the steel surface at 40°. On heating the treated steel surface to 400°, however, some changes occurred. As shown by spectrum C, the P–O–C bands near 1190 and 1242 cm^{-1} disappeared, as did the prominent 975-cm^{-1} band. As spectrum C shows remnants of the 1300-cm^{-1} band and of the 1500- and 1600-cm^{-1} aromatic bands, this suggests that cleavage of the P–O–C linkage occurred in the tricresyl phosphate that remained on the surface and did not evaporate, some products containing P–O groups and aromatic systems remaining bound to the steel surface after the 400° heating.

The feasibility of measuring low-temperature emission spectra has been shown by these as well as by other experiments during which the infrared emission spectra of oleic acid on aluminum surfaces at 22° were measured with results (*1*) similar to those observed at higher temperatures. Numerous applications of the method to topics such as boundary lubrication or catalysis or biological systems readily come to mind. However, some difficulties remain. The resolution is relatively poor at present, but this particular failing is more than offset by the ability to observe spectra. The resolution problem, technological in origin and beyond the scope of the present discussion, is being improved. Also, the intensity–temperature behavior of emission bands, the total change in emission when a surface reaction occurs, the stability of a surface during long scanning periods and similar effects, some of which will be characteristic of the system examined, can be expected to cause some difficulty in the interpretation of emission data.

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Nature of the Surface of a Platinum-Rhodium Alloy in Electrocatalysis

In recent years alloy surfaces have been used increasingly as electrode materials, particularly in connection with the oxidation of hydrocarbons (*1*). Little is known concerning the nature of the electrode surface of the catalyst. In this communication we report a phenomenon bearing on this for platinum-rhodium alloy catalysts.

In Figs. 1 and 2 are shown the steady state potential–log rate relationships for

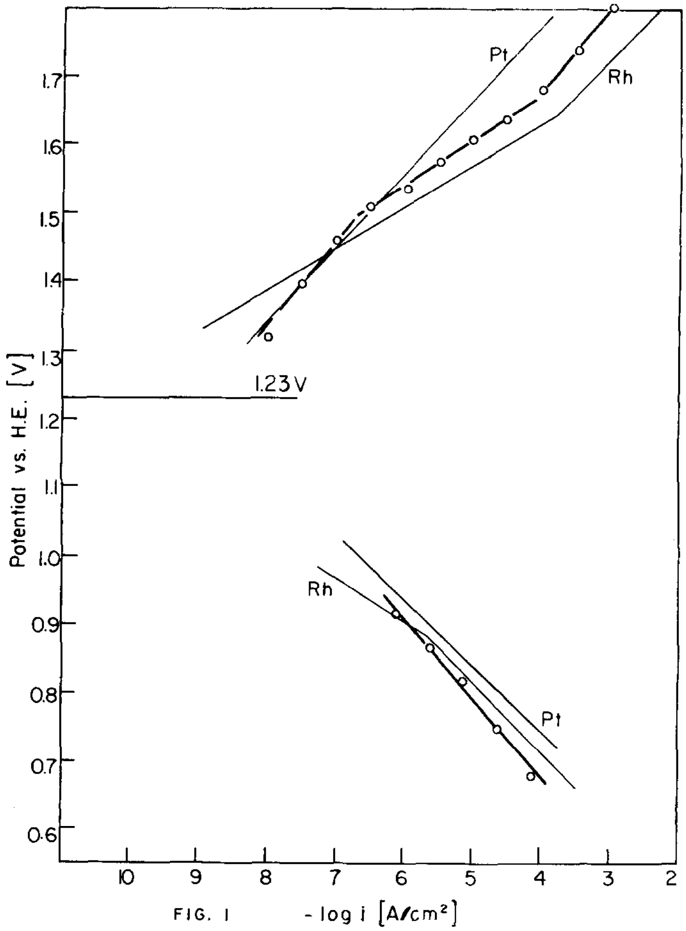

FIG. 1

FIG. 1. Steady state V–log i relation for O_2 evolution and dissolution reactions on a Pt–40 at % Rh alloy electrode (open circles) in acid solution (1 N $HClO_4$). Data for Pt and Rh electrodes are included as full lines (*2*, *3*).

the electrochemical oxidation of water to oxygen and the cathodic reduction of oxygen to water for substrates of rhodium (*2*), platinum (*3*), and platinum-rhodium (*2*) alloy (40 at % Rh). The observed behavior cannot be accounted for by any simple electrode reaction mechanism.

It is clear from the relations given on the alloy electrode that the reactions, both the oxidation to O_2 and the reduction to H_2O, follow the kinetic characteristics corresponding to the individual metals, whichever has the faster rate at a given electrode potential, and not some intermediate value as might be expected had some homogeneous oxide-alloy surface been present. [It is known from other data (*3–5*) that the electrodes under conditions at which the reactions occur are covered with a layer of a few angstroms of oxides.]

