



Title	REACTIONS AT FRESH METAL ELECTRODE SURFACES
Author(s)	ANDERSEN, Terrell N.; ANDERSON, Jeffrey L.; BODÉ, Donald D., Jr.; EYRING, Henry
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 16(1), 449-476
Issue Date	1968
Doc URL	http://hdl.handle.net/2115/24872
Type	bulletin (article)
File Information	16(1)_P449-476.pdf



[Instructions for use](#)

REACTIONS AT FRESH METAL ELECTRODE SURFACES

By

Terrell N. ANDERSEN, Jeffrey L. ANDERSON,
Donald D. BODÉ, JR. and Henry EYRING

Institute for the Study of Rate Processes,
University of Utah, Salt Lake City, Utah, U. S. A.

(Received January 27, 1968)

Abstract

Electrochemical phenomena on bare metal surfaces were studied by measuring the potentials of wire electrodes as their surfaces were scraped off in various aqueous solutions. The scrape potentials were found to be determined by (1) the adsorption of the various species from solution for systems in which the faradaic currents are sufficiently slow and (2) the rates of the various faradaic reactions when the latter are rapid compared to the scraping process. It was found that noble metals conform to case (1) over at least part of the pH range, and in that case the scrape potential can be identified with the potential of zero charge. Over at least part of the pH range for the noble metals studied, solvent reduction is rapid enough that the scrape potentials are described by case (2). All the base metals studied reacted rapidly with the electrolyte over the entire pH range.

Introduction

The structure of the electrical double layer is of basic importance in determining the course of electrode reactions and hence in influencing the catalytic properties of a metal electrode. This paper describes surface renewal studies of solid electrodes which relate to two important aspects of the double layer structure: the potential of zero charge and the relative velocities of various reactions which occur on a bare metal surface to help establish the double layer.

If a fresh metal surface were instantaneously exposed to an electrolyte solution, the open-circuit metal *vs.* solution potential difference would change from zero with time as various charge separation processes occurred. These processes may include orientation of electrons within the surface of the metal, orientation of solvent dipoles adjacent to the metal surface, specific adsorption of various ions onto the metal surface and faradaic currents between the metal

and solution phase. Each of the latter three phenomena also involve electron distribution in the metal due to image forces or bonding, but in these cases the electron distribution is considered separately from the first term since the rate and amount of such distribution is accounted for in the solution-metal phenomena.

The potential *vs.* time transients following surface renewal or the potential obtained upon continuous surface renewal can directly be used for the study of potential distribution in the double layer and kinetics provided that the various relaxation processes are separated in time and the experimental method is sufficiently fast to separate some of the relaxations.

The measurement of the potential of zero charge (pzc) of the streaming mercury electrode is a well-known application of such studies. In this case, the adsorption processes reach equilibrium faster than the surface is renewed (in non-dilute solutions), while faradaic reactions occur much more slowly. Fig. 1 qualitatively shows the relative relaxation times for the various processes in this case. The initial time for electrons in the solid surface to reorient would be expected to be much faster than the relaxation times for the other processes, but it has not been measured and hence is not shown. The relaxation time for dipole orientation on the electrode surface was obtained from double layer resistance and capacitance measurements as a function of frequency.¹⁾ From high frequency capacity measurements on mercury it has been found that the relaxation time for ionic specific adsorption is less than 5×10^{-6} sec,²⁾ the limit of the measuring apparatus. Although this relaxation time is not known, we may take 5×10^{-6} sec as the upper limit for it. Since relaxation implies the attainment of equilibrium between a process and some counter process, we cannot speak of the relaxation time for a given faradaic reaction

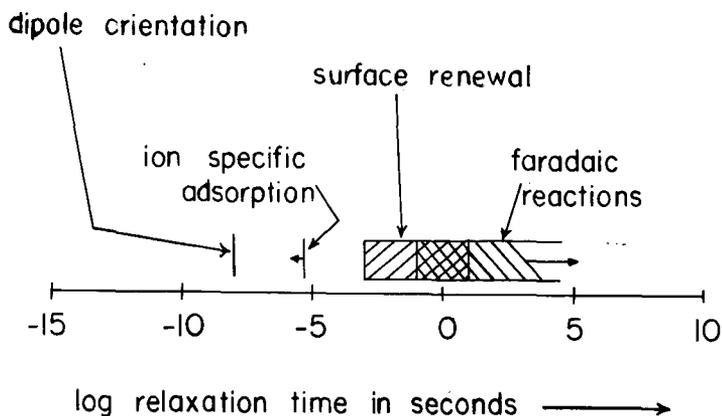


Fig. 1. Schematic representation of various relaxation processes at streaming mercury electrode.

Reactions at Fresh Metal Electrode Surfaces

but only that for the establishment of an equilibrium potential or a mixed potential. For the purpose at hand, we *define* the relaxation time for a faradaic reaction of current density i as the time required for the reaction to change the electrode potential by 10 mV. This definition is chosen so that potential changes caused by faradaic reactions are represented in the same manner as those caused by the previously mentioned relaxation processes. The potential change of 10 mV is arbitrarily chosen since this magnitude is the precision of potential change measurements in the present work. This relaxation time, τ_r , is given in terms of measurable quantities at the electrode by $\tau_r = C\Delta V/i = C(10 \text{ mV})/i$ where C is the differential capacity of the electrode. For example if C is $30 \mu\text{F}\cdot\text{cm}^{-2}$, $\tau_r = 3 \times 10^{-7}/i$ where i is the reaction current in amps cm^{-2} . Fig. 1 shows relaxation times for reactions which occur at Hg in N_2 -saturated aqueous solutions containing "nonreactive" salts such as NaCl. Significant concentrations of readily reducible substances such as Hg_2^{+2} or MnO_4^- ions or O_2 are not considered in Fig. 1 since the purpose of the figure is to show the conditions necessary for measuring the potential of zero charge. For the hydrogen discharge reaction on mercury at the pzc, the relaxation time as defined is of the order of 10^3 seconds. In practice, the reduction of trace impurities such as O_2 or univalent mercury ions are the fast reactions in typical pzc determinations. Experimentally, the relaxation times (as defined) for these impurity reactions are of the order of the slower surface renewal times and somewhat longer; e.g. a calculation of the limiting current (i_l) of dissolved oxygen,³⁾ in equilibrium with 0.1% atmosphere of O_2 yields $i_l \approx 10^{-7} \text{ A}\cdot\text{cm}^{-2}$, such that the defined relaxation time for this reaction is three seconds.

In order to understand the potentials of freshly-exposed surfaces, we shall compare the above relaxation times with the time, τ , for renewal of the surface. Renewal of the Hg surface occurs by drop expansion and by drop renewal. Drop times which have successfully yielded the pzc and thus which have been utilized in double-layer studies are 9 sec and less,⁴⁻⁶⁾ and drops typically expand to about ten times the capillary diameter before detaching from the capillary.⁶⁾ Since this expansion provides for a surface area growth of roughly 100 times, we may approximate the surface renewal time as 0.01 of the drop time. Such calculated surface renewal times are shown in Fig. 1. Thus in the scheme of Fig. 1 surface renewal times faster than approximately 0.1 sec yield the pzc which is the sum of the potential differences from all the charge separations in the double layer except those caused by the faradaic reactions. For τ greater than 0.1 sec in Fig. 1, the measured potential is given by

$$E = \text{pzc} + \int_{t=0}^{\tau} \sum \frac{i}{C} dt \quad (1)$$

if the capacity varies only slowly with the potential.

It is thus understandable that the pzc of Hg is routinely measured by allowing Hg to fall rapidly from a reservoir through a capillary into the solution and by simply measuring the potential difference between the undetached drops and a reference electrode. A significant variation of drop time produces no potential variation when the relaxation times for ion adsorption and faradaic reactions are sufficiently different. This is one of the tests used to indicate whether or not the faradaic reactions are being outrun. The latter test is not sufficient by itself to determine whether or not a "plateau" in the potential *vs.* log time curve corresponds to the pzc; this is apparent since reactions of very different relaxation times may successively change the electrode potential in a manner which produces plateaus in the potential *vs.* log *t* relationship.

Considering various systems other than mercury in simple salt solutions, we note that relaxation times for ion adsorption may vary from less than 10^{-5} sec (as obtained for simple ions on mercury) to several hours (for the case of I^- ions on platinized platinum).⁷⁾ Also, reaction rates vary from negligibly small values to more than 10^4 A·cm⁻².⁸⁾ Thus, with realistically conceivable surface renewal methods, one would expect transients characteristic of various processes or combinations thereof by studying different electrochemical systems.

For solid electrodes, the open circuit scrape method has been developed⁹⁾ which purports to be the solid electrode analogue of the streaming electrode. A metal wire electrode is encased in a Teflon sleeve so that only the cross sectional end is exposed to the solution. This is scraped off with a cutting tool made from a suitable insulating material such as glass, sapphire, or carborundum, and the open-circuit potential is measured during the scraping, tantamount to measuring the streaming Hg electrode potential. Other methods of surface renewal which utilize the basis of Fig. 1, such as the dip method,¹⁰⁾ have previously been reported. A comparative study of this method and the open-circuit scrape method is underway in this laboratory.

Obtaining the potential of zero charge as the scrape potential is more difficult than is obtaining it for the streaming mercury electrode. Reasons for this are: (1) solid metals usually react with solutions much more rapidly than does mercury, so that faradaic currents often cannot be outrun; (2) when reactions are slow, it is usually over a limited pH range; thus, the scrape potential is not constant over long pH ranges indicative of the pzc as the streaming potential is for Hg; (3) satisfactory electrocapillary curves have not been obtained for solid electrodes such that a comparison between the scraped electrode and the potential of the electrocapillary maximum (ecm) can be compared; furthermore, as demonstrated by FRUMKIN *et al.* for Pt,¹¹⁾ when a reactive

Reactions at Fresh Metal Electrode Surfaces

adsorbable component exists in the solution at the pzc, that zero charge potential and the potential of the ecm do not necessarily coincide. In short, it requires careful consideration in order to verify whether or not the faradaic reactions have been outrun in a typical scrape experiment.

