which are referred to as such because they reflect not only the fraction of the charge transferred from the adsorbed species to the electrode but also the change in the parameters of the double layer caused by the adsorption process. In the adsorption of hydrogen atoms on the electrode surface the formal charge transfer coefficient n_2 may be calculated from the equation

$$n_2 = (\partial\Gamma_{H^+}/\partial\Gamma_\Sigma) = -X/Y, \qquad (6)$$

where $\Gamma_\Sigma = \Gamma_H + \Gamma_{H^+}$. The results of the calculation of n_2 indicate an appreciable polarity of the bonds between platinum and rhodium on the one hand, and oxygen on the other[138,158,163]. The chemisorption of an ion j on a platinum electrode is characterised by two formal charge-transfer coefficients:

$$n_j' = (\partial\Gamma_H/\partial\Gamma_j)_{\Gamma_{\Sigma,\varphi}} \qquad (7a)$$

and

$$n_j'' = (\partial\Gamma_{H^+}/\partial\Gamma_j)_{\Gamma_{\Sigma,\varphi}}, \qquad (7b)$$

where Γ_j is the Gibbs adsorption of the ion.

VI. THE INFLUENCE OF THE pH OF THE SOLUTION ON THE STRUCTURE OF THE ELECTRODE/SOLUTION INTERFACE

The thermodynamic theory yielded relations between z.t.c.p. and z.f.c.p. on the one hand and the concentration of the neutral salt at a constant pH (and also at a constant concentration of the acid or alkali in solution) on the other[101,123]:

$$(\partial\varphi_r/\partial\mu^{\pm}_{CA})_{Q,\mu_{H^+}} = -(\partial\Gamma_{C^+}/\partial Q)_{\mu^{\pm}_{CA},\mu_{H^+}} - (\partial\Gamma_{A^-}/\partial Q)_{\mu^{+}_{CA},\mu_{H^+}}; \qquad (8)$$

$$(\partial\varphi_r/\partial\mu^{\pm}_{CA})_{\Gamma_{H^+},\mu_{H^+}} = -2(\partial\Gamma_{C^+}/\partial\Gamma_{H^+})_{\mu^{\pm}_{CA},\mu_{H^+}} - 2(\partial A_H/\partial\mu_{CA})_{\varphi_r,\mu_{H^+}}/(\partial\Gamma_{H^+}/\partial\varphi_r)_{\mu_{H^+},\mu^{\pm}_{CA}}, \qquad (9)$$

where $\mu^{\pm}_{CA}$ is the average chemical potential of the salt ions. These expressions can be referred to as the relations for the Esin–Markov coefficient in the case of platinum metals. Owing to the presence of two total charges (Q and Γ_{H^+}), there exist two Esin–Markov coefficients for platinum metals, in contrast to mercury. When a comparison is to be made with a mercury electrode, one should evidently use the quantity $(\partial\varphi_r/\partial\mu^{\pm}_{CA})_{\Gamma_{H^+},\mu_{H^+}}$.

Eqns. (8) and (9) become identical and the same as the relation for mercury when the electrode surface is free from adsorbed hydrogen and oxygen atoms (the double-layer potential range). Direct determinations of the Esin–Markov coefficients in the double-layer region[101] led to the conclusion that they are equal to −1, i.e. that there is no discreteness effect in the adsorption of anions on platinum metals. This phenomenon has been explained by pronounced charge transfer from the anions to the surface of the metal.

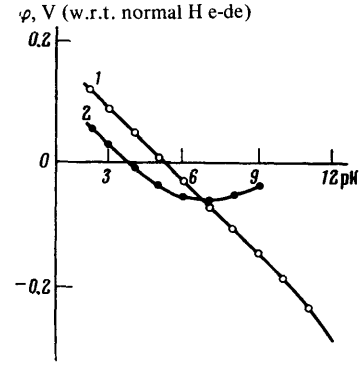


Figure 2. Variation of z.t.c.p. (curve *1*) and z.f.c.p. (curve *2*) with solution pH for a platinised platinum electrode in 0.1 N KCl (according to the data of Frumkin et al.[130]).

The variation of z.t.c.p., z.f.c.p., and Γ_{H^+} with solution pH is of special interest, The variation of z.t.c.p. for platinum and rhodium with pH over the entire range of the latter was found directly by the method of potentiometric titration under isoelectric conditions[127-131] (Fig. 2). It was found that at lower pH values, the potential $\varphi_{Q=0}$ shifts in a negative direction by 35–50 mV (depending on the composition of the solution and the nature of the metal) when pH is increased by unity. This relation becomes somewhat more marked at higher pH values and, for example in the case of the rhodium electrode in 0.1 N Na_2SO_4 at pH 7–12, the shift of $\varphi_{Q=0}$ amounts to about 58 mV per pH unit. According to the thermodynamic theory, we have for solutions with an excess of the salt[120]

$$(\partial\varphi/\partial\mu_{H^+})_{Q=0} = [1 - (\partial\epsilon/\partial A_H)_{\mu_{H^+}}]^{-1}. \qquad (10)$$

The observed relations between $\varphi_{Q=0}$ and pH imply that at lower pH values $(\partial\epsilon/\partial A)_{\mu_{H^+}} < 0$, i.e. the free charge becomes more positive when φ_r shifts. At pH values in the alkaline region $(\partial\epsilon/\partial A_H)_{\mu_{H^+}} \simeq 0$, which corresponds to the relatively weak dependence of Γ_{H^+} on φ_r in alkaline solutions.

