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CATALYSIS BY PALLADIUM-GOLD AND RELATED ALLOYS

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Summary

After a theoretical introduction, results for the following reactions on PdAu alloy wires are reviewed in relation to other work; $pH_2 \rightarrow oH_2$, HCOOH dehydrogenation, $CO + O_2$ and N_2O decomposition. The reactions are all faster on Pd-rich alloys, and the higher apparent activation energies found for the last two reactions arise from heat of adsorption terms. The present evidence favours the view that holes in the d-band are a dominant factor for reactions involving either hydroge or oxygen.

BERZELIUS,[1] as is well known, was the first to define catalysis, which he explained in terms of a catalytic force. Although the force concept is now abandoned, some of its postulated properties strike a chord in the mind of the modern investigator. BERZELIUS said "it is evident that the catalytic force acts principally by means of the polarity of the atoms, which it augments, diminishes or changes. In other words, the catalytic force manifests itself by the excitation of electrical relations, which up to the moment have escaped our investigation."

The present paper is concerned with metal catalysis, and we express the "excitation of electrical relations" in terms of the chemical potential of the conduction electrons in a metal, as defined by the Fermi level. LENNARD-JONES[2] discussed how the Fermi level influenced chemisorption of gases on metals. His idea was that the approaching gas atom drew a conduction electron into a localised surface energy state, and formed a covalent electron pair link with it (Fig. 1).

$$M + \frac{1}{2}H_2 \longrightarrow M - H$$
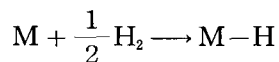
In addition, complete transfer of an electron to form an ionic bond might occur, e. g. with oxygen,
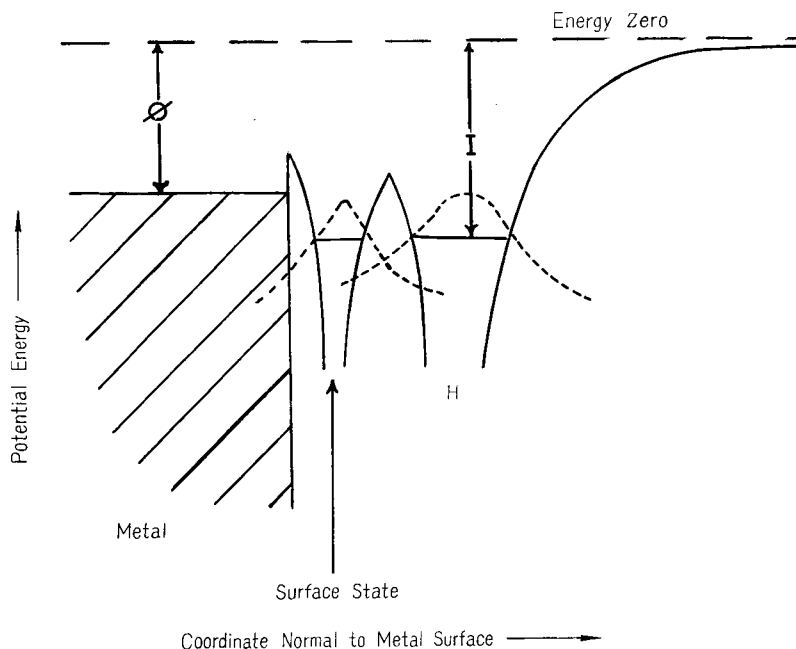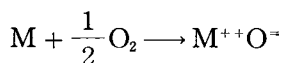
Fig. 1. A Lennard-Jones diagram for the potential energy of an electron normal to the metal surface containing a chemisorbed H atom; $\phi =$ work function for the metal, I the ionisation potential of the H atom, and the dotted lines denote work functions.

$$M + \frac{1}{2} O_2 \longrightarrow M^{++} O^{=}$$

DOWDEN[3] has applied this picture to catalysis in general.

It was shown by TAMM[4] that surface electron energy states will also arise on a metal due to the termination of the periodic potential. In general we expect electrons in these states to be in equilibrium with the bulk Fermi level, although in certain case the surface states need not communicate with the bulk crystal energy band.[5] The reader is referred to a recent review of surface states.[6] So far the concept has been most developed for semiconductors rather than metals.

