

The Parahydrogen Conversion on Palladium-Silver Alloy Films

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The para-ortho hydrogen conversion has been studied on a series of evaporated silver-palladium alloy films, of composition 50% Ag-50% Pd, 70% Ag-30% Pd, 80% Ag-20% Pd, and 100% Ag, in the temperature range 273° to 413°K.

Details are given for the preparation and characterization of homogeneous palladium-silver alloy films (~2000-Å thickness), which were formed by controlled evaporation from palladium-silver alloy wires. X-Ray diffraction and X-ray fluorescence techniques were used to analyze the films throughout the reaction vessel. The compositions were constant to within 3% over geometric film areas of 120 cm².

The activation energy for the conversion increased with silver content of the alloy, with a sharp rise between the 50% Ag and 70% Ag alloy. A linear compensation effect between the activation energy and frequency factor for the conversion on the alloy series was observed. Heats of adsorption of hydrogen on the alloy films were calculated from the pressure dependency of the reaction at constant temperature. By comparing the experimentally determined entropy changes upon adsorption with calculated values it is concluded that the adsorbed hydrogen film, on the silver-rich alloys, is mobile.

INTRODUCTION

The electronic properties of the transition metals vary discontinuously when proceeding across a period since electrons are added in increments of one. However, if an alloy of adjacent metals can be formed, a continuous variation of electronic structure may be obtained. The electronic structure of alloys between Group VIII and IB metals are of the most interest as catalysts because as the IB metal is alloyed with the Group VIII metal, the valency *s* electrons of the former fill the "holes" in the *d* band of the latter. According to the Band Theory or the Valence Bond Theory, there are, respec-

tively, about 0.6 *d*-band vacancies or 0.66 unpaired *d* electrons per atom in nickel and palladium. These figures correspond to a composition of about 60% to 65% of the IB metal in the alloy (1, 2). Evidence that these percentages are correct has been supplied by the physical properties of the alloys. For the palladium-gold alloys, the magnetic susceptibility progressively decreases as gold is added to palladium until it reaches zero at a composition of about 60% gold (1). Similar behavior is found for palladium-silver alloys (3).

One of the early publications to show the effect of the filling of *d*-band vacancies on the catalytic activity of metals was that of the well-known work of Couper and Eley (1). In this paper they reported measurement of the activation energy of the para-ortho hydrogen conversion on a series of gold-palladium alloy wires, and showed that there was a marked rise in the activation energy for the conversion

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near the composition at which there were just sufficient *s* electrons from the gold to fill the vacancies in the palladium *d* band.

In several reported studies on Group IB-Group VIII alloy systems (4) the change in activity for hydrogen reactions does not always occur at the exact composition at which the *d* band is filled. The possibility of *d*-*s* promotion of electrons in the Group IB element and the donation of *s* electrons to the *d* band by adsorbed hydrogen should not be overlooked, in addition to the thermodynamic considerations discussed below.

In the present paper we describe a study of the parahydrogen conversion on a similar alloy system, palladium-silver, in which the catalyst is in the form of an evaporated film. Palladium-silver and palladium-gold alloys are well suited for studies of the electronic factors involved in catalysis, because they form a complete series of solid solutions having the face-centered-cubic structure and because the lattice constants in each series vary by only 5%. However, even the palladium-silver system is not as ideal as might first appear to be the case. Work by Kleppa (5) and Pratt (6) has shown that the thermodynamic properties of palladium-silver systems are really quite complex, with large negative excess entropies of mixing. At 1000°K the formation of a random solid solution of 50% Pd and 50% Ag is accompanied by a net reduction in entropy. It is considered that these thermodynamic effects are of electronic and magnetic as well as vibrational origin. Also, palladium absorbs hydrogen, and Kowaka (7) has shown that pretreatments of palladium ribbons with hydrogen poison the surface for the hydrogenation of ethylene, but under the same conditions hydrogen has little effect on palladium-silver alloy ribbons. The same author found that the palladium-rich alloys did absorb hydrogen. The rates of absorption, at pressures of 100 torr, decreased with increasing silver content, and became zero at about 60% silver.

The palladium-silver alloys have previously been used in catalytic studies involving formic acid decomposition, (8),

ethylene hydrogenation (7), and the hydrogen-oxygen combination reaction (7).

The ultimate goal in the preparation of an alloy thin film for catalytic work is to obtain a completely homogenized film with a uniform composition over the extended area of the reaction vessel. Holland (31) has given a brief review of the preparation of alloy thin films by vacuum evaporation techniques. More recently, Belsar (9) has made an extensive study of the preparation of the alloy films of 20 metal pairs. However, these films were deposited over the limited area of a microscope slide.

There are essentially three methods for obtaining the desired alloy films: by alternate deposition of two component metals with subsequent heat treatment to establish homogeneity, by simultaneous evaporation of two component metals from separate sources, or by evaporation from an alloy source. Each of these methods depends somewhat upon adequate interdiffusion for complete homogeneity. The first technique, however, depends upon this to the greatest extent, since each component is originally deposited in separate layers. Thus, homogeneity may be difficult to achieve. For the method of simultaneous evaporation from separate sources, the positioning of the sources is quite critical if a uniform composition over an extended area is to be achieved. This is also a factor in the first method. Both of these methods, however, do have the advantage that the composition of the final film may be determined by the weight loss from the different sources.