Nevertheless, the capabilities of the scrape method seem important to study since methods for determining the potential of zero charge of solid electrodes in the presence of specific adsorption are very sparse. Also, the method appears promising as a tool to study the relative velocities of simultaneous reactions which determine steady state electrode potentials.¹²⁾

The open circuit scrape transients have been studied for Au and Ag electrodes in aqueous solutions of varying ions, ion concentrations and pH^{9,13)} and for Ga electrodes in a few acidic solutions.¹⁴⁾ In these cases the transient potential peak was identified with the pzc except in a few solutions for which faradaic processes were shown to outrun the rate of surface renewal (*i.e.*, to significantly change the recorded potential from the pzc). It was experimentally shown that the employed scraping speed (of 15,000 rpm) could just outrun the effects of reactions of velocity $.2 \text{ mA}\cdot\text{cm}^{-2}$ for an electrode having a capacity of $80 \mu\text{F}\cdot\text{cm}^{-2}$.

The present study applies the open-circuit scrape method to Pt, and to a lesser extent to Ir, Rh, Ni, Sn, Pb, Al, and Ti in N₂-saturated aqueous solutions at room temperature (approximately 24°C). A variety of metals were studied in order to ascertain the limitations of the open-circuit scrape method as a tool for determining the pzc. Some preliminary data have been given for platinum⁹⁾ but the methods employed for obtaining the data, and the sparsity of data were such that definite conclusions could not be drawn regarding which processes had reached steady-state at the scrape potential.

Experimental Section

The experimental setup was the same as in reference 13. It should be noted that care must be exercised in the choice of the sleeve which encases the wire electrode. Whereas pure Teflon (Du Pont's TFE polymer) acts as an inert electrode holder in the case of the metals studied here, other plastics may cause erroneous scrape potentials as the scraper alternately cuts the plastic and the wire. For example, the scrape potentials of .020 in.-diameter Pt wires in polyethylene or nylon sleeves were several hundred millivolts negative of those for Pt sealed in Teflon or glass. The latter values were in agreement with those for experiments in which plastic was not scraped or cut simultaneously with the metal surface. This experiment was accomplished by

Terrell N. ANDERSEN *et al.*

scraping a wire the diameter of which was just larger than the sapphire bit (and encased in any of the above-mentioned plastics). Scraping speeds of up to approximately 24,000 rpm (*i.e.*, surface renewal rates of about 1/800 sec) were employed.

The metal purities were 99.999 and 99.99% for Pt, 99.99% for Ni, 99.95% for Sn, Pb and Al, 99.9% for Rh and Ir, and 99.8% for Ti. For most of the experiments the metals were studied "as received" except for washing of the surface to remove grease, *etc.*; any variations of this procedure are stated.

Experimental Results and Discussion

Platinum

The steady state (or pre-scrape) potentials for Pt were several tenths of a volt more positive than the scrape potential, V_{sc} , similar to those for Ag, Au and Ga. Commencing with the electrode's being scraped, the potential abruptly changed to V_{sc} , and finally decayed back to the rest potential when scraping ceased. The characteristics of the potential decay indicated that O_2 impurity in the cell was primarily responsible for the observed decay.

The experimental results were independent of scraping speed over the experimental range of less than 7,000 rpm to 24,000 rpm.

Effect of pH and anions

The scrape potentials for Pt are shown as a function of pH for various solutions in Fig. 2. Although the ionic strengths of the solutions were not kept constant over the entire pH range for most solutions, the observed changes in V_{sc} are due solely to the pH change as shown by studies of salt concentration *vs* V_{sc} (Fig. 3). The reproducibility of V_{sc} is given by the vertical lines in Fig. 2 and was noted to be better in acidic than in neutral and basic solutions. The results of many independent experiments run on different days with different electrodes, scraping bits, *etc.* were used to obtain the range of values listed. In order to properly place the various curves with respect to each other, successive experiments were run with only the electrolyte being changed. The same technique was also employed in determining the best line through the data in Fig. 3.

Effect of cations

In neutral 0.1 N Cl^- solutions the V_{sc} values for Na^+ , K^+ , Cs^+ , Ba^{+2} and $(C_2H_5)_4N^+$ solutions were within experimental error and it was hence concluded that cation adsorbability was small.

Reactions at Fresh Metal Electrode Surfaces

Anion concentration

The scrape potential on Pt as a function of solute concentration is shown in Fig. 3. The spread of data is greater, for several of the solutions, than is the change of V_{sc} with concentration, and it is concluded that the scrape potential is independent of salt concentration for Na_2SO_4 and for KCl, KBr and KI at the higher concentrations. A concentration effect is apparent in

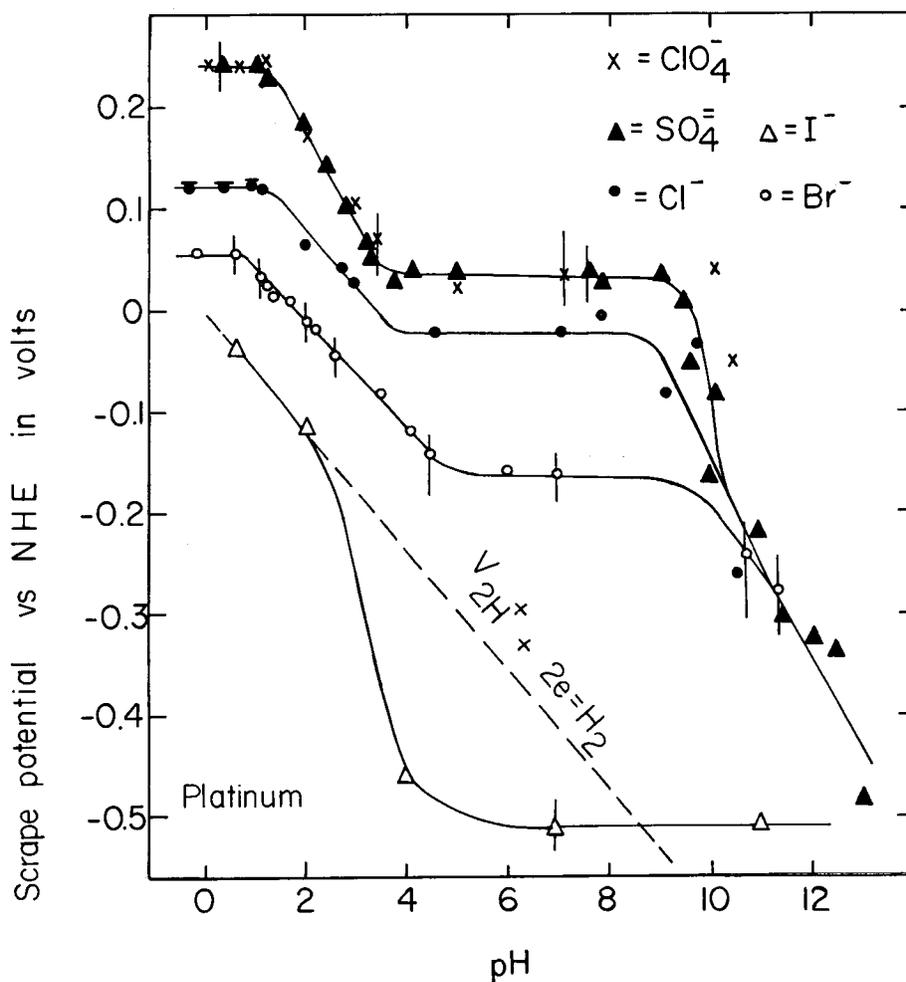


Fig. 2. Scrape potential vs. pH for Pt electrode in various solutions. Alkaline solutions prepared by addition of NaOH to neutral salt. Other solutions: $\times = .03 \text{ N NaClO}_4 + \text{HClO}_4$;

$\blacktriangle = 0.1 \text{ N K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$; $\bullet = 0.1 \text{ N (KCl + HCl)}$; $\blacksquare = 3.0 \text{ N (HCl + KCl)}$;
 $\circ = 0.1 \text{ N KBr} + \text{H}_2\text{SO}_4$; $\triangle = 0.1 \text{ N KI} + \text{H}_2\text{SO}_4$

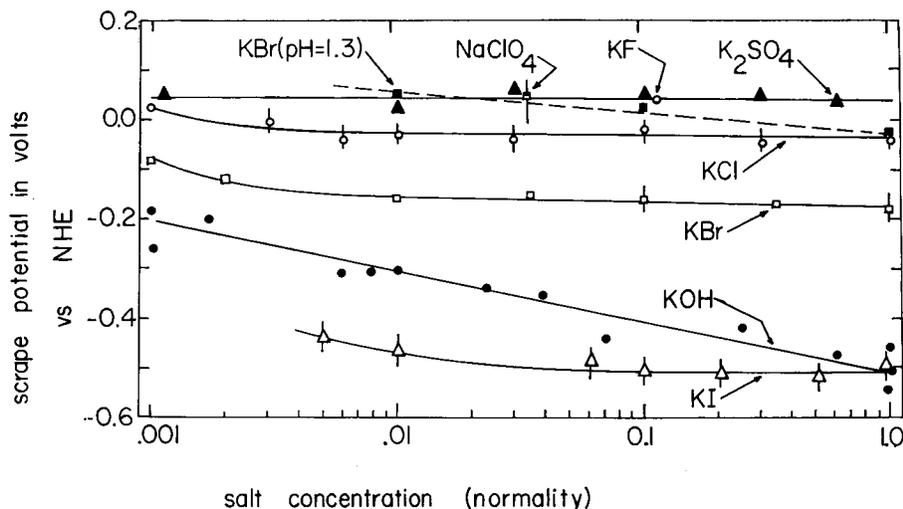
Terrell N. ANDERSEN *et al.*

Fig. 3. Scrape potential *vs.* solution concentration for Pt in various electrolytes.

the cases of OH⁻ ions, for Br⁻ ions in acidic solutions, and for Cl⁻, Br⁻ and I⁻ in dilute solutions.

