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A STUDY OF THE ADSORPTION MECHANISMS ON OXYGEN ELECTRODES

Y. L. SANDLER

Report No. 1

Contract DA-36-039 AMC-00136 (E)

dated 29 January 1963

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First Semi-Annual Report, 6 September to 31 December 1962

File No. 5385-PM-63-91 (4105)

U. S. Army Electronics Research and Development Laboratory
Fort Monmouth, New Jersey

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Prepared by

Y. L. Sandler

WESTINGHOUSE RESEARCH CORPORATION
Research Laboratories
Pittsburgh 35, Pennsylvania

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I. OBJECTIVE

A study is carried out of the oxygen adsorption mechanism at the surface of materials that could be incorporated in oxygen electrodes for operation in aqueous electrolytes or other electrolytes at moderate temperatures. Information resulting from these studies is to provide a new basis for further oxygen electrode development work.

II. ABSTRACT

The work reported here is a continuation of the work done under a previous contrast DA-36-039-SC-89138.

An improved method for studying the exchange of oxygen with O^{18} pre-adsorbed on a metal surface is reported. Detailed information on the nature of the chemisorbed oxygen on silver and the isotopic exchange mechanism at 200°C was obtained. The rates of chemisorption and dissociation were determined, which are two distinct processes beyond a certain oxygen coverage.

Oxygen pressure versus temperature characteristics and isotopic exchange reactions on carefully cleaned silver and silver-gold alloy powder surfaces are reported. The powders were all prepared by a spark erosion method. A strong increase in the exchange activity was obtained at elevated temperatures by dilution of the silver.

With pure silver at room temperature a dissociative oxygen exchange was observed which decreased with time. A palladium powder (of commercial origin) was active only above 100°C.

In presence of water, the chemisorption of oxygen on silver was strongly retarded at moderate temperatures. On palladium, under similar conditions, no exchanged oxygen was found in the gas phase although the isotopic composition of the water showed that oxygen had exchanged with it. Oxygen in presence of water at moderate temperatures thus appears to be reactive only in form of adsorbed OH.

III. INTRODUCTION

The work presented in this report is a continuation of the investigation under the previous Contract DA-36-039-SC-89138. Most of the methods employed in the present work are essentially the same as previously described. For a better understanding of the methods and the purpose of the measurements the reader is advised to consult the Final Report (Report No. 3) of the previous contract.

IV. RESULTS

1. Oxygen Exchange on Gold

A final experiment was performed with a carefully cleaned gold surface (cf. Final Report, page 46). In the presence of water vapor 0.2 atmospheres of a $O^{16}_2 + O^{18}_2$ mixture was contacted with the gold at room temperature. No measurable amount of $O^{16}O^{18}$ was formed within one week. The half life of the exchange must have been larger than 40,000 hours. Clean gold does not activate oxygen with or without water present. We calculate that an electric current (if it could be produced via a dissociative oxygen adsorption mechanism under our experimental conditions) would certainly have to be smaller than 10^{-10} amp per cm^2 of effective surface area.

2. The Exchange of Oxygen with Pre-Adsorbed Oxygen on Silver (V) at 200°C

The exchange experiments with pre-adsorbed oxygen on silver were continued in order to obtain more information on the mechanism of the exchange reaction. The previous experiments (cf. Final Report, page 35) had shown the existence of a molecular chemisorption in addition to an atomic adsorption at 200°C.

The method has now been improved, allowing the study of the kinetics of adsorption and exchange in considerable detail. As will be seen from the experiments described in the following pages, adsorption of oxygen beyond a certain coverage takes place in form of molecules; adsorption and exchange then are two distinct consecutive processes. Kinetic data on these separate processes have been obtained and it is hoped that a correlation with electrode mechanisms will be possible when the corresponding electrochemical experiments have been carried out.

Experimental Procedure:- Seven runs were made with 20 gm of silver powder (Handy and Harman, 99.999% pure) in a vessel of about 140 cc. Proper choice of the vessel size and surface/volume ratio made it possible to make a large number of measurements in each run without appreciable depletion of the gas in the system. Neon (in excess) was admixed to the O^{16}_2 and argon to the O^{18}_2. In part of the experiments O^{16}_2 was pre-adsorbed and O^{18}_2 added later, in the others the reverse procedure was adopted. Small gas samples were withdrawn at regular time intervals. The absolute amount in cc (at 1 atm. and 25°C) was determined for each component by measuring the pressure of the sample in a standard 3 liter volume and by analysis of the composition in the mass spectrometer (Consolidated Electrodynamics Corp., Model 21-103C). At the end of a run the entire amount of neon and of argon left in the vessel was measured by repeated expansion into the standard 3 liter volume and analysis. The amount of each type of oxygen in the gas phase as well as in the absorbed phase at any given time can then be calculated. The sample was first degassed several days on a separate vacuum system at increasing temperatures, cleaned with oxygen and hydrogen up to 520°C and again pumped. After the first run, immediately before a new run was started, the sample was subjected, at 500°C, to short contacts with oxygen and hydrogen, followed by pumping for half an hour and cooling to the reaction temperature (200°C) in helium.

For the sake of brevity, only the results of two runs will be given which represent the two extremes in coverage so far investigated. Table 1a gives the mass spectrometric analyses of the first run. The oxygen adsorption is easily recognized qualitatively from the change of the ratios Ne/O^{16}_2 and A/O^{18}_2 given in the last two columns in Table 1a. Table 1b is a balance sheet, giving the total amounts of the various gases added and

TABLE 1a

EXCHANGE OF PREADSORBED O^{16}_2 + Ne with O^{18}_2 + A on Ag V at 200°C, Run No. 1

MEASUREMENTS

Time Min.		MOLE %							
		Neon	A	$O^{16}O^{16}$	$O^{16}O^{18}$	$O^{17}O^{18}$	$O^{18}O^{18}$	$\frac{\text{Neon}}{O^{16}O^{16}}$	$\frac{\text{Argon}}{O^{18}O^{18}}$
0	Admitted 25 mm O^{16}_2 + Neon Mixture	88.24		11.55	.05			7.64	
20	O^{16}_2 + Neon, Sample No. 1	93.78		6.22				15.08	
50	Added O^{18}_2 + A Mixture, 25 mm		92.11	.06	1.08	.04	6.71		13.73
55	O^{16}_2 + Ne, O^{18}_2 + A, No. 2	42.77	50.47	2.97	.53		3.26	14.40	15.48
65	O^{16}_2 + Ne, O^{18}_2 + A, No. 3	42.90	50.22	3.27	.55		2.76	13.12	18.30
80	O^{16}_2 + Ne, O^{18}_2 + A, No. 4	42.91	50.49	3.64	.68		2.28	11.79	22.14
110	O^{16}_2 + Ne, O^{18}_2 + A, No. 5	42.70	50.71	3.93	1.06		1.60	10.86	31.69
170	O^{16}_2 + Ne, O^{18}_2 + A, No. 6	43.12	50.41	4.07	1.59		.81	10.59	62.23
230	O^{16}_2 + Ne, O^{18}_2 + A, No. 7	42.35	51.10	4.11	1.90		.54	10.30	94.63
290	O^{16}_2 + Ne, O^{18}_2 + A, No. 8	44.18	49.48	4.02	1.97		.35	10.99	141.37

TABLE 1b

BALANCE SHEET FOR OXYGENS IN ENTIRE SYSTEM, RUN NO. 1

	cc. of Neon	A	$O^{16}O^{16}$	$O^{16}O^{18}$	$O^{17}O^{18}$	$O^{18}O^{18}$
O^{16}_2 + Neon added	2.7685		.3623	.0015		
Sample No. 1 withdrawn	.0494		.0032			
Balance:	2.7190		.3590	.0015		
O^{18}_2 + A added		2.8501	.0018	.0334	.0012	.2076
	2.7190	2.8501	.3609	.0349	.0012	.2076
Sample No. 2	.0184	.0217	.0012	0.00023		.0014
	2.7005	2.8283	.3596	.0347		.2062
Sample No. 3	.0252	.0297	.0019	.0003		.0016
	2.6753	2.7986	.3577	.0344		.2045
Sample No. 4	.0228	.0268	.0019	.0003		.0012
	2.6524	2.7718	.3558	.0340		.2033
Sample No. 5	.0214	.0254	.0019	.0005		.0008
	2.6310	2.7463	.3538	.0335		.2025
Sample No. 6	.0227	.0266	.0021	.0008		.0004
	2.6082	2.7197	.3516	.0327		.2021
Sample No. 7	.0234	.0283	.0022	.0010		.0003
	2.5848	2.6914	.3494	.0316		.2018
Sample No. 8	.0215	.0241	.0019	.0009		.0002
	2.5632	2.6672	.3474	.0306		.2016
Removed at Room Temp.	2.5632	2.6672	.2244	.1122		.0195
Residuals	0.0	0.0	.1230	-.0816		.1821
Total O_2 added			.3642	.0349		.2076
Total O_2 removed			.2412	.1165		.0255
			.1230	-.0816		.1821

withdrawn from the system.

In Fig. 1 the changes taking place in the gas phase are represented. The amounts (in cc) of various types of oxygen and their totals are plotted as a function of time. Of the 0.36 cc of O^{16}_2 admitted, about one half is adsorbed. After 50 minutes 0.207 cc of O^{18}_2, plus some $O^{16}O^{18}$ contained in the heavy oxygen, are admitted. It is seen from the curve "Total Oxygen" that some further adsorption of the mixture takes place. Immediately upon contact of the O^{18}_2, O^{16} is evolved in molecular form. It is particularly significant that in the initial 20-30 minutes after contact of the O^{18}_2 no $O^{16}O^{18}$ is formed. The overall atomic exchange reaction thus consists of two distinct consecutive steps: the molecular chemisorption and the atomic exchange reaction in the surface layer. The experiment shows in a particularly clear manner the existence of a molecular chemisorption.

Data of another run, performed at lower pressures, are given in Tables 2a and 2b (run No. 2). The changes in the gas phase are represented in Fig. 2. Here O^{18}_2 was admitted first and in smaller amount. The isotopes were interchanged to study the importance of isotope effects and to explore a possible exchange with residual oxygen left in the bulk of the silver. Both effects exist but were found not to change the results significantly.

