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Surface Thermodynamics of Metal/Solution Interface: the Untapped Resources

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I. INTRODUCTORY REMARKS

Platinum metals electrochemistry is closely associated with electrocatalysis. This wide and highly mobile field is occupied by extremely different types of researchers, who consider electrocatalytic phenomena at various levels, from industrial to atomic. All of them are fighting for one and the same result (roughly, as high as possible activity and stability of the catalyst), but they surely see the events at catalyst/solution interface by different eyes. Some researchers approached electrocatalytic field from the classical electrochemistry side, but a lot of people were involved from other areas of chemistry and physics. This situation is typical for electrochemical material science, with its mounting increase of publications around mainstreams and some risk of a gradual loss of fundamentals. However it is not over yet to remind some of them.

Electrochemical surface thermodynamics is a boundless science. For ideally polarisable (*mercury-like*) electrodes it is to a great extent fixed in textbooks and courses. On the contrary, for

C.G. Vayenas (ed.), *Interfacial Phenomena in Electrocatalysis*, Modern Aspects of Electrochemistry 51, DOI 10.1007/978-1-4419-5580-7_2,

perfectly polarasible electrodes (assuming coadsorption of ions and atoms) thermodynamical knowledge is less disseminated, still available mostly in original papers and brief reviews.[1-4] Today this knowledge is connected mostly with hydrogen-adsorbing platinum group metals.

In what follows, only a small portion of platinum interfacial electrochemistry is discussed. The boundaries of this review are very sharp:

(a) aqueous solutions,
(b) inorganic adsorbates (with accenting adsorption of anions, with only selective information about cations adsorption),
(c) equilibrium interface (no faradaic processes are discussed),
(d) pure metals (not alloys or surfaces modified by foreign metal adatoms).

However just inside these boundaries we have a hope to find key information concerning reaction zone of electrocatalytic processes, as hydrogen- and oxygen-containing species, as well as supporting inorganic anions, are unavoidable components of any interface in fuel cells and other important configurations. The basic problems of catalytic activity and reactivity prediction are still by and large based on the separation of *electronic* and *structural* factors (if possible) and understanding of their interrelation (if exact separation fails). This problem traces its roots to the period when only macroscopic observations were possible, and any experimentally measured quantity reflected the interplay of numerous molecular level factors. At that stage thermodynamic relationships were applied to construct a self-consistent description of various observations. During a modern period, when electrocatalytic studies are already well equipped with various microscopic and spectroscopic techniques, people operate with precise information about certain molecular aspects, but it is still impossible to get the complete set of data about all details of reaction layer. This means that some details should be understood or assumed indirectly, in particular from comparison with thermodynamic quantities.

Some details discussed in this review are of more routine importance, as the total charge quantity is actively used for in situ determination of electrodes true surface area of various perfectly polarisable electrodes.[5]

Even with the restriction of content mentioned above it is impossible to collect the literature exhaustively. To overcome this problem, some recent reviews related to application of various in situ techniques are cited instead of numerous original papers. Publications of active research groups working systematically in the field are cited selectively (if these studies present a long-term series, typically the latest papers are mentioned). Citations of rarely available papers are more sizeable (still not exhaustive), to avoid a loss of original sources. Illustrations attempt to present some less known data in a compact form.

II. PREHISTORY AND VISIBLE HORIZON

The pronounced progress of platinum electrochemistry is indepted to the existence of platinized platinum, Pt/Pt (first applied by Kolraush[6]). Starting from 1930s Frumkin initiated a systematic study of Pt/Pt, including comparison of hydrogen adsorption at metal/solution and metal/gas interfaces.[7-9] Most important results are available in his review,[10] including the grounds in favor of monolayer hydrogen coverage at zero RHE potential and discussion of experimental data in terms of Temkin isotherm. Other highly dispersed platinum materials (Adams platinum resulting from reduction of PtO_2, platinum black, skeletal platinum) were studied as well. Their specific surface areas were in the range of 10–40
$m^2 \cdot g^{-1}$, but after stabilization (ageing) in solution the usual values were of the order of $m^2 \cdot g^{-1}$. Systematic comparison of various dispersed platinum materials was reported later.[11,12] Despite of pronounced difference in fabrication protocols, all dispersed materials demonstrate similar hydrogen adsorption isotherms, with significant distinction from smooth polycrystalline platinum. For the latter, complete hydrogen desorption takes place at lower potentials (*lower bonding energy*). In the absence of modern techniques for structural characterization and with the use of a limited number of electrochemical techniques it was hardly possible to get more information about structural/morphological effects, which later appeared in the centre of attention.

Electrochemistry of other platinum group metals was also roughly characterized before 1960s (see, e.g., Refs. 13–15 for Rh

and Ir, and Ref. 16 for Os and Ru). The studies of Pd formed a separate area,[17,18] because hydrogen absorption in metal bulk attracted a principal attention, not interfacial processes. Separation of hydrogen adsorption and absorption for dispersed metals is rather complicated.

When the fact of hydrogen adsorption on platinum metals was well documented, a search for self-consistent models started, aimed to description of surface hydrogen coverage dependence on electrode potential and temperature. Breiter was the first who studied the temperature dependence of hydrogen adsorption on smooth platinum, rhodium and iridium.[13,14,19] He demonstrated a possibility to present experimental dependences typical for polycrystalline platinum by combination of two Frumkin isotherms[20] (see below in Section IV.5).

To do the same with dispersed platinum metals, one had to overcome its fast ageing at elevated temperatures, accompanied by decrease of true surface area. This problem was addressed[21] by measuring galvanostatic charging curves and rather fast voltammograms (0.2–0.5 V s^{-1}) of preliminary aged Pt/Pt, and 15–20% increase of the charge in H UPD region was found when temperature was increased from 20 to 80°C. This effect (absent for smooth Pt and powder-type dispersed materials)[12] was assigned to higher accessibility of specific surface regions, like narrow pores. An alternative hypothesis of hydrogen penetration into Pt bulk had never found solid confirmation. For other dispersed platinum metals, no anomalous increase of hydrogen coverage was observed.

The data on coverage-dependent differential heat of hydrogen adsorption and coverage-potential dependences formed a set of the most early quantitative thermodynamic information reported for both smooth platinum metals and electrodeposited dispersed Pt, Rh, and Ir in acidic and alkaline solutions. The following tendencies appeared to be general:

(a) the heat of adsorption decreases with hydrogen surface coverage;
(b) coverage of 0.3–0.4 separates the regions with more and less sharp decrease mentioned above, and simultaneously separates two voltammetric desorption peaks (both features are the most pronounced for platinum);

(c) heat of adsorption decreased in a sequence KOH > H_2SO_4 > HCl (at least at low and mid coverage, for which the accuracy was better).

The particular disagreements found for the behavior of *two forms* of hydrogen at smooth and dispersed platinum were probably induced by a limited accuracy of data treatment, as well as by still not exactly proven assumption of complete coverage at zero RHE potential.

Looking back one can easily notice that before mid 1960s the thermodynamics of adsorption phenomena on platinum was considered mostly in terms of temperature dependence. This traditional approach was not specific for electrochemical thermodynamics, but there was no serious basis to involve other parameters. Another remarkable point is discussion exclusively in terms of hydrogen adsorption, under more or less transparently formulated assumption of complete charge transfer with formation of uncharged adatom. It is slightly strange: future surface thermodynamics was outlined already in 1936,[8,9] and its principal point was the interplay of ionic and atomic adsorption, but even 30 years later ionic contribution was still accounted only as very formal subtraction (*double layer correction*). When the idea of this interplay was first presented by Frumkin in more comprehensive form,[22] it met immediately Breiter's support.[23]

The main reason of slow intervention of the evident atomic-ionic interplay concept was a lack of experimental techniques to discover contributions of various coexisting adsorbates. Further development consisted in subsequent separation of strongly interrelated contributions from hydrogen adatoms, various ions, and (much later) water molecules. Running a few steps forward from early temperature dependences, we should refer to the most recent advancement: temperature effect on in situ scattering X-ray spectroscopy (SXS) response of platinum, currently available for very few systems,[24] confirms temperature-induced adsorbate reordering and temperature-dependent adsorbate-induced surface reconstruction/deformation. By involvement of these phenomena into general consideration of interfacial equilibria we really have a chance *to complete the picture*, and to arrange a solid link between observations and atomic/molecular models. The progress depends

equally on high-level experimental techniques[25-32] and reflecting, again and again, on the reliable electrochemical data.

The early thermodynamic data are effective quantities related simultaneously to hydrogen adsorption and numerous accompanying phenomena, but they are still not hopeless for deeper analysis. In addition we should not underestimate the importance of this early period for accumulating the experimental experience,[33] as platinum metals electrochemistry requires rather specific techniques of surface and solution preparation, to avoid contaminations.

Terminology originating from this early period appeared to be rather stable. Namely, the conditional separation of the overall potential interval into *hydrogen region*, *double layer region*, and *oxygen region* still holds much favor, as well as the names *strongly bonded* and *weakly bonded* for hydrogen adsorbed at higher and lower potentials (or for lower and higher hydrogen coverages). These historic names are still actual for polycrystalline platinum (with some reservations). UPD (underpotential deposition) notion appeared later, owing to Schmidt and Gygax studies of metal submonolayers on foreign supports,[34,35] and became widespread after the first conceptual paper publication.[36] However it took some time to realize that hydrogen adsorption with charge transfer at positive RHE potentials (hydrogen adatoms formation) presents the same phenomenon. Now H UPD became a usual term, which never hinders the use of historic notions.

III. A BREAKTHROUGH: FRUMKIN-PETRII SURFACE THERMODYNAMICS

1. Rarity: Equilibrium Techniques to Study Adsorption

The initial approach to platinum surface thermodynamics[7-9,37] was based on mercury-like double layer experience. In particular the adsorption of H^+ ions was treated as purely electrostatic, which means the complete replacement of these ions by any other cations when the latter are in large excess. This assumption works when H^+: cation molar ratio is below 0.1, and valid at least for pH ≤ 3 and salt concentrations up to 1 M.

Rather concentrated set of basic equations was published in a large conference paper[22] and simultaneously in a brief Frumkin's note.[38] The results of versatile experimental verification of this theory were briefly reviewed in Ref. 39 and then subsequently in Refs 1–4. Important review of experimental facts collected before the 1960s can be found in Ref. 10, Section 4. Finally, the last Frumkin's book[40] completed and published by Damaskin and Petrii contains a representative selection of data and the most reliable tabulated values.