The variation of z.f.c.p. and Γ_{H^+} with pH was first observed by Shlygin et al.[6] Subsequently interest in this problem was aroused by the study of Kheifets and Krasikov[167]. The influence of pH on the z.f.c.p. values for platinum metals has been investigated[109,115,116,168,169]. The most complete data have been obtained by the method of potentiometric titration under isoelectric conditions[130,131]. Fig. 2 illustrates the variation of z.f.c.p. with pH for a platinised platinum electrode in 0.1 M KCl solution. A similar variation of z.f.c.p with pH was also found for platinised platinum and rhodium electrodes in 0.1 N Na_2SO_4. It follows from Fig. 2 that in the pH range 2.3–5 z. f. c. p. shifts with increasing pH towards cathodic values by about 35 mV when the pH is altered by unity. In the pH range 5–9 the shift of z. f. c. p. is small, and at pH > 7 z. f. c. p. begins to shift in the positive direction as the pH is increased. The complex variation of $\varphi_{\Gamma_{H^+}=0}$ with pH is due to the fact that $\varphi_{\Gamma_{H^+}=0}$ shifts from the hydrogen to the double layer region and then to the region where adsorbed oxygen is deposited. The following relation holds for the variation of z.f.c.p. with pH:[106,107,109]

$$(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}=0} = [1 - (\partial\epsilon/\partial A_H)_{\varphi_r}]^{-1}, \qquad (11)$$

which shows that the shift of z.f.c.p. in the negative direction with increasing pH corresponds to $(\partial\epsilon/\partial A_H)_{\varphi_r} < 0$. When $A_H = 0$, we obtain $(\partial\varphi/\partial\mu_{H^+})_{\Gamma_{H^+}=0}$, and when $(\partial\epsilon/\partial A_H)_{\varphi_r} > 1$, the shift of z.f.c.p. may be in the positive direction. Then pH ~7, $\varphi_{Q=0} = \varphi_{\Gamma_{H^+}=0}$ (Fig. 2). In this case $\varphi_{Q=0}$ and $\varphi_{\Gamma_{H^+}=0}$ correspond to the double layer region of the platinum electrode, i.e. to the region of its ideal polarisability where $Q = \Gamma_{H^+}$.

The results made it possible to plot the variation of z.f.c.p. with A_H and to find its value for $A_H = 0$, i.e. for the platinum surface free from hydrogen and oxygen. It proved to be −0.06 V (relative to the normal hydrogen electrode). Thus z.f.c.p. for the platinum surface free from hydrogen and oxygen is more positive by only 0.2–0.3 V than z.c.p. for mercury. The difference $\varphi^{Pt}_{\epsilon=0} - \varphi^{Hg}_{\epsilon=0}$ is inconsistent with the familiar relation between the electron work function and z.c.p.,[170–172] since the difference between the electron work functions of platinum and mercury is 0.9–1.0 V according to ultrasonic measurements[173]. The problem of the causes of the discrepancy requires further study. Possibly it is associated with the different structures of the adsorbed layers of water on platinum and mercury and with the difference between the structure of platinum crystallites grown in contact with water or platinum subjected to anodic-cathodic activation on the one hand and platinum treated with ultrasound at a high temperature on the other.

Fig. 3 presents the variation of the free surface charge of a platinised platinum electrode with potential in 0.1 M KCl solution at different pH values obtained by the method of potentiometric titration under isoelectric conditions[130]. These data make it possible to put forward the hypothesis of a gradual transition with increasing pH to an electrode surface negatively charged throughout the entire range of φ_r. Such a phenomenon is typical for all platinum metals. Its interpretation is based on allowance for the simultaneous influence of two factors: the shift of the range of potentials in which measurements are made in the negative direction and a more pronounced overlapping of the regions corresponding to the adsorption of hydrogen and oxygen as the pH is increased. Hydrated surface oxide groups are probably weakly acidic and split off hydrogen ions in alkaline media, adsorbing cations. Thus in alkaline solutions there is a transition from the adsorption of cations, caused by the ionisation of the adsorbed hydrogen and decreasing over a range of φ_r values, to the adsorption of cations on the surface of oxide groups, which becomes more marked also over a range of φ_r values.