The O^{18}_2, admitted at a pressure of 0.85 mm Hg, was taken up quantitatively to give a coverage of 0.116 cc. 0.139 cc of O^{16}_2 were then admitted. It is seen from the Figure that there is now an immediate evolution of $O^{16}O^{18}$, leading to a relatively fast isotopic equilibrium. The half-life for the $O^{16}O^{18}$ formation now is less than 3 minutes as compared to a few hours in the first run. This in spite of the fact that the oxygen coverages differ only by a small factor. The other runs made gave results

TABLE 2 a

EXCHANGE OF PREADSORBED O^{18}_2 + A with O^{16}_2 + Ne on Ag V at 200°C, Run No. 2

MEASUREMENTS

Time Min.		Neon	Argon	$O^{16}O^{16}$	$O^{16}O^{18}$	$O^{17}O^{18}$	$O^{18}O^{18}$	$\frac{\text{Neon}}{O^{16}O^{16}}$	$\frac{\text{Argon}}{O^{18}O^{18}}$
0	Admitted O^{18}_2 + Argon, 12 mm		92.36		1.05		6.59		14.02
10	O^{18}_2 + Argon, Sample No. 1		99.99						
20	O^{18}_2 + Argon, No. 2		99.99					Complete uptake	
25	O^{16}_2 + Neon, 9 mm	88.35		11.65				7.58	
30	O^{18}_2 + A, O^{16}_2 + Ne, No. 3	38.06	58.15	3.25	.47		.07	11.71	830.71
40	O^{18}_2 + A, O^{16}_2 + Ne, No. 4	38.58	57.97	2.39	.91		.15	16.14	386.47
55	O^{18}_2 + A, O^{16}_2 + Ne, No. 5	37.73	58.93	2.07	1.12		.15	18.23	392.87
85	O^{18}_2 + A, O^{16}_2 + Ne, No. 6	37.42	59.13	2.11	1.20		.14	17.73	422.36
145	O^{18}_2 + A, O^{16}_2 + Ne, No. 7	37.75	59.18	1.92	1.06		.09	19.66	657.56
205	O^{18}_2 + A, O^{16}_2 + Neon, No. 8	37.35	59.57	2.00	1.02		.06	18.68	992.83
265	O^{18}_2 + A, O^{16}_2 + Neon, No. 9	37.74	59.10	2.01	1.01		.14	18.78	422.14

TABLE 2b

BALANCE SHEET FOR OXYGENS IN ENTIRE SYSTEM, RUN NO. 2

	cc. of Neon	A	$O^{16}O^{16}$	$O^{16}O^{18}$	$O^{18}O^{18}$
O^{18}_2 + A added		1.6227		.0184	.1158
Sample No. 1 removed		.0617			
		1.5610			
Sample No. 2		.0573			
		1.5036			
O^{16}_2 + Neon added	1.0568		.1393		
	1.0568	1.5036	.1393	.0184	.1157
Sample No. 3	.0220	.0337	.0018	.0003	.0000
	1.0348	1.4699	.1374	.0181	.1157
Sample No. 4	.0238	.0358	.0014	.0005	.0001
	1.0104	1.4340	.1359	.0176	.1156
Sample No. 5	.0275	.0430	.0015	.0008	.0001
	.9833	1.3910	.1344	.1067	.1155
Sample No. 6	.0212	.0336	.0012	.0006	.0001
	.9621	1.3573	.1332	.0161	.1154
Sample No. 7	.0235	.0368	.0011	.0006	.0000
	.9385	1.3205	.1320	.0154	.1154
Sample No. 8	.0252	.0403	.0013	.0006	.0001
	.9133	1.2801	.1307	.0147	.1153
Sample No. 9	.0244	.0382	.0013	.0006	.0001
	.8888	1.2419	.1294	.0141	.1152
Removed during cooling period	.8888	1.2419	.0585	.0283	.0034
	0.0	0.0	.0708	-.0142	.1118

intermediate between the two cases discussed.

The essential difference between the two runs is that in the first all atomic sites are covered with the first admitted dose of oxygen. The second dose of oxygen then has to cover molecular sites. In the second case, at least the larger part of the second dose of oxygen is also adsorbed on atomic sites. This accounts for the very rapid initial exchange in the second case.

We conclude from our experiments that there are distinct atomic and molecular sites on the silver. This point had not been clear until now.(1),(2)

The hump in the O^{16}_2 curve is probably not an experimental inaccuracy, but is due to a surface rearrangement taking place. Spontaneous gas evolutions of this type are visible on many of the curves and also appeared in some of our pressure-temperature experiments at about 200°C.

3. Results with Sparked Powders

a. Experimental: Silver (VI) and silver-gold alloy wires were produced from purest materials available (better than 99.999%) by levitation melting and swaging. Tests by solid mass-spectrometry showed that the low impurity level was maintained. For carbon removal, the wires were heat-treated at temperatures above 750°C for 3 days in oxygen. The wires were then sparked under high purity water for production of a fine powder. (For details, cf. Final Report). The reaction vessel, of about 18 cc volume, consisted of a quartz bulb joined to Pyrex tubing, a thermistor, a small "finger" for condensing water or condensable impurities, and a Hoke metal valve.

The cleaning treatment finally adopted was the following:- before filling in the powder, the system was degassed, with the quartz bulb kept at about 600°C and the remainder of the system at 200°C. Occasionally small amounts of O_2 were admitted for cleaning the surfaces. The powder was then deposited in the quartz bulb and the system closed by means of a H_2 flame (to avoid any contact with carbonaceous gases). After evacuation the temperature was gradually raised to the given maximum degassing temperature. Oxygen and/or hydrogen were admitted at certain intervals at a gradually decreasing pressure to clean the surfaces. The gases were occasionally pumped into a mass spectrometer for analysis. This was done either directly via a dry ice trap or, for cleaner work, by condensing the impurities in a liquid-nitrogen cooled trap and subsequent warming up of the trap after isolating the reaction vessel. Each time before a new run was made, the powder was brought close to the maximum degassing temperature and subjected to treatment with oxygen (or hydrogen) at decreasing pressures, down to 10^{-3} - 10^{-4} mm Hg, followed by only a few minutes final pumping and chilling to the reaction temperature in helium. In this way the diffusion of fresh impurities (carbon or oxygen) from the bulk to the surface was minimized.

The areas of the powders were measured by krypton adsorption and usually were carried out in situ after a certain series of experiments was terminated. More frequent determinations proved impractical because of contamination of the powders by the measurement. Since a certain amount of sintering always took place during the prolonged experiments, the given areas may in some cases be only reliable to a factor of approximately 2.

b. 25% Silver-Gold Alloy:- Some preliminary measurements were already reported (Final Report, p. 50). These were carried out after pretreatment of the powder at 280°C with oxygen. An approximate temperature dependence of the half life τ of the $O^{16}_2 + O^{18}_2$ exchange reaction is shown in Fig. 3, curve 1. A pressure-temperature plot was already given in the Final Report (Fig. 1a). It showed the same general characteristics as previously obtained with 100% silver, but the adsorption, both at -195°C (physical) and above room temperature (chemical) was stronger with the alloy. This is in part due to the larger surface area of the alloy, which was determined to be 14,000 cm^2 (1.5 gm). The coverage amounted to only 1.3% of a monolayer.

The powder was then further degassed and treated with hydrogen up to 500°C. Two pressure-temperature curves thus taken are shown in Fig. 4.

Again the same type of behavior is seen, but the adsorptions are now weaker than in the first run (Final Report, Fig. 19) because of the higher relative oxygen coverage.

The isotopic oxygen exchange reaction was also measured again. The results are shown in Fig. 3, curve 2. The first 4 points, giving a good straight line, point 5 was taken 1 day later, point 6 2 days later. The deviation of the last point from the straight line probably indicates poisoning of the surface at the relatively low temperatures.

The surface area at the end of these experiments amounted to 1,600 cm^2. This is 9 times smaller than the area found after run No. 1 (curve 1). The exchange rate is about 20 times slower than in run No. 1. The discrepancy by a factor of 2 may be due to the uncertainty in the surface areas at the actual time of the runs, (see above, p. 12). At any rate, the pretreatment of higher temperatures and cleaning with hydrogen does not seem to have had a considerable effect on the rates observed above 200°C.

c. 4% Silver-Gold Alloy:- This sample was pretreated with oxygen to 280°C. A pressure-temperature curve, shown in Fig. 5, was then taken. The curve is similar to the previous curves but the amount of chemisorption now was much smaller; it only caused a 25% pressure drop before the pressure increase at 200°C. This confirms, at least qualitatively, that the concentration of silver on the surface itself has actually become smaller and that spark erosion is a suitable method for the production of alloy surfaces.

The results of the oxygen exchange measurements are indicated in Fig. 6, Ag 4%. The half-life at 200°C is seen to be about one half of the half-life obtained with Ag 25%. (The latter curve is the same as the upper curve in Fig. 3.) The surface area was 7400 cm^2, as compared with 1600 cm of the 25% sample. The rate per unit area, therefore was only about 2 times lower for the 4% sample while the silver content was about 6 times lower than for the 25% sample. Thus, the rate of the dissociative exchange reaction per surface silver atom appears to be slightly improved by the dilution of the silver. Also, the apparent activation energy, calculated from the curves appears somewhat decreased (29,500 as compared to 33,000 cals/mole).

The dilution effect, however, appears considerably greater when comparing the 2 alloy curves with the corresponding curves obtained with a silver sample prepared by the same method ("Ag VI"), as described later.

In Table 3 results of a desorption experiment are given, performed immediately after the last exchange experiment on the 4% alloy at 194°C. The reaction vessel was evacuated for about 10 seconds, when the gas phase contained about 23.8% $O^{16}O^{18}$ (see analysis, first line). The subsequent samples collected by desorption from the surface are still not in equilibrium with respect to $O^{16}O^{18}$. The expression $[O^{16}O^{18}]^2 / [O^{16}_2][O^{18}_2]$ should be equal to the equilibrium constant = 4 if the gas was rapidly randomized on the surface. The lack of equilibrium is in agreement with the results already reported with 100% silver (Ag V, Chapter IV 2). The ratio O^{16}_2/O^{18}_2, given in the last column, shows that the gas gradually becomes richer in O^{16}. This must be due to O^{16} retained in the bulk during the degassing period appearing at the surface. An isotope effect would give a change in the opposite direction. The effect is much stronger with pure silver.

d. <u>100% Silver (Ag VI)</u>:- The previous experiments with pure silver had been carried out with a powder from commercial sources. The uptake of oxygen at room temperature had been found to be very slow (cf. Final Report). This suggested that the silver surface might not be atomically clean. Furthermore the strong paramagnetism found (by means of the low temperature parahydrogen conversion) when the silver was pretreated with hydrogen also suggested the presence of impurities. For this reason, and also in order to permit a better comparison with the performance of the alloy powders, a silver powder (Ag VI) produced by our sparking method was tested. For comparison, the same experiments were performed after hydrogen - and after oxygen - pretreatment.

TABLE 3

DESORPTION OF OXYGEN FROM 4% Ag-Au ALLOY

	Temperature °C	Time (min.)	Pressure in Vessel mm Hg	O^{16}_2	$O^{16}O^{18}$	O^{18}_2	$\frac{[O^{16}O^{18}]^2}{[O^{16}_2][O^{18}_2]}$	Half-Life min.	$\frac{O^{16}_2}{O^{18}_2}$
Admitted Sample	194.5°	0	100	48.4	6.2	45.4	0.057	1330	1.06
	194.5°	988	100	39.5	23.8	36.7	0.39		1.07
Pumped	194.5°	.2	0						
Desorption:									
1	194.5°	9.5	.039	34.6	40.4	25.0	1.9		1.38
2	194.5°	19.5	.035	33.3	45.9	20.8	3.0		1.65
3	194.5°	29.5	.034	33.0	47.4	19.6	3.5		1.63
4	194.5°	41	.034	31.9	48.8	19.3	3.9		1.65
5	194.5°	51	.034	31.3	49.5	19.2	4.1		1.63
6	194.5°	63	.034	31.9	48.8	19.3	3.9		1.65
7	194.5°	220	.028	31.4	49.2	19.4	4.0		1.62
8	270°	overnight	>>0.5	32.4	49.2	18.4	4.05		1.76

d-1. H_2-pretreated Silver: The powder was cleaned with oxygen up to 420°C and was then treated for several hours with hydrogen up to 500°C at pressures up to 1 cm. On pumping a slow desorption of gas was observed at 500°C which at first mainly consisted of hydrogen, but later mainly of water vapor. After 1 hour about 6×10^{-4} mm gas was collected in the 18 cc volume of the reaction vessel in 4 minutes; over 85% of this was water vapor. At 400°C no measurable desorption occurred in the same time span. In this state the vessel was cooled to -195°C and a pressure-temperature run was made with oxygen. Fig. 7 shows the result. Contrary to the previous results obtained with silver, a fast chemisorption to very low pressures ($\sim 10^{-4}$ mm) took place at -86°C, the lowest temperature at which the continuous temperature rise started (cf. Final Report, p. 7). The physically adsorbed gas desorbing at -86°C is seen to be readsorbed immediately. The fast uptake probably is characteristic for a clean surface.

