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CORRELATIONS BETWEEN ELECTROCHEMICAL ACTIVITY AND HETEROGENEOUS CATALYSIS FOR HYDROGEN DISSOCIATION ON PLATINUM

By

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Abstract

Hydrogen-deuterium exchange rates on platinum surfaces have been compared to equivalent hydrogen molecule and adsorbed hydrogen atom electrochemical oxidation rates on the same surfaces. Over a temperature range of 293 to 360°K the first order rate constants for H_2-D_2 exchange and hydrogen molecule electrochemical oxidation are the same, showing that the adsorption-dissociation reaction (TAFEL,BONHOEFFER-FARKAS) is rate controlling. The rate of oxidation of the adsorbed hydrogen atom reaction involving electron transfer (VOLMER) is an order of magnitude larger.

The hydrogen evolution reaction has been the subject of numerous mechanistic investigations which has resulted in the determination of reasonably accepted mechanisms for a number of substrates. All the acceptable reaction paths have one reaction step in common which, in acid electrolyte, is the electronation of hydrogen ions to form neutral hydrogen species adsorbed on the electrode surface.

$$M + H^+ + e^- \rightleftharpoons MH$$

This charge transfer step was originally discussed by ERDEY-GRUZ and VOLMER¹⁾, and subsequently has been referred to as the Volmer reaction. Two different reaction paths for hydrogen evolution may be distinguished. These two paths differ in the manner in which the adsorbed hydrogen atoms are desorbed from the surface to form molecular hydrogen. TAFEL²⁾ suggested a desorption step which did not involve charge transfer,

$$2MH \rightleftharpoons H_2 + 2M$$

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which is a purely chemical step and often referred to as catalytic recombination or TAFEL recombination. It is termed in this work as the TAFEL reaction. A second possible desorption step is desorption accompanied by charge transfer.

$$MH + H^+ + e^- \rightleftharpoons H_2 + M$$

The latter reaction is attributed by VETTER3) to HEYROVSKI4) and is usually referred to as the Heyrovski reaction. For any given electrode material, the reaction path for hydrogen evolution could be either of the two pairs of sequential steps, VOLMER-TAFEL or VOLMER-HEYROVSKI, and any one of the three individual steps could be the rate-determining step. BOCKRIS5) has catalogued the probable reaction paths and rate-determining steps for hydrogen evolution from a number of electrode materials in acid electrolyte. In the particular case of Pt electrocatalysts in acid electrolyte, the VOLMER-TAFEL sequence is most probable.

The electrochemical oxidation of molecular hydrogen historically has received less attention and the mechanism for this reaction is not necessarily identical to the mechanism for hydrogen evolution. Hydrogen evolution is observed at potentials where (at room temperature) for most transition metals the electrode surface contains at least a monolayer of adsorbed hydrogen6). Hydrogen oxidation occurs at more positive potentials, where the hydrogen coverage is generally less than a monolayer for these metals7). Since one would expect the coverage of the electrode surface by adsorbed hydrogen to play a critical rôle in either of these hydrogen reactions, it is quite clear that the mechanism may change in going from cathodic to anodic potential regions. Of all possible mechanisms, the TAFEL-VOLMER and HEYROVSKI-VOLMER sequences are again most probable. A non-dissociative adsorption of hydrogen to form a hydrogen molecule-ion intermediate was proposed by HORIUTI8) as the rate determining step for some substrates. The Horiuti mechanism can be represented as

$$H_2 + M \rightleftharpoons H_2M \rightleftharpoons H_2^+M + e^-$$
$$H_2^+M \rightleftharpoons MH + H^+$$

BAGOTZKY *et. al.*9) recently proposed a mechanism similar to the HORIUTI mechanism for hydrogen oxidation on Pt in acid electrolytes. There are a number of possible variations of the steps in the HORIUTI mechanism, all of them having the same essential feature that the hydrogen molecule adsorption step is not accompanied by hydrogen dissociation and requires only a single isolated site for the reaction. In the HEYROVSKI-VOLMER sequence, hydrogen adsorption is dissociative but requires only a single site. Only the TAFEL-VOLMER sequence requires dual-sites, which are nearest neighbor sites for hydrogen dissociation. The principal question, therefore, is to determine whether an electron transfer step, a molecular adsorption step, or an adsorption-dissociation step is rate limiting. This differentiation is essential for an analysis of the operation of electrochemical fuel cell anode catalysts.

The rate of oxidation of adsorbed hydrogen atoms (VOLMER reaction) on platinum has been measured previously$^{10)}$ and found to be at least an order of magnitude greater than the electrochemical rate of hydrogen molecule oxidation$^{11)}$. Although these results eliminate the VOLMER reaction as the rate limiting step, they do not provide a differentiation between the TAFEL-VOLMER, HEYROVSKI-VOLMER or HORIUTI mechanisms. Such a differentiation could be provided by separately measuring the rates of either the TAFEL or HEYOVSKI reaction for the Pt surface. In gas phase heterogeneous catalysis, the TAFEL reaction corresponds to the dissociative chemisorption of hydrogen molecules on the metal surface and is usually the first step in hydrogen reactions on transition metals (T>200°K). Recent studies$^{12),13)}$ of hydrogen-deuterium exchange reactions over platinum have shown that for T>200°K, both the equilibration and heterogeneous exchange reaction follow the Bonhoeffer-Farkas mechanism,

$$H_2 + D_2 + 4M \rightleftarrows 2HM + 2DM \rightleftarrows 2MHDM \rightleftarrows 2HD + 4M$$