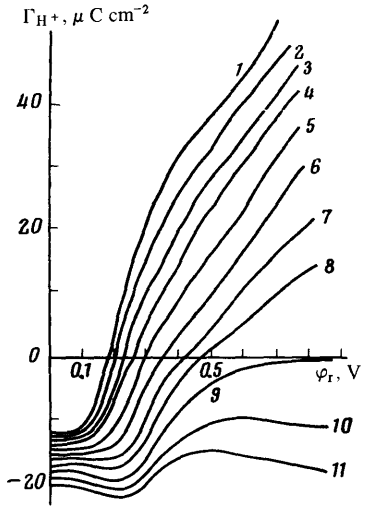


Figure 3. Variation of the free surface charge of a platinised platinum electrode with φ_r in 0.1 N KCl at different pH: 1) 2.3; 2) 3; 3) 4; 4) 5; 5) 6; 6) 7; 7) 8; 8) 9; 9) 10; 10) 11; 11) 12 (according to the data of Frumkin et al.[130]).

The relation between the degrees of adsorption of hydrogen and oxygen ions and atoms leads to the possibility of observing under certain conditions at a constant pH two values of z.f.c.p. corresponding to the reduced and oxidised electrodes. The existence of z.f.c.p. for oxidised platinum followed from the measurements of Balashova and Frumkin[174]. Two values of z.f.c.p., at 0.13 ± 0.02 V and 0.47 V (relative to the normal hydrogen electrode), were found[168] by the radioactive tracer method in a 0.04N Na_2SO_4 solution at pH 6. A similar phenomenon occurs in 0.004N Cs_2SO_4 solution. Two values of z.f.c.p. were observed for iridium in a 1N KI + 0.01N KOH solution[115] (Table 2). Only one value of z.f.c.p. was found for ruthenium[103], in the region corresponding to the adsorption of oxygen, since the z.f.c.p. for the reduced electrode is in the region corresponding to the evolution of molecular hydrogen. Owing to the overlapping of the regions corresponding to the adsorption of hydrogen and oxygen and their involvement in the potential jump at platinum metals, conditions can arise, in principle, over a relatively wide range of potentials where the surface carries almost no free charge (see, for example, curve *9* in Fig. 3).

The rhodium electrode–0.1 M KCl system proved to be particularly convenient for the observation of two values of z.f.c.p. and for the investigation of their characteristics. The results of the determination of the variation of Γ_{H^+} with φ_r for this system by the method of potentiometric titration under isoelectric conditions are

illustrated in Fig. 4. The z.f.c.p. corresponding to oxidised rhodium shifts in the negative direction by 80–140 mV when the pH increases by unity.

At high anodic potentials oxide ions are probably formed with participation of oxygen and the cations and anions of the supporting electrolyte[175–180]. Experiments by the tracer atom method indicate a non-monotonic change with potential in the charge of the metallic component of the ion double layer in this range of polarisations[179,180].

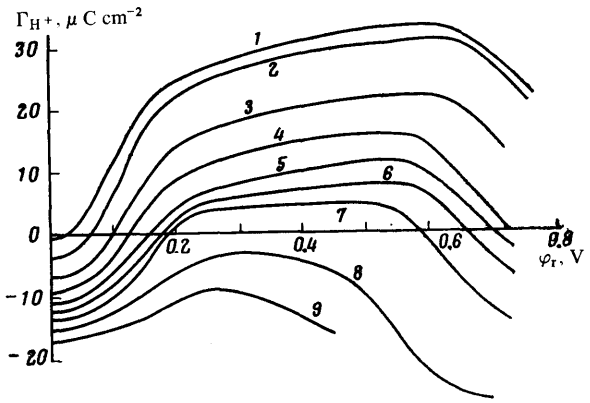


Figure 4. Variation of the free surface charge of a rhodium electrode with φ_r in 0.1 *N* KCl at different pH: 1) 3; 2) 4; 3) 5; 4) 6; 5) 7; 6) 8; 7) 9; 8) 10; 9) 11 (according to the data of R. Notoya's data).

The adsorption of ions is greatly influenced by the inhomogeneity of the surfaces of platinum metals, which has been specially emphasised in a number of publications[20–23]. The inhomogeneity leads to a logarithmic Temkin isotherm for the relation between the adsorption of ions and their concentration in solution and to the Roginskii–Zel'dovich equation for the kinetics of the adsorption of ions[20–23,181–184]. The intrinsic inhomogeneity of the surface of platinum has been demonstrated[185] by differential isotopic methods. Among the interesting conclusions reached in the study of the exchange of ions adsorbed on platinum metals for ions from the solution, the conclusion that a transition state involving both an adsorbed ion and an ion from the solution must be formed in the exchange process[186] is noteworthy.

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