The present approach to catalysis assumes that modifications in the Fermi level of a metal brought about by alloying, will directly influence the free energy of the surface electrons. We shall examine how far this hypothesis may be justified a posteriori in certain instances.

Electron Concentration in Alloys

The idea of electron concentration devolves from HUME-ROTHERY,[7] and

is based on what is now called the Rigid Band Model. Electron concentration for an alloy is defined as the total number of valency electrons divided by the total number of atoms, *e. g.* for Cu_5Sn it is $9/6 = 1.50$. Thus if we add a divalent metal to a monovalent silver we shall raise the electron concentration. H. JONES pointed out that as long as the Brillouin zone remains that for silver, the effect of the additional electrons is simply to raise the Fermi level. At phase changes the crystal structure alters so as to expand the Brillouin zone and lead to a lowering of the Fermi level.

In a classical study G. M. SCHWAB[8] examined the α-phase alloys of silver as catalysts for formic acid decomposition. Raising the Fermi level raised the activation energy for this reaction, which Schwab associated with electron transfer from the acid to the metal. We may adopt a modified mechanism to allow for the formation of surface formate ion, demonstrated by infra-red adsorption, and for a slow step of electron donation to the metal,

$$MH + HCOOH \longrightarrow M^+O\overline{OC}H + H_2$$
$$M^+OOC\overline{H} \longrightarrow MH + CO_2 \text{ (slow step)}$$
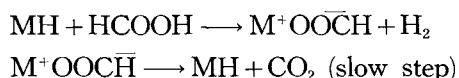
There is infra-red evidence in the case of Cu, Ni and Zn for the presence of formate ion as an intermediate adsorbed species.[9] If this should prove to be so for PdAu alloys, then we may best explain these results in terms of the mechanism of RIENÄCKER and HANSEN[10] above with the assumption that the second step is the slow one.

Group VIII Alloys

RIENÄCKER has published many papers in this field. In his early studies he examined the order-disorder change, and showed that the ordered alloys usually exhibit the lower activation energy for a catalytic reaction. He further found that on adding a group I B metal to a group VIII metal, at a particular concentration of the former, a sudden increase in activation energy for the particular reaction occurred.[11] RIENÄCKER and BOMMER[12] suggested a change in the binding state of the metal electron occurred at this point.

The Palladium-Gold Alloys

The PdAu alloys are substitutional one phase fcc. alloys over the whole range of composition. The change in lattice spacing is relatively small, 3.88 to 4.07 Å, and there is no evidence for a miscibility gap. They are preferable to the CuNi alloys, where there is evidence for phase separation.[13,14] According to the early MOTT and JONES density of states diagram,[15] in PdAg alloys we should have a narrow nd band overlapped by a broad $(n+1)s$ band, and we may infer a similar structure for PdAu, with the nd overlapped by the

