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Hydrogen–Deuterium Exchange on Evaporated Films of Platinum and Platinum–Gold

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The exchange of gaseous hydrogen with deuterium adsorbed on Pt or Pt–Au alloy films, prepared under ultra-high vacuum, was studied in the temperature range 78 to 300 K.

Chemisorptive titration results confirm that the surface composition is equal for all equilibrated Pt–Au films with overall composition within the miscibility gap. The measured ratio of adsorbed H/adsorbed Xe supports our model that the gold-rich phase envelops the crystals of the platinum-rich phase.

The Arrhenius plots of the H/D exchange are linear for the alloys but show a distinct break at ~110 K for Pt. The apparent activation energy and reaction order are identical on the alloys and for the low temperature reaction on Pt. The initial ratio of D_2/HD in the reaction product is in excess of the equilibrium ratio at all temperatures studied. This is interpreted by an appreciable contribution of a Bonhoeffer-Farkas mechanism even at 78 K.

I. INTRODUCTION

In our laboratory catalytic reactions on alloys are systematically studied and some results on reactions of hydrocarbons have been published (*1–4*). Whereas reactions of hydrocarbons and other materials are usually accompanied by self-poisoning due to side reactions, the hydrogen equilibration reaction,

$$H_2 + D_2 \rightleftarrows 2HD,$$

does not suffer from this complication. However, as this reaction proceeds even at very low temperatures (78 K) with an immeasurably high rate on many metals its value as a diagnostic tool is limited. In this respect the related so-called exchange reaction,

$$D_{ads} + H_2(gas) \rightleftarrows HD(gas) + H_{ads}, \qquad (1)$$

is more attractive as it proceeds with a measurable rate on metal films. An additional advantage is that the fraction of the surface which actually participates in the reaction is automatically revealed, in contrast to the equilibration reaction for which it often remains unknown whether it is catalysed by a very small or a large number of active sites.

Both reactions have been the subject of many studies and mechanisms have been suggested by Bonhoeffer and Farkas (*5*), Rideal and Eley (*6*), Couper and Eley (*7*), Boreskov (*8*), and by Schwab and Kilmann (*9*). The question arises whether new relevant information on this controversial subject can be obtained by diluting the active platinum sites in an inactive matrix of gold. This has motivated the work reported in the present paper on the exchange reaction with Pt–Au alloys.

II. EXPERIMENTAL METHODS

Apparatus

The ultrahigh vacuum system was similar to the one described earlier (*1*), but some minor modifications were made to improve the rate of mass transfer. The gas composition was monitored by a bakeable mass spectrometer (MS 10, AEI) connected to the system via a Granville-Phillips valve.

Alloy films were prepared by simultaneous evaporation of the metals, with glass walls kept at 300°C. Both metals were evaporated from tungsten wires placed in the center of the adsorption vessel, acting virtually as "point" sources. After evaporation the films were sintered at 300°C for 3 hr. From xenon adsorption measurements the roughness factor of the films was found to be 1.3–1.4.

Calculations and also an experiment with xenon as diluent gas showed that the measured rate was not mass transfer limited. The upper limit of the measurable rates was given by the speed of response of the mass spectrometer amplifier. The mass spectrometer was calibrated for protium (H_2) and deuterium (D_2) against a condensator manometer. The sensitivity of protium deuteride (HD) was taken to be the average of those of H_2 and D_2.

Materials

Spectroscopically clean metals were used (Drijfhout, Amsterdam). The alloy composition of the films was determined by weighing the tungsten wires before and after evaporation. Neutron activation analysis of samples from different places in the vessel showed a satisfactory homogeneity. The gases used were from l'Air Liquide, Brussels.

Measuring Procedure

The surface area of the film was first measured by deuterium adsorption at 298 K in the pressure range of 1–5 × 10^{-3} Torr (1 Torr = 133 N m^{-2}). The number of adsorbed H atoms is called H_S. Then the pressure of deuterium was increased to about 1 Torr and after 10 min the excess deuterium was pumped away. In a "standard" procedure the pumping proceeded up to a pressure of 1 × 10^{-4} Torr, then the reaction volume was isolated from the pumps and brought to the desired temperature of the exchange experiment. When a stable temperature was attained, about 0.1 Torr of protium was admitted and the reaction followed by the mass spectrometer. When the exchange reaction was ended the system was pumped again. By admitting 1 Torr of deuterium the protium adsorbed on the surface was exchanged against deuterium; subsequently the whole measurement could be repeated. The measured reaction rate was found to be reproducible several times under equal conditions with the same film.

In some experiments the pumping period was prolonged so that an ultimate pressure of about 1 × 10^{-7} Torr was attained ("exhaustive pumping"); in other experiments the adsorption vessel was cooled at a pressure higher than 1 × 10^{-4} Torr ("supplementary adsorption").