The interrelation of techniques applied to determine basic quantities is shown schematically in Fig. 1. The most evident are the total charge Q_t and the total capacity C_t: one can get both quantities from usual electrochemical techniques under (quasi) equilibrium conditions. The establishment of equilibrium can be controlled or estimated from dependence on current density (for chronopotentiometry) or scan rate (for voltammetry). For the former technique, it is possible to measure the equilibrium curves by interrupting polarization from time to time and waiting when potential becomes constant. This approach (equilibrium charging curves, called now the galvanostatic intermittent titration technique, GITT) had been first applied in the study of hydrogen sorption by palladium.[17] To measure the free electrode charge Q_f associated with ionic adsorption exclusively, the direct measurements of Gibbs surface excess of ions were applied by means of the radiotracer technique. Independently, Γ_{H^+} value could be determined under some circumstances from the changes of solution pH induced by adsorption.

The principal interrelations of the basic quantities are well-known and explained in earlier reviews.[1-4] The general approach is based on 3D electrocapillary curve, with its two planar intersects corresponding to two Lippmann equations for constant chemical potentials μ_H = const and μ_{H+} = const, see Refs. 41–43 for additional explanations. Here we mention the most important ratio:

$$Q_t = -F\Gamma_H = Q_f - FA_H \tag{1}$$

where A_H and Γ_H are the surface concentration and Gibbs adsorption of hydrogen adatoms, respectively. The total charge Q_t is what we need to spend when increasing the electrode surface for one

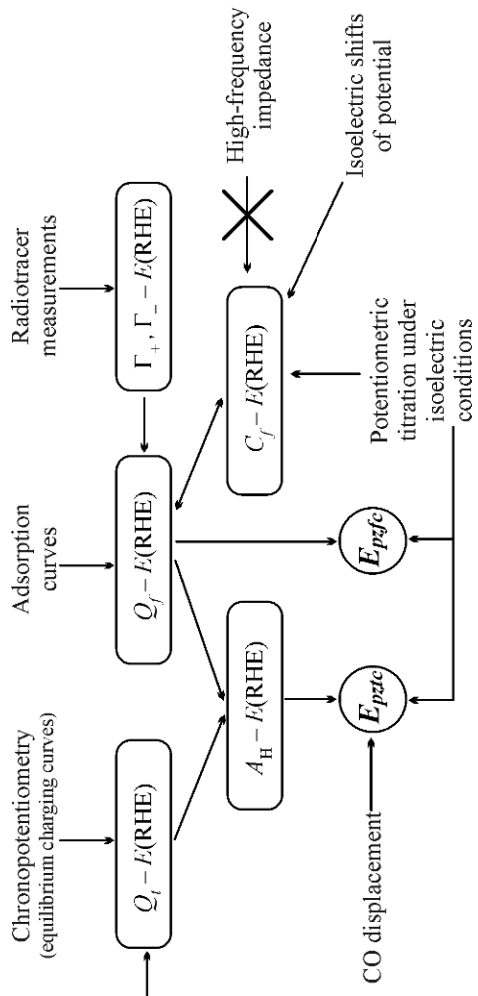

Figure 1. General scheme of the experimental verification applied in Frumkin-Petrii surface thermodynamics to electrodes with high surface area. CO displacement represents the most informative currently developed technique for smooth electrodes.

square unity (to say, 1 cm^2) under condition μ_{H+} = const., i.e., at fixed pH. For the free charge Q_f, it is possible to provide the experimental conditions when $Q_f = F\Gamma_{H+}$: it is true for acidic solutions with excess of supporting salt electrolyte, when

(a) all hydronium ions are displaced from ionic double layer, and
(b) chemical potentials of all ions are constant.

Additional reservation consists in

(c) the absence of hydronium specific adsorption; it is already beyond thermodynamics, and should be always taken into account when some physical models are considered in combination with thermodynamic data.

The majority of original results in 1960-70s were reported just for diluted acids with excess salt additives. For pure acid solutions, the important simple link between Q_f and Γ_{H^+} disappeared, and the scheme of experimental verification had to be more complex. In addition to basic quantities, a number of differential quantities can be determined experimentally. The technique of isoelectric potential shifts[44] gives the derivative $\left(\frac{\partial\Gamma_{H^+}}{\partial E(RHE)}\right)\mu_{H^+}$. It provides a meaning of the equilibrium ionic double layer capacity C_f for certain solution composition because no charge is spent for formation or desorption of hydrogen adatoms. Similar values corresponding to the constancy of other basic quantities were determined from similar potential shifts $\left(\frac{\partial E}{\partial\mu_{H^+}}\right)_{\Gamma_{H^+}}$ and $\left(\frac{\partial E(\mathrm{RHE})}{\partial\mu_{H^+}}\right)_{Q_t}$ in experiments with replacement of one solution by another. Relative replacement techniques could be applied to determination of ions adsorption, see a systematic series.[45-47]

For correct arrangement of these experiments, a lot of routine details had to be controlled, to avoid artefacts. Special cells with separated compartments allowed to replace solutions independently in the chambers of working and reference electrodes, as well as in the bridge between these solutions. Contributions from molecular hydrogen had to be minimized, especially in the vicinity of zero

RHE potential, when the amount of molecular hydrogen in equilibrium with hydrogen adatoms is already high enough. These details are explained at great length in the early papers.[44,48,49]

To measure the quantities related to free charge, and to escape the effect of oxygen traces in experiments with solution replacement, one needs to use electrodes of very high true surface areas (1–10 m^2), which is possible if the geometric area of the electrodes covered by the layer of dispersed electrodeposited platinum metals runs up to dozens of cm^2. For this configuration, the accuracy of Γ_{H^+}determination is ca. ±2 $\mu C \cdot cm^2$. Radiotracer techniques available in the 1960s required only one order lower true surface areas, with the obligatory operation of taking the electrode out of the cell. This is the reason why the role of radiochemical data in the studies of equilibrium adsorption was initially rather limited. However in mid 1970s the improvement of this technique increased its contribution to the area, see e.g., Refs 50–52 and Section IV.2 below.

The most laborious experiments related to free charge determination turned out to be more effective when the technique of potentiometric titration under isoelectric conditions was worked out.[53] Using the cell shown in Fig. 2, it became possible to collect the data without solution replacement and to avoid the establishment of certain potential in the hydrogen region by equilibrating the system with hydrogen gas.

The two subsequent sections address frequently missed or misunderstood aspects of Frumkin-Petrii thermodynamics.

2. True Double Layer Capacity

It is usually believed that high frequency capacitance obtained from impedance spectroscopy can represent ionic double layer capacity. However in general this is not the case for platinum electrode, this is the reason why one arrow in Fig. 1 (in the left) is crossed. In contrast to C_f measured under equilibrium conditions (by means of isoelectric potential shifts), non-equilibrium impedance response can contain a contribution from A_H (and/or A_O, surface concentration of oxygen-containing species). These contributions are determined by A_H and A_O potential derivatives and their free electrode charge derivatives, and in general can be either positive, or negative.

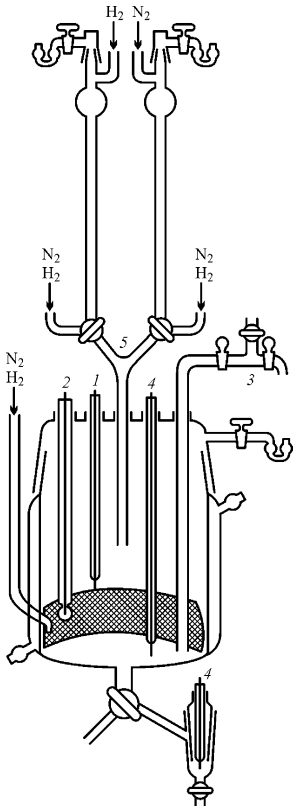

Figure 2. Schematic representation of the cell used for potentiometric titration under isoelectric conditions.[53] Working electrode (gauze with a layer of electrodeposited dispersed metal) (1), glass electrode (2), salt bridge for connection with the reference electrode compartment (3); counter electrodes (4); a set of burettes for deareated solutions of acid and base containing the excess of supporting electrolyte (5). This technique allows avoiding solution replacement in the course of measurements of isoelectric potential shifts. Reprinted from Ref. 53, Copyright (1974) with permission of Nauka Publ.

The role of true double layer capacity in so-named *double layer correction* of total capacity was specially considered in a rarely available paper,[54] with illustrations reproduced in Fig.3. Curves 2 demonstrate that ionic contributions to total capacity in the hydrogen potential region are non-monotonous, and deviate from horizontal dashed line (extrapolation of current in double layer region, typically used for approximate correction). For chloride, and especially for bromide solutions, the ionic contribution to total capacity in the hydrogen region surely exceeds the contribution formally estimated from horizontal interpolation. In particular, this formal procedure results in pronounced underestimation of true surface area determined from H-UPD charge (up to 15–20%).

For sulfuric acid solution, there is a sort of mutual compensation of ionic contributions in the regions of weakly and strongly bonded hydrogen (C_f in these regions is below and above horizontal line, respectively, see Fig.3a). Another aspect of this compensation is as follows: the observed doule layer capacity at E(RHE) > 0.4 V is essentially higher than ionic capacity because oxygen-containing species start to adsorb. Curves 3 and 4 in Fig. 3a demonstrate the results of approximate and more reliable correction. The corresponding difference is slightly higher than usual coulometric accuracy (at least 5%). Similar problems arise when other UPD-based techniques are applied to true surface area determination.[5]

Figure 3a presents also an example of negative true double layer capacity. In this case the sign is changed mostly due to a high negative contribution from A_O derivatives. It is the most obvious illustration to keep the reader from considering high-frequency capacity values (never negative in the absence of faradaic reactions) as C_f. An example of negative true double layer capacity in a wider potential interval is known for iridium: in alkaline solution the sign changes already at ca. 0.1 V RHE.[55]

Another useful illustration goes from comparison of true and high-frequency capacity values. Namely, application of Dolin-Ershler scheme to impedance data for 40 Hz–50 kHz frequency range[56] results in 2–3 times lower values of double layer capacity in the region of high hydrogen coverage, as compared to curves 2 in Figs.3 a-c. The specific shape of capacity peaks determined by anion nature is qualitatively the same, but several details are smoothed or even lost in high-frequency data.

