AD NUMBER: AD0083341

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 1 Feb 1956. Other requests shall be referred to Office of Naval Research, Washington, DC.

AUTHORITY

ONR LTR 9 NOV 1977

REPORT NO. 49

DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR

Prepared for the
Office of Naval Research
Contract No. N5ori-07819
NR-092-008

BY

C.N. Satterfield
T.W. Stein

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemical Engineering Cambridge, Mass.

Division of Industrial Cooperation Project 6552
February 1, 1956

REPORT NO. 49

DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR

Prepared for the
Office of Naval Research
Contract No. N5ori-07819
NR-092-008

BY

C. N. Satterfield
T. W. Stein

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemical Engineering Cambridge, Mass.

Division of Industrial Cooperation Project 6552
February 1, 1956

INTRODUCTION

The heterogeneous decomposition of hydrogen peroxide vapor has been the subject of several investigations. Data have been reported for the rates of decomposition at partial pressures of hydrogen peroxide from 5 or 6 mm of mercury up to 1 or 2 cm, at temperatures from room temperature up to 400°C, and on such surfaces as soft glass, Pyrex, quartz, aluminum and tin. The work of previous investigators has been recently summarized (30). However, there have been many inconsistencies in the data available and an explanation of the fundamental nature of the heterogeneous decomposition of hydrogen peroxide vapor has been lacking. One of the purposes of this work was to try to obtain a clearer picture of the important factors which affect the surface decomposition rate. A second objective was to ascertain under what conditions homogeneous decomposition becomes appreciable. Aside from these more theoretical reasons, there is an engineering need for determining those materials which will cause the minimum decomposition on contact with hydrogen peroxide vapor. In the present work substantially greater H_2O_2 vapor concentrations than previously were studied, as well as a much greater variety of surfaces.

Previous studies indicate that any surface has an accelerating effect on hydrogen peroxide vapor decomposition. Most investigators have reported that the reaction rate can be expressed by a first order equation, although second order reactions, both retarded and unretarded by water, and zero reactions have also been suggested (10,16,17). The reaction is reportedly unretarded by additions of moderate quantities of air, or CO_2.

The rate of reaction is much higher on metals or soft glass than on Pyrex or quartz although it can be varied by one or more orders of magnitude on a Pyrex surface alone by changing its chemical and physical properties. The reported activation energies have ranged from 5-20 Kcal./gm.mole, but most frequently have been in the vicinity of 10 Kcal./gm.mole.

The homogeneous decomposition of hydrogen peroxide vapor has been observed primarily only in studies of flames and explosions. The explosion limits of hydrogen peroxide vapor at various total pressures have been determined (28,29) and it was found that these limits were dependent only on the hydrogen peroxide concentration in the vapor and were unaffected by the ratio of water to oxygen. The decomposition of the vapor in boric oxide reaction tubes in the temperature range from 470-540°C has been observed (19) and an activation energy was reported that was in the range of 40-50 Kcal/gm. mole. On the basis of the magnitude of this quantity and the effect observed when the surface to volume ratio of the reaction tubes were changed, it was concluded that the decomposition was at least partially homogeneous.

EXPERIMENTAL

The experimental apparatus comprised two sections, a vaporization section, depicted on Figure 1, and a decomposition section, shown in Figure 2.

The vaporization section was capable of producing a steady flow of hydrogen peroxide vapor at a constant concentration. A hydrogen peroxide-water solution was fed continuously to an electrically-heated Pyrex boiler through a levelling device (see insert on Figure 1) which maintained a constant liquid level in the boiler. The boiler pressure was regulated by an external helium system; the helium, being lighter than the hydrogen peroxide-water vapors, was prevented from entering the system by maintaining in the reflux condenser, atop the boiler, a helium-vapor interface, which is visible.

The hydrogen peroxide-water vapor mixture from the boiler first passed through an entrainment separator and then through an electrically heated Pyrex preheater (see Figure 2). A portion of the vapor at this point was withdrawn for analysis by condensing it at 5°C, and analysing the condensate for hydrogen peroxide content by potassium permanganate titration. The remainder of the vapor flowed through the reaction tube, and was then similarly condensed and analysed. The division of vapor flow between the upstream and downstream condensers was controlled by control of the pressure, this being set by bubbling the oxygen leaving each condenser through a column of water before passing it through a wet test meter. The collectors in which the liquid samples accumulated were so constructed that the samples could be removed without affecting the pressures in the condensers, so as not to affect the flow division.

The reaction tubes used in the study of glass surfaces were usually one inch in diameter and approximately two foot long, with ball and socket joints on the ends with which the tube was clamped in the system. When plastic surfaces were to be studied, the samples were placed in the glass reaction tubes. In the study of metallic surfaces, metal rods about 3/32 inches in diameter and 6.5 inches long rested coaxially, on small aluminum supports, in a Pyrex tube about one foot long. The ends of this Pyrex tube had a diameter of one inch, but the central portion in which the metallic sample was placed had a diameter of 3/16 inches.

Each reaction tube was immersed in a constant temperature bath to which it was sealed by stuffing boxes, using asbestos tape as the gasketting material. At temperatures below 180°C, "Nujol", a mineral oil, was used in the bath; at temperatures above 180°C, a molten salt mixture containing 7 wt.% sodium nitrate, 40 wt. % sodium nitrite, and 53 wt.% potassium nitrate, was used. The bath was agitated by a stirrer and its temperature was regulated to within $\pm$ 2°C by a thermoswitch which controlled a heater lying along the length of the bath. The temperatures were measured with iron-constantan thermocouples at three locations--in a well at the exit of the preheater and in the two ends of the constant temperature bath.

The range of experimental variables studied in this work was:

Partial pressure of hydrogen peroxide	0.02-0.23 atm.
Temperature	110-490°C
Total pressure	1 atm.

The partial pressures of hydrogen peroxide studied were higher than those hitherto investigated and closer to those likely to be encountered in practical operations.

The data obtained in each set of experimental conditions were the amount and composition of the hydrogen peroxide-water liquid sample collected from each condenser, the volume of oxygen leaving each condenser, the upstream and downstream pressures, the temperature of the vapor leaving the preheater and the temperature of the bath. At each of the combinations of experimental conditions, three sets of data were collected to avoid fortuitous errors. By means of a material balance, the rate at which each component enters and leaves the reaction tube can be calculated and from this the rate of decomposition of the hydrogen peroxide.