When the powder was evacuated for 2 hours at 500°C, further desorption of water was observed. The sample was then cooled to -195°C and the parahydrogen conversion was measured. A fast conversion was obtained with a half-life of only 2 minutes. A previous, presumably less pure, silver sample (Ag IV, Final Report, p. 27) has given a similar result. It was then tentatively concluded that the strong paramagnetism causing the observed conversion is probably due to carbonaceous impurities. In view of the fact now observed that large amounts of hydrogen are retained by the surface, it is more likely that this main impurity, presumably in form of OH ions, is the cause of the paramagnetism (see Discussion).

After pumping overnight at room temperature the isotopic oxygen exchange reaction $O^{16}_2 + O^{18}_2 \longrightarrow 2\, O^{16}O^{18}$ was measured. The results are presented in Table 4. The "half-life τ" was calculated under the assumption of an exponential decay between two subsequent measurements, the equilibrium value of $O^{16}O^{18}$ being given by an equilibrium constant = 4. For a roughly equimolar mixture of $O^{16}{}_2$ and $O^{18}{}_2$, the equilibrium concentration of $O^{16}O^{18}$ is 50%. As seen, a fairly fast formation of $O^{16}O^{18}$ now occurred at room temperature, not previously obtained with the other silver samples. This must be a true $O^{16}{}_2 + O^{18}{}_2$ exchange on a clean surface. An exchange of oxygen with an adsorbed OH ion (or any impurity oxide) would lead to a decrease in the $O^{18}{}_2$ concentration, initially equal to the increase in $O^{16}O^{18}$: $-OH^{16} + O^{18}{}_2 \rightarrow -OH^{18} + O^{16}O^{18}$. This was not found to be the case at room temperature. The continuous slowing down of the reaction (increasing τ) is probably due to poisoning by impurities arriving at the surface from the bulk or the gas phase.

d-2. Oxygen-Pretreated Silver: After alternate oxygen treatment and pumping for 24 hours at 500°C, a pressure-temperature run was again made. As Figure 8, curve 1, shows, again a strong uptake was obtained at low temperatures. The rate of chemisorption was not as high as after hydrogen pretreatment (Fig. 7), but the percentage of surface covered with oxygen probably was larger in the present case because of a decrease in surface area that may have occurred during the high temperature treatment between the two series of measurements. The absolute amounts of oxygen admitted to the system were the same. With a surface area determined to be 1330 cm^2 (for about 1-1/2 gm of silver) the coverage now amounted to about 0.1 monolayers.*

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* Note: The oxygen coverage in all cases was calculated as though the oxygen was physically adsorbed, i.e. by assigning to the adsorbed oxygen "molecule an area of 16 A^2. This was done because the true number of adsorption sites was not known.

TABLE 4

$O^{16}_2 + O^{18}_2$ EXCHANGE ON Ag VI, AFTER H_2 PRETREATMENT

Date		Pressure mm Hg	Temp. °C	Time at Temp. mins.	O^{16}_2	$O^{16}O^{18}$	O^{18}_2	Half-Life τ mins.
					Mole %			
10/30	Mixture admitted	3.5	24	0	46.85	6.29	46.86	350
	Sample No. 1		24	33	46.21	9.29	44.50	
	2		24	123	45.35	11.27	43.38	↓
	3		24	196	45.00	12.20	42.80	
	4		24	405	44.28	13.81	41.82	
10/31	5		24	1500	41.91	17.83	40.16	3400
	6		101	125	40.11	18.87	40.02	
	7		175	50	38.65	20.40	39.95	
	8		175	1065	46.94	28.03	25.23	
11/2	Mixture admitted	3.5		0	47.8	6.2	46.0	
	Sample No. 1		200	30	48.2	6.5	45.3	
			200	90	48.2	7.0	44.8	~4000
			250	0	49.0	10.4	40.6	
			250	15	49.0	13.5	37.1	130
			250	31	50.0	15.7	34.3	
			250	57	50.2	18.8	31.0	
			250	99	50.4	22.1	27.5	↓
			250	132	50.6	24.4	25.0	
			250	160	51.1	25.9	23.0	
			250	193	51.1	27.5	21.4	
			250	226	51.0	29.1	19.9	250

A second dose of gas was added on the following day at room temperature to give a total coverage of about 0.3 monolayers. The curve obtained (Fig. 8, curve 2) now resembled the curves obtained with the less pure silver powders (Final Report, Fig. 10): the chemisorption is now much slower and more incomplete before it becomes reversible at 230°C (changing slope). In part, this behavior may have been due to accumulation of impurities during the long time elapsed since cleaning of the surface. Some condensable impurities were now detected in the gas phase. The pressure dips indicated in curve No. 2 occurred when the glass-"finger" was immersed in liquid nitrogen.

The strong and fast chemisorption with Ag VI, irrespective of whether hydrogen or oxygen pretreated, indicated that the sample prepared by the sparking method has an atomically cleaner surface than the previous commercial samples (Ag I-V, Final Report).

The $\underline{O^{16}{}_2 + O^{18}{}_2}$ reaction was also remeasured on the oxygen-pretreated surface. The results are again similar to those obtained for the hydrogen pretreated surface, although the rates are now somewhat lower at room temperature. As seen from Table 5, an exchange occurred at room temperature having an apparent half-life changing from about 1200 to 13,000 minutes, as compared to 350 to 3400 minutes with the H_2-pretreated sample.

It can be seen from both Tables, 4 and 5, that above 200°C the amount of $O^{16}O^{18}$ formed is just about equal to the amount of $O^{18}{}_2$ disappearing with time from the gas phase. The fact that the oxygen pretreated sample shows the same effect (compare also Final Report, page 31) proves that the exchange is not caused by the presence of hydrogen: $-OH^{16} + O^{18}{}_2 = -OH^{18} + O^{16}O^{18}$.

The reaction taking place here appears to be an exchange of $O^{18}{}_2$

TABLE 5

$O^{16}_2 + O^{18}_2$ EXCHANGE ON Ag VI, AFTER OXYGEN PRETREATMENT AT 500°C

Date	Pressure mm Hg	Temp. °C	Time at Temp. mins.	O^{16}_2	$O^{16}O^{18}$	O^{18}_2	Half-Life mins.
					Mole %		
11/12 Mixture admitted	3	24.0	0	48.18	6.21	45.61	
		24.0	23	48.58	6.78	44.64	1200
		24.0	56	48.07	7.05	44.88	2100
11/13		24.0	1065	47.08	8.51	44.41	13000
		222	0	46.95	9.87	43.18	
		222	34.5	47.65	11.50	40.83	
		256	0	48.48	14.59	36.93	
		256	24.5	50.89	18.49	31.42	147
		256	53	51.15	21.61	27.24	190
Evacuated at 460°							
Mixture admitted	3	280	0	48.39	6.39	45.22	
		280	30	47.69	16.82	35.49	76
		280	47	47.74	18.24	33.02	
		280	60	47.35	21.16	31.49	95
		280	985	45.00	43.89	11.16	

with dissociatively adsorbed O^{16} (which can be considered a surface-"oxide"). This in turn at higher temperature rapidly exchanges with oxygen in the sub-surface layers, not successfully removed during the pumping. The surface -- sub-surface exchange is so fast that most of the dissociatively adsorbed surface gas remains O^{16}. The effect is a consequence of the very high solubility of oxygen in silver. The exchange with the sub-surface is slow at 200°C, (the temperature chosen for the experiments with pre-adsorbed oxygen - Chapter IV 1), but rapidly increases as the temperature is raised. At the higher temperatures also a rapid depletion of the oxygen from the gas phase was noticed. (In the later experiments with palladium where similar effects were noticed, argon was admixed to the oxygen allowing the observation of sorption effects from a change in the argon/oxygen ratio).

Both effects, the change of the ${O^{16}}_2/{O^{18}}_2$ ratio and the slow sorption of oxygen, are connected with the same phenomenon, viz. an increase in mobility of successive layers as the temperature rises, beginning with the surface layer itself at about 200°C.

The results of the exchange on Ag VI are also plotted in Fig. 6. The points do not lie on a good straight line because of the dependence of the rate on prehistory. (The powder was pumped before the high temperature point was taken.) Nevertheless the comparison with the Ag-Au alloys shown in the same Figure is valid. At 200°C no effect of prehistory is found and the rate at this temperature is far below the rates found with the alloys. A good straight line was obtained with the 25% Ag-Au alloy. The solubility of oxygen in the alloys is considerably lower(5) than in pure silver and, accordingly, no change in the ${O^{16}}_2/{O^{18}}_2$ ratio was found with the alloys.

A temperature-rise experiment was carried out in presence of water vapor. In this experiment the silver powder was initially kept at -41°C and a small amount of water in the finger next to the reaction vessel was maintained at -45° by means of a thermistor controlled iso-octane bath, cooled by a stream of cold nitrogen (cf. Final Report, Fig. 2). A standard amount of oxygen was admitted. The result is shown in Fig. 9. The high pressure peak probably is of no particular physical significance. It appears to be due to rapid desorption of a large quantity of water initially adsorbed on the silver. Reestablishment of the equilibrium pressure with the water kept at -45° was slow. The chemisorption of oxygen above this temperature is seen to be very slow. At +91°C the water was condensed by placing a liquid nitrogen bath on the finger containing the water. An appreciable pressure is seen to remain in the gas phase. In the absence of water (Fig. 8) the pressure had practically vanished at this temperature. The direct chemisorption of oxygen is thus strongly inhibited by water.

On evaluating the amount of oxygen adsorbed, we find that about 1/4 of the oxygen in the vessel is already adsorbed at -45°C. The estimate is uncertain, particularly because it is based on the assumption that the thermistor voltages obtained for the two gases (O_2, H_2O) are additive.

After cleaning the surface again at 500°C, the adsorption of water as a function of coverage was measured at 3 different temperatures. The heat of adsorption, determined from these isotherms, showed a maximum of about 1/3 coverage (as high as 30,000 cals/mole). Such behavior has been previously reported(3); however, before drawing conclusions, we intend to check the reliability of the results. The slowness of establishment of the equilibrium and the relatively small surface area presents considerable experimental difficulties.

Further work will have to be done on the system Ag + O_2 + H_2O at low temperatures. In particular, the exchange reactions in the presence of water has not been studied yet.

4. Surface Rearrangement Effects

The small pressure peak found in the pressure-temperature curve of Fig. 4, curve 1 is probably real and is of the same type as the pressure bursts found in the oxygen exchange experiments on silver V (Fig. 2). The phenomenon was observed at about 200°C, i.e. at the temperature at which the silver surface becomes reactive (CO_2 formation, start of reversibility of the oxygen adsorption). Some kind of surface rearrangement appears to take place. This is possibly a rearrangement of the metal surface as recently observed by Germer(4) with nickel by means of his low energy electron diffraction technique. Spontaneous gas desorptions and readsorptions as observed by us do not seem to have been previously reported.