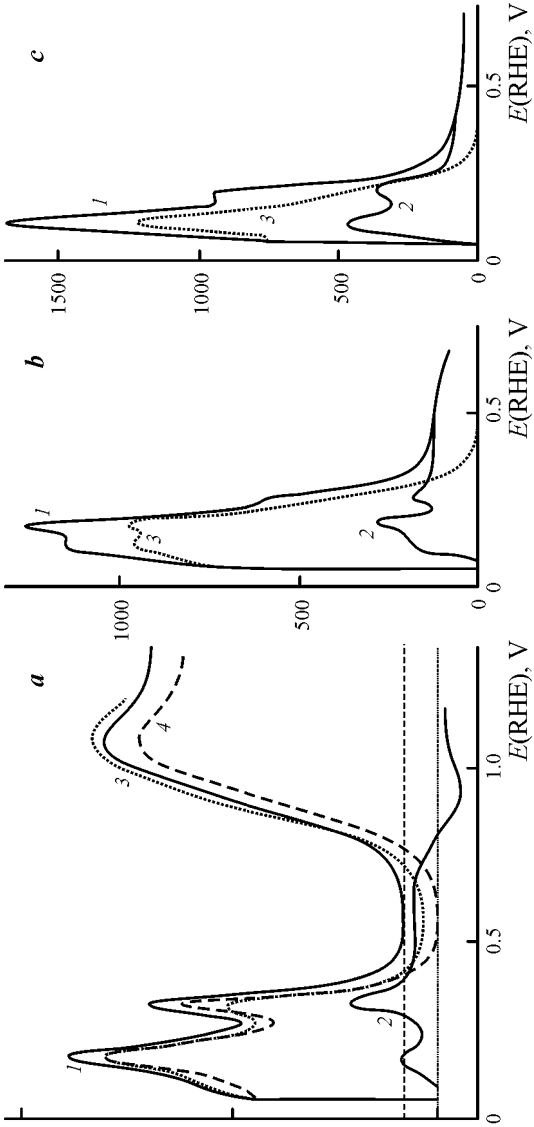

Figure 3. Cyclic voltammograms representing total capacities C_t (1), and true double layer capacities C_f (2) in 1 N H_2SO_4 (a), HCl (b) and HBr (c). Dashed lines (3) correspond to the difference of curves (1) and (2). In Figure 2a, dashed curve 4 corresponds to formal double layer correction (applied under assumption of purely double layer intermediate region between hydrogen and oxygen adsorption regions). From Ref. 54, with modifications.

A sharp right peak of sulfate contribution to C_f (curve 2 in Fig. 3a) is an interesting feature, as it somewhat reminds the famous Clavilier's butterfly at voltammograms of Pt(111)[57,58], the most intriguing feature of platinum single crystalline electrochemistry. It is a sort of *screened butterfly*: for the majority of disordered polycrystalline materials this feature finds itself inside the hydrogen region. It is surely sensitive to surface structure, which was never controlled in early equilibrium experiments. To estimate its possible position along the potential axis, we collect three sulphate adsorption curves definitely measured by various techniques and on different platinized platinum electrodes in sulfate solutions of close composition[59-61] (Fig. 4a). Figure 4b presents two limiting cases of *screened butterfly* obtained by differentiation of these equilibrium curves. The difference in curves 1 and 2 in Fig. 4b is far beyond inaccuracy of our treatment.

Probably some unusual voltammetric features of certain polycrystalline platinum samples, like *the third hydrogen peak*,[62] can result from structure-sensitive sulfate adsorption.

3. Potentials of Zero Charge: General Trends

One of the most psychologically embarrassing aspects of platinum metals electrochemistry is the existence of two types of potentials of zero charge (pztc and pzfc for total and free charges, solid and open circles in Fig. 5 respectively). Figure 5a compares some data for Pt, Ir and Rh in solutions of various pH, and Fig. 5b collects the data for platinum (most actively studied) in solutions of various anionic composition. Other symbols in Fig. 5 mark several representative values for single crystas. The experimental approach to determine these values was discussed in a general context of zero charge problem in Ref. 63. The basis of this approach is CO displacement technique, which the Alicante group started developing jointly with Clavilier.[64,65] It was consequently developed and improved by Feliu and co-workers, and a number of their results[66-72] ploted in Fig. 5 are discussed below in Section IV.2.

The number of platinum group metals in Fig. 5a is limited to three because other metals are less studied. For Pd, complications appear because of hydrogen absorption at potentials below ca. 0.1–0.15 V (RHE). This interval is so wide because highly defective dispersed palladium absorbs a lot of hydrogen in the α-phase, to

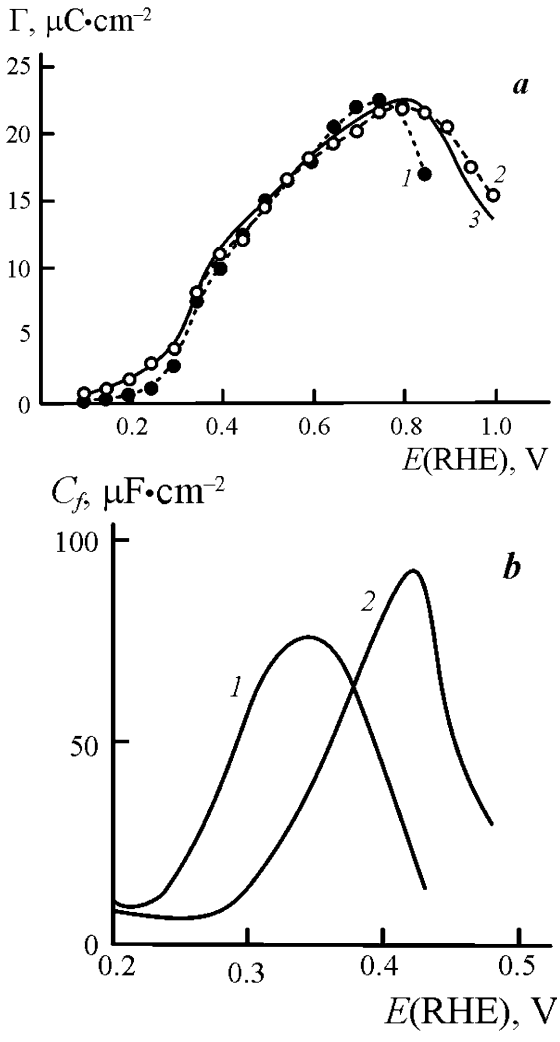

Figure 4. Equilibrium data on sulfate adsorption (a) and two limiting versions of their potential derivatives (b) for 3 - 10 mM H_2SO_4 with 0 – 10 mM additives of Na_2SO_4. Curves 1-3 (a) for this treatment are taken in original form from PhD theses of L.Yu. Lukyanycheva (conductivity technique, curve 1), Zh. N. Malysheva (radiotracer technique, curve 2), V.V.Topolev (adsorption curves technique, curve 3); corresponding published plots are in smaller format,[59-61] and can contain some distortions.

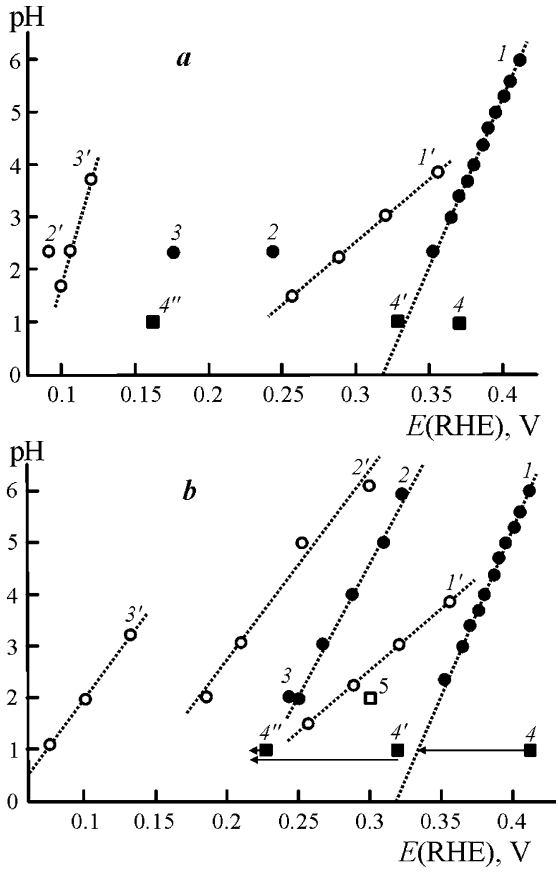

Figure 5. Potentials of zero total (solid symbols) and free (open symbols) charges of various dispersed electrodeposited metals in sulfate solutions (a) and of platinized platinum electrode in solutions of different anionic composition (b). The data for Pt (a - 1, 1'), Ir (a – 2, 2') and Rh (a – 3, 3') are plotted jointly with later determined values of the pztc of Pt(100) (a- 4)[66], Pt(111) (a – 4')[67] and Pt(110) (a – 4'')[68] in 0.1 M H_2SO_4. The data for polycrystalline electrodeposited platinum in sulfate (b – 1, 1'), chloride (b – 2, 2') and bromide (b – 3, 3') are compared with pztc values for Pt(100) (b - 4)[69], Pt(111) (a – 4')[72] and Pt(110) (a – 4'')[68] in 0.1 M $HClO_4$ Arrows demonstrate the shifts of pztc with the density of (111) steps. Triangle (b – 5) demonstrates the estimate of pzfc of platinized platinum in perchlorate solution.[70] Original Refs for 1-3 and 1'-3' can be found in the text, Section III.3.

say nothing about formation of concentrated hydride β-phase below 0.06 V (RHE).[73,74] Limitations result from the fact that the charge spent for equilibrium hydride formation is usually much higher than for any interfacial process. Despite of these troubles, a number of adsorption experiments with palladium were successful.[75,76] Zero charge potentials are available for 0.05 M sulphate solution of pH 3. Unfortunately, there are no data for other metals in exactly the same solution, but it is evident that both pztc and pzfc of Pd are closer to the same values for Pt than for other metals.[75]

Complications with ruthenium are induced by *early* oxygen adsorption, as well as by the shift of research interest to its catalytically outstanding alloy with platinum (see recent review).[77] Only one paper[78] contains some data on free electrode charge of electrodeposited Ru and Pt-Ru in alkaline and acidic chloride medium. The most important result is the shift of pzfc for Pt-Ru (ca. 0.06 V towards less positive values), as compared to Pt under the same conditions. As can be judged from some curves, pzfc of pure (non-oxidized) Ru finds itself in the region of negative RHE potentials.

For osmium, *early oxidation* problems are even more pronounced, and no systematic thermodynamic study was completed. A number of important experimental facts about electrodeposited osmium (or better to say, osmium oxohydroxide?) electrochemistry are collected in Ref. 79.