III. RESULTS

1. Surface Composition

Figure 1 shows the adsorption of hydrogen at 298 K per unit xenon adsorption (i.e., per unit total surface) as a function of the alloy composition. The parameter α is defined by

$$\alpha = \frac{\text{atoms } H_{\text{ads}}}{\text{atoms } Xe_{\text{ads}}}.$$

Assuming that the hydrogen adsorption at 2 × 10^{-3} Torr and 298 K is specific for the platinum atoms in the surface (gold does not adsorb molecular hydrogen under these conditions), Fig. 1 shows that the surface composition is constant for a wide range of alloy concentrations.

2. Exchange on Platinum

The time course of exchange at 78 K is illustrated in Fig. 2 by the recorded ion currents for masses 3 and 4. Similar graphs are recorded at higher temperatures. Two stages of exchange can be distinguished: (I) An initial fast exchange where the formation of HD is accompanied by desorp-

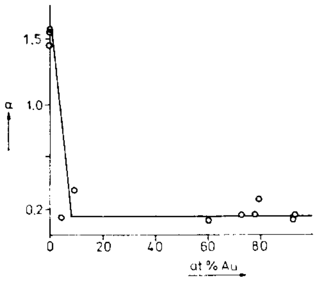

FIG. 1. α as a function of the alloy composition.

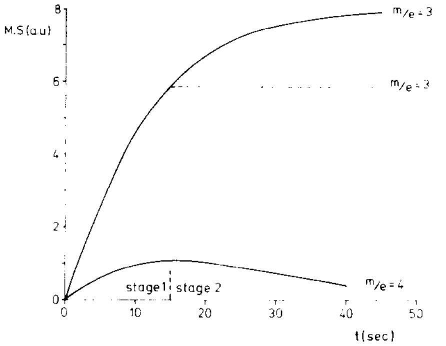

FIG. 2. — Time course of the exchange reaction on Pt ($T = 78$ K). --- Reaction with atomized deuterium on Pt ($T = 78$ K).

tion of significant quantities of D_2 ($t < 15$ sec); and (II) a slow exchange where the equilibration $H_2 + D_2 \rightleftarrows 2HD$ contributes to the formation of protium deuteride while the D_2 concentration decreases ($t > 15$ sec). It is evident that the overall exchange is a complicated process. A similar behavior was found by Eley and Norton (*10*) and Boreskov (*11*) with nickel. In the present results, however, the formation of D_2 in a large excess compared to the quantity expected on the basis of simple statistics shows the occurrence of a reaction which we shall call an R'' process in generalizing the terminology introduced by Klier *et al.* (*12*) on the exchange reaction of oxygen isotopes. The existence of an R'' process in hydrogen isotope reactions had been reported previously by us for the reactions of gaseous deuterium with potassium anthracene complexes (*13*).

The time course of the overall exchange process can be linearized in semilogarithmic coordinates as can be seen from Fig. 3. This kind of plot was obtained for more than 300 experiments, indifferent of temperature, pressure, and catalyst composition. Always a perfect straight line was obtained for the points $t > 15$ sec and the points at $t < 15$ sec were always significantly above this line. For $t > 15$ sec the correlation coefficient was better than 0.95, but inclusion of the points for $t < 15$ sec resulted in a far worse correlation coefficient and did not justify the inclusion of these points in the linear plot determined by the other points.

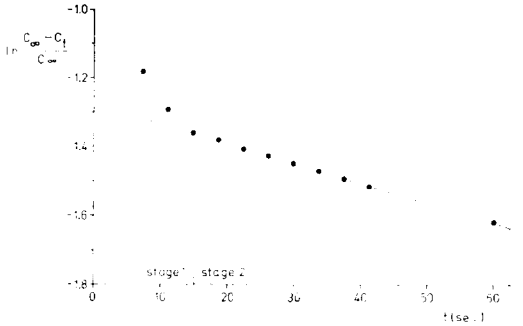

FIG. 3. Semilogarithmic plot of the time course of the exchange reaction on Pt ($T = 78$ K).

The exchange thus follows the formal kinetics of

$$\frac{d \ln(1 - C_t/C_\infty)}{dt} = \frac{k}{C_\infty} = K, \qquad (2)$$

where C_t is the concentration of HD at $t = t$; C_∞ is the concentration of HD at $t = t_\infty$, in the present case $t_\infty = 15$ min. Stage I and stage II have different rate constants k' and k'', respectively, and different values of C_∞' and C_∞. The constant K was found to be independent of temperature and pressure; consequently C_∞ and k depend on T in an identical manner. The relative contributions of stages I and II can be influenced by various factors: (1) Exhaustive pumping (see Experimental) causes a relative *increase* of stage I and (2) supplementary adsorption of D_2 leads to a relative *decrease* of stage I. If at 78 K