Except for a few runs at the very highest temperatures studied, the inlet and exit concentrations were not greatly different, so that the reaction tube may in general be regarded as a "differential reactor". The correct method of averaging inlet and exit concentrations is therefore relatively unaffected by the order of the reaction. If, for example, the inlet and outlet partial pressures were to differ by as much as a factor of 2, the log-mean partial pressure, the correct mean for a first order reaction, would differ from the geometric-mean, the correct mean for a second order reaction, by only 1.5%. The differential rate of decomposition, $\frac{-dN_{H_2O_2}}{A\ d\Theta}$,

is therefore calculated as the difference between the rate at which hydrogen peroxide enters and leaves the tube, divided by the total surface area. A few surfaces, Pyrex coated with boric oxide and 2S aluminum, were studied over a range of temperatures and compositions sufficiently extensive that the results could be expressed in a mathematical form based on the Langmuir adsorption model. Other surfaces were studied less extensively and frequently at only one temperature. In these cases the activity of a surface is expressed by plotting the differential rate of decomposition observed against the geometric mean of the inlet and exit partial pressure of hydrogen peroxide. The partial pressure of oxygen and water vapor might also have some slight effect, but essentially the same concentration of liquid hydrogen peroxide was boiled in all studies of surface activities so that the concentrations of oxygen and water vapor were functions of the average hydrogen peroxide concentration only. The independent variables were thus reduced to three--the type of surface, temperature, and the partial pressure of hydrogen peroxide.

The rates of heterogeneous reaction studied here were sufficiently low that the rate of diffusion of H_2O_2 from the bulk vapor to the surface was neglected as a limiting factor. This introduces a slight error in a few cases. Thus, the difference between the interfacial and bulk partial pressure was estimated, by means of the correlation for laminar flow in a wetted wall column (32), to be about 15% in the studies with the most reactive glass tube (tube 17,

a Pyrex tube with silver present) when the average bulk partial pressure of hydrogen peroxide was 0.02 atm. In an average Pyrex tube (tube 19) the maximum error was only 8% at an averaged bulk partial pressure of about .04 atm. This diffusional error would not affect the qualitative comparison of two surfaces because the error is greater on the more reactive surface. For those surfaces on which a wide range of hydrogen peroxide concentrations were studied and for which equations were derived, the difference is greater at the higher concentrations than at the lower. For example, on a boric oxide coated tube (tube 9) at 180°C the difference increased from 2% at 0.03 atmosphere of hydrogen peroxide partial pressure to 11% at a partial pressure of 0.2 atm. Similarly on an aluminum surface it increased from 3% at a bulk hydrogen peroxide partial pressure of 0.045 atm. to 13% at 0.14 atm. However neglecting the effect does not affect the form of the equation derived for expressing the data, and the value of the correction factor called for is generally less than the reproducibility of the data.

In studies of heterogeneous decomposition where a reaction tube itself was the surface studied, the area on which the reported rate is based was taken to be the entire area of the tube, including the slight portion which protruded outside the bath. The connectors to upstream and downstream condensers were acid-treated Pyrex and had an area of about 5% of the reaction tube. Except when studying the most inert surfaces, any decomposition on connector surfaces could be neglected;in a few cases a small correction factor was applied based on the known decomposition rate on acid-treated Pyrex.

RESULTS AND DISCUSSION

The experimental results are given in Table I.

Heterogeneous Decomposition

1. Glass

Glass surfaces of various compositions were studied most extensively because they are the least active surfaces known. Various alterations were made in the chemical and physical natures of the glass surfaces in order to find what factors affect the decomposition rate of the vapor. Attempts were then directed towards removing or avoiding those elements which are the sources of catalytic activity on a surface.

Unaltered Surfaces

The rates of decomposition of hydrogen peroxide vapor were measured on the following commercially available glass surfaces, in the form of glass tubes: fused silica, boric oxide fused onto Pyrex, soft glass and lead glass. Several of the tubes were subjected to various chemical treatments to alter their surface. To distinguish between the subsequent differences in behaviour, the tube condition after each of these treatments is designated by a different letter.

Borix oxide films were fused onto several Pyrex tubes by a method suggested by Cook (4). The rates of hydrogen peroxide vapor decomposition on these surfaces are shown on Figure 3. Tube 7

TABLE

SUMMARY OF EXPERIMENTAL DATA

T_{av} -- Average temperature of gas entering reaction tube and reactor wall temperature. -- °C

$P^{1}_{H_2O_2}$ -- Partial pressure of hydrogen peroxide vapor entering reaction tube. -- atm.

$P^{2}_{H_2O_2}$ -- Partial pressure of hydrogen peroxide vapor leaving reactor tube. -- atm.

P_{H_2O} -- Arithmetic average of the inlet and exit partial pressures of water vapor. -- atm.

P_{O_2} -- Arithmetic average of the inlet and exit partial pressures of oxygen. -- atm.

n -- Flow rate of vapor entering reactor tube. moles/min.

A -- Area of the catalytic surface. cm^2

V -- Volume of reaction tube. cm^3

t -- Time elapsed since surface was exposed to hydrogen peroxide vapor. hr.

r -- Differential rate of heterogeneous decomposition. moles/min. $cm^2 \times 10^6$

R° -- Differential rate of heterogeneous decomposition at 120°C on metals plus Pyrex reaction tube. moles/min. $\times 10^6$

R -- Differential rate of decomposition in homogeneous range. moles/min. $\times 10^6$.

TUBE 3 (Continued)