The third method, evaporation from an alloy source, is unique, at least, in the simplicity of deposition. However, the success of this technique depends upon the vapor pressure of the respective components. The component with the higher vapor pressure volatilizes preferentially from the alloy source which results in a film more rich in the volatile component. This, however, is of no consequence if the vapor pressure difference is not extreme and if the composition of the film can be determined by a separate means.

From the above discussion, it is apparent

that the properties of the components in an alloy, such as vapor pressures and diffusion constants, determine the best vacuum evaporation technique for that alloy. For copper-nickel alloy films, Sachtler and Dorgelo (10) reported that evaporation from an alloy wire was unsuccessful due to a large difference in vapor pressures between the components. They concluded that the successive evaporation method with subsequent heat treatment was the best technique. Since they reported well-homogenized films, adequate interdiffusion must take place. They did, however, report variations of composition even over the limited areas used.

From diffusion data reported for palladium in an 80% silver-palladium alloy (11) and for silver in a range of silver-palladium alloys (12), the self-diffusion of these components in an 80% silver-palladium alloy was calculated. For a time of 1 hr at room temperature, 200°, and 400°C, palladium atoms will diffuse distances of 0.83, 470, and 11,000 Å, respectively, while silver atoms will diffuse 2×10^{-7} , 0.15, and 160 Å. Thus, to homogenize any silver-palladium film, a temperature of at least 400°C is necessary. If the palladium and silver, at the outset, are completely separated, as they are in the successive evaporation process, longer times and higher temperatures are predicted to be required.

Moss and Thomas (13) obtained thin films of palladium-silver alloys principally by successive and simultaneous evaporation. In agreement with the above predicted results, they found that successively

evaporated layers of silver and palladium required a heat treatment above 500°C for a period of some hours to obtain a homogeneous film. By a simultaneous evaporation technique, they obtained homogeneous films with a few percent variation in composition over the extent of a spherical vessel. To obtain the latter, the poisoning of four sources in the center of the vessel was quite critical.

EXPERIMENTAL

Evaporation Technique and Film Analysis

For this work each palladium-silver film was obtained from an alloy wire source. The reaction vessel design for the vacuum deposition of the palladium-silver alloy thin films is shown in Fig. 1. These vessels were made from 25-mm OD Pyrex tubing, and they were 15 cm long. Before use, these vessels were thoroughly cleaned by a method described by Tichane (14) which is claimed to be superior to a chromic acid wash. The filaments used in the reaction vessels were made from 10-mil tungsten wire. Several loops, approximately $\frac{3}{4}$ inch apart, were put into the filament, as shown in Fig. 1. These loops primarily served to absorb the thermal expansion of the wire during the evaporation process in order to prevent sagging. They also prevented the beading and running together of the wire being evaporated. Neither silver nor palladium form low-melting alloys with tungsten (31). These tungsten filaments were cleaned by electrolysis in a 10% KOH solution with nickel as the other electrode. The alloy wire to be evaporated

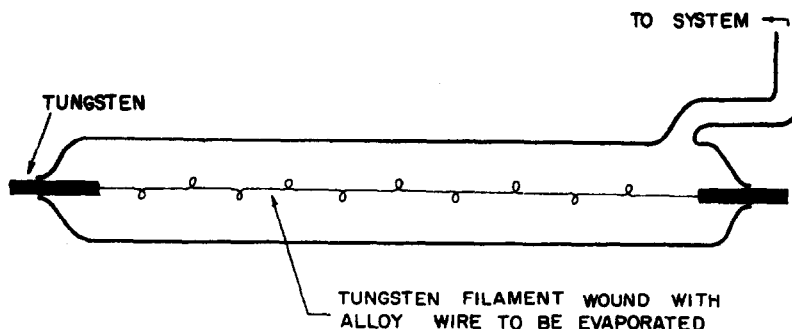


Fig. 1. Reaction vessel used for the preparation of alloy films.

was wound around this filament with the aid of a lathe and speed reduction gear. This wound filament was weighed on a Mettler Balance before and after evaporation to determine the weight loss during evaporation. Before the filaments were sealed into the reaction vessel, small diameter tungsten rods were spot-welded through nickel sleeves to each end. These were then sealed through the Pyrex reaction vessel using a special glass, Corning Code 3320, as shown in Fig. 1. The completed reaction vessel was then joined into the vacuum system, and the thin film was deposited.

To obtain the homogeneous alloy films used in this work, the following evaporation procedures were used: After overnight baking out periods at about 500°C, the vessel temperatures were brought down to 400°C. This heat was supplied by a Nichrome heating tape. With vessels at 400°C, the alloy wires were evaporated. Evaporation currents from 3.5 to 5.5 amp and evaporation times of 3 min were used. The deposited films were then annealed for 1 hr at 400°C before being cooled to room temperature. Parahydrogen conversion studies then commenced.