Summary of the data in Fig. 5b is also incomplete, and two other types of solutions should be mentioned. For perchloric acid solutions, application of a nuber of techniques shown in Fig. 1 is complicated by chloride formation taking part in parallel with H UPD, see below in Section IV.4. Nevertheless, the dependences of platinum free electrode charge on potential for 0.005 M H_2SO_4 + 0. 5 M Na_2SO_4 and 0.01 M $HClO_4$ + 1 M $NaClO_4$ were compared.[70] The values of pzfc are very close (~0.3 V RHE), despite of lower perchlorate adsorption. Zero charge potentials of both types were also measured in fluoride-based solutions of pH 2.4 (0.3 M HF + 0.12 M KF), representative papers of this series are Refs. 80 and 81. Both pztc and pzfc of platinum and rhodium are found to be ca. 0.03 V more positive than in sulfate solutions of the same pH (with slightly different ionic strength). These results for both relatively weakly adsorbing anions, perchlorate and fluo-

ride, are in agreement with general tendency demonstrated in Fig. 5b.

The data on zero charge potentials in alkaline solutions are mostly available for platinum and rhodium,[82-84] being closely related to the studies of oxygen adsorption. Oxygen UPD phenomena is beyond the frames of this review, but some intersections are inescapable, as just for these systems an interesting phenomenon of *inverted* pzfc is the most pronounced.

In fact, only the values of so-named *normal* pzfc are given in Fig. 5 and discussed above, but (as it was predicted already in 1930s) two pzfc can exist in each system. The second (*inverted*) pzfc results from oxygen adsorption and its contribution to free charge, this is why its shift to less positive potentials in RHE scale with pH is expected. The pH dependence of electrode charge required a lot of experimental efforts, and initially was approached from *acidic* and *alkaline* edges.[85-87] Owing to improvement of isoelectric potential shifts technique and the arrangement of titration under isoelectric conditions[53,88-92] it became possible to cover the overall pH interval and to get the reliable dependences of pztc and *normal* pzfc on solution pH (both dependences for Pt in chloride media are presented in Fig. 6a).

Direct experimental observations of both pzfc in solutions of certain composition were reported for the following systems: for Ir in alkaline iodide-containing solutions;[93] for Pt in sulphate solution, pH 6;[52] for Rh in chloride solutions, pH 5–9;[92] for Ru in chloride solution, pH 2.[78]

There are also many examples of free charge vs. potential curves demonstrating the pronounced decrease of free charge in the oxygen adsorption region, when more positive *inverted* pzfc is approached, but not attained. An example for rhodium is presented by curves 1–3 in Fig. 6b. The subsequent curves 4–7 at higher pH already contain two zero points. The most surprising behavior in this series (curves 8 and 9 at the most high pH) is the absence of pzfc in potential interval under study. The same type of curves was observed in earlier studies of alkaline solutions.[55,83] It is important that strongly adsorbing bromide or iodide additives induced the appearance of the *lost* region of positive free charge, due to their ability to compete with adsorbed oxygen. We do not discuss iodide-containing systems now, as many of them are strongly irre- for both relatively weakly adsorbing anions, perchlorate and fluo-

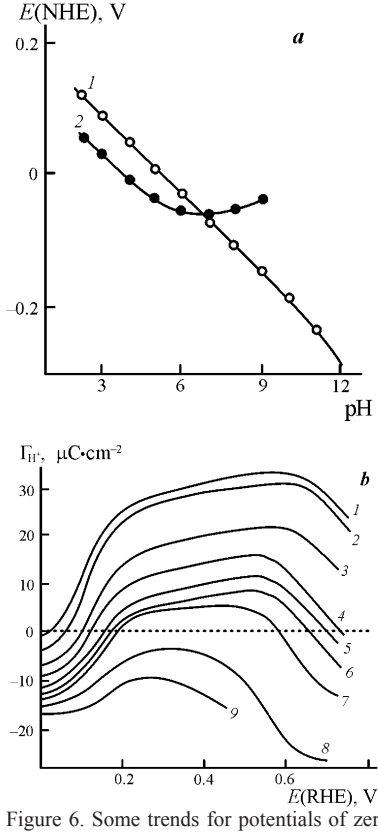

Figure 6. Some trends for potentials of zero charge as a function of solution composition: (a) pH dependences of platinum pztc (1) and pzfc (2) in 0.1 M KCl;[90] (b) example of pzfc inversion for rhodium in 0.1 M KCl; free charge curves are presented for pH 3(1), 4 (2), 5 (3), 6 (4), 7 (5), 8 (6), 9 (7), 10 (8), 11 (9);[92] (c) (see p. 126) platinum pzfc depencence on salt concentration c and anion nature in 3 mM HCl + c M KCl (1), 3 mM HBr + c M KBr (2), 3 mM KOH + c M KBr (3), 3 mM KOH + c M KI (4).[103] In Refs 90, 92, pH was adjusted with HCl or KOH. Reprinted from Refs. 90(a), 92(b), and 103(c), Copyright (1975), (1976) and (1977), respectively, with permission of Nauka Publ.

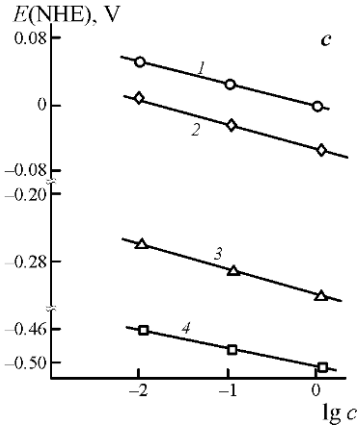

Figure 6. Continuation.

librium with hydrogen, but works as a sort of *surface modifier* (see representative Refs. 94 and 95).

Qualitatively, the initial hypothesis never contradicted the data on normal and inverted pzfc: residual negative charge of oxygen atoms (or hydroxide adsorption with charge transfer) decreases the adsorption of anions and supports the adsorption of cations. Finally the charge of adsorbed ions changes its sign, which means that the free electrode charge passes a new zero point. When superposition of hydrogen and oxygen adsorption is very pronounced (e.g., in alkaline media), the anomalous adsorption of cations starts at lower potentials, and these systems usually demonstrate no pzfc in the overall potential range. Attempts to support this hypothesis by quantitative data induced the interest to cations adsorption.

This topic should be separated, as it opens the door to the large area related to surface thermodynamics on metals modified by foreign adatoms. In the 1970s, the knowledge of metal UPD was still limited, and both electrostatically adsorbing cations and that adsorbing with pronounced charge transfer were studied in a similar manner. It is worth to mention a visual comparison of platinum pzfc shifts of the opposite sign in sulfate medium induced by iodide and thallium adatoms.[95] More weakly adsorbing cations only slightly affect platinum and rodium pzfc: 20 mV shift to more

positive values is observed when one goes from Li^+ to Cs^+;[96-99] comparable or even smaller shifts are induced by alkaline earth cations,[100] and it does not correlate with cation charge and surface coverage. Namely, the effect increases when going from barium to zinc,[101] despite of comparable Gibbs adsorptions of both cations. Most probably the reason is Zn UPD. Interplay of the effects of adsorbed cations and hydrogen adatoms was noticed, but never considered quantitatively.

Cations adsorption is of interest for interpretation and prediction of pzc dependences on salt concentration, considered in a general form in Ref. 102. Experimental data for solutions of various anionic composition[103] (Fig. 6c) demonstrate no pronounced slope difference for anions of essentially different adsorption behavior. All slopes are very low (even lower than expected in the absence of Esin-Markov effect studied earlier for similar systems.)[104] The decrease of slope can result from two contributions (decrease of cations adsorption with potential and displacement of hydrogen with increase of anion concentration). This result means that the straightforward interpretation of Esin-Markov coefficients for platinum metals (if any) should take into account that these values can be underestimated.

It is easy to see that a self-consistent thermodynamical consideration of hydrogen and ions adsorption ignored (at least in an explicit form) the existence of water at the interface. In reality water is expected to participate in all interfacial events, and can contribute to both *atomic* and *ionic* quantities if its orientation/location is changed with electrode charge and adsorbate coverage. This is a natural weak spot to be understood by some additional means.

General trends of zero charge potential behavior for electrodeposited platinum metals were formulated 20 years prior to the period of active thermodynamical studies of single crystalline surfaces. In what follows we try to catch similarities and disagreements missed or scarcely discussed earlier.

IV. SINGLE CRYSTALS AND *OLD* PLATINUM ELECTROCHEMISTRY TRY TO MEET HALF-WAY

1. From Poorly to Well-Defined Surfaces

Platinized platinum and relative dispersed electrodeposited metals of 1960s–1970s were extremely poorly-defined materials of complex structure. Protocols for electrode fabrication were of the same type as the standards of technical galvanics.[105] In particular, galvanostatic deposition was typically used, and concentration of chloride bath was not fixed precisely because of several subsequent depositions from one and the same portion of solution. Nowadays we know a lot about dependence of the structure of electrodeposited platinum on deposition potential and bath composition (see Ref. 106 and Refs. therein). Late data on SEM, TEM and XRD of platinum electrodeposits demonstrate that galvanostatic modes applied to prepare the electrodes for thermodynamic studies corresponded to very low RHE potentials (sometimes even below zero) and had to result in formation of rather loose agglomerates of 10–20 nm size crystals with relatively low defectiveness, weak mutual coalescence, and slightly pronounced bulk texture. Lamellar shape of platinum crystals formed in this region of deposition potentials is typical, but nobody can be sure about reproducibility of structural details when depositing at constant current. The specific surface areas were close to 10 $m^2 \cdot g^{-1}$ or higher, when the thickness was few μm.

A long period, between Will's pioneering studies of platinum single crystals[107] in 1965 and Clavilier's invention of the technique to prepare well-ordered platinum low-index surfaces[57,58,108] in 1980, still remained *poly Pt epoch*, as all the results published for single crystalline electrodes were reconsidered later. During the next decade major attention was devoted to thorough coulometric analysis of voltammetric data and attempts to separate hydrogen and anions contributions (well-known Clavilier's papers[109,110] can be mentioned as a very relative end of this period). In the 1990s, the most active period started: Aldaz, Feliu and coauthors created a worldwide school of single crystal electrochemistry based experimentally on Clavilier's technique. Simultaneously, a lot of important studies were carried out with larger commercial single crystals, a famous example is Ref. 111. This approach (initially

most popular in USA) is predominantly electrocatalytic, and now it places emphasis on bimetallic systems.

Two groups of electrode materials (electrodeposited platinum metals and single crystals) missed each other for a long time, and people simply certified the pronounced difference of electrochemical responses for poly Pt and single crystals. Some occasions to recognize each other appeared already in XXI century, when a lot of better characterized polycrystalline materials became available.

