Measurement of Charge Carriers in the Palladium-Hydrogen System*

The catalytic activities of various metals and alloys have been studied for a wide range of reacting systems (*1*). One of the interesting observations has been the effect of hydrogen on the catalytic properties of palladium and nickel, and their respective alloys with gold and copper. Thus for the parahydrogen conversion (*2*) it was reported that pre-exposure of the pure metal, Pd, to hydrogen markedly reduced its catalytic activity. More recently the work on the hydrogenation of some olefins on Ni and Ni-Cu alloys (*3*, *4*) and on Pd and Pd-Ag alloys (*5*) demonstrated that pretreatment with hydrogen promoted the activity of the alloys while it reduced that of the pure transition metals. It is highly speculative whether this effect of hydrogen sorption may be attributed to geometric or electronic factors, or whether it is a surface or bulk phenomenon. Some information concerning the electronic properties of a catalyst may be obtained from measurements of the Hall coefficient.

In this paper we describe some recent experimental measurements of the Hall coefficient of palladium in the presence of hydrogen. These data are compared with those found for the Pd-Au and Pd-Ag alloys.

The deflection of charge carriers in a metal or semiconductor when exposed to a magnetic field has become a valuable tool in solid state research. These measurements yield valuable information on the polarity of the carriers, their mobility, and their density. In a conductor (thickness d) placed in a magnetic field (of strength B_Z) perpendicular to the direction of current flow, a voltage is developed across the sample in a direction perpendicular to both the current and the magnetic field. This Hall voltage V_{H} is proportional to the product of the input current I_X and the magnetic flux density: $V_{\mathrm{H}} = R_{\mathrm{H}} I_X \ (B_Z/d)$. The proportionality constant R_{H} is commonly referred to as the Hall coefficient, which is taken to be negative for materials in which electrons are the majority carriers, and positive where holes are the majority carriers. Thus for a sample of fixed thickness the Hall coefficient may be obtained from measurements of the Hall voltage as a function of magnetic field strength at constant input current (*6*).

The two-band model commonly employed relates the Hall coefficient to the additive contributions of electrons and holes

$$-R_{\mathrm{H}} = \frac{1}{N|e|} \frac{n_{\mathrm{e}}\mu_{\mathrm{e}}{}^2 - n_{\mathrm{h}}\mu_{\mathrm{h}}{}^2}{(n_{\mathrm{e}}\mu_{\mathrm{e}} + n_{\mathrm{e}}\mu_{\mathrm{e}})^2} = \frac{1}{N|e|n^*} \quad (1)$$

where N is the number of atoms per cubic centimeter; e, the electronic charge; n, the number of charge carriers per atom; μ, their mobility; and the subscripts e and h refer to electrons and holes. The parameter n^* is the effective number of conduction electrons in analogy to the free-electron model (*7*, *8*). In solid metals the free-electron value is to be expected for a spherical Fermi surface and an isotropic relaxation time. Departures from the theoretical free-electron value are observed.

The palladium specimens used were metal strips (15 mm long, 2 mm wide, and 0.5 mm thick) with two extensions on one side (3 mm long and 0.5 mm wide) and a similar one on the opposite side. These extensions were for making the contacts for the Hall-voltage leads. The pair of extensions were connected to a potentiometer and electrically balanced to match the single lead on the opposite side. Palladium wires were used in order to eliminate generation of thermoelectric effects. The specimens were vacuum-annealed before assembling.

Electric currents of up to 5 A were used. These were supplied by a heavy-duty automobile battery. It was necessary, however,

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to mount the battery on a grounded metal plate in order to eliminate pickup of extraneous fields by the battery.

With the magnet used in the Hall measurements (4-inch Varian) field intensities of about 14 kOe could be obtained. The Hall voltage was fed into a 150 A microvolt-ammeter (Keithley) which acted chiefly as a preamplifier, since the Hall voltage was recorded on an x–y recorder (Electronics Associates). With this arrangement useful measurements could be made by plotting Hall voltages at 0.4 μV/inch.

The palladium was charged with hydrogen electrolytically at room temperature. The electrolyte was 0.1 N H_2SO_4 and the current around 6 mA. Charging times of up to 12 hr were used.

The usual procedure consisted in removing the specimen from the electrolytic cell. After washing the sample in distilled water and alcohol, an electrical resistivity measurement was made. Attempts to make immediate Hall measurements were unsuccessful because of the large fluctuations in the Hall voltage which occurred intermittently. After letting the specimen rest for several hours these intermittent changes disappeared and satisfactory plots of Hall voltage vs. applied field could be obtained. The resistivity measurements were related to the hydrogen content of the sample. These measurements showed little loss of hydrogen for periods as long as 12 hr.