GLASSES AND PLASTICS

RUN	T_{av}	$P^{1}_{H_2O_2}$	$P^{2}_{H_2O_2}$	P_{H_2O}	P_{O_2}	n	r	A
				TUBE 4 PYREX				
30A	180	.0841	.0673	.941	.010	.1023	2.68	619
B		.0698	.0650	.940	.012	.1008		
C		.0698	.0641	.931	.012	.1204	2.53	
25A	180	.0385	.0347	.969	.020	.1389	3.371	619
B		.0342	.0318	.971	.020	.1284	0.519	
C		.0340	.0299	.969	.022	.1203	0.866	
26A	180	.103	.091	.908	.026	.2816	3.08	619
B		.101	.093	.908	.028	.2328	3.07	
21A	215	.0841	.069	.942	.018	.4642	4.36	619
B		.0843	.0814	.947	.021	.2600	5.01	
24A	215	.0289	.0225	.974	.014	.3481	1.31	619
B		.025	.021	.978	.026	.2618	1.28	
C		.024	.020	.976	.028	.2527	1.41	
27A	215	.0907	.0637	.913	.026	.1395	5.74	619
B		.0821	.0638	.919	.026	.1453	4.34	
C		.0821	.0622	.919	.026	.1389	4.20	
30A	215	.1181	.0977	.918	.016	.2702	5.86	619
B		.095	.087	.914	.019	.2743	2.56	
C		.1005	.088	.916	.017	.2813	5.71	
32A	250	.0492	.030	.951	.052	.4084	5.81	619
B		.0462	.0328	.952	.036	.1562	3.34	
C		.0418	.0289	.902	.086	.1562	3.49	
25A	250	.0156	.0126	.978	.031	.2236	0.982	619
B		.015	.012	.981	.030	.2261	0.97	
C		.0141	.2118	.978	.033	.2243	1.0	
28A	250	.0713	.0499	.926	.043	.1789	5.81	619
B		.0688	.0486	.910	.048	.1737	5.33	
C		.0688	.0485	.938	.04	.1904	5.65	
31A	250	.0638	.0421	.933	.021	.2867	8.40	619
B		.0634	.0800	.931	.022	.2309	8.40	
C		.0647	.0599	.928	.029	.2462	8.58	
				TUBE 5 PYREX				
33A	180	.128	.110	.885	.014	.1022	2.86	626
B		.129	.114	.878	.022	.0890	3.18	
34B	180	.0863	.0865	.943	.006	.2645	3.98	626
C		.0659	.0591	.940	.016	.3022	3.02	
29A	180	.0814	.0262	.983	.008	.1391	1.35	626
B		.0843	.0651	.982	.005	.1044	1.50	
42A	180	.1521	.1168	.876	.006	.2329	12.3	626
B		.129	.099	.918	.006	.2800	10.0	
C		.1115	.0981	.906	.008	.2476	8.5	
44A	180	.213	.172	.870	.013	.2774	13.8	626
C		.219	.171	.817	.013	.2116	14.7	
49A	180	.0796	.0718	.941	.010	.2887	3.34	626
B		.106	.087	.974	.006	.3504	10.4	
C		.1054	.0842	.927	.007	.3413	8.20	
34A	215	.1115	.0587	.903	.030	.0838	4.45	626
B		.1287	.0992	.845	.029	.1304	6.81	
37A	215	.0617	.0415	.947	.010	.1290	3.98	626
B		.0599	.0413	.945	.013	.1162	3.36	
C		.058	.040	.953	.010	.1310	3.82	
40A	215	.0297	.0218	.986	.008	.2056	1.96	626
B		.0273	.0217	.983	.008	.1972	1.81	
C		.029	.021	.985	.007	.2122	2.06	
43A	215	.1028	.0744	.912	.016	.2363	9.39	626
B		.103	.084	.903	.020	.2166	8.16	
C		.1022	.0767	.914	.013	.2957	11.3	
47A	215	.172	.119	.695	.185	.1940	15.0	626
B		.153	.111	.773	.121	.2047	14.3	
C		.167	.126	.694	.184	.1972	13.6	

RUN	T_{av}	$P^{1}_{H_2O_2}$	$P^{2}_{H_2O_2}$	P_{H_2O}	P_{O_2}	n	r	A
				TUBE 5 (Continued)				
50A	215	.0984	.0704	.932	.010	.1993	8.12	626
B		.1047	.0782	.926	.010	.2333	9.38	
38A	250	.1144	.0504	.888	.048	.0868	8.44	626
C		.110	.087	.891	.042	.0988	8.03	
48A	250	.0492	.0348	.951	.016	.2816	4.80	626
B		.0528	.0345	.950	.017	.2088	5.88	
C		.0414	.0318	.954	.019	.2116	5.18	
41A	250	.019	.013	.990	.013	.1628	1.40	626
B		.019	.014	.991	.011	.1761	1.19	
C		.0195	.0145	.992	.009	.1934	1.51	
44A	250	.084	.066	.927	.022	.1747	7.89	626
B		.090	.069	.916	.027	.1586	7.26	
C		.092	.069	.922	.026	.1616	7.80	
51A	250	.086	.069	.931	.017	.2850	7.01	626
B		.088	.068	.934	.015	.2872	8.73	
C		.088	.068	.932	.016	.2782	8.26	
				TUBE 6 (Condition A) PYREX				
52A	180	.022	.017	1.108	.009	.2812	2.02	626
B		.022	.017	1.01	.009	.2122	1.66	
53A	180	.086	.055	.962	.016	.2767	4.37	626
B		.086	.064	.964	.015	.2822	4.71	
C		.086	.051	.962	.016	.2358	5.45	
54A	215	.022	.016	1.003	.019	.2973	2.56	626
B		.021	.015	1.003	.017	.2978	2.50	
C		.021	.015	1.009	.016	.3068	2.64	
56A	215	.056	.030	.964	.026	.1491	6.16	626
B		.056	.032	.968	.026	.1498	5.40	
C		.054	.032	.969	.026	.1601	5.59	
58A	260	.017	.010	.978	.022	.2.18	2.58	626
B		.017	.010	1.003	.020	.3498	3.56	
C		.018	.009	1.001	.021	.2978	3.10	
57A	260	.040	.021	.975	.030	.1874	5.26	626
B		.037	.021	.975	.030	.1998	4.96	
C		.038	.020	.978	.017	.2013	5.01	
				TUBE 6 (Condition B) PYREX Pre-treated with 2% H_2O_2				
58A	180	.043	.039	.995	.003	.3389	1.89	626
B		.044	.039	.994	.005	.3389	2.19	
C		.044	.040	.994	.005	.3700	2.51	
59A	215	.033	.031	.997	.008	.2181	0.72	626
B		.037	.033	.997	.008	.2161	1.31	
C		.036	.032	.998	.008	.2340	0.80	
62A	215	.080	.066	.958	.007	.1278	3.78	626
B		.079	.066	.961	.006	.1554	3.72	
C		.077	.065	.960	.008	.1268	2.21	
60A	260	.029	.026	.997	.013	.1483	0.64	626
B		.032	.027	.999	.010	.1698	1.20	
C		.027	.024	.998	.018	.1484	0.74	
63A	260	.066	.057	.968	.010	.2134	3.94	626
				TUBE 6 (Condition C) PYREX				
64A	180	.040	.038	.982	.001	.0842	2.88	626
B		.035	.033	.993	.004	.3337	0.96	
C		.036	.028	.996	.001	.3695	0.48	
65A	215	.034	.032	.998	.004	.3106	0.58	626
B		.039	.026	.997	.006	.1926	1.08	
66A	260	.028	.025	.998	.008	.1848	1.14	626