Characterization of Films

Since silver does have a higher vapor pressure than palladium, a separate method for composition analysis was required. X-Ray fluorescence and diffraction techniques were used in conjunction to determine both the composition and homogeneity of the evaporated thin films. After the reaction studies, the vessels were disconnected from the system and cut into five equal sections. These sections were then broken. In some cases, it was found that the alloy films could be floated off the vessel fragments in a bath of water. However, in other cases, a bath of concentrated hydrofluoric acid was required. These films were then transferred to microscope slides for X-ray examination. At least one sample from each of the five sections was examined to determine the concentration over the extent of the vessel.

1. X-Ray fluorescence analysis. Standard

X-ray fluorescence techniques (15, 16) were used for the quantitative analysis of the alloy films. This work was performed on a General Electric XRD-6 emission spectrometer. The compositions were determined from the relative intensities of the Ag $K\alpha$ and Pd $K\alpha$ fluorescence X-ray emissions. The $K\alpha$ emissions were chosen rather than the $K\beta$ emissions because of their greater intensities and because the $K\beta$ peak of silver is very close to the absorption edge of palladium. However, because the K spectra of silver and palladium are so close (Ag $K\alpha$ and Pd $K\alpha$ peaks occur at 2θ angles of 23.87 and 25.00 degrees, respectively) the choice of X-ray fluorescence for analysis is an excellent one.

For this work, a calibration curve was determined and is shown in Fig. 2. Pal-

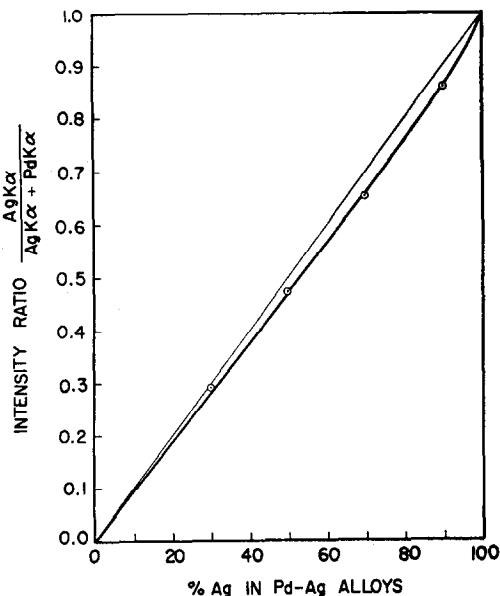


Fig. 2. Calibration curve for X-ray fluorescence.

ladium-silver alloy wires of known composition were used for this calibration. The 10% and 30% silver-palladium wires were obtained from J. Bishop and Co. The 50% silver-palladium wire was obtained from Engelhard Industries Inc. A sample of 70% silver-palladium wire was generously supplied also by Engelhard Industries Inc. The silver and palladium from which these wires were made were claimed to be spec-

troscopically pure. The percentages of each component in the final alloy wires were given by weight and were claimed to be within 0.5% of their reported values. Since relative peak intensities were used, any differences resulting from sample form, wires or films, were assumed to be small and were neglected. The slight deviation from linearity in the calibration curve is caused by the enhancement effect of silver on palladium. Film from different sections of the vessel was stripped and examined to ensure the uniformity throughout the vessel. For each measurement, the tungsten target tube was used and was operated at 65 kV and 55 mamp. A topaz crystal was needed to resolve the K spectra of silver and palladium. The goniometer was operated on the slow speed, 0.5 degrees/min, and peak intensities minus the background were measured from the recorder chart. The average of at least three relative peak intensities was then converted into percent silver content using the calibration curve in Fig. 2. Experimental variations amounted to less than $\pm 1\%$ in the final alloy compositions reported by X-ray fluorescence. The data thus acquired are purely quantitative. By itself, fluorescence neither determines the homogeneity of a film nor, indeed, even the existence of a single alloy phase. Therefore, this method must be used in conjunction with X-ray diffraction.

2. X-Ray diffraction analysis. All samples were measured by standard X-ray diffraction techniques (17, 18) using a General Electric XRD-5 diffractometer. The film compositions were determined from lattice parameter measurements. Coles (19) has accurately determined the relationship between lattice parameter and decomposition for bulk palladium-silver alloys, as shown in Fig. 3. Differences between lattice parameters of bulk silver and silver thin films (1000 Å) have been reported to be approximately 0.05% (20). Larger deviations were observed for thinner films. The thicknesses of the films in this work were all greater than 1000 Å.