In order to examine our experimental technique the Hall coefficients of two pure metals, Pd and Ni, were measured (Table 1). Subsequently hydrogen was introduced into the Pd specimen and the resistivity and Hall coefficient evaluated as a function of the atomic ratio H/Pd. From the data listed in Table 1 it may be seen that no change in Hall coefficient occurs with the addition of hydrogen to palladium. This behavior is entirely different from that observed during the alloying of Pd with a Group IB metal, such as Ag (*9*). Under these conditions, an increase in the Hall coefficient is measured, with a maximum appearing near 40 atom % silver (*10*). It is of interest that the maximum in the Hall coefficient occurs near the same Pd-Ag alloy composition for which a maximum in the hydrogenation rate of ethylene has been reported (*5*). A quantitative theoretical analysis of this problem is hampered by the complexity of the band theory of metals, especially transition metals. However, the data presented suggest a contributing role played by electronic carriers in heterogeneous reaction. The most likely parameter affected by the addition of hydrogen or Group IB metal to Pd is the carrier density and carrier mobility. Magnetic susceptibility measurements indicate a monotomic decrease in hole density with additive. It may be surmised therefore that carrier mobility is the important parameter. The formation of a substitutional alloy in the case of Pd-Ag as compared to an interstitial one in the case of Pd-H would be expected to modify carrier mobility in different ways for the two systems under consideration. Most likely the interstitial hydrogen offers a larger scattering cross section to the holes and electrons than the substitutional silver.

TABLE 1

HALL COEFFICIENT OF PALLADIUM IN PRESENCE OF HYDROGEN AT 297° ± 3°K

Metal	Resistivity ($\mu\Omega \cdot$ cm)	H/Metal[a] (atom ratio)	Hall coefficient (cm^3/coulomb) × 10^5		
			This work	Literature	
Ni	7.36	0	−5.6[b]	−5.7[c]	−6.1[d]
Pd	11.22	0	−7.6	−6.8[d]	−7.5[e]
Pd	12.47	0.10	−7.3[f]		
Pd	15.95	0.48	−7.3[f]		
Pd	19.46	0.78	−7.4[f]		

[a] From resistivity data of R. J. Fallon and J. W. Castellan, *J. Phys. Chem.* **64,** 160 (1960).

[b] Due to ferromagnetism of Ni the extraordinary Hall coefficient was also measured and found to be 7.68 × 10^{-2} cm^3/coulomb in good agreement with the published value (footnote[c]).

[c] Gray, D. E., ed., "American Institute of Physics Handbook," pp. 5–237. McGraw-Hill, New York, 1957.

[d] Condon, E. U., and Odishaw, H. eds., "Handbook of Physics." McGraw-Hill, New York, 1963.

[e] Schindler, A. J., *J. Phys. Chem. Solids* **1,** 42 (1956).

[f] The apparent small decrease in Hall coefficient can be attributed to the increase in specimen thickness inherent to the absorption of hydrogen.

Further work is in progress to clarify the relationship between electronic structure and catalytic reactivity.

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Selective Poisoning of Al_2O_3 Catalysts

In connection with fundamental research into the catalytic properties of gamma alumina for the isomerization of the *n*-butenes important information could be obtained from poisoning experiments using triethylamine. An instrument comprising a microreactor with 200 mg of catalyst and a gas-liquid chromatograph was used to determine the activity by means of the pulse technique. With a fresh (conditioned) catalyst three pulses had to be injected into the carrier gas stream before a constant conversion was found. Then small amounts of triethylamine dissolved in cyclohexane were injected in a sequence. After each injection the catalytic activity was measured in the indicated way. The amine strongly poisoned the catalyst while the activity was not affected by the cyclohexane alone.

Typical results obtained with the *n*-butenes on samples of the same catalyst batch are given in Fig. 1a,b,c. In certain parts of the graphs linear relations are found and in some cases the slopes are found to change rather abruptly. The horizontal parts of some curves are due to the fact that interconversion of butene-1 (b-1) and *cis*-butene-2 (c.b-2) is rapid and easily leads to equilibrium compositions. The results seem to show that two points on the horizontal axis are relevant for the different feed materials and reaction products. The original part of the curve valid for formation of *trans*-butene-2 (t.b-2) from b-1 or c.b-2 can be extrapolated to the same end point on the horizontal axis as the curves for conversion of the t.b-2. This seems to indicate that for reactions in which t.b-2 is involved one should distinguish between two types of active centers. The sites which are poisoned selectively from the beginning are active for conversion and formation of t.b-2. The sites which are poisoned in second instance have no activity for t.b-2 conversion and only a limited activity for t.b-2 formation. For the conversion of b-1 and c.b-2 both active centers behave identically.

For the interpretation of the results it seems important to note that t.b-2 because of its structure cannot come with its double bond near to a flat surface. The shortest distance is approximately 1.5 Å as compared to 0.6 Å for the other butenes (*1*). This could mean that certain active centers can easily interact with the π electrons of b-1 and c.b-2 but not with the π electrons of t.b-2. On those sites formation of t.b-2 is