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$(n+2)s$ band. The dependence of susceptibility on composition for PdAg,[16,17] PdAu,[18] and the interstitial PdH[19] also, plotted in Fig. 2, show the susceptibility decreases to zero at an atomic concentration of Ag, Au or H of about 0.6. The data plotted in Fig. 2 show the zero susceptibility values occur at 0.52 atoms of Au or Ag, and 0.64 atoms of H, the difference between relating to the different character of the two types of solution. It was con-
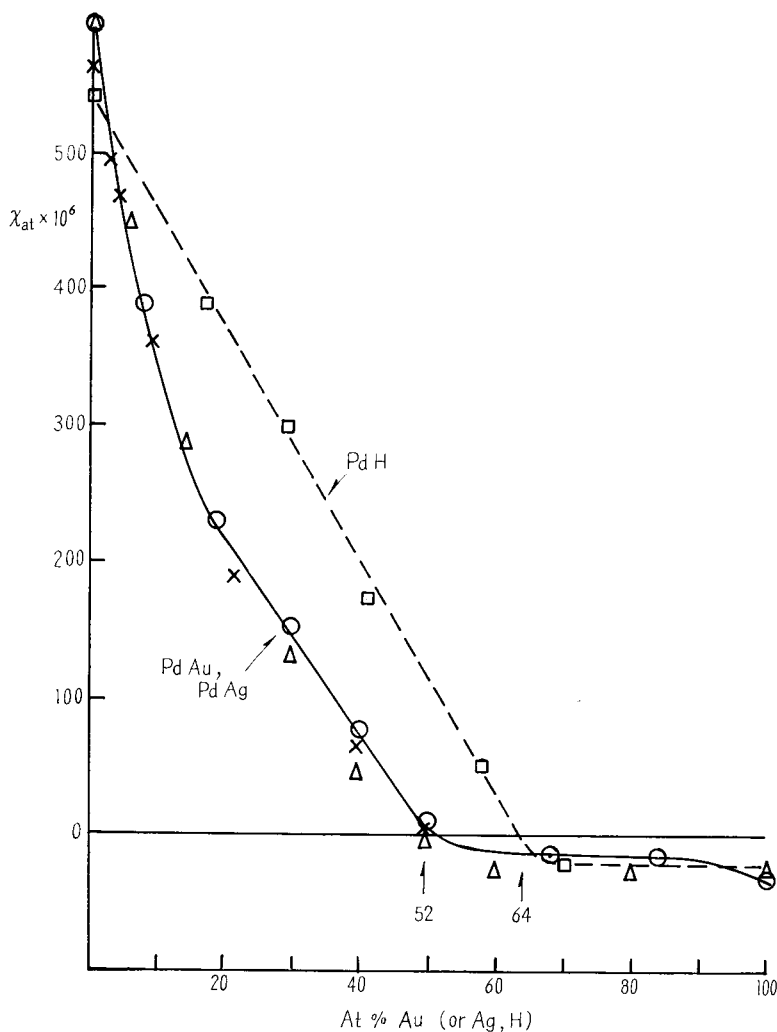

Fig. 2. The atomic susceptibility of PdAu alloys, ○ PdAu (VOGT, 1932), △ PdAg (SVENSSON, 1932), × PdAg (HOARE, METTHEWS and WALLING, 1953) and □ PdH (SIEVERTS and DANZ, 1937).

cluded that the d^{10} structure in the Pd atom had become $d^{9.4}$ $s^{0.6}$ in the bulk metal, *i. e.* there were 0.6 holes/atom in the d band of Pd (also for Ni.) In fact, since the s band overlaps the d band it would be more correct to say 0.45 holes in the d band, 0.15 holes in the s band. This consideration is raised by HOARE and YATES,[20] in a paper in which they derive from thermal and magnetic data the density of states curve for Pd shown in Fig. 3. The Fermi level is shown, and we have added a hypothetical Fermi level for Au also. This number 0.45 is more easily reconciled with the recent value of 0.36 holes in the d band determined from the de Haas-van Alphen effect.[21]
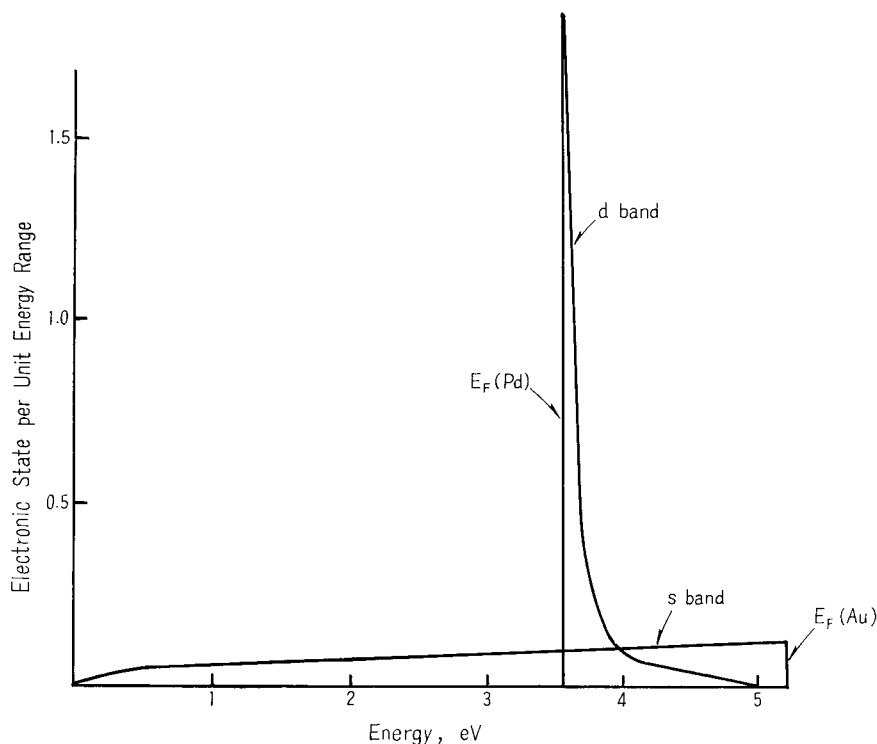