RUN	T_{ev}	$P_{Fe_2O_3}$ [1]	$P_{K_2O_3}$ [2]	P_{H_2O}	P_{O_2}	n	r	A
						-	-	-
				TYPE 7 (Condition A)				
				PYREX				
69A	180	.029	.028	1.001	.009	.8227	1.61	617
B		.027	.026	1.000	.009	.1763	0.78	
C		.032	.028	0.993	.010	.1479	0.96	
64A	215	.040	.036	0.995	.009	.1741	1.39	617
B		.038	.027	0.996	.009	.2852	1.85	
C		.027	.023	0.999	.007	.3637	1.52	
67A	250	.030	.029	1.000	.008	.2448	2.62	617
C		.026	.021	1.000	.006	.2823	2.04	
				TYPE 7 (Condition B)				
				TREATED WITH CHROMIC ACID				
72A	180	.053	.44	.974	.007	.0956	1.21	617
B		.046	.051	.964	.009	.0788	0.70	
C		.055	.050	.968	.008	.0897	0.68	
75A	180	.033	.032	.989	.008	.1662	0.29	617
B		.030	.029	.994	.009	.1761	0.47	
C		.036	.031	.989	.007	.1649	0.81	
71A	215	.045	.040	.980	.008	.1470	1.09	617
C		.050	.048	.974	.008	.1099	0.81	
74A	215	.039	.038	.987	.005	.2284	0.66	617
B		.038	.036	.986	.006	.2044	0.57	
76A	250	.026	.023	.999	.005	.1107	0.50	617
B		.030	.028	.995	.006	.0960	0.46	
70A	250	.039	.036	.988	.005	.2270	1.18	617
C		.039	.038	.988	.005	.2015	1.55	
				TYPE 7 (Condition C)				
				PYREX				
78A	180	.060	.52	.934	.019	.2195	2.88	617
C		.049	.056	.944	.020	.2192	3.75	
77A	215	.056	.054	.938	.033	.1431	2.87	617
B		.054	.044	.961	.016	.1228	4.04	
79A	250	.047	.047	.945	.009	.3415	3.86	617
B		.050	.044	.947	.011	.3011	3.17	
C		.045	.054	.956	.010	.2151	2.22	
				TYPE 7 (Condition D)				
				TREATED WITH 4% SODIUM HYDROXIDE				
82A	180	.077	.060	.945	.008	.30349	17.2	617
B		.071	.062	.962	.008	.3410	16.0	
C		.068	.062	.970	.007	.3452	14.9	
87A	180	.030	.018	.996	.011	.2530	4.41	617
B		.030	.018	.996	.012	.2401	4.74	
C		.030	.018	.996	.012	.2348	4.63	
83A	215	.047	.022	.978	.011	.1710	12.84	617
B		.073	.021	.974	.011	.1803	15.30	
C		.069	.021	.972	.013	.1586	12.84	
84A	215	.033	.017	.991	.016	.1364	6.11	617
B		.038	.016	.995	.012	.2317	6.56	
C		.032	.018	.995	.013	.2402	8.69	
86A	250	.029	.013	.986	.013	.1282	9.34	617
B		.028	.013	.983	.013	.1346	8.70	
C		.028	.014	.988	.013	.1376	9.52	
85A	250	.036	.018	1.000	.008	.2857	7.55	617
B		.034	.020	1.000	.004	.3279	7.97	
C		.013	.022	1.01	.002	.4797	7.94	
				TYPE 7 (Condition E)				
				SURFACE COATED WITH MOBIC OXIDE				
94A	180	.064	.053	.937	.016	.2892	3.89	617
B		.072	.056	.935	.015	.2258	6.31	
C		.065	.054	.938	.015	.2327	5.87	
98A	180	.026	.036	.978	.010	.2904	0.72	617
B		.025	.027	.974	.014	.3035	1.07	
C		.033	.028	.969	.012	.3164	2.35	
95A	215	.049	.044	.948	.015	.2329	5.27	617
B		.055	.044	.939	.023	.1985	3.37	
C		.058	.045	.939	.020	.2065	4.86	
98A	215	.030	.028	.967	.014	.3023	0.76	617
B		.029	.026	.974	.012	.3436	1.39	
C		.029	.026	.976	.012	.3572	1.52	
96A	250	.060	.042	.941	.019	.2863	6.90	617
B		.058	.043	.940	.021	.2808	5.28	
C		.053	.031	.943	.025	.1923	4.49	
97A	250	.037	.028	.970	.010	.3009	4.47	617
B		.033	.029	.966	.014	.2797	1.57	
C		.038	.029	.962	.012	.2341	2.08	
				TYPE 8				
				PYREX COATED WITH MOBIC OXIDE				
88A	180	.062	.48	.940	.012	.1840	3.75	592
B		.065	.051	.940	.008	.1428	5.58	
C		.070	.050	.931	.018	.1210	3.79	
93A	180	.019	.015	.977	.013	.2769	1.71	592
B		.019	.016	.981	.014	.2671	1.20	
C		.019	.017	.974	.014	.2656	1.06	
891	215	.065	.047	.932	.017	.1812	5.29	592
		.064	.045	.934	.017	.1838	5.31	