In the temperature region between 300–500°K, the rate of surface diffusion is very rapid and the rate limiting step is indicated to be the dissociative chemisorption of hydrogen and deuterium, rather than the exchange in the atomically held layer. It is, therefore, possible to measure the rate of gas phase hydrogen dissociative chemisorption on platinum in the temperature region of interest for electrochemical kinetics but in the absence of an electron transfer step. With the hydrogen dissociation step rate determining, the rate of hydrogen-deuterium exchange will be given by

$$r_{HD} = k_{HD} C_{H_2} (1-\theta)^2 - k_r \theta^2 \qquad (1)$$

where θ is the coverage of the metal surface by adsorbed hydrogen and deuterium at the conditions of exchange (total pressure, temperature), k_{HD} is the hydrogen (or deuterium) dissociation rate constant, and k_r is the hydrogen (or deuterium) desorption rate constant. If for the electrochemical oxidation of hydrogen the TAFEL-VOLMER sequence is correct, then with the hydrogen dissociation step rate determining the anodic current density will be given by

$$i_A = nFk_{at}C_{H_2}(1-\theta)^2 - nFk_{ct}\theta^2 \qquad (2)$$

where θ is the coverage of the metal surface by adsorbed hydrogen, k_{at} and k_{ct} are the anodic and cathodic rate constants, respectively. Comparison of (1) and (2) indicates that the forms of the expressions are identical, differing only by the conversion from chemical units, *mole/cm*^{2}, to electrochemical units, *amp/cm*^{2}. Therefore, the gas-phase rate constant k_{HD} and the electrochemical rate constant k_{at} refer to the same elementary step, the dissociation of molecular hydrogen by the transition metal surface but differ in the nature of the chemical environments of the hydrogen molecule-metal surface systems. The absolute magnitudes of k_{HD} and k_{at} may or may not be the same, depending on the degree to which either a) the molecules in the electrolyte, or b) the electric field gradient at the electrolyte-metal interface alter the shape of the potential energy surface along the H_2-metal reaction coordinates or the nature of the H_2-metal transition state. This complication, however, does not affect the conclusion that can be drawn from a *positive* correlation of the hydrogen-deuterium exchange rate constant with the electrochemical hydrogen oxidation rate constant. A positive correlation is possible only if the TAFEL-VOLMER sequence is the operating mechanism and only if the electrolyte and electrified interface do not affect the absolute rate of hydrogen dissociation. This paper presents the results of studies of H_2-D_2 exchange and electrochemical hydrogen oxidations on platinum, showing a correlation between the rate of H_2-D_2 exchange and electrochemical hydrogen oxidation rate parameters at equivalent temperatures and hydrogen concentrations, providing a resolution of the mechanism for the electrochemical oxidation of hydrogen on platinum.

THEORY OF CYCLIC VOLTAMMETRY

Cyclic triangular wave voltammetry provides a direct measure of electrode reversibility because the potential at which oxidation and reduction occur are observed directly. At sufficiently low potentiodynamic scan rates a condition of quasi-equilibrium is maintained at the electrode surface. Under these conditions the separation of anodic and cathodic current peaks potentials is about $59/n\ mV$, where n is the total electron transfer for the reaction, the reaction is reversible and under total diffusional control. When the potentiodynamic scan rate is increased, a point is reached at which the kinetics of electron transfer become comparable to the rate of potential change and the separation of the oxidation and reduction current peaks becomes greater than $59/n\,mV$. NICHOLSON[14] has shown that the standard (chemical) rate constant is in general a calculable function of the frequency at which the current peaks separation is greater than $59/n\,mV$. For the reversible hydrogen reaction on platinum in acid, it is not possible to measure both an oxidation and reduction peak due to the inequality of the reactant and product concentrations $C_{H^+} \gg C_{H_2}$. Since, therefore, it may be assumed that under kinetic interference both the oxidation and reduction peaks will shift symmetrically about a mid-point when the transfer coefficient is 0.5, measurements obtained on the oxidation peak potential of dissolved hydrogen as a function of the potentiodynamic scan rate will suffice. From potentiodynamic i/ε traces for the oxidation of dissolved hydrogen, a peak shift from the quasi-equilibrium peak potential can be measured experimentally as a function of sweep rate from which the kinetic rate constant can be calculated.

NICHOLSON[14] has developed the theory of cyclic voltammetry for electron transfer reactions described by the electrochemical absolute rate equation. In NICHOLSON's derivation, the current-potential relation at a plane electrode for the reaction

$$2H^+ + 2e^- \overset{k_s}{\rightleftharpoons} H_2$$

is

$$i = nFk_s \exp\left[-2\alpha F(\varepsilon - E)/RT\right]\left[(C_{H^+}^0) - (C_{H_2}^0)\exp\left[2F(\varepsilon - E)/RT\right]\right] \tag{3}$$

where ε is the electrode potential, E the standard potential, k_s is the standard (chemical) rate constant at $\varepsilon = E$, α is the (cathodic) transfer coefficient and $C_{H^+}^0$ and $C_{H_2}^0$ are the hydrogen ion and hydrogen molecule concentrations at the electrode surface, respectively. This expression was used to derive a relation between the separation in the anodic and cathodic potentiodynamic current peak potentials ΔE_p and a kinetic parameter containing the rate constant, k_s, and the potentiodynamic sweep rate. This relation is valid for $\alpha = 1/2$ and for the experimental condition where H_2 (or in general, the reduced species) is absent initially in the electrolyte. NICHOLSON's theory can be applied directly to the hydrogen reaction at a Pt electrode only in approximate sense. The pre-exponential terms in Equation (3) measure the rates of the anodic and cathodic partial currents at the standard potential and the exponential terms describe the retarding or accelerating effect of the potential on the partial reactions. This will be true only if k_s is independent of potential. For a Pt electrode at $\varepsilon \leq 0.2\ V$ (nhe) this will generally not be true, since hydrogen adsorption will affect the rate of the hydrogen reaction. NICHOLSON's theory has, therefore, been modified to account for the changing surface condition during the potential sweep.

The correct current-potential relation for the hydrogen reaction at a plane electrode is

$$i = i_0\left[1 - \frac{C_{H_2}}{C_{H_2}^0}\exp[2F(\varepsilon - E)/RT]\right] \tag{4}$$

where i_0 is the exchange current density for the hydrogen oxidation reaction, C_{H_2} and $C_{H_2}^0$ are the hydrogen concentrations at the electrode surface and in the bulk of the electrolyte, respectively. This expression is derived in detail elsewhere$^{15)}$, and is valid for a number of different mechanisms when the electrode potential, ε, is close to the equilibrium potential, E, as is the case experimentally.