2. Potentials of Zero Charge – Occasion to Draw Together

Single crystal electrochemistry started to approach surface thermodynamics from attempts to get the basic quantities shown in Fig. 1. Application of a number of already known techniques was impossible because the surface areas of single crystals are several orders lower than required for tracing adsorption phenomena by any *bulk* technique applied to solution (changes of solution composition resulting from adsorption are negligible even if the volume is very low).

Under these circumstances two principal approaches were possible: to increase a sensitivity of techniques or to work out the alternative tools. The former approach was successful only for radiotracer techniques,[112] but their application is limited to certain ions and is typically helpless for hydrogen adsorption studies. Among alternative (purely electrochemical) techniques, the most successful was surely CO displacement recently reviewed in Ref. 72. There are also other probes besides CO (see, e.g., the comparison of CO and N_2O probes).[66]

Displacement techniques were helpful for collecting the data on the total charge and corresponding pztc for low index and stepped single crystal surfaces in solutions of various composition. For pure acids (mostly studied by this technique) the quantitative comparison with Frumkin-Petrii school data is limited by the difference in pH and solution composition. If to consider extrapolation of sulfate series (curve 1 in Fig. 5a), pztc values for dispersed Pt/Pt appear to be closer to pztc of Pt(111) (point 4'). It is suggestive to join this coincidence and the *screened butterfly* discussed above in Section III.2, and to assume that the surface of electrodeposited platinum contains (111) terraces, but we should keep ourselves from too straightforward conclusions: for stepped surfaces,

pztc's should be more negative.[66,68,69,72] In view of this fact the similarity of Pt/Pt and Pt(100) pztc's (point 4 in Fig. 5a) should be also considered. At the same time, the pztc for Pt(110) (point 4'' in Fig. 5a) is much more negative.

The values for two Pt and Rh single crystal surfaces in 0.5 M H_2SO_4 were compared.[113] Surface crystallography effects on pztc values are qualitatively the same: 0.38 V for Pt(100) versus 0.15 V for Pt(110) and 0.14 V for Rh(100) versus 0.10 V for Rh(110). The authors accented the location of all pztc points inside hydrogen adsorption region, but the quantitative difference was not analysed (in later papers as well). Comparison of single crystalline and electrodeposited Rh (its pztc is presented by point 3 in Fig. 5a) results in approximately the same conclusion like for platinum: polycrystalline material behaves more likely as (100) than as (110). Recent data of Wandlowski's group[114] for three low index Rh surfaces in 0.1 M H_2SO_4 demonstrate pztc sequence another than a sequence for platinum: Rh(111) (0.105–0.120 V) ≤ Rh(110) (0.110–0.130 V) < Rh(100) (0.140–0.155 V). Current hypothesis consists in a key role of strong sulphate adsorption on Rh(111) in the negative shift of pztc. This observation is very promising for interpretation of various surface crystallography manifestations affected by metal nature.

Unfortunately, for a majority of systems the available techniques for pzfc determination are still limited to high surface area electrodes and solutions with excess of supporting salt electrolyte, and there is a very small chance to compare with single crystals. However deep analysis of thermodynamic relationships and a proper choice of solution gives a principal possibility to determine pzfc if it is located in purely double layer region,[71,72] and this is the case for Pt(111) in perchloric acid. For this interface, pzfc appeared to be very close to its earlier known pztc (marked by pont 4' in Fig. 5b). This finding at first sight contradicts previous *polycrystalline* trend: for platinum and rhodium at pH below 5–6 pzfc is always lower than pztc. At low pH, the difference amounts to several dozens of mV and decreases with pH. For sulfate media, extrapolation of these dependences to pH 0–1 results in pzfc values of 0.22–0.23 V RHE. A single available point for perchlorate solution (point 5 in Fig. 5b) is very close to sulfate pzfc value (curve 1' in Fig. 5b), being evidently shifted from pztc in the same

solution. As there are no other systems to compare, we cannot judge whether it is some fundamental difference.

The values of pztc for low-index platinum surfaces in perchlorate medium (points 4, 4', and 4'' in Fig. 5b) are more positive than in sulfuric acid, but the dependence on surface crystallography follows the same trend. Horizontal arrows demonstrate the negative shifts of pztc with step density for stepped surfaces of all terrace orientations (shift is very small for originally stepped Pt(110) and attains 0.1 V for two other surfaces). From detailed analysis with inclusion of high vacuum data[63] one can assume that for pzft the negative shift can be even more pronounced, and it is confirmed by very few values reported now for stepped surfaces.[72] The general trend of halide ions effect is the same for single crystals and electrodeposited platinum, as can be concluded from available total charge curves.[71,115]

Basically, the comparison of zero charge potentials gives very rough notion concerning similarities and difference in thermodynamic behavior of single crystals and highly disordered metals. However even being affected by numerous factors, this comparison demonstrates that metal nature and strongly adsorbing anions nature play a major role for materials of any surface structure. Further clarification requires additional experimental facts for single crystals, especially the reliable pH dependences of zero charge potentials. To address this problem experimentally, it is important first to clarify the behavior of adsorbed OH species on single crystal electrodes.[116]

Another challenge is to widen the knowledge concerning other metals, besides platinum. Good examples of Ru[117,118] and Ir[119] single crystal electrochemistry were published, but systematic thermodynamic treatment is still absent.

As for already existing data on zero charge potentials and related values, they are of great interest for the studies of more and more complex real less characterized materials.

3. From Well-Defined Surfaces to More and Less Defined Materials

A rather natural idea is to present the behavior of polycrystalline surfaces as an additive behavior of their fragments having different

crystallographic orientations. There are dozens of examples where such attempts seemed to be successful.

A possibility to consider polycrystalline platinum surface as some combination of low index surfaces or as some disordered single crystalline surface surely cannot be immediately concluded from the values of zero charge potentials exclusively. Experiments with some *intermediate* model systems more or less *reduceable* to simple additive combinations of several planes, or of terraces and steps, are of increasing interest. Microfacetted electrodes,[120,121] various types of nanoparticles prepared by precise non-electrochemical techniques,[122,123] non-coalesced electrodeposited particles,[124] and single platinum *microspheres* deposited on micro-electrodes,[125] as well as highly ordered templated electrdeposits[126] can be considered as most ordered real platinum materials helpful to discover structural effects at atomic level. However they all are still *too simple* to compare with, to say, platinized platinum, and attempts to electrodeposit the dispersed metallic multilayers of more and more ordered type[106,127] are also relevant.

Very specific type of platinum materials hopefully able to form a bridge between less and more ordered surfaces is the so-called facetted polycrystal. Since the pioneering work of Cerviño et. al.[128] in the 1980s, the electrochemical faceting procedure of different metal surfaces to produce preferred crystallographic orientations was widely employed and investigated. The application of fast repetitive periodic potential pulses in different potential ranges to produce faceting of platinum, gold, palladium, rhodium is a highly reproducible procedure developed by Arvia and coworkers.[129-133] The structure and morphology of this sort of electrodes is already well characterized by scanning electron and scanning tunnelling microscopy (as well as their catalytic properties).[134-136] The mechanisms of faceting processes is also clarified.[137] A similar type of surface treatment was proposed later,[138-140] and some comparison with what was previously and carefully studied by Arvia's team for a huge number of systems surely makes sense, as the faceting process involves very similar phenomena. Representative examples of early and more recent electrochemical faceting studies can be found in Refs. 141, 142. Recent review on faceting and roughening of metals is also available.[143] The main goal to involve these materials is to collect as manifold as possible experimental arguments supporting contribu-

tion of faceted regions and intermediate areas into electrochemical responses.

However it is evidently senseless to reduce single crystal electrochemistry to material science, a tool to solve some puzzles of real materials, but it is easy to see that appealing to various materials widens a field of vision. The same is with inadequacy of idea to put this area in frames of classical thermodynamic scheme. Following its own way, single crystal experiments collect more and more information about behavior of all adlayer components, but keeping some traditions of data treatment would not be out of place for this advanced field. The subsequent Sections touch briefly three points of most visible intersection.

4. Adsorption of Anions

A sort of asymmetry is observed in the studies of ions adsorption on platinum group metals: anions attract more attention than cations. The reason is probably a prevalence of acids among electrolytes, and just the sulphuric acid remained one of the most popular for a long period. It was stated already in Ref. 9 that platinum capacity in the double layer region exceeds the capacity of ionic double layer in sulfuric acid. This was confirmed more directly by comparison of the slope of galvanostatic charging curves and the values of sulphate adsorption:[144] more than a half of capacity formally determined from electrochemical data could not be attributed to sulphate adsorption. However this ratio estimated by various means, as well as the observed double layer capacity, were not quanitatively reproducible for various polycrystalline materials, leading to the assumption that competitive adsorption of sulfate and OH species is very sensitive to surface structure.

Unbelievable progress in sulfate adsorption studies took place during the single crystalline era, especially after direct visualization of adlayer and phase transition in 2D sulfate adlattice on Pt(111).[145] Partly similar observations vere reported for Ir(111).[146] In addition, quantitative agreement of sulfate surface coverage on Pt(111) determined by radiotracer technique[112] and results of thermodynamic analysis[147] made Pt(111) a really famous electrode and inspired the studies of more general problem: order-disorder in adlayer. It was a real shift to atomic level electrochemistry.

Parallel events in the field of in situ IR spectroscopy (for a review of sulfate IR studies, see Ref. 26) resulted in a coupled shift to molecular level: bi-sulfate anion was recognized in sulfate adlayer even in solutions with predominating sulfate. It was completey new situation, when chemical equilibrium is affected by adsorbate-surface interaction. In usual terms of solution equilibria, the effect corresponds to increase of pK_a from its bulk value (ca. 2) to 3.3–4.7 (pK_a is potential-dependent).[148] To agree this situation with *bulk* thermodynamics, one should simply use electrochemical potential instead of chemical. The phenomena of adsorption-induced protonation is relative to UPD, when adsorbate-surface interaction shifts redox equilibria. In more *molecular* terms, the species determined as bi-sulfate ions are probably interfacial ion pairs,[149] i.e., the phenomenon can be considered as coadsorption. This situation is screened in purely thermodynamic analysis, as excess surface protonation is hidden in Gibbs adsorptions of sulfate and H^+. However it becomes important for any further model consideration, as it can affect lateral interactions and the order in the adlayer. The excess adsorption-induced protonation of various anions is a very attractive field. In particular it is the only chance to explain why multicharged oxoanions can form complete monolayers on platinum.[150,151]

This unique sulfate developments attracted more attention to reference systems with weaker adsorbing anions. Fluoride and perchlorate looked the best candidates for a long period, despite both require special efforts to keep the surface pure.[152] Double layer capacity values and the data for various anions adsorption are always very sensitive to imputrities in acids (the problem was specially addressed recently in Ref. 153). Perchlorate *self-contamination* by reductive chloride formation takes place at positive RHE potentials on Pt and especially on Rh. Kinetics of these processes was studied systematically by Horanyi and co-workers (see Ref. 154 for earlier references). At Rh electrode, the reduction starts already at ~0.5 V RHE, when for Pt measurable amounts of chloride appear only after polarization at potentials closer to zero RHE. According to Ref. 155, for typical modern experiments with single crystals the concentration of chloride in 0.1 M $HClO_4$ does not exceed 0.01 μM, leading to negligible effects on voltammograms. However for long-term experiments contamination can be much higher. The only available perchlorate adsorption data for

electrodeposited platinum[70] were surely obtained in presence of chloride impurities. Actually, no chloride in solution was found (analytical technique applied in Ref. 70 provided sensitivity not better than 0.01 mM), but the directly determined quantity of adsorbed chloride was rather high (several $\mu C \cdot cm^{-2}$, with a maximum at E(RHE) = 0.4 V), so the reported data on perchlorate adsorption could be affected by this fact.