RUN	T_{ev}	$P_{Fe_2O_3}$ [1]	$P_{K_2O_3}$ [2]	P_{H_2O}	P_{O_2}	n	r	A
						-	-	-
				TYPE 8				
				(Continued)				
92A	215	.027	.026	.986	.014	.2617	1.88	592
B		.032	.030	.972	.019	.1986	0.78	
C		.027	.026	.986	.014	.2697	1.06	
90A	250	.058	.044	.937	.019	.3563	6.93	592
B		.055	.043	.936	.020	.4378	6.86	
C		.055	.044	.938	.021	.3297	5.99	
91A	250	.030	.027	.960	.015	.2421	1.20	592
B		.030	.026	.964	.011	.3380	2.38	
C		.031	.027	.958	.022	.1693	1.32	
				TYPE 9 (Condition A)				
				PYREX TUBE COATED WITH MOBIC OXIDE				
100A	180	.030	.028	.994	.008	.2874	1.78	592
B		.028	.024	.995	.009	.2876	1.65	
106A	250	.039	.029	.991	.009	.2864	2.97	592
B		.036	.029	.991	.009	.2286	2.50	
C		.038	.028	.988	.010	.2481	2.60	
101A	215	.034	.018	.992	.006	.2738	2.78	592
B		.031	.020	.988	.010	.2908	1.20	
C		.030	.020	.988	.008	.2733	0.76	
				TYPE 9 (Condition B)				
				REACTED WITH AMMONIUM HYDROXIDE				
109A	180	.099	.069	.897	.022	.1228	5.21	592
B		.096	.070	.902	.016	.1148	4.93	
C		.102	.067	.904	.018	.1052	6.00	
103A	180	.030	.026	.976	.012	.2258	1.37	592
B		.029	.026	.974	.013	.2366	1.40	
C		.029	.026	.974	.014	.2228	1.58	
108A	180	.064	.049	.946	.013	.2496	6.00	592
B		.066	.051	.944	.010	.2543	6.38	
C		.075	.058	.937	.015	.2458	7.60	
104A	215	.026	.019	.977	.014	.2363	2.28	592
B		.028	.019	.976	.014	.2160	2.74	
C		.026	.019	.980	.012	.2272	2.63	
107A	215	.070	.047	.942	.015	.2746	1.28	592
B		.068	.045	.946	.012	.2877	10.85	
C		.068	.044	.946	.015	.2642	10.78	
112A	215	.93	.068	.902	.021	.2892	4.62	592
B		.92	.066	.906	.019	.2891	9.95	
C		.092	.066	.905	.021	.2365	9.93	
111A	250	.074	.040	.919	.029	.1864	10.00	592
B		.074	.040	.921	.026	.1864	11.00	
C		.078	.042	.911	.032	.1928	10.10	
105A	250	.024	.016	.979	.014	.2247	2.85	592
B		.021	.013	.978	.014	.2215	3.04	
C		.023	.014	.983	.012	.1429	3.73	
110A	250	.065	.039	.948	.020	.1958	8.75	592
B		.061	.037	.956	.017	.1949	13.58	
C		.070	.039	.936	.024	.1747	8.83	
				TYPE 9 (Condition C)				
				MOBIC OXIDE COATED WITH A MIXED OF VAPOUR AREA				
114A	180	.061	.031	.970	.016	.1612	3.22	1450
B		.064	.029	.967	.018	.1504	3.44	
C		.061	.027	.972	.016	.1561	3.50	
116A	180	.037	.020	1.008	.010	.2884	3.28	1480
B		.037	.020	1.008	.017	.2938	3.31	
118A	180	.098	.060	.942	.014	.1950	6.71	1450
B		.100	.045	.936	.019	.1947	6.62	
C		.096	.041	.941	.019	.1696	6.08	
106A	180	.220	.079	.848	.038	.4338	39.6	1450
B		.214	.077	.855	.035	.4589	40.4	
C		.222	.076	.865	.043	.4235	40.5	
121A	180	.166	.062	.880	.024	.4 15	27.4	1450
B		.155	.059	.893	.029	.4328	26.0	
C		.156	.062	.896	.042	.4331	26.3	
114A	215	.034	.008	.999	.013	.2579	4.46	1450
B		.032	.008	.999	.012	.2460	4.09	
C		.031	.007	.999	.013	.2469	3.92	
117A	215	.067	.033	.966	.018	.3561	7.85	1480
B		.061	.033	.917	.017	.3793	7.02	
C		.058	.030	.971	.016	.3907	7.00	
119A	215	.094	.031	.936	.028	.2961	12.46	1450
B		.090	.030	.941	.026	.3069	12.28	
C		.093	.030	.950	.029	.3079	12.9	
125A	215	.197	.061	.866	.041	.4885	41.2	1450
B		.199	.063	.861	.042	.4528	38.8	
C		.200	.061	.867	.048	.4313	39.0	
122A	215	.148	.047	.891	.038	.4100	27.4	1450
B		.132	.049	.900	.037	.5008	27.6	
C		.129	.051	.902	.036	.5163	28.7	
117A	250	.027	.008	1.001	.014	.2428	3.76	1480
B		.027	.004	1.008	.013	.2428	3.76	
C		.027	.003	1.001	.014	.2428	3.76	
112A	250	.056	.014	.978	.019	.3093	4.70	1450
B		.055	.014	.977	.020	.3155	8.58	
C		.054	.014	.978	.019	.3328	8.98	
120A	250	.076	.015	.966	.038	.2640	9.98	1450
B		.075	.015	.965	.038	.2638	9.79	
C		.073	.014	.966	.036	.2639	9.53	
126A	250	.160	.046	.893	.046	.3896	38.6	1480
C		.169	.043	.875	.058	.3257	36.7	
123A	250	.118	.046	.892	.055	.5736	27.9	1480
B		.119	.048	.900	.048	.5806	28.3	
C		.118	.046	.902	.044	.5899	27.6	