For diffusion to a plane electrode we have

$$D\frac{\partial^2 C_{H_2}}{\partial x^2} = \frac{\partial C_{H_2}}{\partial t} \tag{5}$$

$$t = 0, \quad x \geq 0 \quad C_{H_2} = C_{H_2}^0 \tag{6}$$

$$t \geq 0, \quad x \to \infty \quad C_{H_2} \to C_{H_2}^0 \tag{7}$$

$$t \geq 0, \quad x = 0 \quad \frac{\partial C_{H_2}}{\partial x} = \frac{i_0}{2FC_{H_2}^0}\left[C_{H_2}^0 - C_{H_2}\exp[2F(\varepsilon - E)/RT]\right] \tag{8}$$

and $\varepsilon - E = vt$, $v \equiv d\varepsilon/dt$, for an anodic potentiodynamic scan.

This system of partial differential equation may be converted into a single linear Volterra integral equation by using Laplace transfoms. The rasult is

$$\frac{X(y)e^{-y}}{\phi} = 1 - e^{-y} - \int_0^y \frac{X(z)dz}{\sqrt{y-z}} \tag{9}$$

where

$$X(y) = \left(\frac{D\partial C_{H_2}}{\partial x}\right) / C_{H_2}^0\sqrt{\pi a D}$$

$$\phi = i_0/(2FC_{H_2}^0\sqrt{\pi a D}) = k_s/\sqrt{\pi a D}$$

$$y = \frac{2F}{RT}vt = at$$

The integral equation was solved numerically to generate potentiodynamic curves of $X(y)$, *vs.* y from which the potentials at the current peak

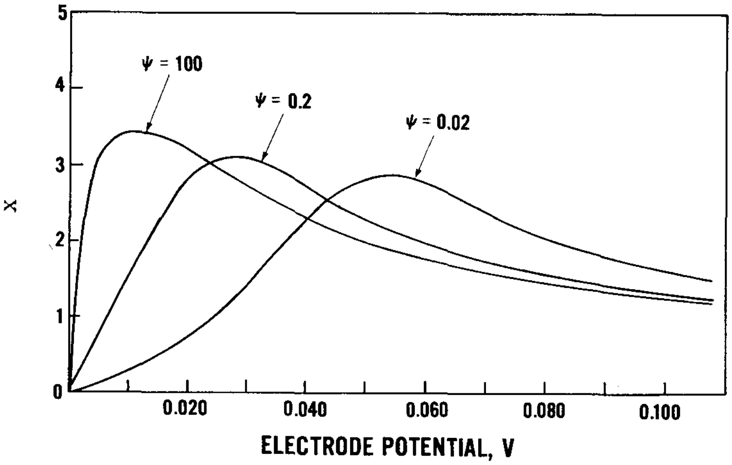

Fig. 1. Computer generated potentiodynamic scanning curves for the hydrogen molecule oxidation current showing the shift in the anodic current peak potential with increasing scan rates $\psi = k_s/\sqrt{\pi a D}$.

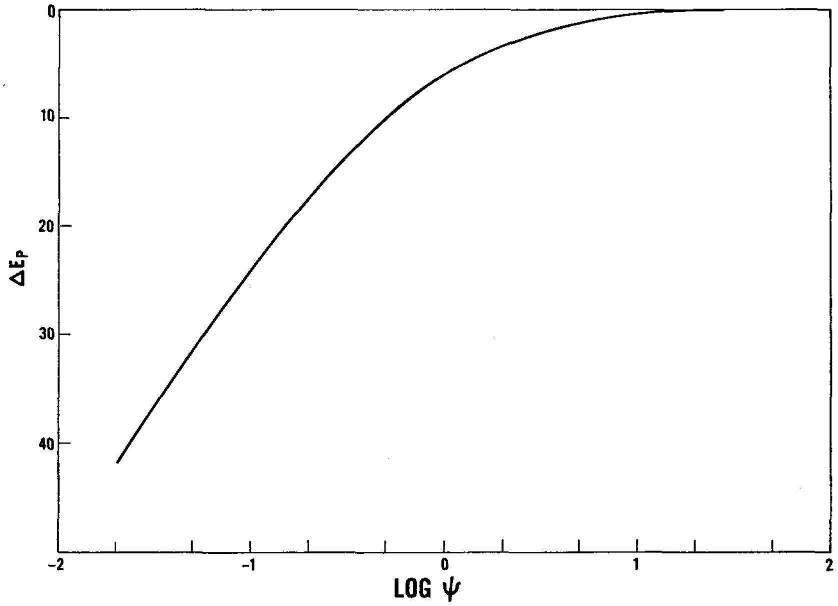

Fig. 2. Working curve for calculating hydrogen molecule oxidation rate constants from the shift (ΔE_p) in the anodic current peak potential from the quasi-equilibrium peak potential.

maxima could be selected. Examples of computer generated anodic potential sweep curves are shown in Figure 1 for different values of the kinetic parameter ψ. The reversible, quasi-equilibrium, hydrogen molecule oxidation current peak for a potential scan starting at zero potential (nhe) occurs at $10.67\,mV$ (nhe). An increase in sweep rate from this reversible condition by a factor of 500 results in a shift in current peak potential of $16.83\,mV$ from the reversible peak potential with a broadening of the peak shape. In general, as the sweep rate increases, the hydrogen molecule oxidation current peak potential shifts to higher potential, the peak shape broadens, and the peak maximum, which is proportional to $i_p/\sqrt{v}$, where i_p is the maximum in the oxidation current, drops slightly. A new working curve of ΔE_p *versus* ψ for the application of cyclic voltammetry to hydrogen molecule oxidation is shown in Figure 2. This working curve may be used to calculate a first-order reaction rate constant $k_s=(i_0/2FC_{H_2}^0)$, the corresponding first-order reaction rate, $k_s\,C_{H_2}$, and the exchange current density, $2F\,k_s\,C_{H_2}^0$, for hydrogen molecule oxidation.

EXPERIMENTAL DETAILS

Electrochemical Hydrogen Molecule Oxidation Kinetics

A conventional three chamber gas tight cell was used with extensive purification of the electrolyte. The test electrode consisted of a small platinum disc sheathed with PTFE. Purified nitrogen was passed through the cell, after which the electrolyte was saturated with hydrogen by the passage of hydrogen through the cell. For experiments above ambient temperature, the entire cell was placed in an oven with temperature control of ±1°K. A WENKING potentiostat programmed by a WAVETEK Model 112 signal generator was used for potentiodynamic scanning and the *i*-*V* curves recorded by a TEKTRONIX 561A oscilloscope with camera attachment. Both continuous cycling between 0 *V* (nhe) and 1.25 *V* (nhe), and single sweep scans from 0 *V* (nhe) were used. The internal resistance between the test electrode and the reference probe was measured by a current interrupter technique because at high potentiodynamic scan rates a significant error in the current peak potential shift can be introduced.