5. Results with Palladium (Pd I)

A palladium powder was tested by the same methods as described for silver, gold and their alloys. The powder was supplied by Engelhard Industries and guaranteed to be of 99.99% purity. 4.0 gm were used in a vessel of 18 cc. The surface area (at the end of the experiments) was 5100 cm^2.

a. Degassing: The powder was degassed for a period of two weeks at a slowly increasing temperature up to 550°C. Addition of oxygen was found to increase the rate of CO_2 evolution. The oxygen, added at a pressure of about 1 mm Hg, was taken up almost quantitatively. Contrary to the rare metals used so far, Pd forms a stable oxide phase at these pressures. In order to avoid possible complications due to residual OH on the surface, no hydrogen was used for cleaning.

b. Exchange with Preadsorbed O^{18}_2: After a final pretreatment at 550°C at decreasing oxygen pressures down to 10^{-3} mm followed by 1 minute pumping, the powder was cooled to room temperature. Small successive doses of O^{18}_2 were then adsorbed. The uptake was fast and practically quantitative to a coverage of about 750 cm^2 (cf. note, page 18). No desorption took place on pumping. 1 mm Hg of O^{16}_2 was then admitted. No isotopic exchange was found within 64 hours.

c. $O^{16}_2 + O^{18}_2$ Exchange: After short pumping, 10 mm of the isotopic mixture were admitted. Practically no exchange was found at room temperature and up to 100°C. In order to follow the oxygen loss by sorption at higher temperatures, a small amount of argon was added to the isotopic mixture and a new run was made. Table 6 gives the results obtained on two successive days. The uptake of oxygen can be seen from the increase in the argon percentage in the gas. The reaction rates per unit area at elevated temperatures are of the same order as with silver - faster than with Ag VI, but slower than the commercial silver samples. Even more than with silver, the rates are uncertain at the highest temperatures due to the fast bulk uptake of oxygen. The apparent activation energy for the $O^{16}O^{18}$ formation on the Pd is roughly 35,000 cals/mole.

d. Oxygen Exchange in Presence of Water: 8.5 mm Hg of water vapor and an equal amount of a $O^{16}_2 + O^{18}_2$ + A- mixture were brought in contact with the

TABLE 6

$O^{16}_2 + O^{18}_2$ EXCHANGE ON Pd I

Date			Pressure mm Hg	Temp. °C	Time at Temp. min.	O^{16}_2	$O^{16}O^{18}$	O^{18}_2	Argon	Half-life τ min.
						Mole %				
12/13/62	Mixture admitted		9 mm	23.5	0	46.2	5.8	43.8	4.3	
	Sample No.	1		"	60	48.0	6.1	42.3	3.7	
		2		100°	56	48.8	6.3	41.3	3.7	
	(Mixture remeasured					47.4	5.8	42.7	4.0)	
		3		.'	123	48.1	6.5	41.6	3.9	
		4		229°	0	48.1	6.6	41.1	4.2	
		5		"	27.5	46.3	7.2	41.2	5.3	
		6		"	57	44.8	7.8	40.7	6.8	~1200
12/14/62	24° overnight. continued	7		230°	0	41.4	11.6	39.0	8.1	
		8		"	27	37.8	12.5	36.9	12.8	
		9		260°	2	19.2	9.3	22.8	48.6	
	Recalculated without argon	7				45.0	12.6	42.4		
	"	8				43.4	14.3	42.3		380
	"	9				37.5	18.1	44.4		
	New mixture		12 mm	261°	0	47.1	5.8	43.1	4.0	
		1		"	31	31.6	15.7	32.4	20.4	~60
				"	53	~0	~0	~0	99.9	

palladium at room temperature. The results of this run are given in the first part of Table 7. It is seen that no $O^{16}O^{18}$ was formed at room temperature in 6 days. Some $O^{16}O^{18}$ was formed at 150°C in 46 minutes. After pumping the gas through a liquid nitrogen trap, the contents of the trap were released into the spectrometer and - surprisingly - were found to contain water of 6% O^{18} content.

In a better controlled experiment, the powder was first carefully cleaned and degassed at 550°C. The vessel was then saturated with water vapor of 9.8 mm pressure (in equilibrium with liquid water at 11°C), while the powder was kept at 300°C. The water vapor was then condensed in the finger kept at liquid nitrogen temperature and the metal powder was cooled to room temperature. 8.5 mm of the oxygen mixture were then admitted. The measurements, given in the same Table 7 show that no $O^{16}O^{18}$ was formed at room temperature or at 150°C within one hour. After 6 days at room temperature, still no change in the $O^{16}O^{18}$ concentration was found. However, the water again was found to be enriched in O^{18}; it contained 4.6% H_2O^{18}.

The only interpretation which we can offer at present is that the oxygen chemisorption on the palladium is irreversible, while the water adsorption, at least in part, is reversible. An exchange between adsorbed oxygen and water takes place on the surface. The H_2O^{18} then exchanges with water in the gas phase, while the $O^{16}O^{18}$ remains bound to the surface or diffuses into the bulk.

It appears that at low temperatures and in the presence of water the activation of oxygen on a palladium (and also silver) electrode would involve an OH ion or radical rather than the dissociation of oxygen on the bare metal.

TABLE 7

$O^{16}_2 + O^{18}_2 + H_2O^{16}$ EXCHANGE ON Pd I

Date		Temp. °C	Time at Temp. min.	O^{16}_2	$O^{16}O^{18}$	O^{18}_2	A	O^{16}_2	$O^{16}O^{18}$	O^{18}_2
				Mole %				Mole %, excluding A		
12/21	$O^{16}_2 + O^{18}_2$ + A Mixture			47.7	5.9	42.5	3.9	49.6	6.1	44.2
	Sample No. 1	23.5	32	47.8	5.7	42.5	4.0	49.7	6.0	44.3
12/24	2	23.0	2750	47.6	5.8	42.0	4.7	49.9	6.1	44.0
	3	150	5	55.5	4.9	35.4	4.2	58.0	5.1	37.0
	4	150	25	42.6	5.6	45.9	5.9	45.2	6.0	48.8
		150	46	43.2	6.2	43.2	7.3	46.7	6.7	46.7
1/3/63	Mixture			46.9	6.0	43.3	3.9	48.8	6.2	45.0
	Sample No. 1	24.2	25	47.8	5.8	41.9	4.6	50.1	6.0	43.9
	2	24.0	53	48.3	5.8	41.8	4.0	50.4	6.1	43.6
	3	24.5	93	47.7	5.8	47.3	4.2	49.8	6.0	44.2
	4	150	2	47.3	5.8	42.3	4.6	49.6	6.1	44.3
	5	149	16	47.1	5.8	41.9	5.3	49.7	6.1	44.2
	6	150	57	46.8	5.7	42.2	5.3	49.4	6.0	44.5

e. Equilibrium Oxygen Pressure over Pd: Immediately after the exchange experiment, the oxygen pressure over the oxygenated Pd powder was measured for a continuously rising temperature (see Figure 10). The pressure was not in equilibrium with the system. Several equilibrium points were then taken in the region of 500°C by (a) allowing a dose of oxygen to absorb and to come to equilibrium and (b) by pumping some oxygen off and allowing the pressure to come to a stationary value. Equilibrium is only slowly established at this relatively low temperature. The points in Fig. 10 thus obtained are seen to lie approximately on a straight line obtained by extrapolating the log equilibrium pressure versus 1/T-curve for the dissociation of Pd O (taken from literature(5)) down to the lower temperatures.

In the final cleaning stages of the palladium the oxygen admitted was kept below this pressure ($\sim 10^{-2}$ mm at 500°C).

V. FURTHER DISCUSSION AND CONCLUSIONS

By means of an improved mass spectrometric technique, the experiments with pre-adsorbed oxygen on silver (Ag V) have now shown a considerable amount of detail about the nature of the adsorbed phase and the kinetics of the isotopic exchange reaction. The existence of a molecular as well as an atomic chemisorption has now been very clearly demonstrated. The two types of chemisorption occur on distinct sites: there is a sharp transition from atomic to molecular chemisorption as the coverage increases. Obviously at higher temperatures - as the coverage decreases at constant pressure - the atomic adsorption will become the prevalent form. Also the rate constant of the surface exchange will become faster and may overtake the rate constant for desorption of the molecules. The rate of ad- and desorption will then be equal to the overall exchange rate. This is the case, for example, with hydrogen on transition metals like platinum or nickel which form reversible hydrogen electrodes. An electrochemical investigation of the transition to this state would be of great interest.

At the time when these exchange experiments were performed, it was not yet realized that the hydrogen used for cleaning the surface at high temperatures was tenaceously held to the surface. Therefore, to make quite sure that our conclusions are correct, some confirming experiments with pre-adsorbed oxygen will be made in the future.

The experiments on Ag VI and the silver-gold alloys prepared by the same method have shown a striking increase in the exchange rate at elevated temperatures as the silver becomes more diluted. In the following table the half-lives τ are given for silver Ag VI and the two silver-gold alloys at 220°C. The product τ x A reduces τ to equal areas. The gas volume was the same in all cases. f is the fraction of silver in the alloys.

TABLE 8

HALF-LIVES τ FOR SILVER AND SILVER-GOLD ALLOYS AT 220°C

	Half-life mins.	Area A meter^2	τ x A min. m^2	τ x A x f min. m^2	Apparent Activation Energy cals/mole
Ag VI	10,000	0.133	1,330	1,330	43,000
25% Ag-Au	520	0.205	107	27	33,500
4% Ag-Au	270	0.740	200	8	29,500

On comparing the rates on a basis of equal silver content (column τ x A x f), it is seen that the 4% alloy produces an exchange rate 170 times faster than the pure silver. Also, the activation energy is lower for the alloys. From this it appears that the alloys may have interesting oxygen-electrode properties at elevated temperatures.

When we compare the properties of the sparked silver sample Ag VI with those of the previously studied silver samples of commercial origin some remarkable differences become apparent which probably are connected with the mode of preparation. Sample Ag VI gave a fairly fast exchange at room temperature, but its activity at elevated temperatures was low. On the other hand, the silver powders of commercial origin previously studied gave no activity at room temperature but were more active at elevated temperature. Also, inspite of the more prolonged heat treatment at higher temperatures given to the sparked sample Ag VI, it underwent less sintering than the commercial samples and its surface area remained larger.

A microscopic study of the surface structure of the various samples to be carried out may show some interesting differences.

Pretreatment of silver with hydrogen at 500°C in addition to the oxygen treatment produced a more active - presumably cleaner - surface at room temperature, but part of the hydrogen was retained and only slowly desorbed as water in 1-2 days at 500°C. No direct effect of the retained hydrogen on the oxygen exchange rates - by exchange with OH-groups - could so far be established. The retained hydrogen may have been the source of the strong paramagnetism found by the parahydrogen conversion after hydrogen treatment, and not carbonaceous impurities as previously suggested. Probably Ag_2OH is formed on the surface, which would be paramagnetic.

In no case was a reversible oxygen adsorption found at room temperature in presence of water. With silver it was shown that the presence of water inhibits the chemisorption of oxygen. In case of palladium, no exchanged oxygen was found in the gas phase although the oxygen exchanged with the water. This shows that oxygen on these metals at room temperature is labile only in the form of -OH.

VI. PROGRAM FOR THE NEXT SIX MONTHS

(1) To round off the reported studies with silver and palladium, the following experiments are planned: The exchange experiments with pre-adsorbed oxygen on silver (Ag V) will be checked to make sure that these were not influenced by retained hydrogen. They will also be extended to high pressures.