RUN	T_{av}	$P_{B_2O_3}$ [1]	$P_{B_2O_3}$ [2]	P_{B_2O}	P_{O_2}	n	r	A
TYPE 9 (Condition B) BORON MONOXIDE								
127A	180	.054	.040	.943	.010	.8113	7.68	592
B		.052	.038	.950	.011	.7929	8.21	
C		.051	.038	.984	.011	.3386	8.68	
130A	180	.129	.096	.917	.010	.4089	20.3	592
B		.126	.094	.908	.012	.3890	17.5	
C		.131	.099	.906	.012	.3981	19.6	
135A	180	.341	.139	.771	.023	.3188	108.0	592
B		.340	.113	.781	.020	.3020	73.6	
C		.340	.143	.772	.019	.3842	120.8	
134A	180	.086	.063	.927	.012	.3819	12.3	592
B		.092	.064	.920	.016	.2847	11.6	
C		.095	.063	.917	.020	.2579	17.2	
131A	215	.128	.082	.901	.026	.3288	21.1	592
B		.131	.085	.895	.030	.3180	22.8	
C		.133	.086	.902	.021	.3130	28.1	
128A	215	.049	.028	.946	.023	.1135	2.80	592
B		.051	.032	.935	.014	.2806	8.80	
C		.046	.033	.900	.014	.2992	6.28	
144A	215	.338	.037	.776	.019	.4062	128.00	592
B		.336	.078	.790	.033	.3767	31.80	
C		.335	.140	.791	.022	.4660	164.00	
137A	215	.100	.066	.916	.020	.3421	16.0	592
B		.096	.060	.914	.027	.1839	13.6	
C		.097	.062	.908	.022	.2994	15.2	
140A	215	.196	.130	.792	.021	.4448	126.0	592
B		.275	.112	.805	.021	.4338	118.0	
133A	280	.122	.048	.91	.036	.1899	19.1	592
B		.120	.046	.895	.044	.1430	26.5	
C		.122	.063	.910	.029	.2961	36.1	
136A	280	.316	.062	.799	.035	.3096	78.5	592
B		.312	.065	.799	.043	.1470	58.1	
C		.309	.064	.804	.041	.1597	61.8	
148A	280	.091	.036	.920	.023	.3168	19.1	592
B		.091	.052	.915	.029	.2736	17.6	
C		.091	.054	.914	.028	.3132	18.8	
129A	280	.063	.026	.998	.020	.2733	7.68	592
B		.060	.026	.997	.020	.2644	6.84	
C		.061	.025	.999	.025	.2631	6.94	
TYPE 10 (Condition C) TREATED WITH CHROMIC ACID HBO_3								
176A	180	.064	.042	.958	.006	.2536	5.76	592
B		.064	.041	.956	.006	.2479	5.13	
C		.069	.046	.948	.006	.2631	5.99	
178A	180	.028	.020	.967	.007	.2081	1.96	592
B		.028	.020	.966	.007	.2086	2.02	
C		.028	.020	.966	.007	.2031	2.13	
174A	215	.027	.021	.965	.008	.2881	2.08	592
B		.026	.021	.964	.008	.2849	1.77	
C		.027	.020	.966	.008	.2260	2.28	
175A	215	.062	.048	.936	.011	.1909	5.20	592
B		.064	.044	.942	.012	.1778	5.67	
C		.052	.039	.951	.014	.1366	4.98	
170A	280	.052	.038	.938	.015	.2124	6.07	592
B		.053	.037	.936	.018	.2118	5.36	
C		.053	.036	.937	.017	.2106	6.26	
177A	280	.027	.018	.968	.011	.1917	2.48	592
B		.026	.019	.966	.009	.1898	2.28	
C		.026	.019	.966	.009	.1958	2.41	
TYPE 11(Condition A) PYREX								
164A	180	.053	.049	.942	.010	.3866	1.96	559
B		.054	.048	.941	.008	.3646	2.50	
C		.055	.049	.950	.008	.3862	3.09	
161A	180	.028	.027	.976	.007	.4100	.79	559
B		.028	.027	.976	.001	.4205	.80	
C		.028	.027	.977	.008	.3984	.58	
157A	215	.056	.036	.950	.015	.1196	4.56	559
B		.068	.038	.930	.013	.1219	3.88	
C		.059	.036	.948	.018	.1009	3.60	
160C	215	.026	.027	.976	.007	.4308	1.01	559
B		.029	.028	.972	.007	.4268	1.18	
A		.028	.028	.976	.009	.4208	1.08	
159C	280	.027	.028	.976	.009	.4077	1.78	559
B		.027	.028	.978	.007	.4103	1.42	
A		.027	.028	.979	.007	.4129	1.34	
158A	280	.060	.042	.950	.016	.3560	4.1	559
B		.061	.043	.946	.018	.3753	4.21	
C		.060	.042	.948	.017	.3917	4.57	
TYPE 11 (Condition B) TREATED WITH BBO_3								
166A	180	.065	.060	.946	.010	.1866	3.78	559
B		.064	.061	.946	.010	.1658	3.97	
C		.067	.068	.945	.008	.1813	3.62	
173A	180	.031	.027	.976	.008	.1803	1.20	559
B		.033	.026	.977	.007	.1912	1.72	
C		.030	.026	.979	.007	.1967	1.57	
172A	215	.032	.026	.976	.009	.2019	1.87	559
B		.031	.026	.977	.009	.1913	1.86	
C		.030	.026	.979	.007	.1860	1.82	
168A	215	.060	.048	.947	.012	.2580	4.26	559
B		.059	.047	.947	.013	.2587	4.71	
C		.058	.048	.949	.012	.2715	4.42	
171A	280	.029	.019	.986	.008	.1152	1.81	559
B		.029	.019	.979	.010	.1188	1.87	
C		.030	.021	.984	.009	.1657	2.00	
170A	280	.060	.038	.936	.020	.1284	3.46	559
B		.049	.031	.955	.018	.1007	3.32	
C		.049	.032	.955	.019	.1163	3.34	
TYPE 12 (Condition A) PYREX TREATED WITH B_2O_3								
180A	215	.052	.044	.963	.013	.3277	4.30	548
B		.058	.048	.961	.013	.3421	4.50	
C		.058	.046	.961	.013	.3616	4.15	
D		.053	.048	.962	.013	.3940	4.30	
TYPE 12 (Condition B) TREATED WITH $A_s BO_3$								
182A	215	.062	.017	.971	.010	.4729	20.60	548
B		.062	.018	.970	.020	.4741	20.40	
C		.048	.018	.968	.020	.4842	20.60	
D		.044	.018	.969	.020	.4770	20.20	
TYPE 13 (Condition A) PYREX TREATED WITH $A_s BO_3$								
191A	215	.048	.028	.945	.080	.4679	22.70	555
B		.047	.026	.948	.080	.4612	21.90	
C		.047	.026	.947	.080	.4679	22.20	
D		.047	.026	.947	.080	.4681	21.80	
TYPE 12 (Condition B) TREATED WITH $B_A BC_3$								
144A	215	.049	.019	.941	.080	.3596	19.10	558
B		.049	.018	.939	.024	.3388	18.50	
C		.048	.018	.941	.023	.3466	18.80	
TYPE 10 (Condition A) PYREX								
156A	180	.064	.062	.938	.008	.3894	3.24	592
B		.067	.061	.939	.008	.4024	3.57	
C		.067	.061	.939	.008	.3784	3.71	
155A	180	.024	.028	.977	.009	.3452	0.61	592
B		.024	.024	.979	.008	.3515	1.21	
C		.024	.022	.979	.008	.3570	1.13	
154A	215	.029	.024	.974	.008	.2738	1.52	592
B		.027	.024	.975	.008	.2713	1.27	
C		.027	.024	.976	.009	.2809	1.80	
151A	215	.062	.046	.941	.012	.4394	5.46	592
B		.063	.047	.940	.012	.4477	5.74	
C		.063	.046	.938	.014	.3998	5.52	
153A	280	.027	.025	.970	.008	.3998	1.42	592
B		.028	.025	.976	.009	.3988	1.62	
C		.029	.026	.975	.008	.3961	1.80	
150A	280	.053	.047	.943	.017	.4437	4.76	592
B		.054	.046	.944	.017	.4308	5.4.	
C		.053	.046	.943	.017	.4332	5.28	
TYPE 10 (Condition B) TREATED IN CHROMIC ACID SLUP OF METAPHOSPHORIC								
162A	180	.049	.039	.955	.008	.3448	4.11	592
B		.049	.038	.956	.008	.3828	4.04	
C		.051	.041	.952	.010	.3880	4.10	
147A	180	.029	.026	.974	.009	.2898	1.27	592
B		.029	.026	.973	.009	.2736	1.44	
C		.028	.025	.975	.009	.2797	1.44	
146A	215	.029	.026	.972	.009	.3274	1.72	592
B		.028	.026	.973	.010	.3363	1.78	
C		.028	.025	.975	.008	.3288	1.78	
168A	215	.062	.050	.936	.014	.3217	4.48	592
B		.062	.052	.938	.013	.3385	5.40	
C		.060	.051	.937	.015	.3299	4.71	
164A	280	.052	.036	.944	.020	.1918	5.08	592
B		.052	.037	.944	.020	.1988	4.91	
C		.052	.037	.945	.020	.2022	5.08	
146A	280	.028	.023	.974	.019	.3569	2.88	592
B		.028	.023	.976	.009	.3583	2.70	
C		.027	.023	.974	.009	.3829	2.61	