Hydrogen-Deuterium Exchange

The apparatus for measuring H_2–D_2 exchange rates is depicted in Figure 3. The reactor, gas mixing and sampling system were constructed entirely from Pyrex. The H_2, D_2 and HD concentrations were measured with a CEC mass-spectrometer, Model 21–614. A cylindrical Pyrex tube reactor

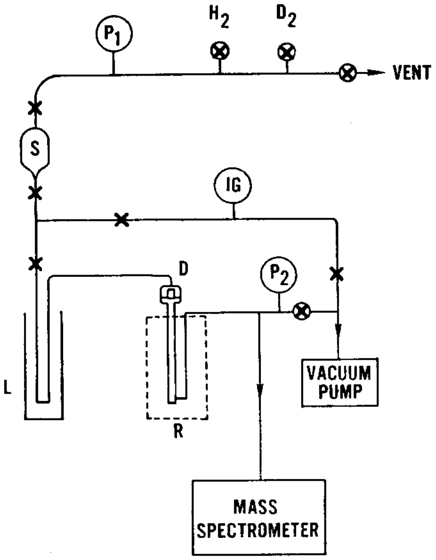

Fig. 3. Schematic of hydrogen-deuterium exchange apparatus. P_1, P_2, micro-pirani gauges; IG, Bendix G-17 ionization gauge; S, gas mixing bulb; L, liquid nitrogen trap; D, ground glass Dekker valve; R, catalytic reactor; X, 6 mm glass stopcocks; ⊗ needle valves.

containing the Pt wire catalyst was connected to the vacuum manifold and gas mixture bulb via a magnetically operated ground glass Dekker valve with intervening liquid N_2 trap, and to the mass-spectrometer sampling system by a 3 ft. length of 250 μm Pyrex capillary. Precision Gas Products Research Grade D_2 (97.5% D_2) and Precision Gas Products Ultra High Purity Grade H_2 (99.999% H_2) gases were separately metered into the storage bulb with partial pressures monitored by a calibrated micropirani gauge. Sampling from the reactor was continuous and at constant pressure, with the rate adjusted by a micrometer calibrated fine metering valve. Experiments carried out in an empty reactor confirmed there was no exchange in the gas handling system or on the walls of the mass-spectrometer.

Prior to sealing the platinum wire catalyst in the reactor tube, the platinum was electrochemically cleaned by potentiodynamic cycling and the absolute area obtained from the hydrogen atom adsorption in the usual manner16). This gave a determination of the true platinum surface area as opposed to the geometric area of the wire. The wire was then dipped into boiling nitric acid, washed in triply distilled water and sealed into the reactor tube. Prior to a run, the system was outgassed in vacuum at

773°K for 12 hours. For the purposes of comparison with BREAKSPEARE *et al.*[12], a cycle of treatments at 1 torr oxygen at 773–973°K followed by reduction in 2 torr hydrogen at 773°K and by outgassing at 773°K was also used. The exchange rate observed following this cycle of treatments was not significantly different from that observed following simple outgassing. The vacuum indicated by the ionization gauge was 2×10^{-6} torr and was limited by the vapor pressure of the silicone stopcock grease at room temperature. Since, however, the stopcocks were separated from the Pt wire catalyst by the liquid nitrogen trap, the effective vacuum in the reactor tube was probably in the ultra-high vacuum range, $\sim 10^{-9}$ torr.

Analysis of Exchange Reaction Kinetics

The H_2–D_2 exchange reaction was carried out batch-wise, by admitting the gas mixture to the reactor and closing the Dekker valve. Time zero was established by the appearance of D_2 in the mass-spectrometer. Due to a residual background of H_2 in the mass-spectrometer, the time progress of the reaction was monitored from the relative heights of the HD and D_2 peaks.

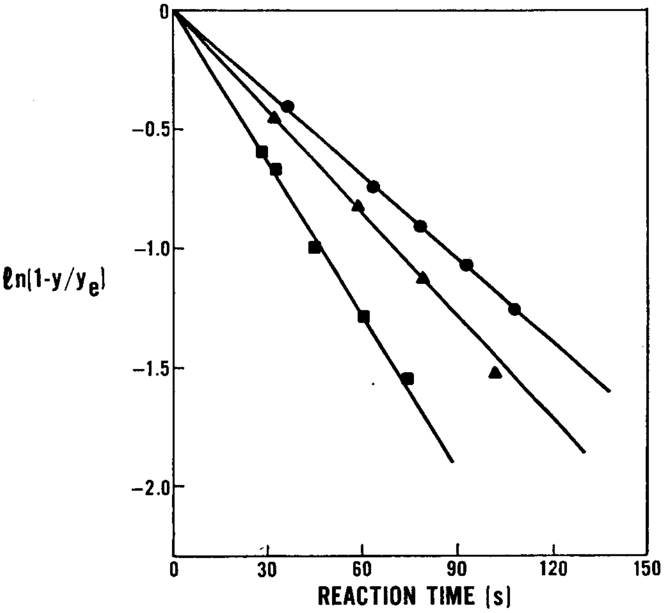

Fig. 4. Temperature dependence of $\ln(1-y/y_e)$ with time for stoichiometric mixtures of H_2 and D_2 on a platinum wire catalyst. 5 torr total pressure. ● 293; ▲ 357; ■ 415°K.