The kinetics of the oxygen exchange with water will be investigated and the thermodynamics of the water adsorption will be further studied.

(2) The effect of carbonaceous compounds on the adsorption and exchange of oxygen on silver and palladium will be explored. These compounds may include CO_2, ethylene and ethylene dichloride. (The latter is known to cause selective poisoning of sites on silver.)

(3) Experiments with pre-adsorbed oxygen (similar to those performed with Ag V) will be performed on a silver-gold alloy to study the effect of alloying on molecular as well as atomic oxygen chemisorption.

(4) The experiments will be extended to other systems, such as Pd-Ag alloys and platinum. Other alloys such as Pt-Au and Pt-Rh may later be studied.

(5) To prepare a suitable system for electrode studies at elevated temperatures, a cell will be designed operating, for the time being, on fused KOH.

Alkali carbonate mixtures and their solution in nitrates and chlorides, and other fused salt mixtures will be prepared and their melting point, conductivity and corrosion properties will be studied in order to see whether they may provide a suitable electrolyte for operating the cell at moderate temperatures.

VII. PERSONNEL

Dr. Y. L. Sandler and Dr. S. Z. Beer worked on this project full time. The measurements on silver Ag V were carried out by the mass spectrometer group under W. M. Hickam.

Thanks are due to Mr. D. D. Durigon for his efficient help with most of the experiments.

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IX. CONSULTATIONS AND LECTURES

A consultation concerning the program of the project took place in August 1962 at the U. S. Army Electronics Laboratory, Fort Monmouth with Messrs. Murphy, Wynn, Franke and Dr. Baars.

A paper "Adsorption Mechanism on Oxygen Electrodes: The Silver-Oxygen System" was delivered at the 142nd National Meeting of the American Chemical Society, Atlantic City, September 1962.

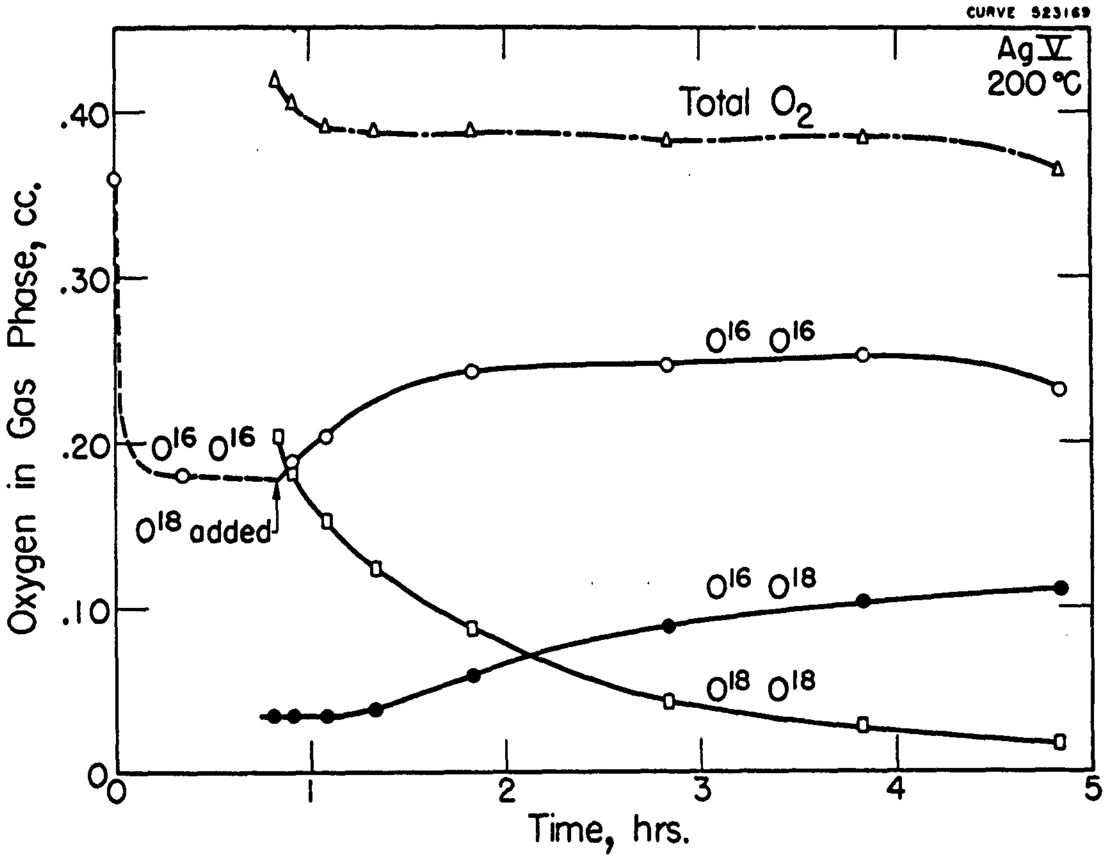

Fig. 1 - Experiment with Pre-Adsorbed O^{16} on Ag V, High Coverage

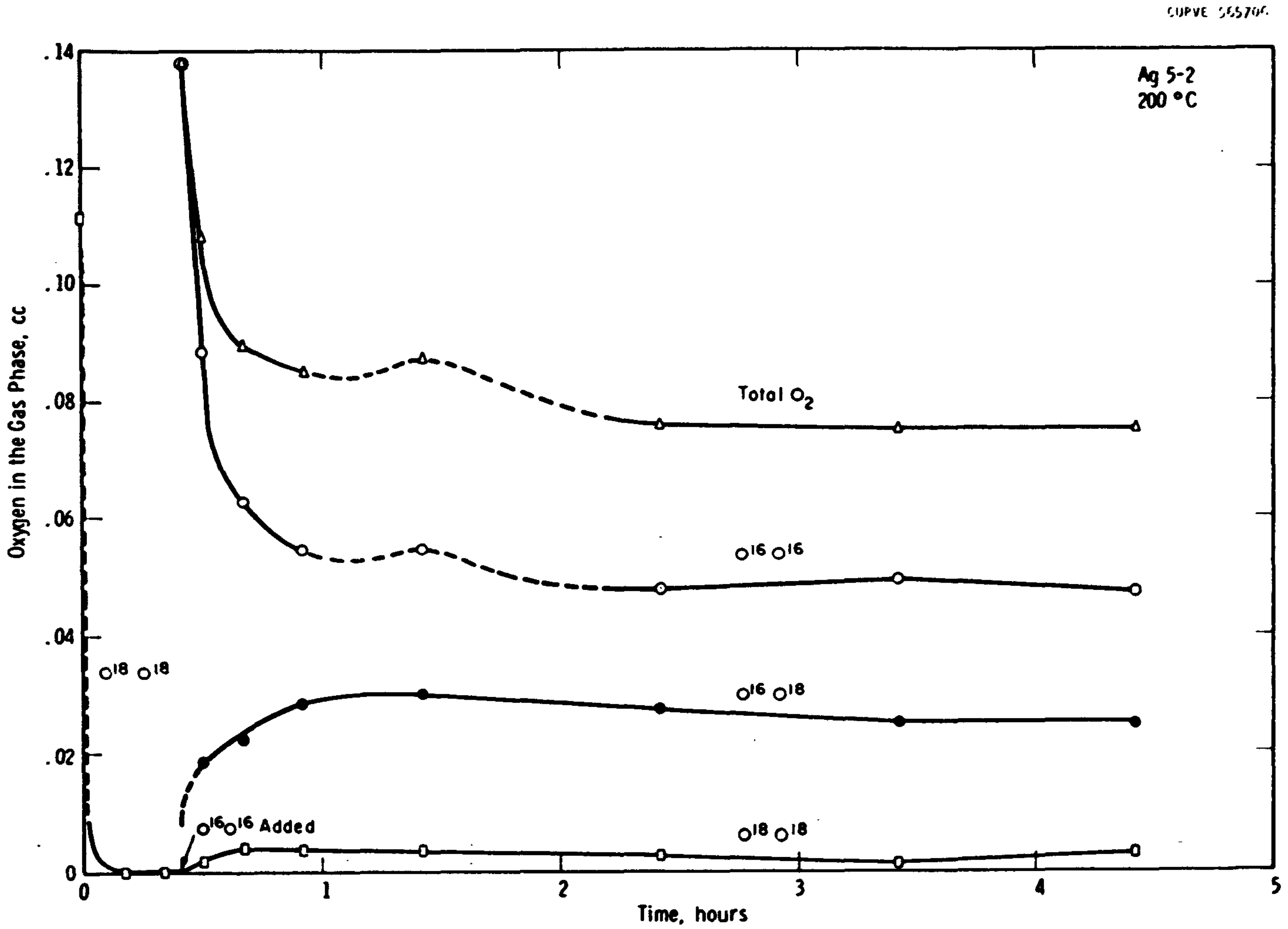

Fig. 2 - Experiment with Pre-Adsorbed O^{18} on Ag V, Low Coverage

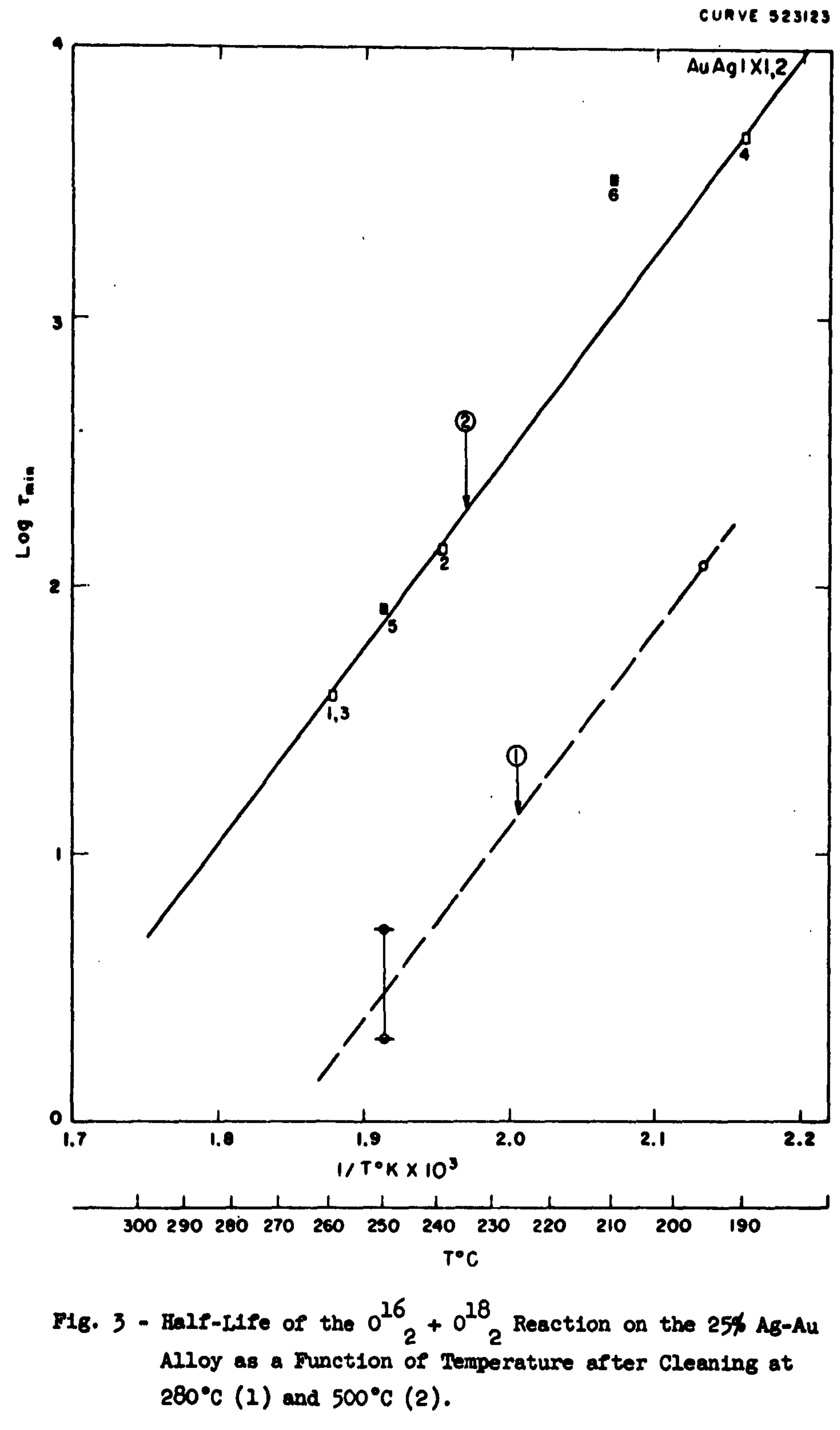

Fig. 3 - Half-Life of the $O^{16}_2 + O^{18}_2$ Reaction on the 25% Ag-Au Alloy as a Function of Temperature after Cleaning at 280°C (1) and 500°C (2).