The samples used for X-ray diffraction were the same as those used for X-ray fluorescence analysis. For each measure-

ment, the copper target tube with a nickel filter was used and was operated at 50 kV and 16 mamp. For the initial diffraction patterns, beam and detector slits of 3 and 0.2 degrees, respectively, were employed; and the goniometer was operated at a speed of 2 degrees/min. For the lattice parameter determinations, the beam and detector slits were 3 and 0.05 degrees for

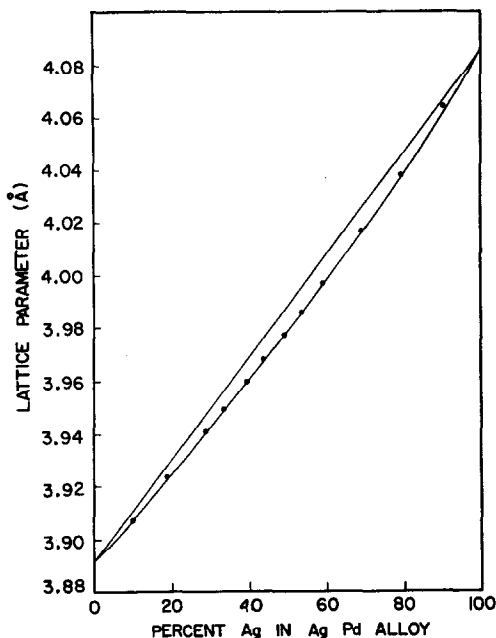


FIG. 3. Lattice parameter variation with composition in Ag-Pd alloys. [From ref. (19)].

better resolution and the goniometer speed was 0.2 degrees/min. In all cases, the soller slit of medium resolution was used. To correct for the low-angle systematic errors of the diffractometer, spectroscopically pure silver powder was run as a standard with each set of measurements. Random errors were reduced by taking the average of at least three measurements for the recorded 2θ values.

Diffraction patterns of all homogeneous alloys clearly showed the (111), (200), (220), (311), and (222) peaks for the face-centered-cubic alloys. From the relative intensities of these peaks, it was established that the alloy thin films were polycrystalline with no preferred crystalite orientation. The lattice parameters were

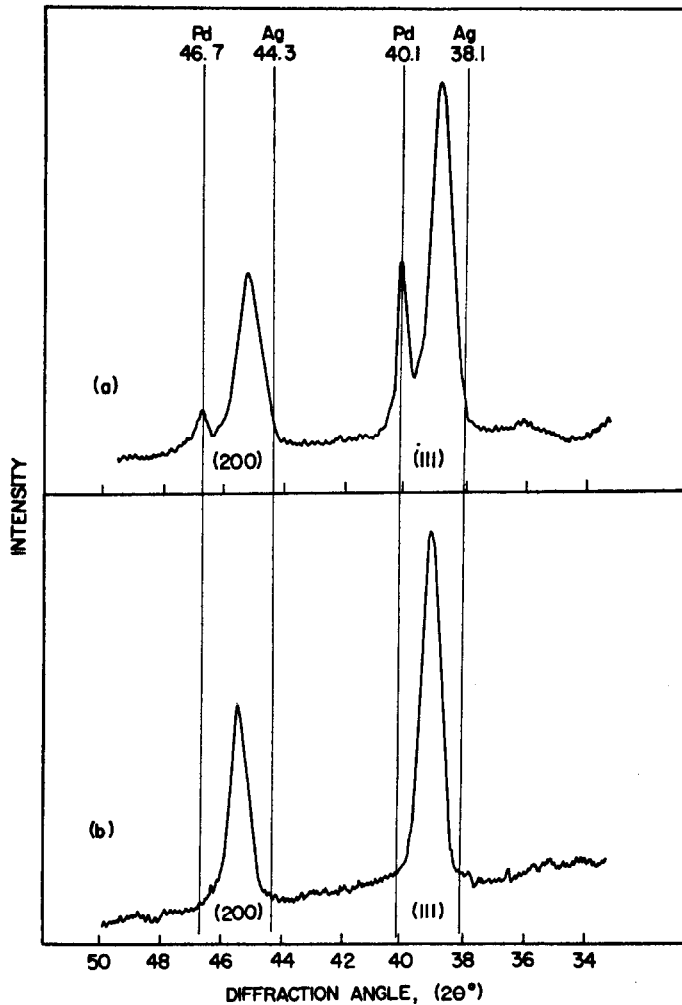


Fig. 4. X-Ray diffractometer patterns [(111) and (200) peaks only]. (a) Film deposited on substrate at room temperature. (b) Film deposited on substrate at 400°C.

calculated from the (111) lattice spacings. Comparisons were made with the lattice parameters calculated from the other planes listed above, but differences amounted to less than experimental errors. Experimental variations cause less than 1.0% error in the final alloy composition reported by the X-ray diffraction.

3. Homogeneity of films. Superficial homogeneity of the alloy films could be observed from their diffraction patterns. For example, Fig. 4 shows two sample patterns: Fig. 4(a) of a film deposited at room temperature and Fig. 4(b) of a film deposited and annealed for 1 hr at 400°C.

Both films were evaporated from a 30% silver-palladium alloy wire. Figure 4(a) clearly shows that for this film homogeneity was not obtained and that some interdiffusion after deposition was required. The film contained an alloy phase and free palladium. The pattern in Fig. 4(b) however, shows a single well-defined peak indicating a homogeneous 50% silver-palladium film.