Let y be the conversion at time t, y_e the conversion at equilibrium.

$$\begin{array}{llll} & H_2 \; + & D_2 \; \rightleftarrows & 2HD \\ \text{Mole fractions:} & \dfrac{1-y}{2} & \dfrac{1-y}{2} & y \\ \text{Partial pressures:} & \left(\dfrac{1-y}{2}\right)P & \left(\dfrac{1-y}{2}\right)P & yP \end{array}$$

If R = (height of D_2 peak/height of HD peak) = P_{D_2}/P_{HD}, then $y = 1/(2R+1)$. The sampling rate was adjusted so that over the time course of the reaction to equilibrium the total reactor pressure changed less than 10%. If both the forward and reverse reactions follow first-order rate laws, then, for constant total pressure,

$$y/y_e = (1-e^{-kt}) \tag{10}$$

It was found that for pressures from 0.5—10 torr and temperatures from 300–500°K, plots of ln $[1-y/y_e]$ *vs.* t yielded straight lines, with slopes $-k$ (sec^{-1}), as shown in Figures 4 and 5. Then the absolute rate of exchange was calculated from

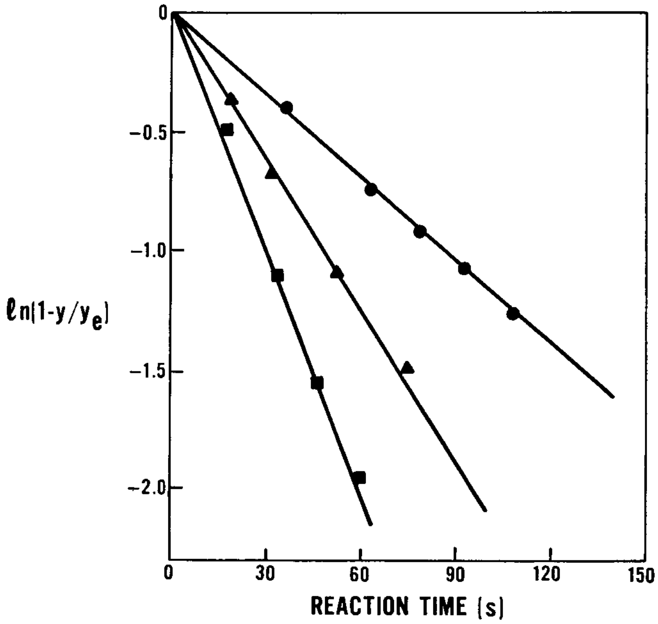

Fig. 5. Pressure dependence of ln $(1-y/y_e)$ with time for stoichiometric mixtures of H_2 and D_2 on a platinum wire catalyst. Temp. 293°K. ● 5.0; ▲ 2;0; ■ 0.5 torr.

$$r\left(\frac{molecules}{cm^2\,sec}\right)=\frac{kN}{A} \tag{11}$$

where N is the number of molecules in the reactor and A the area of the wire. For the purpose of comparison with the electrochemical results, it is convenient to define a rate-constant, k_s, such that the absolute rate is

$$k_s(N/V)=r \tag{12}$$

where V is the reactor volume, and $k_s\,cm/sec$, is equivalent to $\frac{Vk}{A}$.

RESULTS

As easily seen from Figure 5, the first-order rate constant for H_2–D_2 exchange was not independent of the total pressure for the temperatures of this investigation (>293°K). The true order of the reaction over the pressure range of 0.5–5 torr was 0—0.5, tending to zero at the highest pressure. For the purposes of comparing the rate of H_2–D_2 exchange with the electrochemical rate of hydrogen oxidation, the rate constants used were those measured at total pressures such that the coverage of the surface by adsorbed hydrogen and deuterium would approach a monolayer, which was the zero-order region of 5–10 torr total pressure.

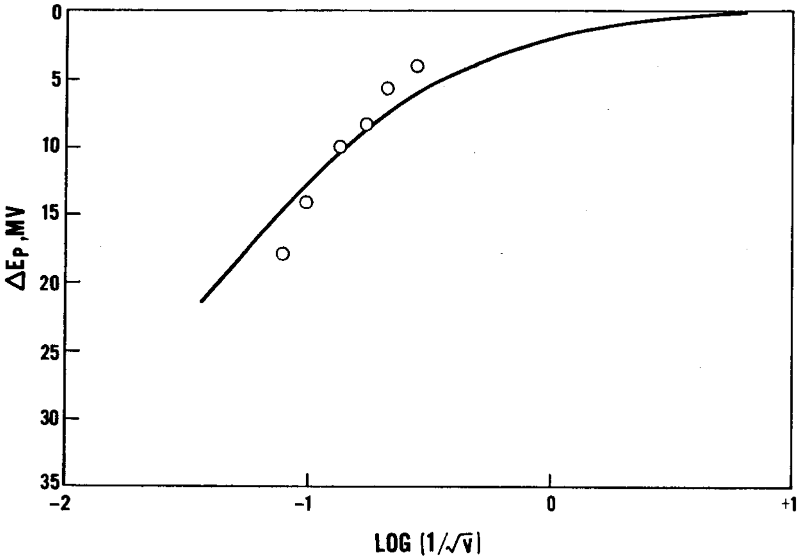

Fig. 6. Comparison of theoretical (solid line) curve for ΔE_p *vs.* $1/\sqrt{v}$ with $k_s=0.23$ cm/sec to the peak shift measured at different scan rates (v) at 293°K.

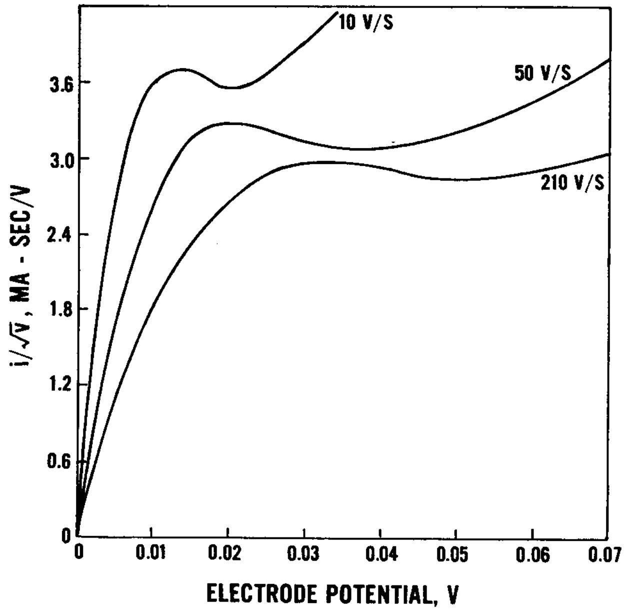

Fig. 7. Observed potentiodynamic scans showing the shift in the normalized anodic current peak potential from the quasi-equilibrium potential with increasing scan rate.