An important detail consists in suppression of perchlorate reduction by sulfate and chloride in mixed solutions. For sulfate-containing systems, it is also important to remember that when chloride appears it suppresses sulfate adsorption and induces smoothing of ascending branch of adsorption vs. potential curves.[156] In any case a search for other reference with weakly adsorbing anions is reasonable.

Among most weakly adsorbing anions, trifluorosulphonic anion[59] and tetrafluoroborate[157] were considered (Fig. 7). BF_4^- highest adsorption value on platinized platinum in 0.01 M HBF_4 solution hardly exceeds 3 $\mu C \cdot cm^{-2}$. To compare, the maximal value for sulphate in 0.005 M H_2SO_4 is close to 20 $\mu C \cdot cm^{-2}$; for fluoride in 0.14 M HF, 12 $\mu C \cdot cm^{-2}$ maximal adsorption was reported.[80,81] Trifluorosulphonic anion adsorption on platinized platinum from 0.005 M solution never exceeds 5 $\mu C \cdot cm^{-2}$.[59] (Trifluoroacetate adsorption was studied for comparison,[59] and was found to be close to sulphate adsorption). All these values correspond to 0.6–0.7 V RHE. Weak adsorption of $CF_3SO_3^-$ anion recently attacted attention,[158,159] and the abovementioned data can be helpful.

Adsorption phenomena in H_3PO_4 are of special interest in view of the role of this electrolyte in fuel cell research and development. Early studies[160,161] induced the suspicion that phosphate adsorption on polycrystalline platinum is irreversible, at least in certain (rather wide) potential region. Manifestations of slow distructive phosphate adsorption were found, probably relative to well-known adsorption behavior of nitrate on platinum group metals.[162,163] The study of phosphate adsorption is surely of interest for basic problem of adsorption-induced protonation. Recent data for Pt(111) indicate no irreversibility, but it is not obligatory contradiction. For metal UPD, there are several examples (thallium UPD on Pt is typical)[165] of reversible behavior at single crystals, despite of completely irreversible adatoms deposition on polycrystalline surfaces.

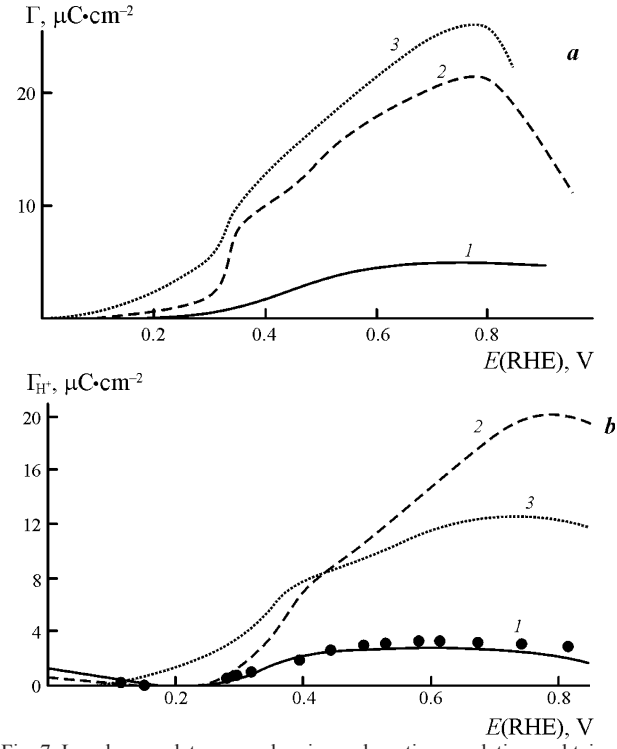

Fig. 7. Less known data on weak anions adsorption on platinum obtained by the conductivity technique. Curves 2 are given for comparison, measured in 2.5 mM H_2SO_4 by the same technique at the same electrodes. (a) Trifluoromethanesulfonic anion adsorption from 5 mM CF_3SO_3H solution (curve 1)[59], compared also with the data for 5 mM CF_3COOH (curve 3). (b) Fluoroborate adsorption from 6 mM HBF_4 solution (curve 1)[157] compared with the available earlier data of isoelectric potential shifts for Γ_{H^+} in 10 mM HBF_4 solution (points). To compare roughly with fluoride adsorption,[81] curve 3 for 0.14 M HF is presented (the activity of hydronium ion in this solution is the same as in 10 mM H_2SO_4). Reprinted from Refs. 59 (a) and 157 (b), Copyright (1981) and (1977), respectively, with permission from Nauka Publ.

Direct experimental results on anions Gibbs adsorption, even if obtained for poorly characterized dispersed platinum, are still of interest for comparison. The effect of potential on the difference of these values for some anions (in particular sulfate and perchlorate)

illustrates the trends of competitive anions and adatoms adsorption, being qualitatively the same for poly Pt and single crystals.

5. Adsorption Isotherms

Temkin isotherm[166] (considered for a long time as the most suitable to describe hydrogen adsorption on platinum, at least at mid coverage) assumes admittedly that interactions in adlayer are repulsive. Early Breiter's analysis[20] in terms of Frumkin isotherm, despite of less satisfactory fit, discovered that the attraction in adlayer is also possible, and more probable for *strongly bonded* hydrogen at low coverage. To compare Breiter's fitting with numerous recent applications of Frumkin isotherm, one should remember that in Ref. 20 the equation of this isotherm was applied in original Frumkin's form,[167] i.e., positive attraction constant corresponded to attraction, not to repulsion, and was twice lower than currently habitual parameter *g*.

Present-day results for poly Pt in the same 0.5 M H_2SO_4 solution, e.g., based on the estimates of hydrogen coverage from integrated IR band intensities,[168] confidently give positive *g* of ca. 3.1, i.e., the result of an opposite sign. It is easy to guess that the difference goes from separation of hydrogen from anions. The latter were actually "mixed up" with hydrogen in Ref. 20.

Appearance of the data for platinum single crystals stimulated many attemplts to apply Frumkin isotherm, in order to provide some quantitative characteristics of lateral interactions in adlayer. Even straightforward double layer correction and fitting of coverage versus potential curves for a single temperature (see, e.g., Ref. 169 and citations in this paper) discovers the pronounced difference in *g* values for hydrogen on Pt(111) from much lower values for Pt(100) and Pt(110). The former value always exceeds 10 in both sulphuric and perchloric media, when both latter values are usually close to each other and even low negative *g* values were reported. To improve the agreement of Frumkin isotherm with experimental curves, more complicated approach (*local Frumkin isotherms*) was proposed,[169] with ironic conclusive comment *the analysis would be only as good as the experimental data*. We should add that the analysis would be as reasonable as the degree of relation of starting corrected values to hydrogen surface coverage.

The approach based on the treatment of temperature dependences[111,170] is more solid, even with the same approximate double layer correction. It confirms very high *g* values (this time 16-18)[111] for Pt(111). However the most serious progress resulted from extraction of entropy terms and application of generalized isotherms, in combination with precise double layer correction based on thermodynamic treatment of voltammetric data.[171-173] Entropy term played a role of effective diagnostical tool, as it discovered the role of water ordering in lateral interaction. This finding provides the direct link to both molecular modeling and interpretation of spectral information related to water at the interface. By these means, the third important adlayer component, besides hydrogen and anions, ceased to be invisible by purely electrochemical techniques.

To adjust the approach based on Frumkin isotherm to deconvolution of experimental curves, the approximations by Gaussian (for repulsive interactions) and Lorentzian (for attractive interactions) were proposed.[173] This approach was helpful to estimate partial contributions from terraces and steps of certain orientation by means of deconvolution of CVs for various high index surfaces. It is interesting to compare contributions from ionic adsorption (known directly for Pt of high roughness factor, as exampled by Fig. 3) with deconvolution based on formal application of Frumkin isotherm.[173] Deconvolution of Breiter's curves and comparison with his fitting parameters can be also of interest, to understand what form of adsorbate is critical for switching from attractive to repulsive fitting parameter. At this stage deconvolution approach already works for ordered platinum nanoparticles with a complex voltammetric response.[122]

Computational efforts to describe lateral interactions and compare the results with experiment in terms of isotherms started much earlier[174] than the experimental information was well prepared. Qualitatively, these initial results obtained in frames of lattice-gas model are interesting, as they demonstrate a possibility of attractive H-H interactions in the case of coadsorption with repulsing anions. Modelling of mixed adlayers at various computational levels was systematically developed by Koper and coworkers,[175-177] and now represents a rather general approach. It can be probably applied to mixed adlayers with short-range interactions of completely different type, earlier considered at phenomenological level (mixed ionic[178] or organic[179] adlayers).

We escape to discuss here a number of hydrogen adsorption isotherms reported on the basis of rather formal kinetic data analysis for hydrogen reactions, like in Refs. 180 and 181. Most frequently the values of surface coverage in this type of studies are extracted from current-time or current-overpotential dependences simply as fitting parameters, and correspond to so-called hydrogen OPD, i.e., the reactive form of adsorbed hydrogen. Ionic double layer effect is ignored under these circumstances.

Besides adsorption isotherms, a model of two parallel capacitors was applied in the 1960s to describe the free charge vs. potential dependence for platinum metals.[185] The authors attempted to take into account contributions of hydrogen and oxygen adatoms in a manner earlier typical for consideration of organic species adsorption. The number of approximations appeared to be too high for further applications, but rereading of this paper 40 years after publication demonstrates that the approach (and the analogy itself) can be of particular interest for analysis of true charge transfer problem addressed in the next Section.