Fig. 3.   Density of states as a function of energy for d and s bands of Pd for one direction of spin (HOARE and YATES, 1957). E_F denotes Fermi level, that for Au being hypothetical.

Modern work[22] modifies this density of states picture to a broad $3d$ band, hybridised to some extent with s and p orbitals, and possessing two maxima. Since the Fermi levels for metals Ni, Pd and Pt lie above the higher narrow maximum, the general behaviour is similar to that predicted earlier on the narrow nd band model.

In the following sections we shall review our own work on PdAu alloy wires, together with related investigations.

Hydrogen Reactions on Pd-Au Alloys

The para-ortho hydrogen conversion on PdAu wires[23] has the lowest apparent activation energy on Pd, which remains constant to 60At% Au, where it abruptly increases, as shown in Fig. 4 a. The frequency factor changes
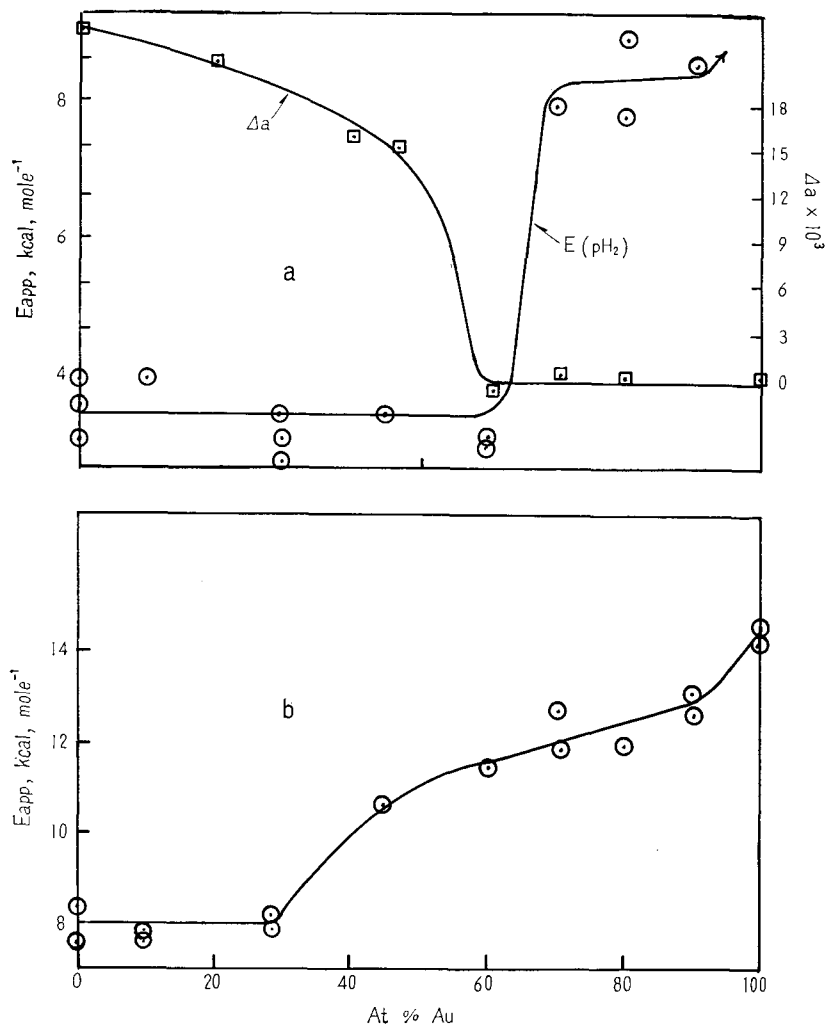