The shifts in oxidation current peak potentials as a function of sweep rate observed at 25°C are shown in Figure 6, and examples of i-ε curves observed at different scan rates are shown in Figure 7. The observed i-ε curves include, of course, the current produced by oxidation of adsorbed hydrogen which causes some overlap with the hydrogen oxidation current peak and produces the rising tail off the end of the peaks. The theoretical calculations were made only for the current produced by hydrogen molecule oxidation and therefore did not contain this background current. Qualitatively, the observed i-ε curves had the same features as the calculated curves, with the oxidation current peaks broadening and the normalized current, $i/\sqrt{v}$, dropping slightly as the peaks shifted with scan rate. The i-ε curves produced by continuous cycling from 0 V to 1.25 V (nhe) were identical to those produced by single sweeps from a rest potential of 0 V (nhe). It was observed experimentally that the switching potential could be lowered below 0 to $-.040$ V (nhe) without affecting the peak shift from the quasi-equilibrium peak. For negative switching $-.020$ V and $-.040$ V (nhe), i-ε curves for hydrogen saturated electrolyte were identical to those observed with the electrolyte purged with nitrogen. Apparently, the cathodic sweep to these negative potentials produces sufficient hydrogen evolution to saturate the diffusion layer around the plane electrode, so that for the anodic sweep, the initial condition is that of a hydrogen saturated electrolyte. The hydrogen molecule oxidation first-order rate constant, k_s, can be calculated from the peak shift observed for a given v and the value of ψ corresponding to the observed peak shift. This procedure yields a slightly different value of k_s for each v. A better procedure is to find the value of k_s which produces the best fit of the theoretical line for ΔE_p *vs.* $i/\sqrt{v}$. This was the procedure followed to find k_s for each temperature.

The first-order rate constants, k_s (*cm/sec*), calculated for H_2–D_2 exchange and the electrochemical hydrogen oxidation are shown in Figure 8 over a temperature range of 294–360°K. In calculating the electrochemical rate constant, the following physical constants were used: the hydrogen solubility in 20% H_2SO_4 was taken as 1×10^{-6} *mole/cm*^{3} and assumed to be essentially invariant over this temperature range; the hydrogen diffusivity was taken as $D=3.34\times10^{-4}\exp(-2\times10^3/RT)$ *cm*^{2}*/sec.* The exponential factor of 2 *kcal/mole* was assumed to be reasonable and the pre-exponential calculated from the observed[9)] diffusivity at room temperature. The apparent activation energy for H_2–D_2 exchange was 2.5 *kcal/mole*, and that for electrochemical hydrogen molecule oxidation was 4.2 *kcal/mole.* In view of the assumed temperature dependencies for the calculation of the electrochemical rate constant, the difference between 2.5 and 4.2 *kcal/mole* cannot be considered significant. In addition, the temperature dependence of the limiting current for hydrogen molecule oxidation in platinum porous layer electrodes[17)] indicated an apparent activation energy[18)] of 3.2 *kcal/mole* (298–433°K, 96% H_3PO_4).

The corresponding absolute reaction rates for $C^0_{H_2}$ (or N/V) of 1×10^{-6} *moles/cm*^{2} for H_2–D_2 exchange and electrochemical hydrogen molecule oxidation are shown in Figure 9, along with the separately measured rates of the oxidation of adsorbed hydrogen (VOLMER reaction). The rates of oxidation of adsorbed hydrogen were calculated from the rate constants for adsorbed hydrogen oxidation reported by STONEHART and LUNDQUIST[10)] and the surface concentration of adsorbed hydrogen on platinum, assumed to be 1.25×10^{15} molecules/cm^2, corresponding to a monolayer of adsorbed hydrogen atoms[12)], and independent of temperature.

DISCUSSION

The two main reasons, other than cleaning, for the electrochemical treatment of the Pt wire prior to insertion in the H_2–D_2 system were, firstly, to obtain an electrochemical measure of the active site area of the wire from hydrogen atom adsorption10) and secondly, to prepare a surface for the gas phase experiments which closely corresponded to the surface in the electrochemical experiments. The results presented in Figures 8 and 9 are based on two different normalizations, one using the nominal geometric area of the wire and the other using the area determined from the hydrogen atom adsorption using a potentiodynamic scan. Potential scanning of platinum in acid electrolyte is known19) to roughen the surface. To some extent, this roughness was lost when the platinum wire was heated to 773°K in the vacuum system. When the wire was removed from the system after the H_2–D_2 exchange experiments, the area determined from the first few potential scans was closer to the geometric area. The cross-hatched regions, therefore, of Figures 8 and 9 represent the uncertainty in determining the active surface present during the measure of the H_2–D_2 exchange rate. On the other hand, the potentiodynamic method of NICHOLSON14) utilized in this work for measuring the rate constant, k_s, for hydrogen oxidation does not depend on the active surface area present, so in this sense the electrochemical rate constants are more accurately determined than the gas phase rate parameters.

The absolute rates of H_2–D_2 exchange measured in this work compare favorably with the results reported by BREAKSPEARE *et al.*12) using Pt cleaned in ultrahigh vacuum (2×10^{-10} torr). In Ref (12), the absolute rate (273°K, 0.4 torr) was reported as 1.2×10^{17} for the wire cleaned by outgassing at $T>1223$°K. In the present work, the absolute rate (293°K, 0.5 torr) calculated from Figure 3 and Equation (2) was 6.6×10^{16} based on geometric area for the electrochemically cleaned wire. This difference is less than a factor of two which could easily be accounted for by differences in the roughness of the surface. The apparent activation energy reported by BREAKSPEARE *et al.*12) for the temperature 300–500°K was 3.0 *kcal/mole*, compared to 2.5 *kcal/mole* in the present work. In the present work, however, cyclic oxidation-reduction treatments of the Pt wire at 773–973°K did not produce a significant increase in the measured rate constant compared to a simple outgassing pre-treatment. BREAKSPEARE *et al.*12) showed an increase by a factor of three (200–500°K) for oxidation-reduction pre-treatment at 1073–1273°K. This enhancement must be associated with the higher temperature of their oxygen treatment and probably produced an increased roughness in the wire surface.