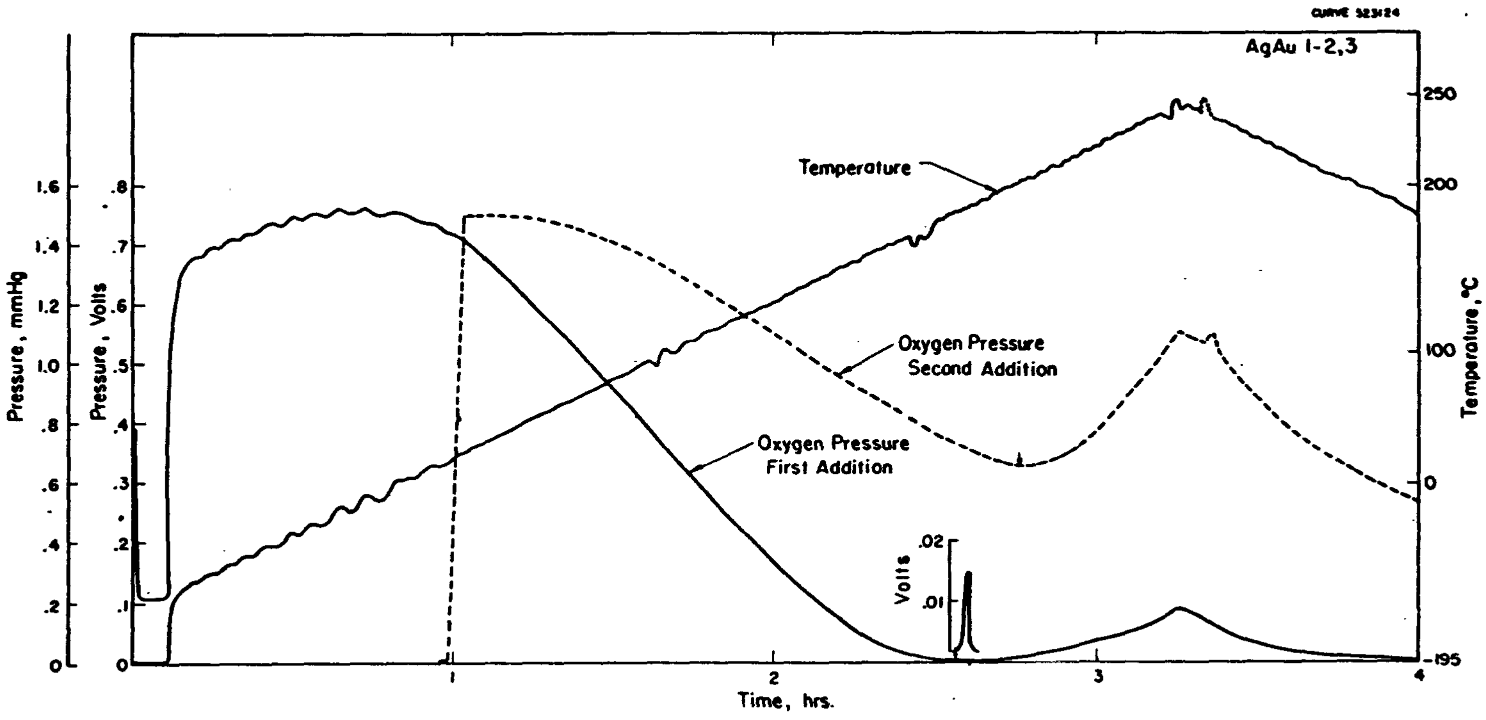

Fig. 4 - Pressure-Temperature Curves for the 25% Ag-Au Alloy

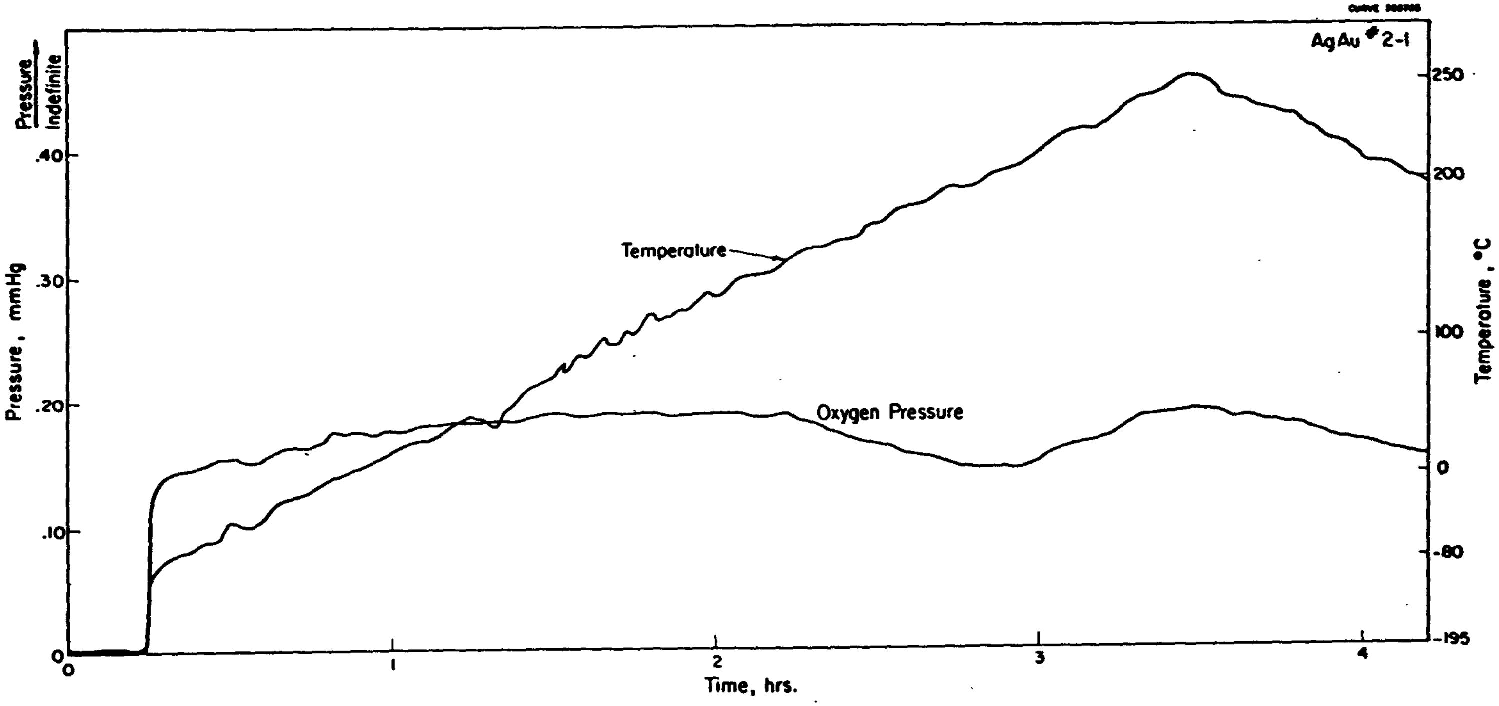

Fig. 5 - Pressure-Temperature Curves for the 4% Ag-Au Alloy

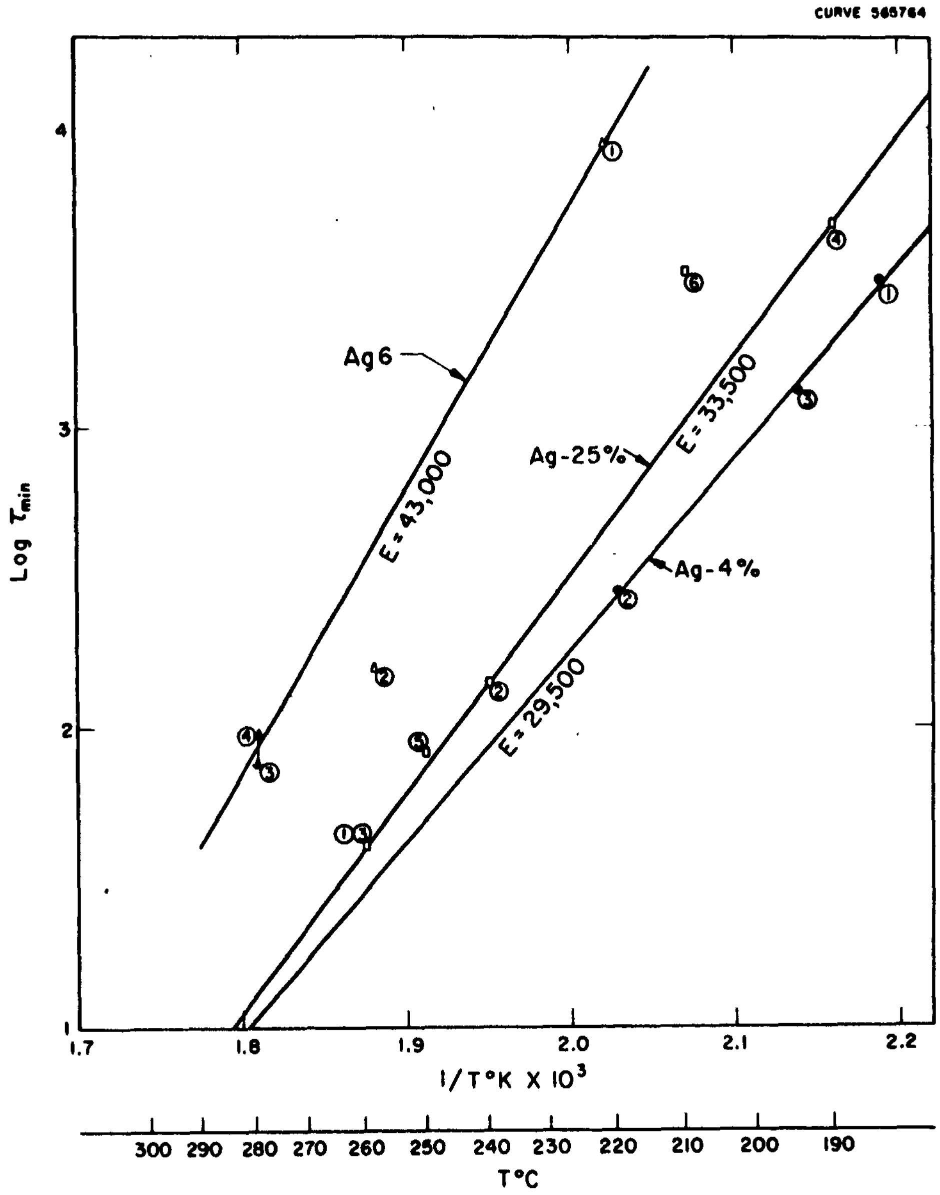

Fig. 6 - Half-Life of the $O^{16}_2 + O^{18}_2$ Reaction as a Function of Temperature on the Sparked Samples: Pure Silver Ag VI, the 25% Ag-Au Alloy and the 4% Ag-Au Alloy