Fig. 4. a) E_{app} for para-ortho H_2 and accommodation coefficient change, Δa, on H_2 adsorption, for PdAu alloys.

b) E_{app} for the formic acid decomposition on PdAu alloys.

relatively little.   It is interesting that the reaction velocity at 500°K is high on pure Pd but increases to a slight maximum at 30At% Au before decreasing rather abruptly to Au, as shown in Fig. 5, a point emphasised recently by BOND.[24]

According to accommodation coefficient measurements,[25] also shown in Fig. 4 a, a big decrease in the concentration of chemisorbed H occurs at 60 At% Au.   It has been suggested[23] that on the Pd rich alloys, the mechanism is

$$pH_2 + HM \longrightarrow MH + oH_2$$

and on the Au rich alloys

$$pH_2 + 2M \longrightarrow 2MH \longrightarrow oH_2 + 2M$$

but this has not been proved conclusively.   The problem is being further examined at Nottingham at present.

RIENÄCKER and SARRY[26] have examined CuPt, and RIENÄCKER and VORMUN[27] PdCu, and a qualitatively similar picture emerges.   The basic idea is that holes in the d band serve to stabilise the activated complex of the reaction, whichever the mechanism.   There are two very recent studies of the parahydrogen conversion on the PdAg system.   On evaporated films[28] there is a very similar abrupt increase in activation energy about 60At%Ag, and on wires[29] something similar at about 80At%Ag, although the authors concerned preferred to draw a parallel between activation energy and Fermi level. On PdAg foils[30] the activation energy rose from 6 kcal at OAg to 9 kcal at 30 At%Ag, then falling to 6 kcal at 53.5At%Ag before rising to a value of 11 kcal for Ag-rich alloys.   However, these foils were much less active than the wires,[29] in spite of their greater area, the reaction temperature being 200°C higher.

In the case of PdH it was found that 8At%H raised the apparent activation energy to 11 kcal/mole, and these results have been confirmed and extended.[31]

For the H atom recombination on PdAu foils in the hydrogen-free condition there is a strong parallel between the effect of composition on reaction rate, with that found for the pH_2 conversion, including the maximum rate at 30At%Au,[32] as shown in Fig. 5.

The superior activity of Pd rich alloys in hydrogen chemisorption on alloy cathodes has also been demonstrated by galvanostatic techniques in electrochemical systems.[33]