For temperatures above 200°K, the absolute rate of H_2–D_2 equilibration over Pt (both isotopes in the gas phase) is equal to the absolute rate of exchange between gaseous H_2 and adsorbed D_2 on Pt.[13,20,21] This result could only be observed if the equilibration of the gaseous isotopes occurs over a Pt surface covered by the amount of adsorbed H and D atoms in equilibrium with the total gas pressure. Thus the rate at which a stoichiometric mixture of $H_2 : D_2$ proceeds to the equilibrium mixture of $H_2 : D_2 : HD$ (the absolute rate of H_2–D_2 exchange) will be controlled by the equilibrium coverage of the Pt surface for the temperature and total pressure of the experiment. There is a consensus among recent investigators[12,13] that the H_2–D_2 exchange over Pt proceeds *via* the Bonhoeffer-Farkas mechnism for exchange temperatures greater than 200°K. It is possible that the rate of this mechanism is limited by the rate of surface diffusion of H (D) atoms rather than the rate of H_2 (D_2) dissociation. Measurements of H (D) atom diffusion rates[22,23] across the metal surface by field-emission microscopy indicated that the collision rate of adsorbed atoms at 400°K was 10^4 greater than the rate of exchange at equivalent conditions and it is, therefore, unlikely that surface diffusion is limiting the rate at the temperatures of this work. The first order rate constant therefore, for H_2–D_2 exchange observed experimentally can be interpreted in terms of the general hydrogen dissociation rate expression of equation 1. When the hydrogen dissociative adsorption is at equilibrium, the rate of H_2 (D_2) dissociation is given by

$$r_{\mathrm{HD}} = k_{\mathrm{HD}} C^0_{\mathrm{H}_2}(1-\theta_0)^2 = (k_{\mathrm{HD}} P_{\mathrm{H}_2}/RT)(1-\theta_0)^2 = k_{\mathrm{HD}}(n/V)(1-\theta_0)^2 \quad (13)$$

where θ_0 is the equilibrium coverage of the Pt surface by H (D) atoms at the total pressure P_{H_2}. By comparison with Equation (12), it is clear that the empirical first-order rate constant $k_s = k_{\mathrm{HD}}(1-\theta_0)^2$.

Similarly, the empirical first-order rate constant for electrochemical hydrogen molecule oxidation can be readily interpreted in terms of the TAFEL-VOLMER mechanism, Equation (2). From (2), the exchange current density for hydrogen oxidation will be given by

$$i_0 = nFk_{\mathrm{at}} C^0_{\mathrm{H}_2}(1-\theta_0)^2 = nFk_{\mathrm{ct}}\theta_0^2 \quad (14)$$

Since $k_s = i_0/nFC^0_{\mathrm{H}_2}$, clearly $k_s = k_{\mathrm{at}}(1-\theta)^2$. Thus, the empirical first order rate constants for H_2–D_2 exchange and electrochemical hydrogen molecule oxidation refer to the same chemical step if, and only if, the hydrogen oxidation proceeds *via* a TAFEL-VOLMER sequence with the hydrogen dissociation (TAFEL) step rate limiting.

The empirical first-order rate constant for both gas-phase hydrogen dissociation and electrochemical hydrogen molecule oxidation contains a term which refers to the coverage of the Pt surface by adsorbed hydrogen.

For a comparison of the absolute value of the rate constants for the two systems to be meaningful, it is necessary that for the experimental conditions of measurement, the coverage of the Pt surface by adsorbed hydrogen be the same for the two systems. The H_2-D_2 exchange reactions were carried out at total pressures (5—10 torr) where, for the temperature range 273—373°K, adsorption of hydrogen on Pt from the gas phase reaches monolayer saturation coverage as indicated by the order of the exchange reaction approaching zero at this pressure. Bett *et al.*[24] have shown

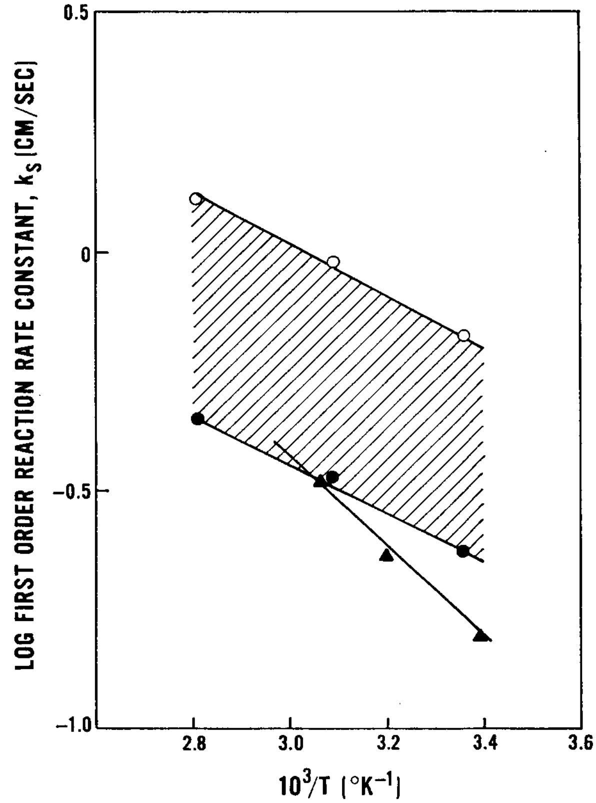

Fig. 8. Comparison of first order rate constants for electrocatalytic oxidation of hydrogen molecules on platinum with the gas phase first order rate constants for hydrogen-deuterium exchange.

▲, Electrocatalytic hydrogen molecule oxidation (real surface area)

○, H_2-D_2 exchange (geometric area)

●, H_2-D_2 exchange ("real" surface area from electrochemical determination of Pt site density).

that the equilibrium coverage of adsorbed hydrogen on Pt in acid electrolyte is equal to the gas-phase saturation hydrogen coverage on Pt at 298°K. This coverage is usually taken arbitrarily as a monolayer for the purposes of surface area calculations. For the purpose here of comparing rate constants, the absolute magnitude of the coverage is not of concern. The necessary and important conclusion is that the hydrogn coverages on Pt are equivalent in the two systems for the experimental conditions of this work.