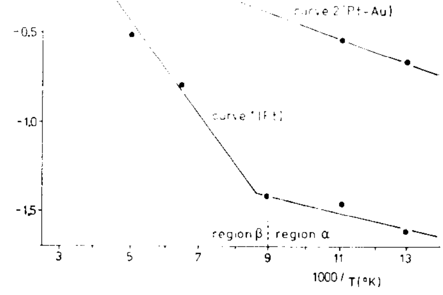

FIG. 4. Arrhenius plot for the exchange reaction on Pt and Pt–Au. Hs is the hydrogen adsorbing surface.

the adsorption of molecular deuterium is followed by adsorption of deuterium atomized by a hot W wire in the vessel, a significant, additional adsorption occurs, up to ten times the normal amount. This additional adsorption leaves stage I unaltered, both in its total extent as well as in its kinetics, but stage II is completely suppressed.

The amount ultimately exchanged, C_∞, and hence also k'' are exponential functions of the temperature as can be seen in Fig. 4. The apparent activation energy is very low, $E_1 = 0.6$ kcal/mol for $T > 110$ K and $E_2 = 0.07$ kcal/mol for $T < 110$ K.

3. Exchange on Alloys

The exchange on alloy films at given pressures and temperatures depends on the surface composition only. In view of the constancy of the surface composition for alloys of differing bulk composition, these alloys show identical exchange activity. This exchange occurred in two stages as found for Pt films (see Figs. 2 and 3). Again stage I is relatively increased by exhaustive pumping and decreased by supplementary adsorption; however, the amount exchanged per surface platinum atom is higher on alloys than on platinum for temperatures below room temperature (see Fig. 4). Temperature dependence of ln C_∞ and hence of ln k'' for the alloys is small and equal to that of platinum in the low temperature range. The Arrhenius plots are linear and unbroken; the apparent activation energy is 0.07 kcal/mol (see curve 2 in Fig. 4).

4. Pressure Dependence

Both for Pt and the alloys the pressure dependence of the amount which is ultimately exchanged at a given temperature can be described by $C_\infty = a \cdot p_{H_2}{}^m$. Values are given in Table 1. The results show that for alloy films m is virtually independent of the temperature, whereas for platinum m decreases from $m \sim .09$ at 78 K to $m \sim 0.2$ at $T > 200$ K.

TABLE 1
PRESSURE DEPENDENCE OF THE AMOUNT OF HD(C_∞) AT $t = t_\infty$[a]

$30\,\mu < p < 100\,\mu$

% Pt	% Au	Reaction temp (K)	m
95.6	4.4	78	0.96
91	9	78	0.89
100	0	78	0.85
95.6	4.4	193	0.92
100	0	193	0.19
100	0	298	0.20

[a] $C_\infty = a \cdot p_{H_2}{}^m$.

IV. DISCUSSION

We shall briefly discuss the following relevant results of this work.

1. The quantity of hydrogen chemisorbed per unit surface area is constant for alloys with widely varying overall composition.

2. By alloying platinum with gold the fraction of adsorbed deuterium which can ultimately be exchanged at 78 K is increased. Its temperature dependence is changed, the broken Arrhenius line for Pt being replaced by a single straight line for alloys.

3. The exchange reaction of hydrogen is always accompanied by an R″ reaction,* characterized by a production of deuterium in quantities markedly exceeding the statistical equilibrium values.

Re 1. The adsorption of hydrogen per unit surface area on platinum and platinum–gold alloys (= chemisorptive titration of surface platinum atoms) is in perfect agreement with the expected behavior according to the thermodynamic data. The phase diagram shows that at 300°C a phase with 85% gold coexists in equilibrium with a platinum-rich phase, containing 2% gold (*14*). In full analogy to nickel–copper alloys photoemission studies showed that the gold-rich alloy forms the surface layer of the alloy film (*14*). On the basis of this model all alloys with compositions inside the miscibility gap are expected to have a surface composition of roughly 15% platinum,

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* This is a generally accepted term in oxygen exchange reactions (*12*). Applied to HD exchange, it means that upon H_2 adsorption by the surface D_2 rather than HD appears in the gas phase.

so the hydrogen–xenon adsorption ratio α should have a value of about $1/7$ of the α value for a clean platinum film. This is precisely what we found experimentally.

Re 2. Hydrogen adsorbed on the surface of the alloys is more reactive than on the surface of platinum (Fig. 4). This higher reactivity suggests that the heat of adsorption of hydrogen is lower on these alloys than on unalloyed platinum. Whereas in platinum metal an adsorbing Pt atom is completely surrounded by other platinum atoms, in the alloys some of its direct neighbors in and below the crystallographic plane are gold atoms which act as "ligands" of the adsorbing Pt atom. Due to their ligand effect, e.g., an electron donation from Au to Pt atoms, the heat of adsorption of hydrogen will be different for an alloy as compared to the pure metal (*15*). Such a lowering of the heat of adsorption by alloying platinum with a Ib element is in line with similar observations on the system Pd–Ag and CO (*16*).