Exchange and Hydrogenation-Dehydrogenation

McKEE[34] found a very similar activity : composition pattern for $CH_4 \cdot\cdot D_2$
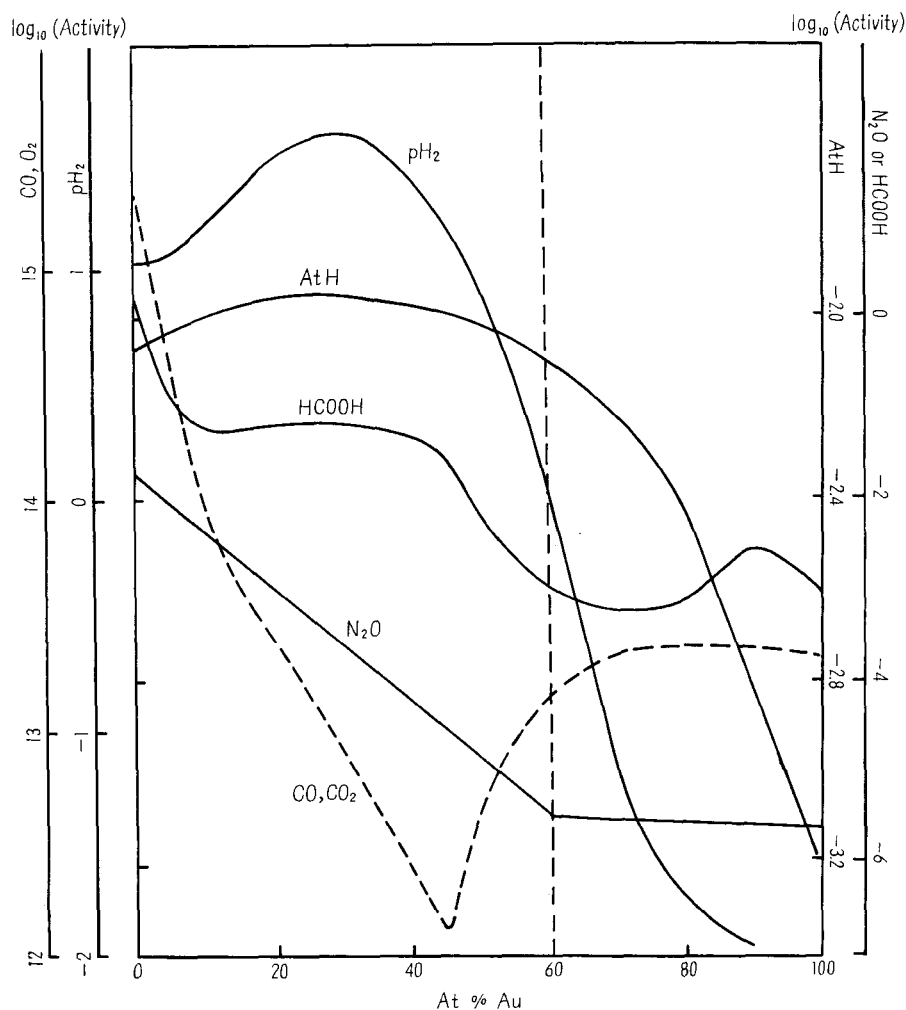
Fig. 5. Activity-composition data for 5 reactions of PdAu wires
(foil in the case of Atomic H).

pH_2 (500°K); H atom (293°K); HCOOH (373°K); N_2O (923°K); $CO+O_2$ (423°K).

on PdAu powders, to the pH_2 conversion, *i. e.* a maximum at 30At%Au
decreasing to zero at 60At%At. The apparent activation energy graph was
complex, with a minimum at 20At%Au.

The hydrogenation of butadiene on PdAu alloy on pumice[35] gave a mark-
ed maximum in the apparent activation energy graph, which abruptly increased
at 60At%Au, but as abruptly decreased at c. 30At%Au.

In the case of formic acid dehydrogenation on PdAu wires,[36] the increase

in apparent activation energy set in at 30At%Au, *cf.* Fig. 4b. It was suggested in the original paper that the difference between this value and the 60At%Au for pH_2, reflected a difference between 2 and 1 hole in the d band associated with the activated complex. We have not as yet been able to bring any further evidence in support of this suggestion.

Reactions involving Oxygen

A new feature appears in the reaction[37]

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$
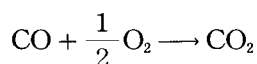
which is found to have the higher apparent activation energy (Fig. 6 a), but also the higher rate of reaction on Pd-rich alloys (Fig. 5). A clue to this behaviour appears from the kinetic orders, which are

$$\text{Pd-rich, } p_{O_2}/p_{CO}^2 \qquad \text{Au-rich, } p_{O_2}^0 \; p_{CO}^0$$
$$\therefore \quad E_{app} = E_t + 2\lambda_{CO} - \lambda_{O_2}, \qquad E_{app} = E_t,$$

where E_t signifies the true activation energy. The high E_{app} for Pd is therefore due to the term $2\lambda_{CO}$, where λ_{CO} is the heat of adsorption of CO on Pd. There is also a point about the Au-rich alloys, where there is no measurable O_2 uptake, so that the zero order reaction must imply adsorption of oxygen on a small number of special sites. The striking minimum in activity at about 42At%Au may reflect a change from one regime to the next.