6. The First Step towards True Charge Transfer

Charge transfer in adlayers presents a subject of dramatic everlasting misunderstandings. To discuss this phenomenon it is necessary first to define the location of transferred charge, i.e., to state that it joins the electronic collective of metal (or leaves it). As there is no experimental tools to observe directly any *boundary* between electrons in metal and solution edge, the only possibility to study true charge transfer is to measure some signal sensitive to free electrons in metal. This is the meaning assumed by Lorenz, who introduced the notion of adsorption with charge transfer.[186,187] In the 1970s, a sharp discussion of so-named *electrosorption valency* γ took place between Frumkin et al.[188,189] and Vetter and Schultze.[190-193] It was finally agreed that γ presents a formal charge transfer coefficient, which relation to basic Lorenz's quantity depends on a plenty of unknown interfacial details, including adsorbate location and its effect on solvent molecules inside the double layer.

The precise values of γ for various adsorbates on platinum single crystals are available now (see examples in Refs 114, 147), and it is probably a challenge to compare their behavior with two

practically forgotten differential quantities available for platinized platinum from combinations of directly measured thermodynamic quantities. These so-named differential contributions of hydrogen atoms (X),

$$X = \left(\frac{\partial E}{\partial A_{\mathrm{H}}} \right)_{\Gamma_{\mathrm{H}^+}} \tag{2}$$

and ions (Y)

$$Y = \left(\frac{\partial E}{\partial \Gamma_{\mathrm{H}^+}} \right)_{A_{\mathrm{H}}} \tag{3}$$

to interfacial potential drop were first discussed in Ref 22, and later calculated more accurately[194] for Pt and Rh (E is the potential in respect to fixed reference electrode, not RHE). The equations for X and Y combine:

(a) isoelectric potential shifts,
(b) the slopes of charging curves , $\left(\frac{\partial Q_t}{\partial E(RHE)} \right)_{\mu_{\mathrm{H}^+}}$ and
(c) the values of the $\left(\frac{\partial \Gamma_{\mathrm{H}^+}}{\partial \mu_{\mathrm{H}^+}} \right)_{E(RHE)}$ derivative.

To determine (c), one should treat a set of adsorption curves for a pH interval as wide as possible.[87] The accuracy of this treatment is not too high, but the reliability of final X and Y values can be checked by comparison with the ratio $X/(X+Y)$ determined independently from another type of data.[82,87]

Despite of numerous accuracy problems going from recalculations of different experimental values into X and Y, the final result is of high qualitative significance: it confirms the existence of at least two physically different forms of hydrogen adatoms on polycrystalline platinum. Positive X values (corresponding to the negative residual charge on hydrogen adatom) are typical for low and mid surface coverage. At high surface coverage, X changes the sign, i.e., the residual charge on the hydrogen adatom becomes

positive. In original papers the effect was presented in terms of hypothetic *dipole of adsorbed hydrogen*.[194] It is important that for polycrystalline Rh, with its single narrow hydrogen adsorption-desorption peak at voltammograms, no changes of X sign were found in the overall interval of surface coverage: X was always positive, indicating negative residual charge of adatoms.

Absolute values of X in sulfate medium were found to be ca. two orders lower as compared to ionic contribution Y. Despite both values are referred to differential effects of introducing the species into adlayer, this difference allows very rough (surely cautious) estimate of the order of residual charge values: hundredth of the electron charge. *Residual* corresponds to conditional (not physical), but fixed metal/adlayer boundary. For halide-containing solutions, the difference is already closer to one order of magnitude, i.e., the residual charge is higher. Other (less pronounced) trends in X and Y behavior were discussed in relation to dependence of zero charge potentials on metal nature and solution composition.[194] This analysis looks self-consistent, but to apply it to exact understanding of charge distribution in the interfacial region one needs to link all charge-related quantities to any independently determined true charge transfer coefficients.

Information on true charge transfer in 1 M HCl and HBr solutions is available from electroreflectance data[195] owing to plasma mechanism of optical signal generation in these solutions. This mechanism was grounded by comparing the experimental electroreflectance spectra with the spectra calculated in frames of plasma electroreflectance theory. This approach cannot be applied in the same manner to any arbitrary system without preliminary analysis. Figs. 8 a,b present the dependence of true charges $|q|$ on adsorbed halide ions (grey areas between two curves in each plot present the interval of possible $|q|$ values, see explanations in Ref. 195 about the attainable accuracy). The potential scales of Figs 8 a, c and 8 b,d are the same, in order to show that for both chloride and bromide systems the behavior of differential X values taken from Ref. 194 (curves 1 in Figs. 8 b, d) is well correlated with decrease and increase of $|q|$. It is also notable that Y behavior correlates with $|q|$,

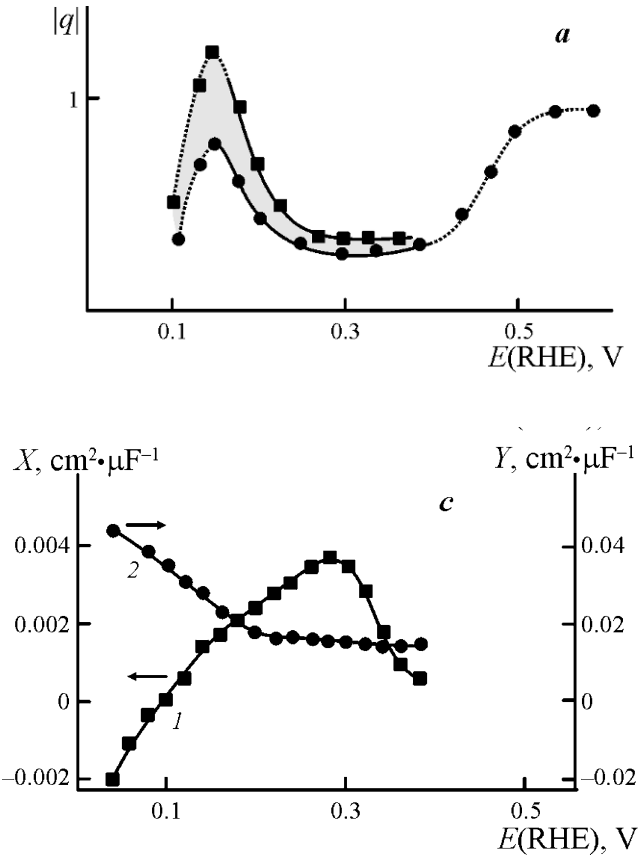

Figure 8. Comparison of true charge transfer coefficients q for chloride (a) and bromide (b) estimated from plasma electroreflectance data[195] (smooth polycrystalline Pt) with X and Y values[194] in solutions of the same anionic composition (c – chloride, d – bromide, dispersed electrodeposited platinum). The area between two curves (a, b) corresponds to unavoidable scatter (boundaries present to limiting versions of q recalculation). Dashed fragments (a) correspond to the region of lower accuracy, as compared to the overall potential region. Reprinted from Refs. 195 (a, b) and 194 (c, d), Copyright (1990) and (1969), respectively, with permission of Nauka Publ.

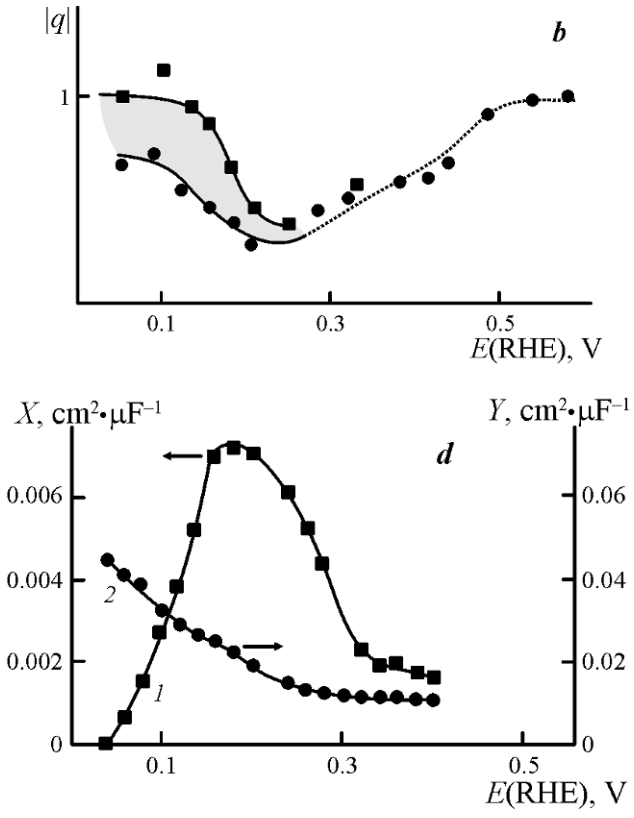

Figure 8. Continuation.

but not with X, i.e., behavior of hydronium ions is coupled mostly with halide ions, not with adatoms. Of course plasma electroreflectance signal can not recognize the nature of atom from which the charge is transferred, so the changes of $|q|$ can involve partial charge transfer from hydrogen adatoms as well, but we are first interested in misterious true charge transfer value.

Further quantitative analysis is hardly reasonable, as the data for comparison should be obtained at exactly one and the same electrode and solution. At this stage we can only conclude from this comparison that the true charge transfer can be used for ca*li-*

bration of the data on formal charge transfer. It looks more visually in differential form with conditional separation of hydrogen atom and ion, but calibration of this sort is basically possible for electrosorption valency as well. The bottleneck is to find the reliable spectroscopic signals sensitive to true charge transfer.

Phenomenological model of effective charge transfer coefficients is presented in Ref. 196. Its application to available thermodynamic data surely can not result in any true charge transfer coefficients, but provides independent possibility to estimate differential effects of solution composition on the electrode charge values. General trends agree with the trends going from *X* and *Y* analysis.

Differential values of *Y* can be also useful for interpretation of electrosorption valency in terms of sulfate vesus bi-sulfate adsorption,[197] as one of mostly untapped resources of platinum electrochemistry. However the main progress is expected from combination of precise electrochemistry, thermodynamic analysis, and independent physical information supported by an appropriate theoretical basis, with necessary links provided by computational community. The final Section contains some brief notes in this respect.

V. REALISTIC AND VISIONARY DREAMS

Fast progress of platinum computational elctrochemistry is stimulated by electrocatalysis, and the studies of CO adsorption predominate.[198] Accumulated experience is extremely useful for modeling the reversible adsorption at the interface, but today the latter looks like a tiny brook in the vicinity of computational mainstream. The closest layer going from electrocatalysis is theoretical/ computational prediction of electrocatalytic activity in hydrogen reactions,[199,200] as it requires the modeling of hydrogen adatoms. The main problem in this case is comparison with experiment, because a lot of factors besides adlayer structure affect the observed reaction rates.