Re 3. Upon discussing the mechanism of the exchange reaction on platinum it appears appropriate to consider separately the two temperature regions defined by the break in the Arrhenius line for platinum (Fig. 4). We thus distinguish a low temperature region α and a high temperature region β.

i. Platinum, Region α

The formation of significant amounts of deuterium in stage I (R'' reaction) shows that upon impact of a hydrogen molecule, two adsorbed deuterium atoms leave the surface as a deuterium molecule. Boreskov *et al.* (*11*) observed the same phenomenon for a nickel catalyst.

Evidently, this reaction cannot be caused by the Couper-Eley nor by the Eley-Rideal mechanism, which both lead to the formation of HD molecules. The results do not exclude, however, that such a mechanism is operating in addition to the R'' reaction.

Two possible mechanisms can be visualized: (a) Adsorbed deuterium is partly present as undissociated deuterium molecules. These are displaced by hydrogen molecules. (b) Deuterium is dissociatively adsorbed. Adsorption of hydrogen increases the degree of coverage and thus causes a weakening of the adsorption bond of deuterium atoms present at neighboring sites. A loosened deuterium atom can react either with a protium atom to form HD, or two adjacent deuterium atoms can leave the surface in pairs as D_2 molecules. This picture thus implies also a Bonhoeffer-Farkas mechanism in combination with a very pronounced induced heterogeneity of the surface, i.e., a strong decrease in heat of adsorption with coverage.

As we find it difficult to see how undissociated molecules, not desorbed during pumping, should spontaneously desorb when molecules of another isotope are present, we are reluctant to accept possibility (a). This reluctance gathers further support from the observation that more exhaustive pumping, to 10^{-7} Torr, does not eliminate this phenomenon. We therefore prefer possibility (b) which is in agreement with our results. Conclusions by Boreskov *et al.* (*11*) seem to support our view as they derived from a kinetic analysis that curves such as those in Fig. 2 can only be obtained if a Bonhoeffer-Farkas mechanism is operating. It is possible, however, that the Bonhoeffer-Farkas mechanism is not the only process occurring in the low temperature region. The high pressure coefficient m of the exchange rate is consistent with a prevailing Couper-Eley mechanism, although it can also be rationalized with other postulates.

ii. Platinum, Region β

The sharp break in the Arrhenius plot for platinum occurs at a temperature where extensive surface migration sets in (*17*). With increasing temperature, therefore, the direct recombination of the now mobile deuterium atoms increases importantly. As a consequence, the reaction via the Bonhoeffer-Farkas mechanism will prevail on platinum in the β region and consequently m decreases.

iii. Exchange Mechanism on Alloys

While for platinum both the apparent activation energy E and the pressure parameter m were different in the temperature regions α and β, it is striking that for the alloys E and m remain constant for the total range of temperatures studied. Again, the high pressure coefficient m can be rationalized either by assuming a pronounced induced heterogeneity in combination with a Bonhoeffer-Farkas mechanism or by a Couper-Eley mechanism or by other postulates between which, however, the results of this paper do not permit us to distinguish. The occurrence of the R″ process with the alloys shows that a Bonhoeffer-Farkas mechanism is at least in part responsible for the exchange.

This interpretation would also explain the exchange results which we obtained by deviating from the standard procedure. Extra pumping should decrease the chance for recombination and, indeed, less deuterium molecules were found to appear in the gas phase. The additional adsorption should have the opposite effect which is, again, in agreement with the experiments. It is possible, however, that in the latter case some deuterium molecules are left on the surface and subsequently displaced by admitted hydrogen molecules.

V. CONCLUSIONS

In summarizing the results of this paper it appears relevant that three phenomenological criteria can be identified for a certain type of exchange reaction. They are (1) initial occurrence of D_2 in excess to equilibrium values, i.e., an R'' reaction. (2) Apparent activation energy $E \sim 0$. (3) Pressure coefficient $m \sim 1$. For platinum, the exchange characterized by these criteria is encountered only in the low temperature α region, but for the alloys it is observed in the whole temperature range of this study. Furthermore, exchange on the alloys has a higher rate constant thus comprising a larger activity of the adsorbate than for platinum at the same temperature. Though the equality of three experimental criteria might be just coincidental, it appears more probable that the same molecular mechanism which prevails on platinum at very low temperatures only, remains predominant on Pt/Au alloys up to the temperature where rates become immeasurable with the present apparatus. This reaction appears to include an appreciable contribution of a Bonhoeffer-Farkas exchange.

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