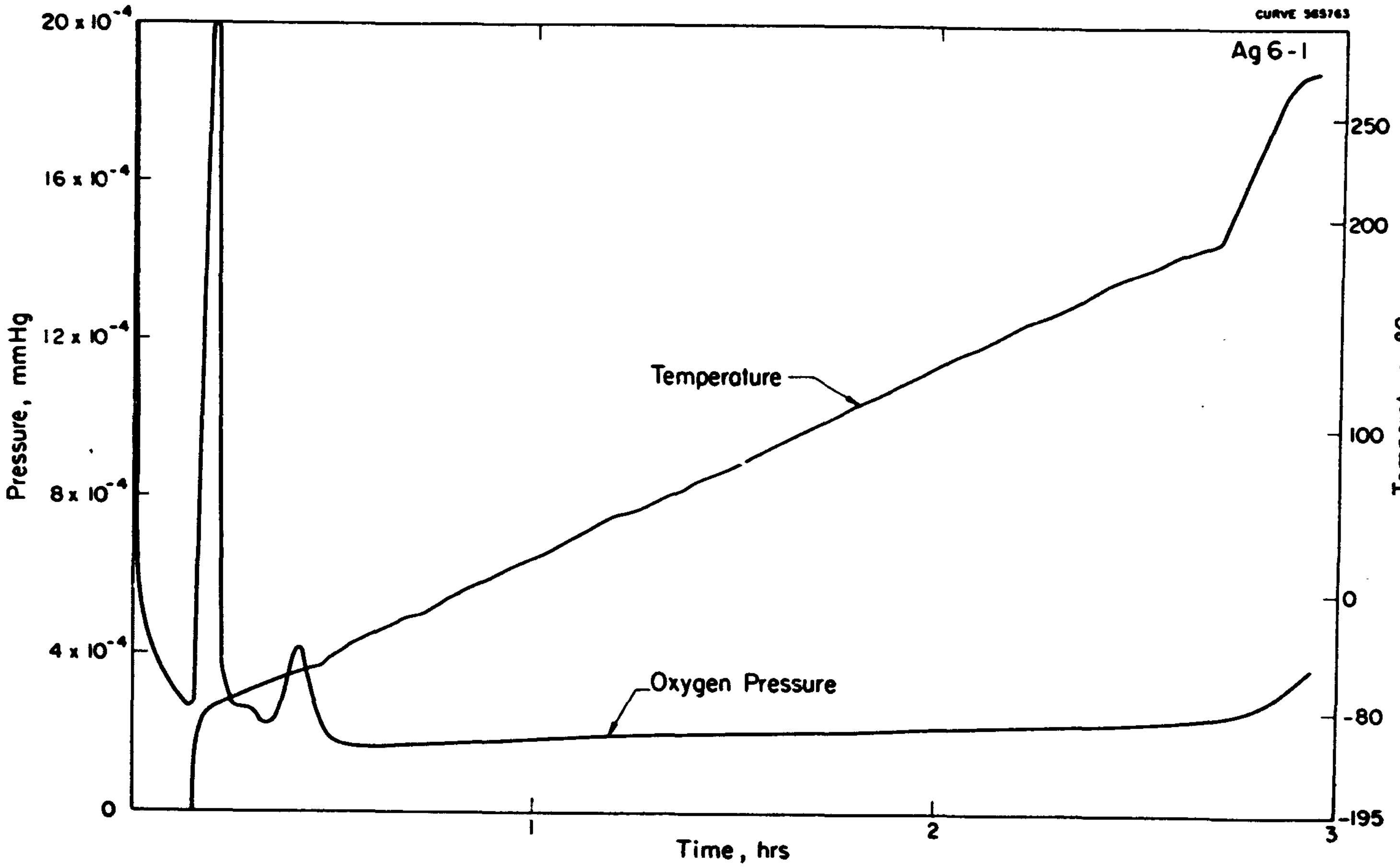

Fig. 7 - Pressure-Temperature Curves for Ag VI after Hydrogen Pretreatment

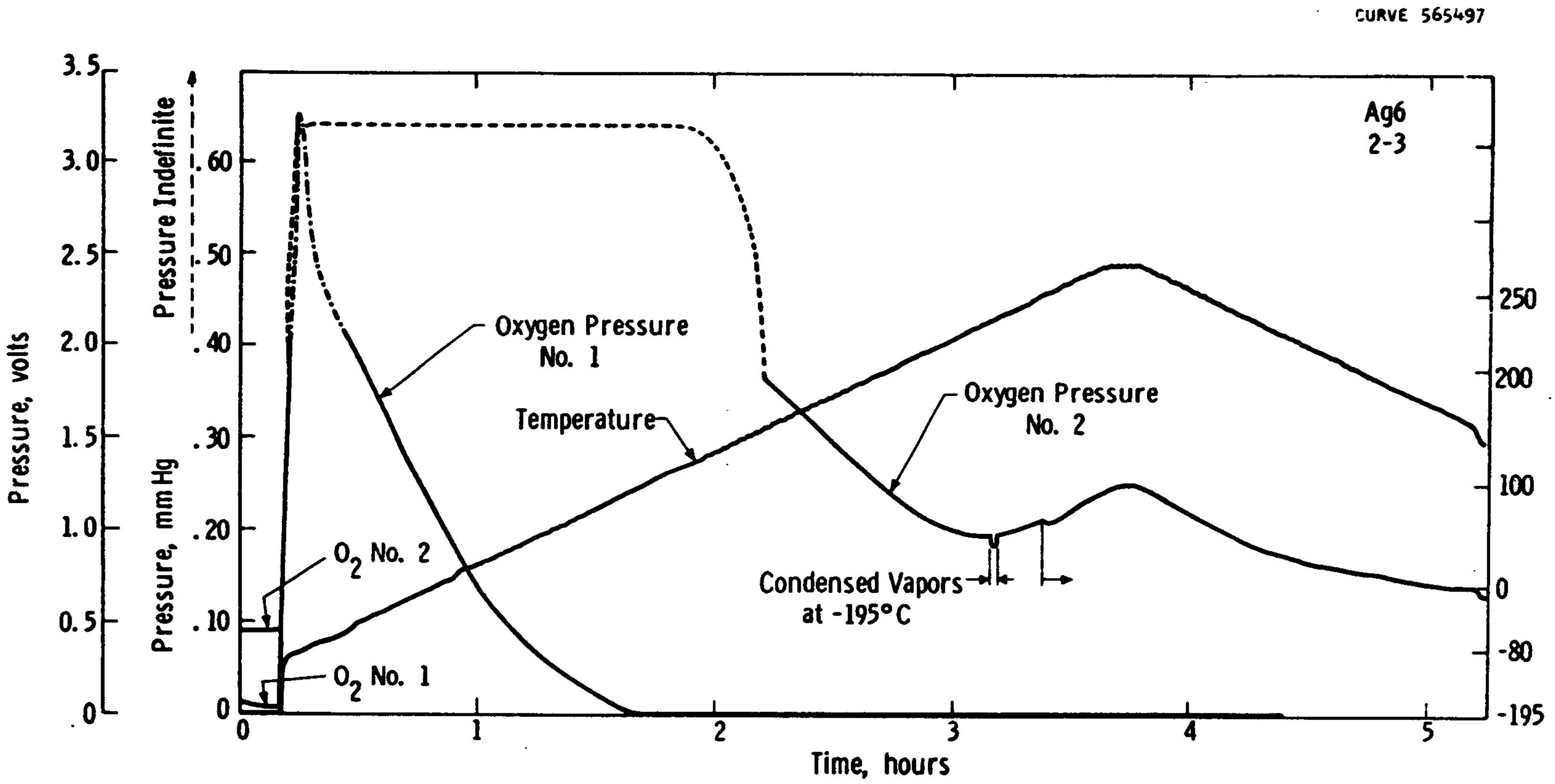

Fig. 8 - Two Pressure-Temperature Curves for Ag VI after Oxygen Pretreatment

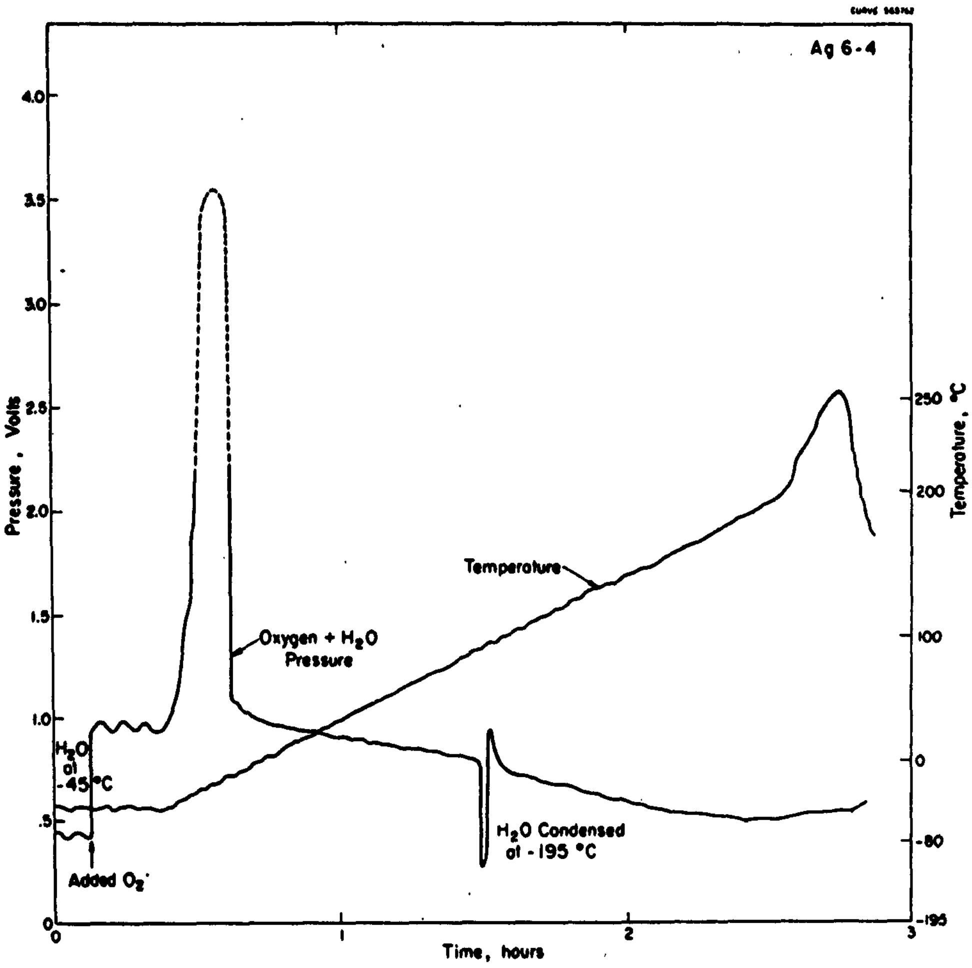

Fig. 9 - Pressure-Temperature Curve for Ag VI with Oxygen and Water Vapor

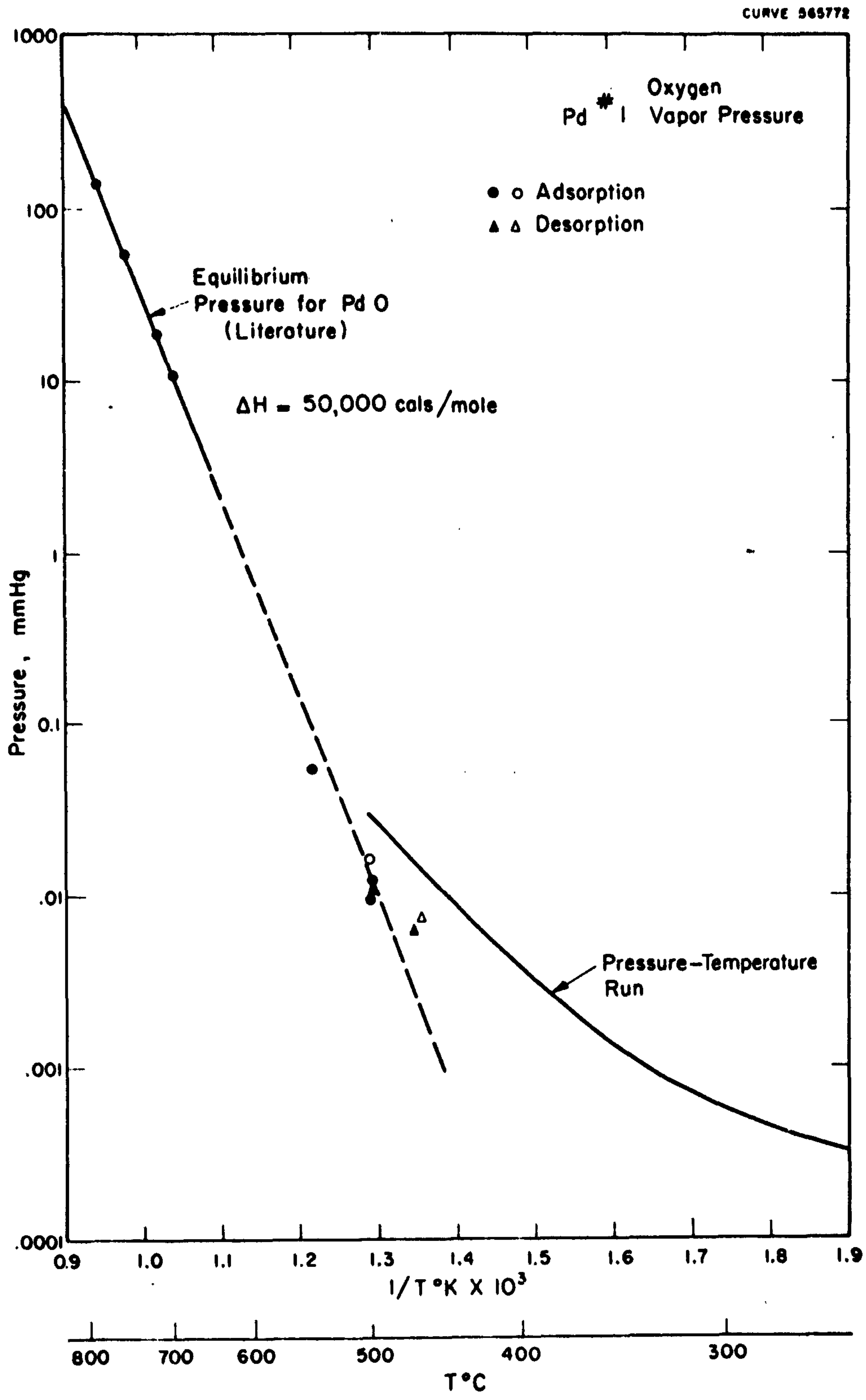

Fig. 10 - Oxygen Pressure over Palladium I.

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U.S.A. Combat Developments Command
ATTN: CDCMR-E
Fort Belvoir, Virginia (1)

Commanding Officer
U.S.A. Communications and Electronics
Combat Development Agency
Fort Huachuca, Arizona (1)

Director
Fort Monmouth Officer
U.S.A. Communications and Electronics
Combat Development Agency
Fort Monmouth, N.J. (1)

Air Force Systems Command
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Corps of Engineers Liaison Office
U.S.A. Electronics Research and
Development Laboratory
Fort Monmouth, N.J. (1)

Marine Corps Liaison Office
U.S.A. Electronics Research and
Development Laboratory
Fort Monmouth, N.J. (1)

AFSC Scientific/Technical Liaison Office
U.S.A. Electronics Research and
Development Laboratory
Fort Monmouth, N.J. (1)

Power Information Center
Moore School Building
200 South Thirty-Third Street
Philadelphia 4, Pennsylvania (1)

Dr. Sidney J. Magram
Physical Sciences Division
Army Research Office
3045 Columbia Pike
Arlington, Virginia (1)

Dr. Ralph Roberts
Head, Power Branch
Office of Naval Research (Code 429)
Department of the Navy
Washington 25, D.C. (1)

Mr. Bernard B. Rosenbaum
Bureau of Ships (Code 340)
Department of the Navy
Washington 25, D.C. (1)

Mr. George W. Sherman
Aeronautical Systems Division
ATTN: ASRMFP
Wright-Patterson Air Force Base
Ohio (1)

Dr. John H. Huth
Advanced Research Projects Agency
The Pentagon, Room 3E157
Washington 25, D.C. (1)

Lt. Col. George H. Ogburn, Jr.
Auxiliary Power Branch (SNAP)
Division of Reactor Development
U. S. Atomic Energy Commission
Washington 25, D.C. (1)

Mr. Walter C. Scott
National Aeronautics & Space
Administration
1520 H Street, N.W.
Washington 25, D.C. (1)

Institute for Defense Analysis
1666 Connecticut Avenue, N.W.
Washington 25, D.C.
ATTN: Dr. Szego & Mr. Hamilton (1)

Director
Advanced Research Projects Agency
Washington 25, D.C. (6)

Commanding Officer
U.S.A. Electronics Research and
Development Laboratory
ATTN: SELRA/Dr, ARPA Coordinator
Fort Monmouth, New Jersey (1)

Dr. R. O. Schlegelmilch
Technical Director
Defense & Space Group
1000 Connecticut Avenue, N.W.
Washington 6, D.C. (1)

Mr. R. A. Osteryoung
Atomics International
Canuga Park, California (1)

Dr. David M. Mason
Stanford University
Stanford, California (1)

Dr. Howard L. Recht
Astropower, Inc.
2962 Randolph Avenue
Costa Mosa, California (1)

Dr. R. T. MacDonald
California Research Corp.
576 Standard Avenue
Richmond, California (1)

Dr. Ralph G. Gentile
Monsanto Research Corp.
Boston Laboratories
Everett 49, Massachusetts (1)

Mr. Ray M. Hurd
Texas Research Associates
1701 Gundalupe Street
Austin 1, Texas (1)

Dr. C. E. Heath
Esso Research & Engineering Co.
Box 51
Linden, New Jersey (1)

Dr. R. J. Flannery