Complete homogeneity was determined by a comparison of the diffraction and fluorescence results. By the nature of the two techniques, the critical sample thickness is much greater for fluorescence than

TABLE 1
PREPARATION AND COMPOSITION DATA FOR THE 80% SILVER-20% PALLADIUM FILM

<i>Preparation</i>					
	Length of wire			19 cm	
	Diameter of wire			0.25 mm	
	Evaporating current			4.5 amp	
	Evaporating time			3 min	
	Substrate temperature			673°K	
	Annealing temperature			673°K	
	Annealing time			1 hr	
	Apparent area			120 cm ²	
	Total reaction volume			500 cm ³	
	Weight deposited			17 mg	
	Film thickness			1300 Å	
<i>Composition and Homogeneity Analysis</i>					
Section of vessel	X-ray diffraction results			X-ray fluorescence results	
	Corrected 2θ ₍₁₁₁₎	a ₀	% Ag	Ag Kα Ag Kα + Pd Kα	% Ag
A	38.57	4.043	82	0.77	82
B	38.56	4.043	82	0.81	85
C	38.55	4.041	81	0.77	82
D	38.56	4.043	82	0.79	83
E	38.56	4.043	82	0.80	85
	Average composition		82% ± 1%		83% ± 2%

TABLE 2
PREPARATION AND COMPOSITION DATA FOR THE 70% SILVER-30% PALLADIUM FILM

<i>Preparation</i>					
	Length of wire			16 cm	
	Diameter of wire			0.25 mm	
	Evaporating current			5.5 amp	
	Evaporating time			3 min	
	Substrate temperature			673°K	
	Annealing temperature			673°K	
	Annealing time			1 hr	
	Apparent area			120 cm ²	
	Total reaction volume			500 cm ³	
	Weight deposited			22 mg	
	Film thickness			1700 Å	
<i>Composition and Homogeneity Analysis</i>					
Section of vessel	X-ray diffraction results			X-ray fluorescence results	
	Corrected 2θ ₍₁₁₁₎	a ₀	% Ag	Ag Kα Ag Kα + Pd Kα	% Ag
A	38.85	4.011	67	0.70	74
B	38.75	4.021	72	0.68	72
C	38.83	4.014	68	0.69	73
D	38.84	4.012	67	0.69	73
E	38.95	4.006	65	0.69	73
	Average composition		68% ± 3%		73% ± 1%

TABLE 3
PREPARATION AND COMPOSITION DATA FOR THE 50% SILVER-50% PALLADIUM FILM I

<i>Preparation</i>					
	Length of wire				60 cm
	Diameter of wire				0.1 mm
	Evaporating current				4.0 amp
	Evaporating time				3 min
	Substrate temperature				673°K
	Annealing temperature				673°K
	Annealing time				1 hr
	Apparent area				120 cm ²
	Total reaction volume				500 cm ³
	Weight deposited				33 mg
	Film thickness				2500 Å
<i>Composition and Homogeneity Analysis</i>					
Section of vessel	X-ray diffraction results			X-ray fluorescence results	
	Corrected 2θ ₍₁₁₁₎	a ₀	% Ag	Ag Kα Ag Kα + Pd Kα	% Ag
A	39.15	3.982	52	0.49	52
B	39.20	3.977	50	0.49	52
C	39.20	3.977	50	0.48	51
D	39.21	3.976	49	0.50	53
E	39.19	3.978	50	0.50	53
	Average composition		50% ± 2%		52% ± 1%

TABLE 4
PREPARATION AND COMPOSITION DATA FOR THE 50% SILVER-50% PALLADIUM FILM II

<i>Preparation</i>					
	Length of wire				60 cm
	Diameter of wire				0.1 mm
	Evaporating current				4.0 amp
	Evaporating time				3 min
	Substrate temperature				673°K
	Annealing temperature				673°K
	Annealing time				1 hr
	Apparent area				120 cm ²
	Total reaction volume				500 cm ³
	Weight deposited				29 mg
	Film thickness				2200 Å
<i>Composition and Homogeneity Analysis</i>					
Section of vessel	X-ray diffraction results			X-ray fluorescence results	
	Corrected 2θ ₍₁₁₁₎	a ₀	% Ag	Ag Kα Ag Kα + Pd Kα	% Ag
A	39.22	3.975	48	0.49	52
B	39.23	3.974	48	0.48	51
C	39.21	3.976	49	0.50	53
D	39.25	3.972	47	0.49	52
E	39.23	3.974	48	0.48	51
	Average composition		48% ± 1%		52% ± 2%

for diffraction. This was shown, for example, by the examination of both sides of the inhomogeneous films which had been deposited at room temperature. Differences between the diffraction patterns of both sides of such a film revealed the expected gradients of silver and palladium. The original atomic layers to be condensed contained an alloy phase rich in silver and often free silver, while the final atomic layers contained an alloy phase less rich in silver and free palladium, as in Fig. 4(a). These results indicated that the diffraction patterns yielded only the surface composition of the films.