Our most recent investigation concerned the decomposition of N_2O on PdAu alloy wires.[38]

$$N_2O \to N_2 + \frac{1}{2}O_2 .$$
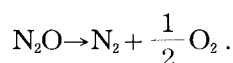
Since this occurred in the range 500–900°C, it is a high temperature reaction. The initial rates were followed by a Pirani gauge. The kinetics found were

$$\text{Pd-rich, } >70\text{At\%Pd} \qquad \text{Au-rich, Pd} < 70\text{At\%}$$
$$v = k''p_{N_2O}/1 + Cp_{N_2O} + C'p_{O_2} \qquad v = k'p_{N_2O} .$$

Added oxygen was found to inhibit the reaction $1/v \propto p_{O_2}$ rather than $p_{O_2}^{\frac{1}{2}}$, so we are concerned with molecular rather than atomic adsorption. Increase in the oxygen pressure was shown to raise the apparent activation energy, and E_{app} and the "true" activation energy, E_t were derived as a function of alloy composition (Fig. 6 b).*)

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*) Since the expression true activation energy is normally defined for Langmuir or related treatments, we have written "true" has in inverted commmas.
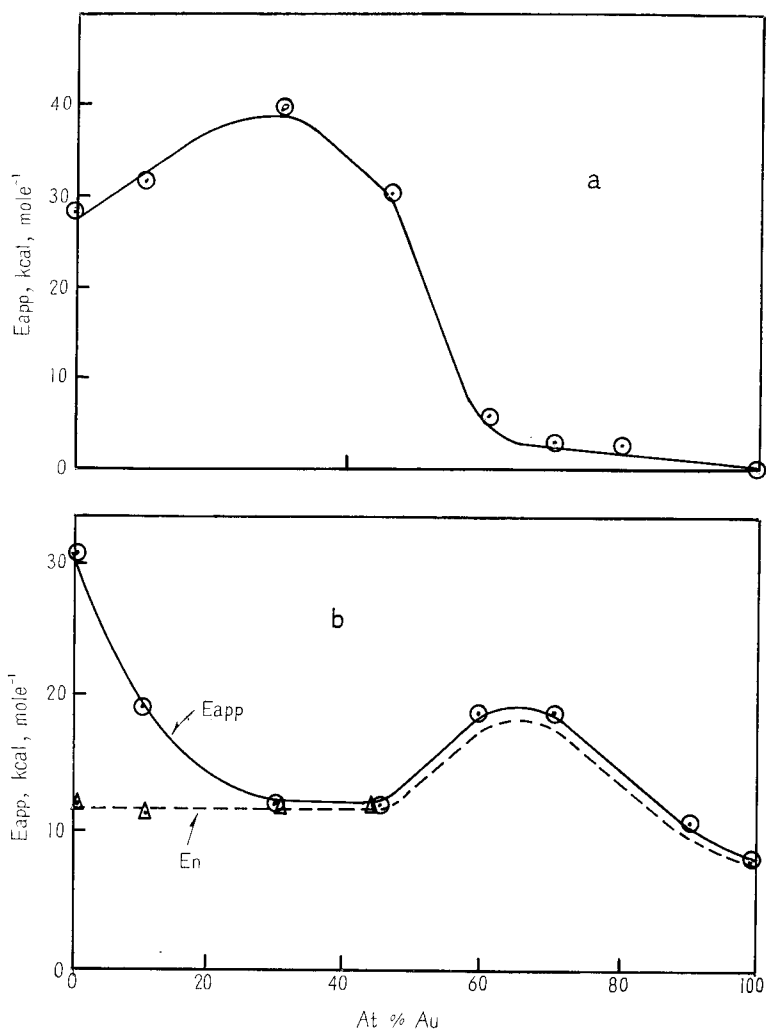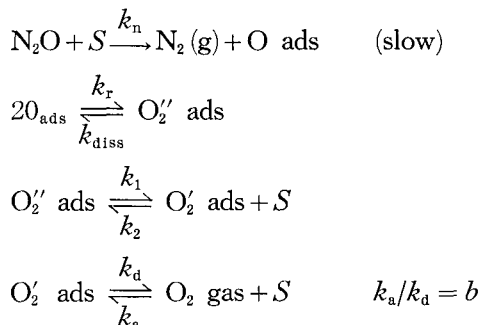
Fig. 6. a) E_{app} for the $CO + O_2$ reaction on PdAu wires.
  b) E_{app} and "true" activation energy E_t for N_2O decomposition on PdAu wires.