Miscellaneous diagnostic tests

Since various impurities could cause reactions which would affect V_{sc} , tests were performed to assess the magnitude of such interference. Also, tests for reaction products seemed desirable such that the cause of the V_{sc} values (adsorption *vs.* faradaic reactions) could be determined.

a. O₂ in solution

For experiments run open to the atmosphere the decay following scraping was faster for all solutions than in the case of an N₂ atmosphere. Upon substituting air for N₂, V_{sc} was unchanged for acidic and neutral solutions, but was often more positive for basic solutions.

b. H₂ in solution

In H₂-saturated solutions, the Pt electrode registered approximately the reversible hydrogen potential. Since this potential was significantly negative with respect to V_{sc} , oxidation of H₂ rapidly occurred at the latter potential causing V_{sc} to be negative from its value in N₂. Accordingly, the potential decay was negative and rapid. The effects of H₂ were greater in neutral and basic solutions than in acidic ones, as would be expected based on the difference between the reversible hydrogen potential and V_{sc} in nitrogen. For example, V_{sc} for Pt in .03 N NaClO₄ was -0.19 V while that in .1 N KBr and pH=1.3 was 0.01 V.

Reactions at Fresh Metal Electrode Surfaces

c. Metal purity

Since the results of section b above show that hydrogen occluded in the platinum metals could cause negative scrape potentials and decays, some effort was made to show that hydrogen (as well as other impurities) was not present in sufficient concentration to be responsible for the results. Potential transients for Pt were unchanged by annealing the metal for three hours at approximately 950°C in a vacuum of 10^{-7} to 4×10^{-8} torr. Furthermore, the results for 99.99 and 99.999% pure Pt were identical.

d. Anodic galvanostatic transients

Various tests have shown that a platinum electrode is covered with approximately a monolayer of hydrogen atoms at the reversible hydrogen potential, and that the equilibrium coverage decreases, approaching zero at a few tenths of a volt positive of the hydrogen potential.⁷⁾

From the scrape potential, obtained either by continuous scraping or by potentiostatting the Pt electrode, anodic constant current was passed through the electrode and the resulting potential *vs.* time plot was recorded. In the case of the acidic solutions ($\text{pH} \approx 1$) arrests (regions of lower dV/dt) were observed from V_{sc} to potentials about 70 mV positive of V_{sc} , after which the potential rose more steeply with time. These "arrests" are typical of electrodes which contain adsorbed hydrogen atoms, and the length of the arrest corresponded to approximately $80 \mu\text{coul}\cdot\text{cm}^{-2}$ (geom.) of metal. The reproducibility of such experiments did not allow a differentiation of θ_{H} in the different acids studied (HBr, HCl and HClO_4). In neutral and basic solutions the potential *vs.* time decay showed only steep slopes characteristic of double layer charging. The solutions studied included ClO_4^- , Cl^- , and Br^- ions.

Iridium and Rhodium

Before the behavior of Pt is discussed, the results will be shown for Ir and Rh since the electrochemical behavior of these metals is quite similar to that of Pt. The scrape potentials are shown as a function of pH for the above metals in Figs. 4 and 5 for 1.0 N KBr and 1.0 N K_2SO_4 solutions to which H_2SO_4 or NaOH were added to fix the pH. Data were collected at only a few values of the pH and the shapes of the curves were estimated on the basis of the results for Pt. The spread of scrape potentials is greater for Ir and Rh than for Pt, the reason seeming to stem from their greater hardness. Even with annealing in He, which softened the metals in terms of one's being able to bend them with more ease, it was still more difficult to effectively scrape the entire surfaces of these metals and to cut the wire away with the surrounding Teflon. Several experiments with different electrodes were run in order to find a satisfactory average value of the scrape potential. It is felt that the

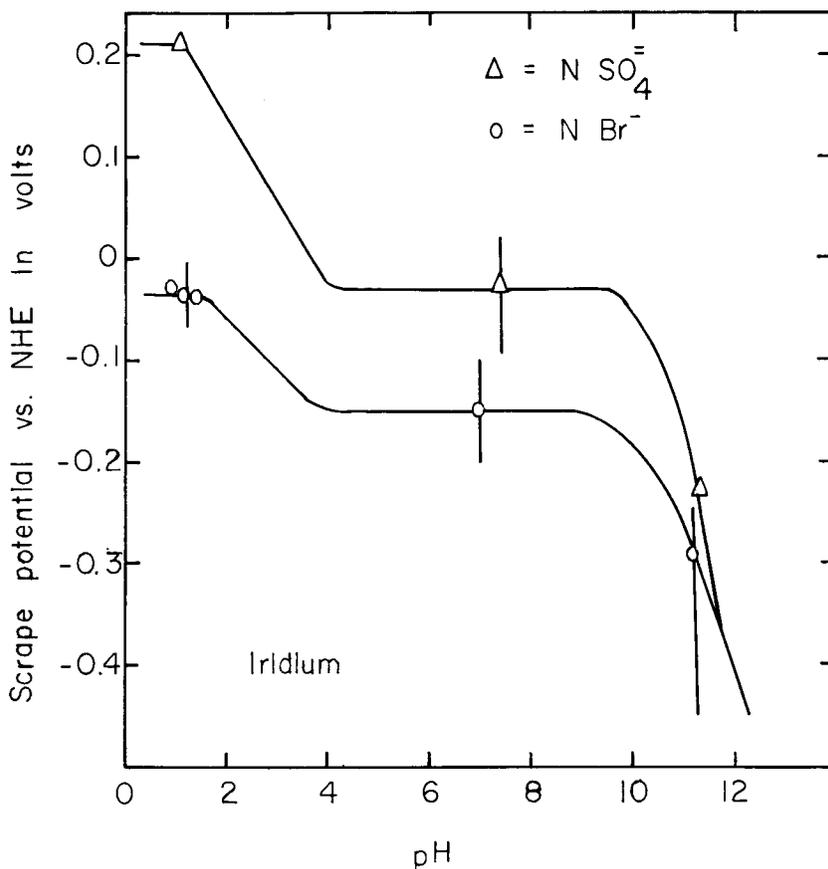
Terrell N. ANDERSEN *et al.*

Fig. 4. Scrape potential *vs.* pH for Ir in 1.0 N K₂SO₄+H₂SO₄ or NaOH (Δ) and 1.0 N KBr+H₂SO₄ or NaOH (○).

more positive scrape values are erroneous (since incomplete scraping would tend to produce values more positive than V_{sc}). From Figs. 4 and 5 a pH effect on V_{sc} is apparent which is similar to that in the case of Pt. Also, the values for Ir and Rh in SO₄²⁻ solutions are about 50 mV more negative than those for Pt (which are equivalent to the values for 0.1 N K₂SO₄ in Fig. 2).

Ir and Rh responded in a manner similar to Pt to other tests. They were more reactive to O₂ gas in the cell and gave "hydrogen regions" in galvanostatic anodic charging curves in acid solutions. The scrape potentials were insensitive to ion concentration in neutral solutions, while lower Br⁻ ion concentrations yielded more positive scrape potentials in acidic solutions.

Reactions at Fresh Metal Electrode Surfaces

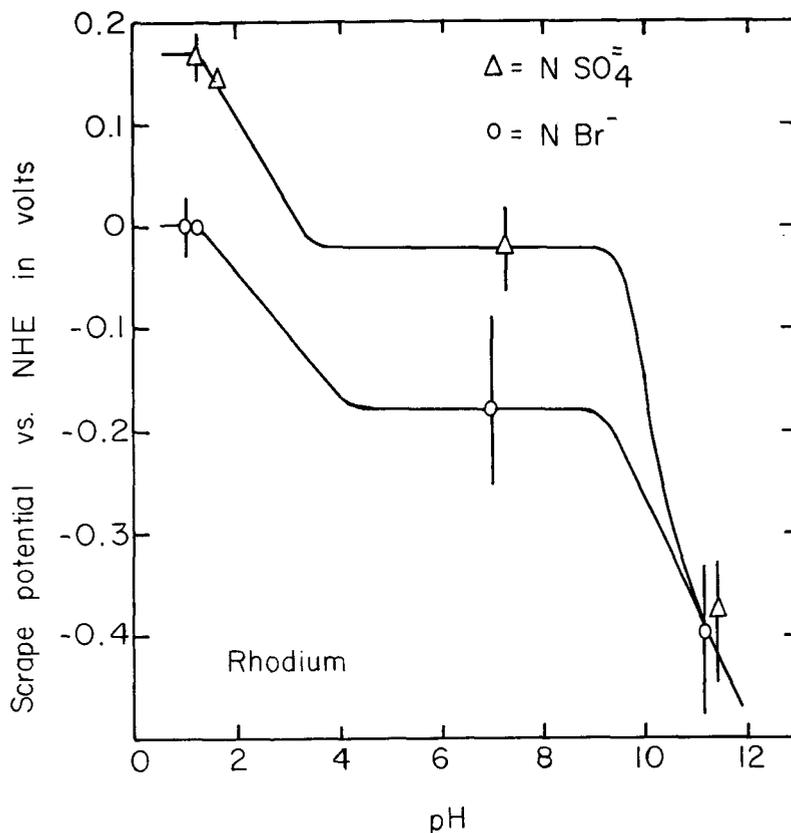


Fig. 5. Scrape potential vs. pH for Rh in 1.0 N K₂SO₄+H₂SO₄ or NaOH (Δ) and 1.0 N KBr+H₂SO₄ or NaOH (○).