The likely interpretation of this result is that the homogeneous alloy substrate has become a heterogeneous mixture of a platinum oxide and a rhodium oxide. Though the reaction takes place on both oxides, the overall rate is determined by the rate for that oxide on which the reaction at the given potential proceeds faster. This means that the reaction will preferentially occur on the specific oxide depending on the electrode potential. Thus, on the anodic side, the reaction at higher electrode poten-

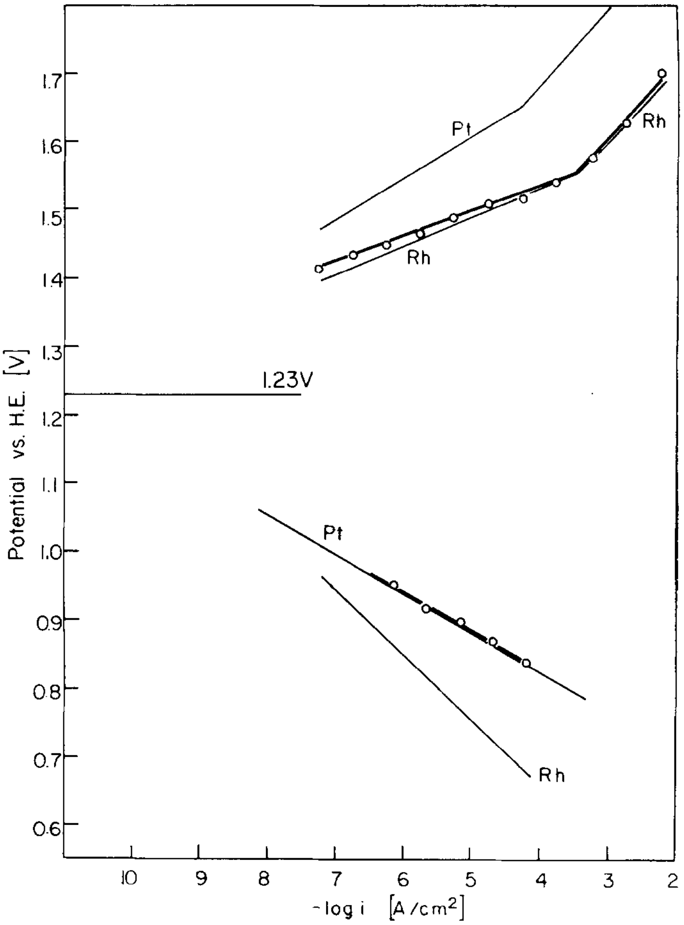

FIG. 2. The same as in Fig. 1 but for alkaline solution (*2, 3*) (1 *N* KOH).

tials occurs predominantly on rhodium oxides. At low anodic potentials in acid solution, the rate of the overall reaction is determined by the rate on Pt oxides (Fig. 1). The cathodic reaction occurs in alkaline solution predominantly on Pt oxides; in acid in the potential range examined both oxides are equally active, and the reaction occurs on both of them.

A reason for this situation may be tentatively suggested as follows. When a platinum-rhodium alloy surface undergoes anodic oxidation, it is probable that the platinum and the rhodium atoms alternatively (since there is almost an equal atomic composition of the alloy) leave the kink sites and diffuse across the surface of the metal. Nucleation at individual patches containing platinum and oxygen, and those containing rhodium and oxygen, must occur *respectively* on the surface, effectively to form platinum oxides and rhodium oxides. The reason that this nucleation occurs to the individual oxide phases and not to mixed oxides is unclear, though the evidence for it presented here is thought to be convincing, and of application in the rational design of alloy catalysts.

The above example illustrates the importance of knowing the nature of an electrode surface, particularly of an alloy electrode at any given experimental condition. The surface of a single-phase alloy electrode may become a true polyelectrode in the sense that the same overall reaction may proceed with different mechanisms and rates on two different electrode sites. This situation should, however, be differentiated from the case (of polyelectrodes) in which two or more different reactions occur simultaneously on the same electrode surface. For the latter, a term like polyreaction seems to be more suitable.

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On the Variation of the Activation Energy of a Catalytic Reaction as a Consequence of the Doping of Semiconductor Catalysts

The search for correlations between the catalytic activity of a semiconductor and its electronic structure, which can be modified by doping, leads one to regard as an argument in favor of the electronic theory of catalysis the fact that *the measured activation energy* of a reaction varies with the introduction of dopes. In this way, for example, the introduction of lithium or gallium into oxides such as ZnO or NiO leads to catalysts for which the activation energy for a catalytic reaction is either decreased or increased with respect to the activation energy observed for the undoped oxide. Since at the same time the Fermi level of these solids is modified by the doping, and also the concentration of charge carriers is decreased or increased, often with a variation of the activation energy of the electrical conductivity, a correlation seems to be found between the electronic structure of the catalyst and its catalytic activity.

The explanation of numerous experimental data relative to the modification of the apparent activation energy for the reaction when dopes are introduced into the catalyst can equally be sought in considering the *variation of coverage of the surface* of the catalyst by the reactants and the products and its effect on the apparent activation energy of the reaction.

I. VARIABLE ORDER OF REACTION

a. Pure catalyst. It is easy to establish (*1*), assuming that the adsorption of the reactant follows a Langmuir isotherm, that for a unimolecular heterogeneous reaction the apparent activation energy, E_a (measured), is the "true" activation energy decreased by the heat of adsorption, Q, of the reactant when this last covers only a small fraction of the catalyst surface

$$E_a = E - Q$$

When on the other hand, the surface is almost completely covered, the apparent activation energy for the reaction is no