On the other hand, no differences were observed in the K spectra of both sides of these inhomogeneous films, indicating that X-ray fluorescence results yielded the bulk composition of the film. Therefore, for films deposited and annealed at 400°C. it was concluded that complete homogeneity was assured when the alloy compositions determined by both techniques were in agreement.

Parahydrogen Conversion Reactions

The apparatus consisted of a conventional high-vacuum system with provision for the preparation and storage of pure normal and para-enriched hydrogen. Full details of the preparation and analysis of reaction mixtures, together with the experimental determination of rate constants and activation energies, have been given previously (21).

RESULTS

The films used in this work had compositions of approximately 50% Ag-50% Pd, 70% Ag-30% Pd, 80% Ag-20% Pd, and 100% Ag. The details of preparation and composition are shown in Tables 1 through 4.

The parahydrogen conversion was found to follow first order kinetics under all experimental conditions studied, the experimental rate constant being given by

$$k = (1/t) \ln (C_0/C_t) \quad (1)$$

where C_0 and C_t are the concentrations of parahydrogen in excess of the equilibrium

value at times zero and t , respectively. The variation of rate constant with temperature is given by the Arrhenius equation, where E is the apparent activation energy and B the frequency factor.

Figure 5 shows the Arrhenius plots for the conversion on the series of alloy films, the percentage of silver being shown in

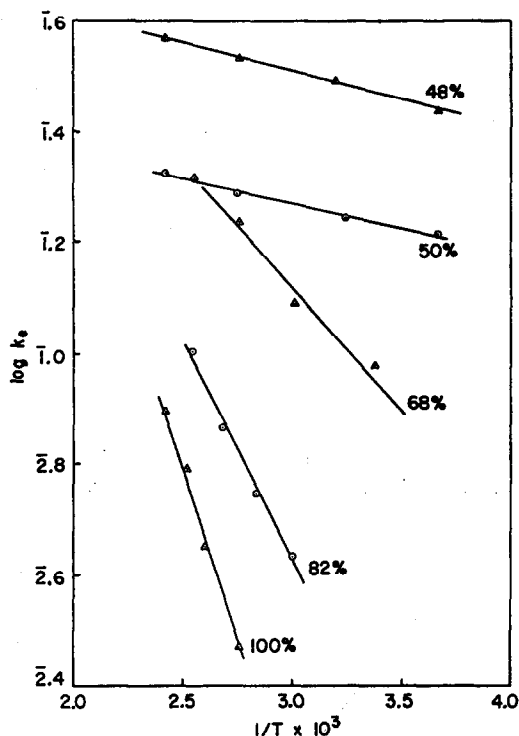


FIG. 5. Activation energy curves for increasing silver content (% Ag indicated).

each case. The marked increase in negative slope (and hence in activation energy) between a silver content of 50% and 68% is clearly seen.

During the kinetic studies on any film no change in activity was observed over its period of use.

The pressure dependency of the conversion was found to follow a Langmuir isotherm

$$1/k = (a/b) + ap \quad (2)$$

the reciprocal of the rate constant being directly proportional to reaction pressure. Figure 6 shows a typical set of pressure

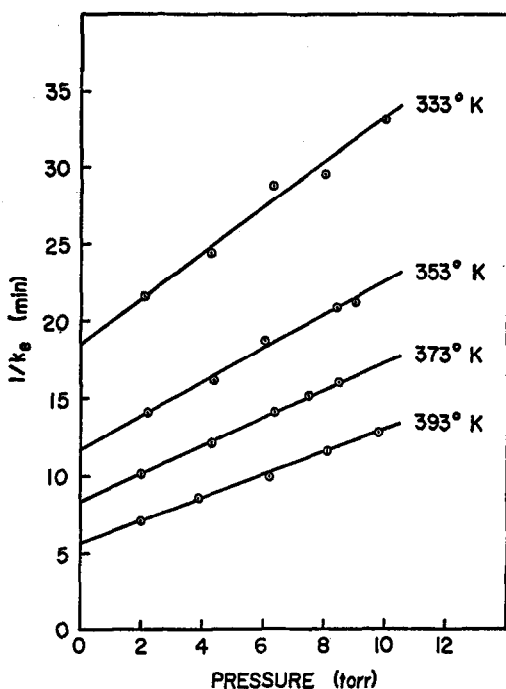


Fig. 6. The pressure dependency of the rate constants for the 80% Ag-20% Pd films.

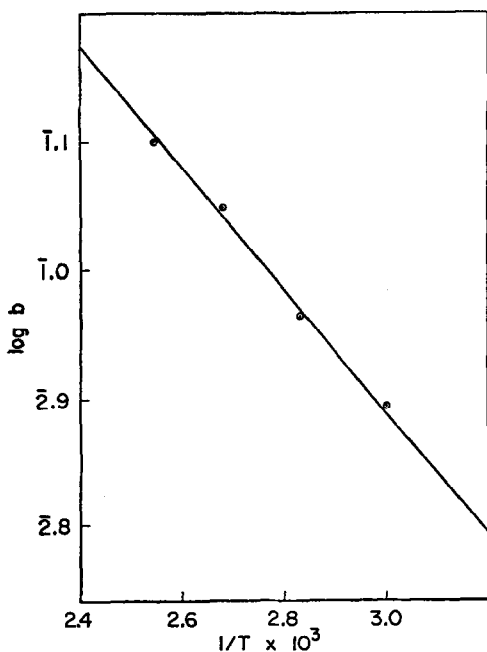


Fig. 7. Determination of the heat of adsorption for the 80% Ag-20% Pd films.

dependency results obtained for the 80% Ag-20% Pd film. Similar results were obtained for all the other films studied, over the same pressure range (approximately 2 to 10 torr).