American Oil Company
Whiting Laboratories
P. O. Box 431
Whiting, Indiana (1)

Dr. Douglas W. McKee
General Electric Company
Research Laboratories
Schenectady, New York (1)

Dr. E. A. Oster
General Electric Co., DECO
Lynn, Massachusetts (1)

Dr. Arthur J. Rosenberg
TYCO, Incorporated
Materials Research Laboratory
Bear Hill
Waltham 54, Massachusetts (1)

Prof. Herman P. Meissner
Massachusetts Institute of Technology
Cambridge 39, Massachusetts (1)

Dr. Donald P. Snowden
General Atomics
P. O. Box 608
San Diego 12, California (1)

Dr. C. Tobias
Chemistry Department
University of California
Berkeley, California (1)

U. S. Army R & D Liaison Group
(9851 DV)
APO 757
New York, New York
ATTN: Dr. B. R. Stein (1)

Director
U. S. Army Engineer Research and
Development Laboratory
Fort Belvoir, Virginia
ATTN: Dr. D. Looft (1)

Chief of Ordnance
Department of the Army
Washington 25, D.C.
ATTN: Mr. J. Crellin (ORDTB) (1)

Engelhard Industries, Inc.
Military Service Department
113 Astor Street
Newark 2, New Jersey
ATTN: Mr. V. A. Forlenza (1)

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Union Carbide Consumer Products Co.
270 Park Avenue
New York 17, N.Y.
ATTN: Mr. R. B. Klopfenstein (1)

United Aircraft Corporation
Pratt & Whitney Aircraft Division
East Hartford 8, Connecticut
ATTN: Mr. J. M. Lee (1)

Melpar, Inc.
3000 Arlington Boulevard
Falls Church, Virginia
ATTN: Mr. R. T. Foley (1)

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Direct Energy Conversion Operations
Lynn, Massachusetts
ATTN: Mr. E. Oster (1)

General Electric Company
Research Laboratories
Schenectady, New York
ATTN: Dr. H. Liebhafsky (1)

ESSO Research & Engineering Company
Products Research Division
P. O. Box 215
Linden, New Jersey
ATTN: Dr. M. A. Weiss (1)

University of Pennsylvania
John Harrison Laboratory of Chemistry
Philadelphia 4, Pennsylvania
ATTN: Dr. J. Bockris (1)

Dr. A. Damjanovic
University of Pennsylvania
John Harrison Laboratory
Philadelphia 4, Pennsylvania (1)

Speer Carbon Company
Research Laboratory
Packard Road at 47th Street
Niagara Falls, New York
ATTN: Dr. W. E. Parker (1)

Monsanto Research Corporation
Boston Laboratories
Everett 49, Massachusetts
ATTN: Mr. R. G. Gentile (1)

Magna Corporation
R & D Laboratories
1001 South East Street
Anaheim, California
ATTN: Dr. Silverman (1)

Dr. H. D. Gregor
150 Lakeview Avenue
Leonia, New Jersey (1)

U.S. Army Signal Research & Development Lab., Fort Monmouth, New Jersey
First Semi-Annual Report, A STUDY OF THE ADSORPTION MECHANISMS ON OXYGEN ELECTRODES, covrng 6 Sept.-31 Dec. 62, dated Feb. 63, 36 p. graphs
Unclassified Report

Oxygen adsorption and isotopic exchange reactions are measured on silver and silver-gold alloys, produced by a spark erosion method, and on a palladium powder. An improved exchange method involving pre-adsorbed oxygen gave detailed information on the nature of the adsorbed phase on silver and the ○ (over)

1. Electrodes - Oxygen Adsorption
I. Contract DA-36-D39 AMC-00136 (E)
II. Westinghouse Research Labs. Pgh. 35, Pa.
III. Y. L. Sandler

U.S. Army Signal Research & Development Lab., Fort Monmouth, New Jersey
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