Discussion of Platinum Metals

The fact that the potential decays are slow and that V_{sc} is insensitive to the rate of removing the surfaces indicates that the surface renewal time lies in between the relaxation times for other processes in a scheme analogous to Fig. 1. In view of the fact that the relaxation times for water orientation on the surfaces of Cu and Hg are 10^{-6} and 10^{-8} sec., respectively,¹⁾ it is expected that water orientation is rapid compared to the surface renewal rate. GILMAN¹⁵⁾ has shown that the slow process in the adsorption of Cl⁻ and PO₄⁻³ ions onto smooth Pt is mass transfer of the ions to the surface. This fact coupled with the nature of the potential decays leads us to believe that ion adsorption is also rapid in the present work, compared to surface renewal. There may be contradiction of this conclusion for the cases of Br⁻ and I⁻ based on the fact that the amount of I⁻ ions adsorbed on platinized platinum in acid solutions¹⁶⁾

Terrell N. ANDERSEN *et al.*

and the electrode impedance of a Pt electrode in HBr near the reversible hydrogen potential¹⁷⁾ both vary with time over many hours. These facts have been attributed to slow adsorption and to changes of the nature of the adsorption bond with time. They are associated with hydrogen equilibration and are more prevalent in acidic than in neutral solutions. Furthermore, the relative magnitude of these effects for smooth *vs.* platinized platinum have not been studied. Hence, we conclude that slow adsorption is not responsible for the trends observed in the present work nor for the values observed except, possibly, for iodide in acidic solutions.

The experimental results are consistent with the interpretation that in Figs. 2 and 4: (1) the potential plateau in the neutral pH range is determined by anionic specific adsorption and solvent adsorption, (2) in the basic range OH⁻ ions coadsorb with the anion of the salt causing the further negative shift of the potential, and (3) in the acidic region the hydrogen ions are involved in a reaction which produces adsorbed hydrogen, such as



A more quantitative description of these scrape potentials in terms of double layer theory follows:

Neutral solutions: The Galvani potential difference of the metal with respect to the solution, ϕ_m , for the case at hand is given by the sum of the potential contributions due to each "condenser" or layer of separated charges between the metal and solution. These dipolar potentials include the surface potential of the metal (χ_m), the oriented solvent molecules on the surface of the electrode (χ_{solvent}), the potential due to the specifically adsorbed anions at the inner Helmholtz plane *vs.* the fully solvated cations at the outer Helmholtz plane (χ_{ions}), and the potential drop within the diffuse double layer, ϕ_2 . Thus we have

$$\phi_m = \chi_m + \chi_{\text{solvent}} + \chi_{\text{ions}} + \phi_2 \quad (3)$$

The contributions χ_m , χ_{solvent} and χ_{ions} have not been separated for Pt or any other metals, and ϕ_2 is only known if the specifically adsorbed charge per unit area, q_1 , is known. In double layer studies on mercury the terms χ_m , χ_{solvent} and χ_{ions} are usually lumped together as the "p.d. between the metal and the outer Helmholtz plane due to specifically adsorbed ions"; *i.e.*

$$\phi_m = q_1(\phi_m - \phi_2) + \phi_2 \quad (4)$$

The value of $q_1(\phi_m - \phi_2)$ is found from the shift of the potential of zero charge due to specific adsorption and a knowledge of the specifically adsorbed charge per unit area, q_1 , from which ϕ_2 is calculated. The latter relationship is given by

Reactions at Fresh Metal Electrode Surfaces

$$\phi_2 = \frac{2RT}{F} \sinh^{-1} \left(\frac{q_1}{A} \right), \quad (5)$$

where $A = (RT\varepsilon C^s/2\pi)^{1/2}$, C^s is the concentration of the solution in ions which are adsorbed and ε is the dielectric constant of the diffuse layer (the same as the bulk solution). $q_1(\phi_m - \phi_2)$ and ϕ_2 are both zero at the pzc for a solution of non-specifically adsorbed ions (*e.g.* NaF for the Hg electrode). For mercury $q_1(\phi_m - \phi_2)$ is related to q_1 as if χ_m and χ_{solvent} could be neglected. *I.e.*¹⁸⁾

$$q_1(\phi_m - \phi_2) = \frac{4\pi q_1 d_{1-2}}{\varepsilon_1}, \quad (6)$$

where d_{1-2} is the distance from the inner- to the outer Helmholtz plane and ε_1 is the average dielectric constant of the compact double layer. Equation (6) describes the experimental $q_1(\phi_m - \phi_2)$ vs. q_1 slope for Hg¹⁹⁻²²⁾ if q_1 is the measured specifically adsorbed charge, and d_{1-2} and ε_1 are "reasonable" double layer values of the order of $d_{1-2} = 2 \text{ \AA}$ and $\varepsilon_1 = 10$. The lack of a precise knowledge of d_{1-2} and ε_1 (or even the relative values for various anions) at the present time prevents a detailed understanding of the contributions from χ_m and χ_{solvent} . The apparent success in neglecting them for mercury suggests that perhaps χ_m is constant for various solutions against a given metal and χ_{solvent} is small or varies linearly with q_1 (at least at small ionic coverages of the surface).²³⁾ For lack of enough data to develop a theory of the double layer of Pt with ionic specific adsorption we shall use equations (3) to (6) to rationalize the gross findings in the present results. These equations are correct at least insofar as they predict the ionic adsorption to be the largest contribution to $q_1(\phi_m - \phi_2)$; *i.e.* the electrode potential at constant charge becomes more negative with increased anionic specific adsorption.²⁴⁾

We can discuss the present results in the neutral pH range by combining equation (4) with a suitable adsorption isotherm. Isotherms which have been quite widely successful in describing ion adsorption onto Hg are of the Langmuir form with allowance for adsorbate particle-particle interaction.^{18,21,22,25)} We shall use the particular form employed by PAIK *et al.*²³⁾ which is of the form

$$\frac{q_1}{q_s - q_1} = \frac{\theta}{1 - \theta} = \frac{2r_i e a_s}{q_s} \exp \left(\frac{-W_0 - ZF\phi_1}{RT} \right). \quad (7)$$

Here a_s is the activity of adsorbate ions in solution, W_0 is the standard free energy of adsorption in the absence of an electric field, ϕ_1 is the Galvani potential at the inner Helmholtz plane (position of the specifically adsorbed ions) with respect to the bulk of the solution, r_i is the radius of the specifically adsorbed ion, q_s is the value of q_1 at saturation coverage, $\theta = q_1/q_s$, e is the

Terrell N. ANDERSEN *et al.*

electronic charge and Z is the valence of the ion. For the type of double layer we are here concerned with

$$\phi_1 = \lambda_{q_1}(\phi_m - \phi_2) + \phi_2, \quad (8)$$

where $0 < \lambda < 1$. We can relate $q_1(\phi_m - \phi_2)$ to θ using equation (6), which results in (9)

$$q_1(\phi_m - \phi_2) = \frac{4\pi q_s d_{1-2} \theta}{\epsilon_1}. \quad (9)$$

If we differentiate equation (7) with respect to $\log a_s$ and substitute in equations (6), (8) and (9) we find that the change of the potential (ϕ_m) with respect to $\log a$ (*i.e.* Fig. 3) is given by

$$\begin{aligned} \frac{d\phi_m}{d \log a} = & \frac{(2.3) 4\pi d_{1-2} q_s}{\epsilon_1} \frac{1}{\frac{1}{\theta(1-\theta)} + \frac{ZF\lambda}{RT} \frac{4\pi q_s d_{1-2}}{\epsilon_1}} \\ & + \frac{d\phi_2}{d \log a} \left[1 - \frac{4\pi d_{1-2} q_s / \epsilon_1}{\frac{1}{\theta(1-\theta)} + \frac{ZF\lambda}{RT} \frac{4\pi q_s d_{1-2}}{\epsilon_1}} \right]. \end{aligned} \quad (10)$$

As an approximation to (10) we shall neglect the diffuse layer contribution (the second term on the rhs). Without knowing q_1 we cannot ascertain the error in such an assumption, but from equation (5) we see that ϕ_2 parallels q_1 in magnitude for a given concentration, and the relative importance of ϕ_2 to $q_1(\phi_m - \phi_2)$ increases as a_s decreases. Using the system Hg/KI_(aq) at the pzc as a guideline we note that $\phi_2 \simeq 1/4 \cdot q_1(\phi_m - \phi_2)$ for 1.0 N KI and $\phi_2 \simeq q_1(\phi_m - \phi_2)$ for .025 N KI.¹⁹⁾ Therefore we would expect $d\phi_m/d \log a_s$ to be approximately equivalent to $d_{q_1}(\phi_m - \phi_2)/d \log a_s$ in more concentrated solutions (*e.g.* 1N) and to be as much as 2 or 3 times larger in dilute solutions.

Considering equation (10) we then note that $d_{q_1}(\phi_m - \phi_2)/d \log a_s$ approaches zero as θ approaches 1 or 0, with the slope being maximal at $\theta = .5$. Fig. 3 shows that $d_{q_1}(\phi_m - \phi_2)/d \log a_s$ approaches zero at higher concentrations for I⁻, Br⁻ and Cl⁻, and is zero for SO₄²⁻ at all concentrations. The result for SO₄²⁻ and the equivalence of V_{sc} for SO₄²⁻, F⁻ and ClO₄⁻ is consistent with the idea that these ions are only slightly specifically adsorbed on Pt. Since cations do not appear to be specifically adsorbed, it appears that Cl⁻, Br⁻ and I⁻ in neutral solutions approach their saturation coverage near .01 N. We do not know the amount of specifically adsorbed charge, q_1 , at $\theta_{anion} = 1$ but may estimate it from the difference in V_{sc} for the 1.0 N halide and the sulfate solutions, assuming the double layer properties to be somewhat similar to those for a Hg electrode. Thus

Reactions at Fresh Metal Electrode Surfaces

$$\frac{4\pi q_{1(\theta=1)} d_{1-2}}{\epsilon_1} \simeq (\phi_m)_{X^-} - (\phi_m)_{SO_4^{2-}} \quad (11)$$

$$\simeq (V_{sc})_{X^-, 1N} - (V_{sc})_{SO_4^{2-}}.$$

Taking $\epsilon_1=10$ and $d_{1-2}=4 \text{ \AA} - r_{X^-}$ we calculate that $q_{1(\theta=1)}=3.2, 9.8$ and $27.1 \mu\text{coul}\cdot\text{cm}^{-2}$ for Cl^- , Br^- and I^- , respectively. These results seem surprisingly low when we consider that a square packed array of ions yields q_1 values of 122, 105 and $86 \mu\text{coul}\cdot\text{cm}^{-2}$ for the same three ions. We may expect that possible errors in double layer parameters and neglect of the water dipolar contribution (χ_{solvent}) could alter the results by 100 or 200%, but the calculated saturation coverages are still much less than a monolayer. Furthermore the present estimates of q_1 are consistent with q_1 values for halides on platinized platinum (from 10^{-3} N solutions)²⁴) measured by radiotracer techniques. We thus conclude that only certain sites on the Pt surface are suitable for ion adsorption and that the heterogeneity of the Pt surface is manifested in this work as well as in other investigations such as hydrogen adsorption studies.