It has been shown previously (21) that from the temperature dependence of the constant b in Eq. (2), which represents

TABLE 5
THERMODYNAMIC DATA FOR
PARAHYDROGEN CONVERSION

Weight % Ag in alloy	Temperature range of reactions (°K)	E (kcal/mole)	$\log B^*$	ΔH^*
48	273-413°	0.47	0.44	—
50	273-413°	0.37	0.27	—
68	296-393°	1.91	1.00	-1.29
82	333-393°	4.29	2.01	-2.11
100	363-413°	5.90	2.64	-2.89
100 ^a	363-413°	5.40	2.20	-2.54

^a Reference (21).

the ratio of the adsorption-desorption rate constants, heats of adsorption may be calculated. Figure 7 shows a typical plot for the determination of heat of adsorption, for the 80% Ag-20% Pd film.

Table 5 shows the apparent activation energies, heats of adsorption, and frequency factors (corrected for unit reaction volume and unit surface area of catalyst), for the conversion on the alloy films studied. For comparison results obtained earlier (21) on a silver film are also included.

DISCUSSION

Activation Energies

Figure 5 shows the increase in activation energies as the silver content of the alloy increases. It is also observed that the activity, k_e , decreases progressively from the 50% Ag-Pd film to the 100% film. Such increases in activation energy or decreases in activity cannot be attributed to geometric factors of the catalysts. The changes in lattice spacing from an alloy of 50% Ag to one of 70%, 80%, and 100% Ag are 0.4, 0.09, and 0.12 Å, respectively. Sherman and Eyring (22, 23) have shown

that the magnitude of the changes in the activation energy for the parahydrogen conversion resulting from such changes in lattice parameters would be at least an order of magnitude lower than the above observed changes.

It has also been suggested (4) that where activation energies change significantly with alloy composition, the activity may be temperature-dependent. This was found to be the case for the hydrogenation of acetylene over Ni-Cu and Ni-Co alloys (2). It was for this reason that all kinetic studies in this work were made over essentially the same temperature ranges.

Figure 8 shows the activation energy as a function of alloy composition. In the bulk Ag-Pd alloys the *d* band of the palladium becomes filled at a composition of

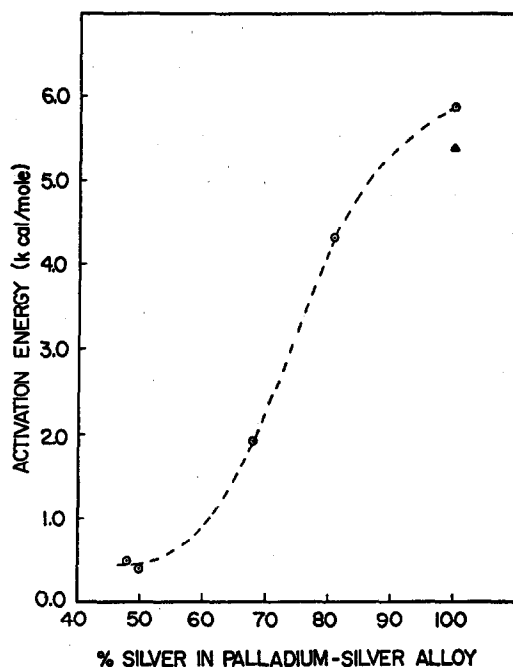


Fig. 8. Activation energy as a function of alloy composition: ○, this work; ▲, ref. (21).

about 60% silver by the *s* electrons from the silver (3, 4). It may be seen from Fig. 8 that the rise in activation energy occurs at a silver content somewhat higher than the expected 60%. It must be pointed out, however, that the exact point at

which the *d* band becomes filled in the bulk alloy has an uncertainty of about 5% (1). It may also be questioned whether or not the point at which the *d* band becomes filled in the bulk is exactly the same point at which all the *d* orbitals in the surface become paired and there are also the other considerations mentioned in the introduction. It is interesting to note that Pratt (6) has shown that the change of total electron Fermic energy, arising from the transfer of electrons from the *s* band of silver to the *d* band of palladium, shows a minimum at 70% silver.