It is surely attractive to model first the structure of adlayers, and to verify the results using more or less direct information from X-ray techniques[30] and probe microscopy.[28,29,32] However the important physical features of the interface can be missed in this

analysis. *Structural* results are necessary to check whether computational approach is realistic, and to supplement further steps.

A field well-prepared to be the second step is experimental modeling of electrochemical interface in vacuum systems[201-204] (see also Section 4 in Ref. 205). These systems give a chance to separate interactions in adlayer (even *artificial*) from any effects going from the solution side. In addition, owing to direct work function measurements in vacuum experimens, one can hope to check the adaptability of certain approaches involved in computational modeling of metal electronic structure. Experimental verification of these approaches with the use of data for real electrochemical systems is usually ambiguous, as the result is simultaneously affected by the uncertainty of solution model. Finally, a strong advantage of vacuum experiments is their already formed stable link with real electrochemical phenomena, constructed in the 1990s by Weaver.[201-203] The data on work functions are available for platinized platinum as well,[206,207] so some feedback with classical data for this electrode material is possible. Current attempts to model the potential of zero charge for platinum/solution interface[208,209] can be probably linked in more natural manner just to experiments done in vacuum.

In situ optical techniques should be considered as a very important tool, because of their natural compitability with the usual configuration of electrochemical cells. The limiting factor is always a model of optical signal, and a lot of important experimental results for platinum/solution interface still wait for physically grounded interpretation.

Laser pulse experiments[210-213] form rather informative link between surface thermodynamics and interfacial molecular features, despite the nature of this technique is still macroscopic, and approximations in separating contributions from dipole, ionic, and surface potential terms are unavoidable. However these approximations are of different nature as compared to classical beyond-thermodynamical assumption. Namely, the experimentally available potential of maximal entropy (pme, considered as a value correlating with pzfc) reflects mostly order-disorder effects, like solvent reorientation. Molecular modeling of *temperature jump* was already reported for mercury electrode,[214] giving the transparent explanation of pioneering experimental results of Benderski and Velichko for mercury[215] in terms of hydrogen bonding in water

adlayer. This computational approach can be also helpful for estimating the difference of pme and pzfc.

Among other optical techniques, reflectance spectroscopy and electroreflectance studies were actively applied to study platinum electrode surface already 40 years ago.[216,217] Before the beginning of 1990s these studies were mostly *polycrystalline* (see Refs. in 195, 218–220), as no well-defined single crystal surfaces were available. These works were concentrated on the assignment of optical signals to certain adsorbates, in particular to various *forms of adsorbed hydrogen*. The specific features of these forms could be explained either by structural factors, or by anions coadsorption, or by charge transfer peculiarities, and the existing theoretical approaches were unable to unriddle this puzzle (however some attempts were reported).[219] A strong effect of oxygen adatoms on the reflectance[219] is still waiting for serious interpretation.

When single crystalline period started, the attention of electrochemical community was already reswitched from optical to in situ X-ray spectroscopic and probe microscopic techniques. Very few electroreflectance results were reported during this period. The earliest data for three low index platinum surfaces[221] were not interpreted in detailed manner. For Pt(111) in sulfate medium, no pronounced signal was observed for hydrogen, excluding butterfly region.[222] For perchloric solutions, electroreflectance was also sensitive selectively to the region of anions highest contribution to electrochemical response.[221] The effects were later reproduced for (111) facets of a platinum microsphere[223]: sensitivity of optical signal to surface crystallography was found to be much higher than for voltammetry.

During the same period in situ IR spectroscopy started its active development. Nowadays the multivarious versions of this technique are widely applied in routine electrocatalytic studies, with predominating attention to adsorption of organic species.[26] However Bewick's IR studies of hydrogen adsorption on Pt poly[224] and on single crystals of several platinum metals[225] should not be forgotten.

Second harmonic generation (SHG) of platinum/solution interface was pioneered by Corn and coworkers,[226-231] who managed to get the response of hydrogen adatoms and coadsorbed anions despite platinum signal is rather low as compared with SHG of Cu, Ag and Au. Further steps[232-234] resulted in a number of particular

findings, mostly used as supplementary information for the studies of organic species adsorption. Possibilities to use SHG for true charge transfer characterization are strongly dependent on signal generation mechanism, which is rarely studied systematically. Simplified contribution in frames of a jellium model gives a semi-quantitative tool to estimate the sign and degree of charge transfer (see discussion in Refs. 150,151). In particular, for polycrystalline platinum the direction of charge transfer for weakly and strongly adsorbed hydrogen appears to be opposite, in (still apparent) agreement with previous consideration[194] of hydrogen adatom contribution to potential drop.

A single attempt was done to use the so-named electroscattering, a modulation technique worked out by analogy with electroreflectance. Its application to Pt poly surfaces faceted in Arvia's style, in combination with linear optics, discovered the inhomogeneity of hydrogen adlayers at relatively low coverage, which was sensitive to microscopic surface morphology.[235]

Recent progress in interfacial optics surely results from combination of linear and non-linear (mostly SFG and SHG) optical techniques.[120,121] At this stage the approach to data interpretation still remains correlative, but a number of newly determined thermodynamic quantities for single crystalline interfaces are involved in these correlations, along with usual coulometrically estimated surface coverages for various adsorbates. SFG application to various platinum/solution interfaces was recently reviewed.[31] SFG is able to provide a reliable separation of contributions from hydrogen (Pt-H band), anions and water molecules,[236,237] and already discovered various types of potential-dependent lateral water bonding. Combination of these results and progress of laser pulse experiments can be highly resultive, but today the data of these two techniques are available for platinum surfaces of different structure.

A challenging problem is to address the effect of adsorbed hydrogen on NMR response of small platinum particles (see Section 3.1.3.2 in Ref. 27). EQCM probably presents a separate possibility to get microscopic information if applied less straightforwardly (not reduced to a weighting instrument). This technique is sensitive to hydrogen adsorption and able to tell the difference of sulfate and perchlorate coadsorption with hydrogen (see Ref. 238 for a brief review of earlier works). Recently developed EQCM

theory coupled with modified EQCM technique (admittance measurements)[239] gives a principal chance to extract local viscosity in the vicinity of interface, an enigmatic feature closely related to the structure of adsorbed water.

Platinum/solution interface is also studied by some techniques with less comprehensible background, like contact electric resistance.[240] Probably the progress of other techniques can later result in some clarification of the meaning of these data. The same is related to immersion techniques applied to determine the potentials of zero charge.[241] Who knows, probably what looks mistaken now can be helpful later, when the nature of disagreement of various techniques shall be interpreted.

No other way out is immediately seen to amplify interactions of electrochemical and spectroscopic techniques, than single-minded computational efforts. If these efforts are concentrated on the modeling of several certain experimentally available signals in frames of unified computational approaches, it is helpful for all consortium. From experimental side, it is highly desirable to apply various techniques to one and the same systems. Usually the quantities more complex for experimental determination are simultaneously more favorable for computational modeling, and vice versa. It can not be helped, but it makes science and life more intriguing.

VI. CONCLUDING REMARKS

This brief review is limited to consideration of platinum group metals in aqueous solutions. Thermodynamic approaches should work in other protic solvents. However these solvents are always of organic nature, and the experimental measurements of any thermodynamic quantities are complicated by irreversible dissociative adsorption of organic species. Another interesting field, still separated, is platinum electrochemistry in aprotic media.[242-247]

Surface thermodynamics of perfectly polarizable electrodes forms a basis for various amphyfunctional approaches being of interest for electrochemistry of oxides[248] and functionally modified electrodes.[249] Beyond platinum metals electrochemistry, this approach is also important for gold, silver and copper when OH adsorption with charge transfer takes place at these surfaces.

The links between our knowledge about ideally and perfectly polarizable electrodes should be thoroughly maintained, as water and ions adsorption are common phenomena for these types of systems. For ideally plarizable (*mercury-like*) electrodes, pzc (pzfc) data are available for much higher number of metals, and the roles of electron work function and water adsorption are more apparent.[250,251]

Frumkin's portrait, jokingly ascribed to Picasso (Fig. 9), was designed by Oleg A. Petrii with assistance of Rein V. Marvet in 1965, i.e., a year before the start of active experimental studies of platinum surface thermodynamics. Correspondingly, this work of art reflects mostly the mercury period of Frumkin school, but the specific asymmetric contour of the face is already formed by platinum-related curves: charging curve from the right and potential shift from the left. Frumkin isotherm, representing the central fragment (nose), consolidates two periods. It is difficult to imagine how the current situation in platinum electrochemistry can be presented in similar style, as many faces with uniquely refined features took part in its development. We already need a whole portrait gallery, and if sooner or later arranged it will surely accumulate this Picasso masterpiece.

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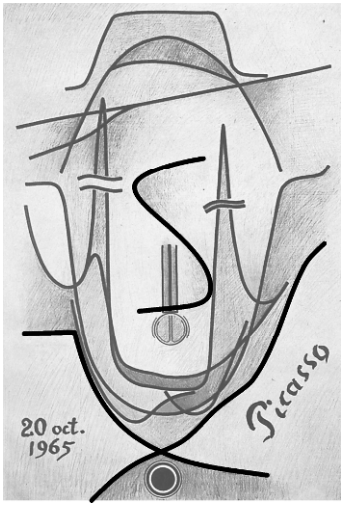

Figure 9. Scientific portrait of A. N. Frumkin representing 1965 state-of-the-art. Features of platinum electrochemistry already became faintly visible: lower part of the face is outlined by potential shift curve (from the right) and charging curve (from the left) of platinum electrode; nose is formed by Frumkin isotherm (S-shaped, corresponding to high lateral attraction). Other features go mostly from mercury electrochemistry, symbolized by a capillary with a mercury drop in the center. Curves, from top to bottom: potential dependences of organic species adsorption (hat) and surface tension (crown of the head); Tafel plots for hydrogen evolution (wrinkle at the forehead); differential capacity curves, including sharp peaks of organic species desorption with splits (eyes), surrounded by *anionic pit* (polarogram of anion electroreduction on the negatively charged surface); intersecting potential energy terms of reactant and product (chin). Rotating ring disc electrode (as adornment at the neck) completes the image. Designed by Oleg A. Petrii with assistance of Rein V. Marvet, originally without thickened curves; first published in 1989 (colored version).[252] With modifications.

notice some *critical points* in interrelations of *old* platinum electrochemistry and current research.

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