RUN	T_{av}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	a	r	A	
TUBE 14 (Condition A) PYREX TREATED WITH $Fe(NO_3)_3$									
184A	215	.037	.028	.939	.021	.3884	20.30	900	
B		.046	.028	.960	.020	.3834	20.00		
C		.046	.028	.960	.021	.3948	20.60		
D		.046	.028	.960	.020	.4036	19.60		
TUBE 14 (Condition B) TREATED WITH Ba NO_3									
186A	215	.037	.019	.966	.021	.4334	12.10	556	
B		.037	.020	.967	.020	.4468	12.60		
C		.036	.020	.964	.020	.4391	12.30		
D		.037	.020	.964	.021	.4561	12.30		
TUBE 15 (Condition A) PYREX TREATED WITH Ba NO_3									
188A	215	.044	.043	.966	.016	.3690	5.90	544	
B		.053	.045	.966	.014	.3710	6.00		
C		.054	.045	.953	.014	.3822	5.30		
D		.048	.043	.956	.017	.3798	5.52		
TUBE 15 (Condition B) TREATED WITH Fe $(NO_3)_3$									
190A	215	.041	.030	.968	.019	.3864	12.10	548	
B		.041	.031	.966	.021	.3970	12.10		
C		.041	.031	.966	.022	.3979	11.30		
D		.041	.030	.967	.020	.3903	11.80		
TUBE 16 (Condition A) PYREX TREATED WITH Ag_2O_3									
187A	215	.038	.011	.976	.021	.3963	14.50	588	
B		.036	.011	.977	.021	.3908	14.20		
C		.035	.011	.977	.021	.4129	14.00		
D		.038	.012	.976	.021	.4189	14.70		
TUBE 16 (Condition B) TREATED WITH $Fe(NO_3)_3$									
190A	215	.056	.021	.971	.02C	.3634	18.70	888	
B		.054	.021	.948	.026	.3781	19.30		
C		.053	.021	.972	.021	.3686	18.20		
TUBE 17 (Condition A) PYREX TREATED WITH Fe $(NO_3)_3$									
184A	215	.053	.032	.956	.017	.4402	14.60	565	
B		.055	.033	.956	.018	.4263	14.90		
C		.053	.031	.957	.018	.4406	14.30		
D		.052	.032	.951	.02C	.4416	13.90		
TUBE 17 (Condition B) TREATED WITH Ag (NO_3)									
191A	215	.042	.011	.978	.024	.3660	17.00	555	
B		.041	.011	.978	.024	.3652	16.70		
C		.041	.011	.979	.024	.3648	16.20		
TUBE 18 (Condition A) PYREX TUBE									
192A	215	.057	.048	.957	.016	.5305	7.96	592	
B		.057	.047	.956	.019	.5087	8.66		
C		.056	.046	.957	.017	.5199	7.73		
TUBE 18 (Condition B) TREATED WITH CrO NO_3									
194A	215	.055	.044	.953	.016	.3348	5.50	592	
B		.053	.043	.953	.018	.3128	5.66		
C		.054	.042	.952	.018	.3302	6.14		
TUBE 18 (Condition C) TREATED WITH HYDROGEN PEROXIDE VAPOR									
196A	215	.055	.043	.949	.016	.2916	5.38	592	
B		.055	.044	.947	.019	.2951	5.57		
C		.054	.042	.948	.018	.2950	5.42		
TUBE 19 (Condition A) PYREX TUBE									
193A	215	.044	.036	.968	.018	.4163	6.26	592	
B		.045	.035	.970	.018	.4216	6.40		
C		.044	.036	.968	.018	.4138	6.48		
TUBE 19 (Condition B) TREATED WITH 2N HNO_3									
195A	215	.030	.027	.990	.012	.3868	1.99	592	
B		.030	.028	.978	.013	.3714	1.28		
C		.030	.029	.978	.012	.4195	1.33		
TUBE 19 (Condition C) TREATED WITH 20C PPM SODIUM STANNATE									
197A	215	.040	.034	.961	.016	.3399	3.20	592	
B		.040	.034	.961	.016	.3388	3.35		
C		.040	.035	.961	.016	.3504	3.17		