The kinetic data obtained on these Ag-Pd alloy films show a linear compensation effect. That is, the corrected pre-exponential frequency factor in the Arrhenius

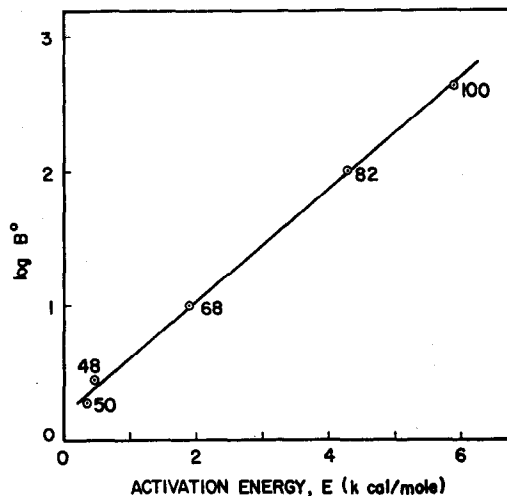


Fig. 9. Compensation effect for the alloy films (%Ag indicated).

equation may be expressed as a linear function of the activation energy, as shown in Fig. 9. This compensation effect can be expressed as

$$\log B^{\circ} = 0.42E + 0.19 \quad (3)$$

E being the activation energy in kcal/mole.

Many interpretations of this effect have been presented in the literature (24-27). The more fundamental approach, based on a linear relationship between the heats and entropies of adsorption, seems to be the most promising. The calculated values

of the heats and entropies of chemisorption for the silver-rich alloys (Table 6) show that such a relationship may exist.

In those cases in which a compensation effect exists it is possible for large variations in the activation energy and pre-exponential factor to produce relatively small changes in the activity.

Bond (4) has shown that when the compensation effect can be expressed in the form of Eq. (3) there must be some characteristic temperature, T_c , at which the reaction rates are equal for a given catalyst series. That is, the Arrhenius plots will converge and cross over at this temperature. (See, for example, ref. 4, Fig. 3, p. 141.) In further developing this point Bond shows that the relationship between the slope of the compensation effect line, m , and the characteristic temperature is

$$m = (2.303RT_c)^{-1} \quad (4)$$

Extrapolation of the lines for the 48%, 68%, 80%, and 100% silver alloys in Fig. 5 shows a convergence at a point represented by the coordinates $\log k_a = 1.6 \pm 0.1$ and $1/T \times 10^3 = 1.85 \pm 0.01$, corresponding to a characteristic temperature of $540^\circ \pm 25^\circ\text{K}$.

From Eq. (4) the value of m may be calculated as 0.41 ± 0.02 , compared with the experimental value of 0.42 from Eq. (3). The marked difference in activity between the 50% and 48% silver alloy films could be due to some contamination of the former, which would lead to a lower activity for apparently equal geometric areas of films.

Heats of Adsorption

The heats of adsorption at equilibrium coverage obtained in this work are shown in Table 5. It may be seen that the heat of adsorption increased with silver content. The value obtained for the 100% Ag film, 2.89 kcal/mole, is in good agreement with previously reported values of 2.54 kcal/mole for a film (21) and 2.5 kcal/mole for a foil (28).

It was not possible to obtain heats of adsorption for hydrogen on the 48% and

50% silver films. The pressure dependency results for these films (similar to Fig. 2) gave good linear plots at constant temperature but yielded negative intercepts. It is possible that this anomalous effect could be due to the occurrence of an absorption as well as an adsorption process on these two films. Although no absorption was detectable from pressure measurements in the constant volume system the possibility of a slight amount of absorption of hydrogen in the 48% and 50% Ag films cannot be discounted.

Little work has been done on the heats of adsorption on alloys, but Bortner and Parravano (29) found that the heat of adsorption of oxygen on Pd-Ag alloy powders also increased with increasing silver content. Shields and Russell (30) showed that the heat of adsorption of hydrogen on a 62% Cu-38% Ni alloy was approximately the same as on pure copper.

Entropy Change upon Adsorption

The change in entropy upon the chemisorption of hydrogen can be calculated as shown previously (21, 24). If the standard state is defined as a surface coverage, θ , of 0.5 and a pressure of 1 atm, then

$$\Delta F_a = RT \ln b \quad (5)$$

where ΔF_a is the free energy change upon adsorption and T the average temperature of the adsorption studies. For the silver-rich alloy films an average temperature of 373°K was chosen and the values of b obtained from the $\log b$ vs. $1/T$ curves, to calculate the data shown in Table 6.

For pure metal catalysts the experimentally determined entropy change may be compared with calculated entropy changes for localized and nonlocalized adsorption. The data for these calculations are not available for alloy systems but it is interesting to note, nevertheless, that calculations for hydrogen adsorption on a silver film (21), for $\theta = 0.10$ yield values of -15.4 e.u. and -29.4 e.u. for nonlocalized and localized adsorption, respectively. From this information it seems reasonable to conclude that the adsorbed hydrogen film on the silver rich alloys is mobile.

TABLE 6
THERMODYNAMIC DATA FOR CHEMISORPTION

Weight % Ag in alloy	Average temp. (°K)	log b	ΔF° (kcal/mole)	ΔH° (kcal/mole)	ΔS° (e. u.)
100	373°	2.94	1.82	-2.89	-12.6
82	373°	1.04	1.65	-2.11	-10.1
68	373°	1.93	0.12	-1.29	-3.8

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