As in the previous reaction, the higher E_{app} and faster rate were found on Pd, and it is immediately seen that this is as a result of λ_{O_2} rasing E_{app}. There is a maximum in the E_t *vs.* At%Au graph, reminiscent of that found for butadiene plus hydrogen.[35]

We have subjected this particular reaction to a very detailed kinetic analysis, based on the elementary steps,

$$N_2O + S \xrightarrow{k_n} N_2 \,(g) + O \text{ ads} \qquad \text{(slow)}$$

$$2O_{ads} \underset{k_{diss}}{\overset{k_r}{\rightleftharpoons}} O_2'' \text{ ads}$$

$$O_2'' \text{ ads} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2' \text{ ads} + S$$

$$O_2' \text{ ads} \underset{k_a}{\overset{k_d}{\rightleftharpoons}} O_2 \text{ gas} + S \qquad k_a/k_d = b$$

Here O_2'' is chemisorbed on 2 sites, and O_2' on one site. In the stationary state

$$\frac{\delta\theta_{O_2''}}{\delta t} = \frac{\delta\theta_{O_2'}}{\delta t} = \frac{\delta\theta_O}{\delta t} = 0$$

and we derive

$$v = \frac{k_n S p_{N_2O}}{1 + \dfrac{k_n}{2k_d} p_{N_2O} + b p_{O_2}}$$

Referring to the graphs, as we increase the At%Au, $k_n S$ (the "activity" in Fig. 5) decreases without change in $E_t = E_n$, becoming zero at 60At%Au. Bearing in mind N_2O does not absorb on Au, we suggest this decrease is due to decrease in S, the number of sites cm^{-2}, rather than k_n, and we associate S with the number of holes in the d band. Since Au does not adsorb oxygen, we attribute the activity of the Au-rich alloy to thermodynamic defects, and show that

$$E_t = E_n + rE$$

where E is the activation energy to form thermodynamic defects. The abrupt rise in E_{app} at 60At%Au is then attributed to the onset of defect activity, since the oxygen inhibition has disappeared at this concentration.

In a study of the methane-oxygen reaction on PdAu on alumina FIRTH[39] found that the apparent activation energy was high on Au and decreased to a value of 60At%Au which remained constant to pure Pd, and the rates are highest on Pd. Similarly for the oxidation of ethylene to CO_2 the rates on PdAg films are highest on Pd, but the rate of ethylene oxide formation is greatest on pure Ag.[40] However Ag is a specific catalyst for this reaction so this last results must be expected.

In his original paper DOWDEN[3] suggested that since oxygen tends to

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accept electrons becoming negatively charged on chemisorption, the reactions of oxygen should go fastest and have the lowest true activation energy on Au (or Ag) and the highest on Pd. He produced some evidence in favour of this for the H_2O_2 decomposition on CuNi alloys.[41] This view is not borne out for the above reactions on PdAu alloys which clearly were fastest on Pd. In a very brief publication HANNA[42] (describing the results of work carried out under Dr. A. COUPER at Bristol) has concluded that H_2O_2 decomposition on PdAu alloy wires is fastest on Au, with the lowest activation energy on this metal, which would fit in with DOWDEN's prediction. At the present time we are further investigating this reaction, and withhold comment until this new work is completed.

In summary, for both hydrogen and oxygen reactions the Pd-rich alloys are generally most active. A good many of the reactions show a sudden change in rate and often activation energy at 60At%Au, where the holes in the d band finally disappear. However, the para-ortho hydrogen conversion remains the clearest example of a really abrupt increase in activation energy at this point, and the simple d hole behaviour may tend to be complicated by the added effects of thermodynamic defects, and in the case of PdAg films, surface enrichment effects. The increasing amount of careful work in progress on PdAu (and PdAg) alloys will allow more quantitative checks on velocity constants and activation energies between laboratories, and should provide a basis for the work of future theoreticians. The use of PdAu wires has preference over other forms of catalyst preparation, from a number of viewpoints, and in particular that of ease of surface cleaning by electrical heating.

Note added in Proof. Heats of mixing of gold and palladium are exothermic over the whole composition range, so there is no tendency for phase separation (J. A. DARBY, Acta Met, **14**, 265 (1966).

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