The slope $d\phi_s/d \log a$ for intermediate ion coverages depends largely on λ , the parameter which determines the potential profile across the compact double layer.¹⁸⁾ If we take $\theta=1/2$, $d_{1-2}=2 \text{ \AA}$, $\epsilon_1=10$, $q_s=30 \mu\text{coul}\cdot\text{cm}^{-2}$ and $\lambda=1$ then $d\phi_m/d \log a_s \simeq 50 \text{ mV}$, while if $\lambda=1/2$ and the other parameters are unchanged $d\phi_s/d \log a_s \simeq 120 \text{ mV}$. Changing q_s over reasonable limits affects the slope to a much smaller extent. It is seen that through a proper choice of λ and a variation in θ that the existent $d\phi_m/d \log a_s$ slopes (OH^- ions and halide ions for $C < .01 \text{ N}$) are easily fitted as are the corresponding slopes for ion adsorption on Hg. An adequate theory with which to predict λ is not available. If the adsorbed charge were uniformly smeared out such that the entire potential drop due to specifically adsorbed ions were between the outer and inner Helmholtz planes, then λ would equal 1. However, since the adsorbed charges are discrete, the field due to such ions extends to the metal making λ less than one (see references 18 and 26 for reviews). Attempts to measure λ for KCl and KI on Hg have been made semiempirically using double layer theory, capacity and adsorption data.^{19,20)} These results predict λ for KI to be larger than that for KCl (the difference being about 0.2 at the pzc). These values substituted into our equation (10) would lead to the electrode-potential *vs.* $\log a_s$ slope to be greater for Cl^- than for I^- . This prediction is born out by experiment (reference 27, p. 160), but the available knowledge would not seem to warrant making the comparison more than qualitative.

Basic solutions: The adsorption approach of the last section can equally well be applied to OH^- ions to explain the scrape potentials as a function of pH

or OH^- ion concentration. The relative value of the scrape potential for OH^- ions compared to other anions would then be a measure of the relative adsorbabilities of these ions. Thus from Fig. 3 we would conclude that anion adsorbability on Pt increases in the order $\text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{OH}^- < \text{I}^-$. Two aspects of OH^- ion adsorption are interesting to note: (1) In Fig. 3 the adsorption of the halide ions appears to reach saturation (for these uncharged electrodes) at solution concentrations near .01 N while for OH^- ions the adsorption continues to increase with concentration; yet the position of V_{sc} indicates that the amount of OH^- ion adsorption is comparable with that for the other ions. (2) In comparing various metal electrodes one notes that the relative adsorbabilities for the halide ions increases in the order $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. However, from the scrape potentials of solid electrodes¹³⁾ and from the pzc of Hg²⁸⁾ one notes that OH^- ions are (a) almost as adsorbable as I^- ions on Pt, (b) more adsorbable than Cl^- but less than Br^- on Au and (c) less adsorbable than Cl^- ions on Ag and Hg. Ag and Hg thus react to OH^- ions as though they were halide ions of a comparable size while there is more specific interaction with Au and Pt. Although it is tempting to suggest specific compound formation in the latter case, it is difficult to rationalize such phenomena in terms of existent data. *i.e.*, on platinum both galvanostatic charging curves⁷⁾ as well as potentiostatic studies²⁹⁾ reveal two separated potential regions at which charge flows to produce or remove chemical compound. That these two compounds are a monolayer of H atoms and a monolayer of oxide is consistent with all existent studies. Furthermore, these results are independent of pH. The reversible formation of a compound similar to equation (12) (which could explain the present scrape data for Pt) does not appear consistent with the above work.



Furthermore, the slow step in the electrochemical oxidation of several organic hydrocarbons on Pt has been found to be the discharge of OH^- ions to form OH radicals.³⁰⁾ The rate of this step (as measured from charging curves) is not adequate to outrun the scraping process. If such a compound (equation (12)) were so tightly chemisorbed that it is never removed nor expanded in the potential range between the reversible hydrogen and oxygen potentials (so that charging studies could not detect it), then it is difficult to understand how it could reversibly interact with OH^- ions in solution.

Although we favor the ionic adsorption approach over the Nernst equation for discussing the neutral and basic scrape potentials, the anomalous results for the OH^- ion effects have not been clarified. The present results show the

Reactions at Fresh Metal Electrode Surfaces

need for additional data relating to double layer phenomena in alkaline solutions. **Acidic solutions:** In the acidic pH range one notes that the scrape potential increases with increasing H_3O^+ ion activity to a pH of approximately 1, and then is independent of further increases in $a_{\text{H}_3\text{O}^+}$. The slope of the V_{sc} vs. pH plot at $\text{pH} > 1$ is approximately -60 mV for Cl^- , Br^- and I^- while it is -90 mV for SO_4^- and ClO_4^- . Unlike the situation in the basic region the anion effect remains distinct throughout the acidic range, although the difference in V_{sc} for the various anions is different in acid than in neutral solutions.

The increase of V_{sc} with H_3O^+ ion concentration is indicative of either cationic specific adsorption or reduction by the electrons of the metal. Specific adsorption appears unlikely because of the small size and strong hydration forces associated with H^+ ions. In substantiation of this fact it is found that the potential of zero charge does not increase with H_3O^+ ion concentration for metals on which H_3O^+ reduction is slow (*e.g.* Hg, Ga *etc.*). Conversely, the charging curves in the present work demonstrate the presence of H atoms (or some similar reaction product) on the surface of the Pt metals at the commencement of the scraping. The fact that the decaying of potential is slow is indicative that the H_3O^+ reduction reaction is near equilibrium. This is further supported by the fact that the exchange current for the reaction $\text{H}_3\text{O}^+ + e = \text{H}_{\text{ads}}$ on Pt is about $10^{-1} \text{ A}\cdot\text{cm}^{-2}$ (*cf.* Fig. 1) and by a substantial amount of electrochemical work dealing with charging curves, potentiostatic measurements and the like.^{7,11,31} Thus we consider the reaction



The rate of the forward reaction can be written as

$$\vec{R} = a_{\text{H}_3\text{O}^+} (1 - \theta_{\text{H}} - \theta'_{\text{A}^-}) \frac{kT}{h} \bar{\kappa} e^{-\vec{\Delta G}_0^\ddagger/RT} e^{-\alpha F\psi_{\text{m}}/RT} \quad (14)$$

and the rate of the reverse one as

$$\overleftarrow{R} = \theta_{\text{H}} \frac{kT\bar{\kappa}}{h} e^{-\overleftarrow{\Delta G}_0^\ddagger/RT} e^{(1-\alpha)F\psi_{\text{m}}/RT}. \quad (15)$$

Here θ_{H} is the fraction of the surface available to reaction (13) which is covered with H atoms and θ'_{A^-} is the fraction of the surface available to reaction (13) which is covered with anions. We note in the present formulation that θ'_{A^-} is in terms of the fraction of the space not available to reaction (13) while in the previous treatment (the neutral pH region) θ_{A^-} was the area of the covered surface compared to that occupied by A^- ions when no more A^- ions could adsorb. $\vec{\Delta G}_0^\ddagger$ and $\overleftarrow{\Delta G}_0^\ddagger$ are the nonelectrical parts of the free energy of acti-

Terrell N. ANDERSEN *et al.*

vation for the forward and reverse reactions. The remainder of the terms in equations (14) and (15) are basic to reaction rate theory.³²⁾ ϕ_m is the Galvani potential of the metal with respect to the solution. At equilibrium, taking the κ 's equal to 1, we obtain

$$\phi_m = \frac{RT}{F} \left(\ln a_{\text{H}_3\text{O}^+} - \ln \frac{\theta_{\text{H}}}{1 - \theta_{\text{H}} - \theta'_{\text{A}^-}} - \frac{\Delta G^0}{RT} \right), \quad (16)$$

where ΔG^0 , the free energy of the reaction with no electric field present, is equal to $\exp\{-\frac{(\overrightarrow{\Delta G^0} - \overleftarrow{\Delta G^0})}{RT}\}$. The anion adsorption is reflected both in θ_{A^-} and ΔG^0 . Increased anion specific adsorption increases the free energy of adsorption of H_2 on Pt^7 and hence should correspondingly cause ΔG^0 to be more positive (and H atoms to be less adsorbed at an uncovered site). An increase in θ'_{A^-} at constant θ_{H} is also seen to decrease ϕ_m . With equation (16) we may discuss the scrape values in acidic solutions. In order to discuss the shape of the V_{sc} vs. pH curve for each salt, we differentiate equation (16) with respect to $\ln a_{\text{H}_3\text{O}^+}$.

$$\frac{d\phi_m}{d \ln a_{\text{H}_3\text{O}^+}} = \frac{RT}{F} \left[\frac{1 - (1 - \theta'_{\text{A}^-}) \frac{d\theta_{\text{H}}}{d \ln a_{\text{H}_3\text{O}^+}} + \theta_{\text{H}} \frac{d\theta'_{\text{A}^-}}{d \ln a_{\text{H}_3\text{O}^+}}}{\theta_{\text{H}}(1 - \theta_{\text{H}} - \theta'_{\text{A}^-})} \right]. \quad (17)$$

Before equation (17) is compared to the results a general estimate of the behavior of the electrode should be made.