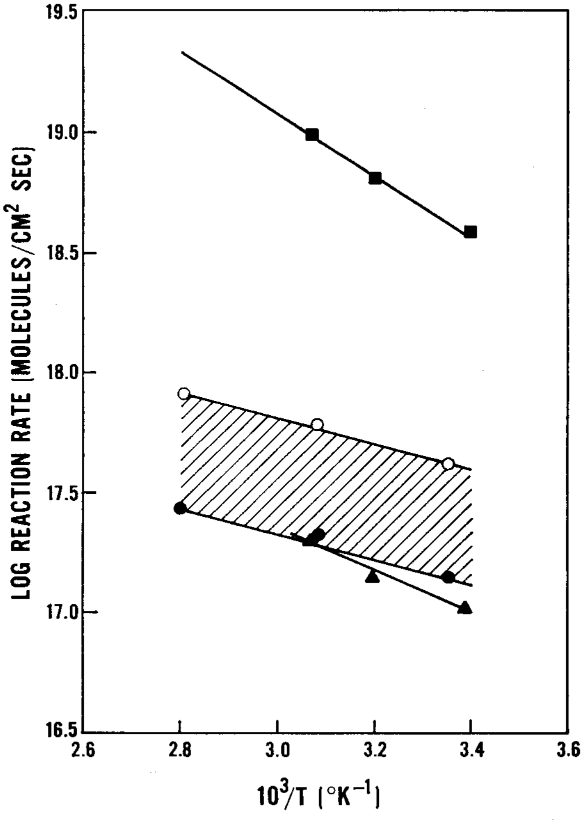

Fig. 9. Comparison of absolute reaction rates for electrocatalytic hydrogen molecule oxidation and adsorbed hydrogen atom oxidation on platinum with the gas phase H_2–D_2 exchange.

■, Electrocatalytic adsorbed hydrogen atom oxidation (VOLMER reaction, real surface area)

▲, Electrocatalytic hydrogen molecule oxidation (real surface area)

○, H_2–D_2 exchange (geometric area)

●, H_2–D_2 exchange ("real" surface area from electrochemical determination of Pt site density).

It is clear from Figure 8 that the first-order rate constants for H_2–D_2 exchange on platinum and electrochemical hydrogen oxidation are in close agreement. The agreement appears even better when the absolute rates of H_2–D_2 exchange and hydrogen molecule oxidation, shown in Figure 9, are compared to the absolute rates of the electron transfer (VOLMER) reaction, which is more than an order of magnitude larger than either of the former reactions. In addition, the activation energy for the VOLMER reaction is twice as great as the hydrogen molecule oxidation reaction and H_2–D_2 exchange (BONHOEFFER–FARKAS) reaction. The results obtained in this work show that the elementary surface reactions on platinum catalysts involving hydrogen molecules are the same in both gas phase and electrochemical catalysis. The proviso is that kinetic comparisons must be carried out at equivalent adsorbed hydrogen coverages. The correspondence between the electrochemical rate data and the gas phase exchange results argues that the rate determining step for the electrochemical hydrogen molecule oxidation is the dissociative chemisorption of the hydrogen molecule (TAFEL reaction) rather than the HEYROVSKI or HORIUTI reactions. It would be extremely unlikely that the rates of either the HEYROVSKI or HORIUTI reactions would be numerically equal to the TAFEL reaction and at the same time give identical activation energies. In any case, the H_2–D_2 exchange reaction can be used as a test reaction for directly determining the activity of model electrocatalysts. This technique has the special advantage that it eliminates the complications that arise from porous electrode structures and electrolyte impurities.

References

1) T. ERDEY-GRUZ, M. VOLMER, *Z. Physik Chem.*, **150 A**, 203 (1930).
2) J. TAFEL, *Z. Physik Chem.*, **50**, 641 (1905).
3) K. J. VETTER, "Electrochemical Kinetics", Academic Press, New York-London p. 519 (1967).
4) J. HEYROVSKI, *Rec. Trav. Chim. Pays-Bas*, **46**, 582 (1927).
5) J. O'M. BOCKRIS and A. K. N. REDDY, "Modern Electrochemistry", Volume 2, Plenum Press, New York, p. 1250 (1970).
6) R. WOODS, *J. Electroanal.* **49, 217** (1974).
7) M. BREITER, "Electrochemical Processes in Fuel Cells", Springer-Verlag, New York, p. 51 (1969).
8) J. HORIUTI and G. OKAMOTO, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo) **28**, 231 (1936) and J. HORIUTI, this Journal **3**, 52 (1954).
9) J. S. BAGOTZKY and N. V. OSETROVA, *J. Electroanal. Chem.* **43**. 233 (1973).
10) P. STONEHART and J. T. LUNDQUIST, *Electrochim. Acta*, **18**, 907 (1973).
11) P. STONEHART and G. KOHLMAYER, *Electrochim. Acta*, **17**, 369 (1972).

12) R. J. BREAKSPEARE, D. D. ELEY and P. R. NORTON, *J. Catalysis,* **27,** 215 (1972).
13) S. TSUCHIYA, T. AMENOMIYA and R. J. CVETANOVIC, *J. Catalysis,* **20,** 1 (1971).
14) R. S. NICHOLSON, *Analytical Chemistry,* **37,** 1351 (1965).
15) W. VOGEL, J. LUNDQUIST, P. ROSS and P. STONEHART, *Electrochim. Acta* **20,** (1975).
16) P. STONEHART, *Electrochim. Acta,* **15,** 1853 (1970).
17) W. VOGEL, J. T. LUNDQUIST and A. BRADFORD, *Electrochim. Acta,* **17,** 1735. (1972).
18) G. NASHICK, Paper #32, Electrochem. Soc. Meeting, Detroit, Mich. 1969.
19) K. KINOSHITA, J. T. LUNDQUIST and P. STONEHART, *J. Electroanal. Chem.,* **48,** 157 (1973).
20) G. C. A. SCHUIT and L. L. Van REIJEN, *Advan. in Catalysis* **10,** 242 (1958).
21) G. K. BORESKOV and A. A. VASSILEVITCH, *Actes Congr. Int. Catal. 2nd* **1960,** 1, 1095 (1961).
22) R. GOMER, R. WORTMAN and R. LUNDY, *J. Chem. Phys.,* **26,** 1147 (1957).
23) R. LEWIS and R. GOMER, *Surface Science,* **17,** 333 (1969).
24) J. A. S. BETT, K. KINOSHITA, K. ROUTSIS and P. STONEHART, *J. Catalysis,* **29,** 160 (1973).