In neutral solutions θ_{H} was found to be zero and at pH=1 the charging curves showed that the amount of H on the electrode was of the order of $80 \mu\text{coul}\cdot\text{cm}^{-2}$. Allowing for a surface roughness factor of 1.5 we conclude that the fractional coverage of the geometrical surface is approximately 1/4. Since the active regions we are dealing with constitute only a part of the total surface, θ_{H} would be more than 1/4. In between a pH of 4 and 1 θ_{H} gradually increases as reaction (13) proceeds more and more to the right (also causing V_{sc} to increase). It was estimated in a previous section that specifically adsorbed anions covered only a few tenths or less of the electrode area at the neutral plateau region of the V_{sc} vs. pH plot. With increasing metal charge caused by H_3O^+ ion discharge, θ'_{A^-} would be expected to increase until finally at pH \approx 1 the entire electrode surface available to reaction (13) is covered with either H atoms or anions. Thus in equation (17) at pH $<$ 1, $1 - \theta'_{\text{A}^-} \approx \theta_{\text{H}}$. Next we make use of the fact that the electrode potential acts as if the regions of anion adsorption and H_3O^+ ion discharge are two capacitors. The sum of the potentials from these capacitors is the electrode potential such that we may write

Reactions at Fresh Metal Electrode Surfaces

$$d\theta_{\text{H}}/d \ln a = K_1 d\phi_{\text{m}}/d \ln a$$

and

$$d\theta'_{\text{A}^-}/d \ln a = K_2 d\phi_{\text{m}}/d \ln a. \quad (18)$$

K_1 and K_2 act as effective electrode capacities for the respective charge changes that they are associated with. Thereby equation (18) becomes

$$\left(\frac{d\phi_{\text{m}}}{d \ln a_{\text{H}_3\text{O}^+}} \right)_{\text{pH} < 1} \simeq \frac{RT}{F} \frac{1}{\left(1 - \frac{K_1 + K_2}{1 - \theta_{\text{H}} - \theta'_{\text{A}^-}} \right)}. \quad (19)$$

Equation (19) predicts that $d\phi_{\text{m}}/d \ln a_{\text{H}_3\text{O}^+}$ approaches zero as $\theta_{\text{H}} + \theta'_{\text{A}^-} \rightarrow 1$, which agrees with experiment. In the approximation that $\theta_{\text{H}} \simeq 1 - \theta'_{\text{A}^-}$ it must be remembered that we are speaking of the potential-controlling regions of a heterogeneous electrode surface so these values cannot be compared to the fractional coverage of the geometrical surface area. Likewise, at more negative electrode potentials other areas of the electrode (with more positive standard free energies of adsorption) may become accessible to adsorption so that more than one such region as defined here needs to be considered to account for all of the measured adsorbed hydrogen. Returning now to equation (17) we see that the condition necessary for obtaining a ϕ_{m} vs. $\log a_{\text{H}_3\text{O}^+}$ slope of 59 mV (quite closely approximated by Cl^- , Br^- and I^- in the present work) is that the second term in brackets be small compared to 1. Since there are four unknowns in this term, the value of the latter may be varied quite widely. However, by assuming that the θ term change by the order of .05 with each pH unit (the sum of them cannot exceed 1 at $\text{pH}=0$ or be less than a few tenths or 0 at $\text{pH}=7$), combinations of θ_{H} and θ'_{A^-} can readily be found which yield values of $\frac{(1 - \theta'_{\text{A}^-}) d\theta_{\text{H}}/d \ln a_{\text{H}_3\text{O}^+ + \theta_{\text{H}} d\theta'_{\text{A}^-}/d \ln a_{\text{H}_3\text{O}^+}}{\theta_{\text{H}}(1 - \theta_{\text{H}} - \theta'_{\text{A}^-})}$ which are .2 or .3.

Turning now to ClO_4^- and SO_4^{2-} solutions we see that equation (17) cannot yield the observed values for $d\phi_{\text{m}}/d \log a_{\text{H}_3\text{O}^+}$ which are approximately 90 mV; the maximum value predicted by equation (17) is 60 mV. The present model can explain the greater slope by allowing for positively charged hydrogen compounds on the surface. Thus if equation (13) for the reaction in the acid range were replaced by equation (20), the observed results for ClO_4^- and SO_4^{2-} solutions could be explained.



Such compound formation and in particular the predicted difference between the halide and SO_4^{2-} solutions is not inconceivable. Charging curves for HCl and HBr solutions yield essentially linear voltage vs. charge (quantity of hy-

drogen) plots while that for H_2SO_4 shows humps.⁷⁾ This indicates that the initial hydrogen on a Pt surface in H_2SO_4 is different from the less-tightly held hydrogen which is added at higher coverages or which is present in halide solutions. Potentiostatic curves also show such a nonuniform heterogeneity of the surface in H_2SO_4 .²⁹⁾ Apparently the more adsorbable anions occupy the low-energy sites such that the compound (equation 20) cannot form in HCl or HBr.

The anion dependence of the V_{sc} vs. pH curves cannot be calculated due to the lack of specific knowledge concerning ΔG_{ads}^0 , θ_H and θ'_A (ΔG^0 also is dependent on θ_H for a given anion). It is interesting, however, to compare the results with the values of the free energy of adsorption of H_2 onto Pt (at $\theta_H=0$) in the different solutions. These adsorption values should parallel ΔG^0 . The standard free energy of adsorption of H_2 onto Pt (at $\theta_H=0$) has been measured at 0°C and is $-8.2 \text{ Kcal}\cdot\text{mole}^{-1}$ for .5 M HClO_4 , $-5.5 \text{ Kcal}\cdot\text{mole}^{-1}$ for .3 M HCl and $-2.9 \text{ Kcal}\cdot\text{mole}^{-1}$ for 0.3 M HBr.⁷⁾ These solutions and temperatures are the closest that could be found to the present conditions. The difference between ClO_4^- and Cl^- solutions corresponds to 117 mV while that between Cl^- and Br^- solutions corresponds to 103 mV. If we compare the present scrape potentials at a comparable pH, the corresponding potential differences are found to be $\sim 120 \text{ mV}$ and 70 mV.

A more quantitative account of the V_{sc} vs. pH curves does not appear warranted in view of the lack of more detailed data. It does serve to show that the gross features of the experimental results can be explained in terms of anion adsorption and equilibrium of H_3O^+ ions with some reduced species on the surface.

Potential of Zero Charge of Pt Metals: From the present results we identify the scrape potentials in neutral and basic solutions with the pzc. In acidic solutions the electrode charge is positive at V_{sc} because of the occurrence of fast reactions. One would infer, however, that the pzc does not change substantially from pH=4 to 1 since H^+ ions are apparently not specifically adsorbed. Table 1 compares the pzc obtained here with a representative portion of the values of other workers. Where the solutions are not the same they are felt to be comparable.

Most of the latter values are taken from a recent review by FRUMKIN *et al.*¹¹⁾ in which the references to the original literature can be found. The referenced values were obtained by various adsorption methods, electrode displacement in an electric field, and double layer repulsion. Table 1 shows that our values for I^- are in agreement with the literature, but that for other solutions the pzc obtained from scrape potentials is negative of that from other

Reactions at Fresh Metal Electrode Surfaces

TABLE I Zero Charge Potential of Pt in Different Solutions *vs.* NHE in Volts

Solution	pzc (present work)	pzc (literature)	references to literature
Solution of minimum specific adsorption	+.05 (neutral)	.16-.19 (mostly acid; 1 study in neutral)	11)
10^{-2} , 10^{-3} N I ⁻	-.51 (neutral & base)	-.55 (acid & base)	24, 33)
N NaBr in 5×10^{-2} N NaOH	-.38	-.26	11)
N Br ⁻	-.17 (neutral)	-.02 (acid)	11)
N Cl ⁻	-.04 (neutral)	.06 (acid)	11)

methods by 100 to 150 mV. It is felt that an important contribution to this difference is the fact that the electrodes in the equilibrium studies referred to in Table 1 contain adsorbed hydrogen whereas ours do not. In order to compare the present pzc values to those in adsorption studies one must consider the dipolar contribution to the latter potentials from the Pt-H bond (χ_H). χ_H cannot be obtained in the present work by adding H₂ to the system since the hydrogen is immediately oxidized resulting in a negative shift of V_{sc} . χ_H can be calculated, however, from a knowledge of the amount of hydrogen on the electrode in adsorption studies and the effective dipolar potential of each H atom. FRUMKIN, BALASHOVA and KAZARINOV¹¹⁾ have obtained $(\partial\phi_e/\partial A_H)_{q_m}$ for N NaCl solutions; this quantity is the change of potential with respect to H atom concentration at constant electrode charge. If we consider the pzc for N NaCl + 10^{-2} N HCl which is given in Table 1, we find¹¹⁾ that the corresponding value of $(\partial\phi_m/\partial A_H)_{q_m}$ is 2×10^3 cm²·farad⁻¹. Since the amount of hydrogen, A_H , on the electrode at the pzc (.06 V *vs.* NHE) corresponds to approximately .2 coverage or 44 μ coul·cm⁻² of electrons,⁷⁾ we calculate the potential contribution χ_H to be $(A_H) (\partial\phi_e/\partial A_H)_{q_m} = .084$ V. This quantity is seen to account for the major part of the difference sought in Table 1. The satisfactory agreement between the adsorption and scrape methods in obtaining the pzc for I⁻ solutions can be explained by the fact that I⁻ ions adsorb so strongly that the H adsorption is almost negligible.

The present results indicate that the pzc shifts cathodic with increasing pH. We agree with BOCKRIS *et al.*³⁴⁾ in ascribing this to OH⁻ ion adsorption.

The present work represents some of the very few results which directly measure the pzc for Rh and Ir. Though the present values unfortunately are quite imprecise, they nonetheless indicate that the zero charge potentials of these metals in K₂SO₄ solutions are approximately 70 mV more negative than that of Pt. This result is in line with the relative work functions of these

metals. Again the lack of adsorbed H must be considered when comparing the present pzc for Rh and Ir with those obtained by other methods.

Base Metals

On many metals reactions are so rapid that the present surface renewal method cannot outrun all the reactions in any pH range. The electrode potential may then be described by

$$\frac{dQ_M}{dt} = \frac{d(C\phi_m)}{dt} = \sum i_c - \sum i_a, \quad (21)$$

where Q_M is the electrode charge, C is the electrode capacity, and i_c and i_a refer to the cathodic and anodic faradaic reactions. In solving (21) for ϕ_m as a function of t one must know ϕ_m at the instant that the faradaic currents start to change the current. If the equilibrium double layer has been established, then $(\phi_m)_{t=0} = \text{pzc}$ and equation (21) reduces to equation (1) (assuming C is approximately constant). This case corresponds to the scheme of relaxations shown in Fig. 1.

Very often adsorption will not reach equilibrium before some reaction transfers a significant amount of charge (such as when metal ions hop into solution). In this case $(\phi_m)_{t=0}$ assumes a value which is difficult to obtain, and the apparent currents in equation (21) will be complicated by corrections to a changing double layer.

Fortunately much of the present work (and apparently all of the work discussed in this section) deals with times which are long enough that adsorption reaches equilibrium and also fast reactions reach their steady-state. *I.e.*, we may neglect $d(C\phi_m/dt)$ in equation (21). Each faradaic current is of the form

$$i_x = Z_x F K_x a_x e^{\pm \alpha_x Z_x F \phi_m / RT}, \quad (22)$$

where the rate constant, K_x , is given by

$$K_x = \kappa \frac{kT}{h} e^{-\Delta G_x^\ddagger / RT}. \quad (23)$$

If we assume an average α and Z which may be used for all reactions (the corrections to this approximation being adsorbed in K changing it to K'), then we may write for (21)¹²⁾

$$\phi_m = \frac{RT}{Z_{\text{ave}} F} \ln \frac{\sum_{\text{cathodic}} K'_c a_c}{\sum_{\text{anodic}} K'_a a_a}. \quad (24)$$

Reactions at Fresh Metal Electrode Surfaces

The latter assumption would not seem to involve undue complication for many systems since the rate determining step for reactions is often found to be a one-electron transfer step for which $\alpha = 1/2$. Film thickening, gas evolution and other such complicating features are fortunately too slow in many cases to enter into the kinetics at our scrape times (an example is the reaction $2\text{H} \rightarrow \text{H}_2$ on Pt).

When only one reaction and its reverse reaction are prevalent, equation (24) reduces to the Nernst equation and ϕ_m is easily identified. For the case of two reactions ϕ_m assumes a value between the pair potentials of these reactions, lying closer to the pair potential of the faster reaction.¹²⁾ This "mixed" potential usually is determined by the anodic current of one reaction (*e.g.* metal dissolution) and the cathodic current of another (*e.g.* reduction of HOH).

We shall now consider the scrape results for Ti, Al, Ni, Sn and Pb in light of equation (24). Although the present work does not analyze the potential decays when scraping has ceased, several qualitative features of them are of diagnostic value in determining the phenomena occurring at the electrodes. Decays may be classified as "fast" or "slow" depending on whether the initial decay slope extrapolates to potentials significantly removed (negative) from V_{sc} at zero decay time. A fast slope obviously means that some one reaction is much faster than the others, according to equation (21) or (24). A slow decay is indicative of practically balancing anodic and cathodic reactions, fast or slow. The "length" of the decay or the potential difference between the scrape and rest potential indicates the stability of V_{sc} as well as the nature of the process responsible for the decay. Thus the decay is long (several hundred millivolts) for the metals on which $V_{sc} = \text{pzc}$ since the pzc is near the pair potential for no reaction, and therefore no process acts to maintain this potential. On the other hand the decays for several of the electrodes (*e.g.* Sn, Pb, Ti, Ni) amounted to the order of 100 mV or even zero in some cases, indicating that the same processes were in effect at V_{sc} and V_{rest} . Short potential decays then correspond to local concentration changes of some species near the electrode or to film thickening.

Ti: V_{sc} for Ti is $-1.18 \pm .02$ V in 0.1 N Na_2SO_4 , .05 N KI or 0.5 N KI solutions, and the decay was short and slow. Since the standard pair potential for the Ti-Ti⁺² couple is -1.63 V³⁵⁾ and that for the hydrogen evolution reaction is approximately $-.6$ to $-.7$ V (the local pH is assumed to be 10-12 due to the water reduction), we expect that the scrape potential is given by

$$\phi_m = \frac{RT}{Z_{ave} F} \ln \frac{K'_{\text{HOH} \rightarrow \text{H}_2}}{K'_{\text{Ti} \rightarrow \text{Ti}^{+2}}} \quad (25)$$

Terrell N. ANDERSEN *et al.*

Since the pair potential for $\text{Ti} + 4\text{OH}^- = \text{TiO}_2 + 2\text{HOH} + 4e$ is -1.45 at $\text{pH} = 10$, this reaction may contribute to V_{sc} , but hydrogen evolution still takes place.

Al: Considering the similarity of Ti and Al in chemical properties, one would expect their scrape behaviors to be similar. For Al $V_{\text{sc}} = -1.56$ in .01N and 1N K_2SO_4 ; $V_{\text{sc}} = -1.58$ in the same solutions at $\text{pH} = 10.8$ and $V_{\text{sc}} = -1.26$ at $\text{pH} = 1.4$. The pair potential for $\text{Al}-\text{Al}^{+3}$ is -1.66 V and that for $\text{Al}-\text{Al}(\text{OH})_3$ is -2.31 .³⁵⁾ It is apparent from the pH effect on V_{sc} that the cathodic current is the reduction of H_2O in neutral and basic solutions while the faster reduction of H_3O^+ ions occurs in acid.

Ni: Fig. 6 shows the scrape potentials for Ni in aqueous sulfate solutions over a broad pH range. Also shown for comparative purposes is the potential/pH diagram for Ni in water.³⁶⁾ In the basic and neutral pH regions we see that predominant reactions are the oxidation of Ni and the reduction of the resulting divalent Ni species. Since the rate of water reduction on Ni near the reversible hydrogen potential is approximately³⁷⁾ $10^{-7} \text{ A}\cdot\text{cm}^{-2}$ we can conclude that the exchange current for the Ni oxidation reactions must be at least an order of magnitude larger. Interestingly, the exchange current of the $\text{Ni}-\text{Ni}^{+2}$ reaction, as obtained from polarization curves, is only the order of $10^{-9} \text{ A}\cdot\text{cm}^{-2}$.³⁸⁾ This anomaly suggests that the solvation of Ni^{+2} ions from the lattice in the polarization experiments³⁸⁾ occurs through a tightly-bonded layer of OH, oxygen or the like, which causes the observed dissociation to be sluggish. In the present work Ni ions from the bare metal may enter the solution much more rapidly. As the pH is decreased from 7 to 0, the hydrogen overvoltage becomes negative at the reversible Ni potential and hence H_3O^+ ion reduction increasingly contributes to the numerator of (24). Thus

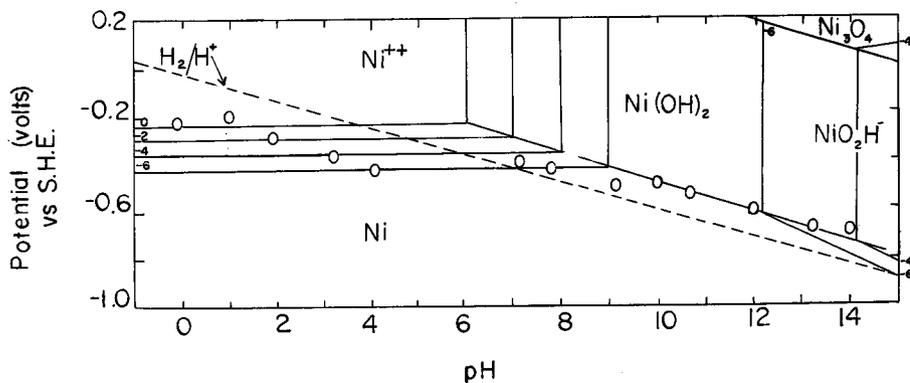


Fig. 6. Scrape potentials (circles) vs. pH for Ni in 0.1N K_2SO_4 + (NaOH or H_2SO_4). Lines show potential/pH diagram for the Ni/ H_2O systems (from reference 36).

Reactions at Fresh Metal Electrode Surfaces

ϕ_m is between the pair potentials for H^+/H_2 and Ni/Ni^{+2} .

Sn and Pb: In order to suppress the effect of the hydrogen evolution reaction such that the phenomena involving the metal might be more prevalent, Sn and Pb were chosen for study. For both of these metals the reaction

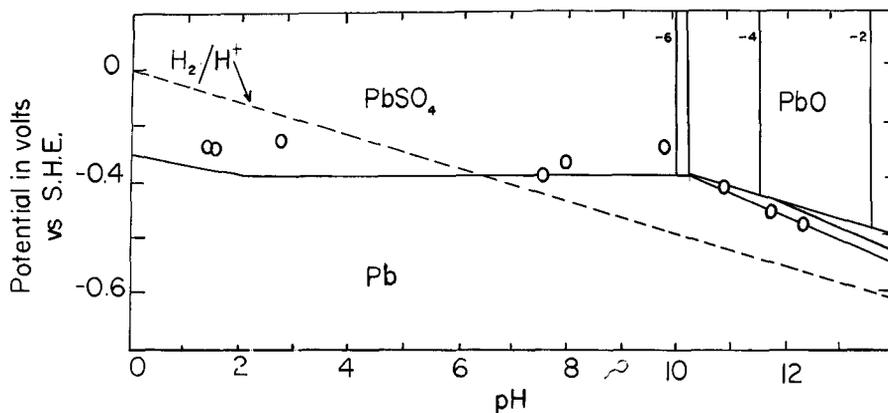


Fig. 7. Scrape potentials (circles) for Pb in 0.1 N K₂SO₄ + (NaOH or H₂SO₄). Superimposed is potential/pH diagram for Pb (from reference 40).

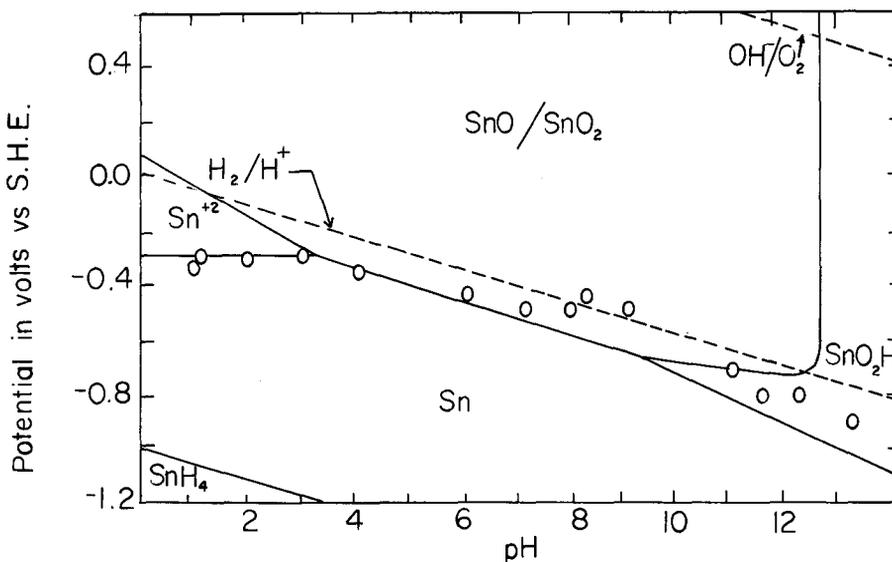


Fig. 8. Scrape potentials (circles) vs. pH for Sn in 0.1 N K₂SO₄ + (NaOH or H₂SO₄). Lines show potential/pH diagram for Sn (from reference 41).

Terrell N. ANDERSEN *et al.*

$\text{H}_3\text{O}^+ + e = \text{H}_{\text{ads}} + \text{H}_2\text{O}$ is known to be the slow step in hydrogen evolution^{38,39)} and the rate of this reaction is so low as to give negligible charge transfer (*i. e.* $0.1 \mu\text{coul}\cdot\text{cm}^{-2}$) in the scrape time at V_{sc} . The scrape potentials for these metals are shown in Figs. 7 and 8 (along with potential/pH diagrams for them)^{40,41)}, from which it appears that equilibrium potentials are attained in times short compared to the time of surface renewal. Thus one redox reaction in equation (24) describes the observed results at any given pH.

Potentials of Zero Charge: It has been demonstrated that reactions occur so rapidly on the five active metals studied here that the scrape potentials do not yield the pzc at any pH. The same is probably true of most other metals which are more electronegative than hydrogen. However, Ga, with a reduction potential of -0.53 V , is an exception to this rule since the scrape potential yielded the pzc in several acidic solutions.¹⁴⁾ The criterion for being able to measure the pzc as V_{sc} is that the rate of hydration of surface metal ions and solvent reduction both be slow. The extent to which polarization curves can be used in the prediction of such rates is questionable, as the present results for Ni have shown. Thus we feel that fresh surface exposure studies are important in understanding the establishment of the double layer as well as in other problems dealing with reactions on bare metal surfaces.

Acknowledgment

The authors are pleased to acknowledge the U. S. Army Research Office (Durham) and the Atomic Energy Commission for the financial support of this work under Contract numbers DA31-124-ARO-D-408 and AT (11-1) 1144, respectively.

References

- 1) J. O'M. BOCKRIS, W. MEHL, B. E. CONWAY and L. YOUNG, *J. Chem. Phys.*, **25**, 776 (1956); J. O'M. BOCKRIS and B. E. CONWAY, *J. Chem. Phys.*, **28** 707 (1958).
- 2) V. I. MELIK-GAIKAZYAN, *Zhur. Fiz. Khim.*, **26**, 560 (1952); A. N. FRUMKIN and V. I. MELIK-GAIKAZYAN, *Dokl. Akad. Nauk, S.S.S.R.*, **77**, 855 (1951).
- 3) G. KORTUM and J. O'M. BOCKRIS, *Textbook of Electrochemistry*, vol. 2, Elsevier Publishing Co., New York, N. Y., 1951, p. 414.
- 4) D. A. JENKINS and R. J. NEWCOMBE, *Electrochim. Acta*, **7**, 685 (1962).
- 5) T. ERDEY-GRUZ and P. SZARVAS, *Z. Phys. Chem.*, **A 177**, 277 (1936).
- 6) I. M. KOLTHOFF and J. J. LINGANE, *Chem. Rev.*, **24**, 1 (1939).
- 7) A. FRUMKIN, *Advances in Electrochemistry and Electrochemical Engineering* vol. 3, ed. by P. Delahay, Interscience Pub., New York, N. Y., 1963.
- 8) N. TANAKA and R. TAMAMUSHI, *Electrochim. Acta*, **9**, 963 (1964).

Reactions at Fresh Metal Electrode Surfaces

- 9) T. N. ANDERSEN, R. S. PERKINS and H. EYRING, *J. Am. Chem. Soc.*, **86**, 4496 (1964);
R. S. PERKINS, R. C. LIVINGSTON, T. N. ANDERSEN and H. EYRING, *J. Phys. Chem.*,
69, 3329 (1965).
- 10) B. JAKUSZEWSKI and Z. KOZLOWSKI, *Roczniki Chem.*, **36**, 1873 (1962).
- 11) A. N. FRUMKIN, N. A. BALASHOVA and V. E. KAZARINOV, *J. Electrochem. Soc.*,
113, 1011 (1966).
- 12) A. G. FUNK, J. C. GIDDINGS, C. J. CHRISTENSEN and H. EYRING, *Proc. Nat'l Acad. Sci.*,
43, 421 (1957).
- 13) D. D. BODÉ, JR., T. N. ANDERSEN and H. EYRING, *J. Phys. Chem.*, **71**, 792 (1967);
D. D. BODÉ, JR., Ph. D. thesis, Univ. of Utah, Salt Lake City, Utah, 1967.
- 14) R. S. PERKINS, Ph. D. thesis, Univ. of Utah, Salt Lake City, Utah, 1967.
- 15) S. GILMAN, *J. Phys. Chem.*, **68**, 2098, 2112 (1964).
- 16) N. A. BALASHOVA and V. E. KAZARINOV, *Élektrokimiya*, **1** (5), 445 (1965).
- 17) T. BIRINTSEVA and B. KABANOV, *Zhur. Fiz. Khim.*, **33**, 844 (1959); quoted in refer-
ence 7.
- 18) P. DELAHAY, *Double Layer and Electrode Kinetics*, Interscience Pub., New York,
N. Y., 1965.
- 19) D. C. GRAHAME, *J. Am. Chem. Soc.*, **80**, 4201 (1958).
- 20) D. C. GRAHAME and R. PARSONS, *J. Am. Chem. Soc.*, **83**, 1291 (1961).
- 21) R. PAYNE, *J. Phys. Chem.*, **69**, 4113 (1965).
- 22) R. PAYNE, *J. Chem. Phys.*, **42**, 3371 (1965).
- 23) W. PAIK, T. N. ANDERSEN and H. EYRING, *J. Phys. Chem.*, **71**, 1891 (1967).
- 24) N. A. BALASHOVA and V. E. KAZARINOV, *Élektrokimiya*, **1** (5), 512 (1965).
- 25) A. N. FRUMKIN, *Z. Physik. Chem.*, **116**, 466 (1925).
- 26) R. PARSONS, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 1,
ed. by P. Delahay, Interscience Pub., New York, N. Y., 1961, Chapt. 1.
- 27) R. PARSONS, *Modern Aspects of Electrochemistry*, vol. 1, ed. J. O'M. BOCKRIS and
B. E. CONWAY, Butterworths Scientific Pub., London, 1954, Chapt 3.
- 28) D. C. GRAHAME, E. M. COFFIN, J. I. CUMMINGS and M. A. POTH, *J. Am. Chem. Soc.*,
74, 1207 (1952).
- 29) M. W. BREITER, *Ann. New York Acad. Sci.*, **101**, 709 (1963); quoted in ref. 18, p. 250.
- 30) H. WROBLOWA, B. J. PIERSMA and J. O'M. BOCKRIS, *J. Electroanal. Chem.*, **6**, 401
(1963); V. DRAZIC, M. GREEN and J. WEBER, *J. Electrochem. Soc.*, **111**, 721 (1964).
- 31) M. W. BREITER, *Electrochim. Acta*, **8**, 925 (1963).
- 32) S. GLASSTONE, K. J. LAIDLER and H. EYRING, *The Theory of Rate Processes*,
McGraw-Hill Book Co., Inc., New York, N. Y., 1941.
- 33) V. E. KAZARINOV, N. A. BALASHOVA and M. I. KULEZNEVA, *Élektrokimiya*, **1** (8),
867 (1965).
- 34) J. O'M. BOCKRIS, H. WROBLOWA and B. J. PIERSMA, *J. Electroanal. Chem.*, **6**, 401
(1963).
- 35) W. M. LATIMER, *Oxidation Potentials*, 2nd ed., Prentice-Hall Inc., Englewood Cliffs,
N. J. 1952.
- 36) E. DELTOMBE, N. DE ZOUBOV and M. POURBAIX, *Proc. CITCE 1955*, Lindau 7,
193 (1957).

Terrell N. ANDERSEN *et al.*

- 37) J. O'M. BOCKRIS and E. C. POTTER, *J. Chem. Phys.*, **20**, 614 (1952).
- 38) J. O'M. BOCKRIS, *Modern Aspects of Electrochemistry*, vol. 1, ed. J. O'M. BOCKRIS and B. E. CONWAY, Butterworths Scientific Publications, London, 1954.
- 39) S. SRINIVASAN, Ph. D. thesis, Univ. of Pennsylvania, Philadelphia, Pa., 1963 p. 58.
- 40) P. DELAHAY, M. POURBAIX and P. VAN RYSSELBERGHE, *J. Electrochem. Soc.*, **98**, 57 (1951).
- 41) E. DELTOMBE, N. DE ZOUBOV and M. POURBAIX, Technical Report No. 25, 1955.