RUN	T_{av}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	a	r	A	
TUBE 20 LEAD GLASS									
198A	215	.089	.086	.955	.018	.4184	60.3	126	
B		.089	.086	.953	.020	.4082	62.0		
C		.086	.086	.956	.018	.4080	56.1		
199A	215	.027	.019	.986	.009	.3860	19.8	126	
B		.027	.019	.986	.009	.4045	19.8		
C		.026	.019	.987	.009	.4014	19.7		
TUBE 21 (Condition A) PYREX COATED WITH MOLYBDENUM									
201A	215	.046	.044	.958	.014	.4352	.52	588	
B		.048	.044	.985	.015	.3841	1.28		
C		.046	.044	.953	.016	.3772	1.37		
TUBE 21 (Condition B) SAME AS USED OVER TUBE 21									
202A	215	.031	.027	.972	.010	.2881	1.76	592	
B		.030	.024	.974	.010	.2198	2.14		
C		.030	.026	.978	.010	.2178	1.64		
TUBE 22 (Condition A) PYREX TUBE									
200A	215	.051	.043	.954	.014	.3941	4.46	592	
B		.052	.043	.952	.015	.2988	4.14		
C		.050	.042	.955	.014	.2972	4.14		
TUBE 22 (Condition B) TREATED WITH 4N H_3PO_4									
203A	215	.068	.057	.938	.012	.3141	3.07	592	
B		.068	.057	.941	.011	.3119	3.23		
C		.068	.057	.940	.011	.3172	3.11		
TUBE 23 LEAD GLASS TREATED WITH 4N H_3PO_4									
204A	215	.058	.044	.943	.015	.2798	37.4	88	
B		.057	.044	.948	.015	.2953	36.4		
C		.059	.044	.948	.014	.3111	36.2		
TUBE 24 (Condition A) PYREX TREATED WITH 5% FACE									
206A	315	.055	.041	.951	.012	.2648	5.96	548	
B		.053	.040	.954	.011	.2538	5.68		
C		.054	.039	.953	.012	.2587	5.50		
TUBE 24 (Condition B) SO_2 GAS PASSED THROUGH TUBE 24									
208A	215	.041	.036	.971	.015	.3786	3.30	548	
B		.041	.036	.970	.014	.3810	3.33		
C		.041	.036	.973	.012	.3735	2.82		
TUBE 25 (Condition A) PYREX TUBE TREATED WITH 4N H_3PO_4									
206A	215	.056	.050	.957	.013	.3654	2.55	592	
B		.056	.050	.957	.013	.3469	2.70		
C		.056	.050	.957	.013	.3438	2.73		
TUBE 25 (Condition B) TEFLON ROD (A = 197 cm^2) ADDED TO TUBE 25									
212A	215	.045	.030	.960	.016	.3927	28.0	197	
B		.046	.030	.960	.016	.3829	24.8		
C		.046	.031	.959	.016	.3988	23.6		
TUBE 25 (Condition C) TUBE ASED									
215A	120	.057	.051	.960	.008	.3383	3.38	592	
B		.057	.050	.963	.008	.3416	4.09		
C		.057	.051	.956	.009	.3473	3.26		
TUBE 25 (Condition D) TEFLON STRIP (A = 120 cm^2) ADDED TO TUBE 25									
216A	120	.048	.040	.969	.010	.2800	4.87	120	
B		.048	.040	.969	.011	.2993	5.34		
C		.048	.040	.969	.012	.2996	6.58		
TUBE 25 (Condition E) POLYETHYLENE STRIP (A = 60 cm^2) ADDED TO TUBE 25									
217A	120	.041	.032	.973	.014	.2599	21.6	60	
B		.041	.031	.974	.015	.1441	26.3		
C		.042	.031	.972	.016	.2835	30.1		
TUBE 25 (Condition F) VERTICAL STRIP (A = 120 cm^2) ADDED TO TUBE 25									
218A	120	.037	.024	.980	.015	.3028	13.26	120	
B		.037	.028	.976	.015	.3129	9.79		
C		.037	.026	.977	.016	.3067	10.05		

TUBE 96

PYREX TUBE TREATED WITH 4N H_3PO_4

207A	215	.049	.047	.962	.014	.3187	1.38	594
B		.050	.047	.962	.014	.3348	1.70	
C		.048	.047	.962	.014	.3309	1.30	

TUBE 97

SILICA TUBE TREATED WITH 4N HNO_3

209A	215	.038	.031	.979	.009	.3217	1.03	844
B		.038	.031	.979	.010	.3116	1.13	
C		.038	.030	.978	.010	.3094	1.34	
210A	215	.066	.061	.963	.015	.3148	3.30	844
B		.065	.060	.963	.015	.3018	3.30	
C		.063	.060	.963	.013	.3223	2.16	

TUBE 98

PYREX COATED WITH 9MI CHLORO METHYL SILANE

211A	215	.060	.056	.963	.018	.3918	2.58	593
B		.057	.054	.963	.010	.3026	1.98	
C		.060	.056	.964	.013	.3158	1.89	

TUBE 99

PYREX COATED WITH METHYL METHACRYLATE

213A	120	.077	.047	.963	.008	.2896	11.66	593
B		.070	.047	.981	.008	.2837	8.86	
C		.068	.046	.950	.008	.2898	8.00	

TUBE 33

PYREX SCARED IN 4N H_3PO_4

277A	215	.026	.022	1.000	.008	.3758	2.38	593
B		.026	.022	.998	.010	.2938	1.94	
C		.026	.028	.999	.010	.1428	1.81	
278A	215	.081	.070	.942	.015	.3523	6.37	593
B		.081	.078	.936	.013	.3778	7.50	
C		.088	.074	.939	.013	.3600	6.78	

TUBE 34

PYREX SCARED IN 4N HCl

282A	215	.076	.056	.943	.013	.2693	7.06	593
B		.075	.059	.958	.014	.2874	8.78	
C		.073	.057	.955	.013	.2644	6.41	
284A	215	.034	.025	.993	.009	.1175	2.16	593
B		.039	.030	.991	.010	.1168	2.36	
C		.037	.028	.994	.008	.1193	2.14	

TUBE 35

PYREX TREATED WITH 1N HF

285A	215	.027	.026	1.000	.007	.3868	1.66	593
B		.027	.026	1.000	.008	.3841	1.39	
C		.027	.026	1.001	.008	.3797	1.63	
286A	215	.069	.064	.956	.010	.4628	3.81	593
B		.070	.064	.954	.010	.4667	4.28	
C		.072	.067	.953	.011	.4628	4.06	

TUBE 36

PYREX TREATED WITH 4N H_3PO_4 HEATED TO 400-430°C FOR 5 HOURS

278A	215	.067	.060	.940	.010	.3828	6.58	593
B		.069	.064	.958	.009	.3844	8.75	
C		.070	.066	.956	.010	.3813	8.79	

TUBE 101 (Condition A)

PYREX TREATED WITH 4N H_3PO_4

287A	215	.042	.033	.966	.016	.1863	2.07	593
B		.043	.035	.969	.016	.1718	2.01	
C		.041	.032	.969	.016	.1841	2.01	
288A	180	.036	.029	.973	.016	.1548	1.87	593
B		.036	.028	.974	.016	.1568	1.97	
C		.036	.028	.973	.016	.1615	1.92	
289A	190	.033	.029	.972	.017	.1955	1.89	593
B		.032	.028	.976	.017	.1832	1.74	
C		.032	.027	.977	.017	.1899	1.68	
260A	117	.026	.021	.979	.016	.2864	2.60	592
B	122	.026	.022	.982	.016	.3070	1.90	
C	116	.026	.020	.981	.017	.3019	2.33	
275A	121	.104	.098	.919	.008	.2852	5.77	593
B		.106	.097	.920	.008	.2456	7.62	
C	120	.103	.094	.922	.009	.3404	6.66	
261A	109	.024	.018	.981	.017	.3391	3.15	593
B	110	.026	.018	.986	.017	.3408	3.47	
C	111	.026	.019	.985	.016	.3783	3.18	
274A	110(116)	.088	.081	.928	.008	.3664	6.26	593
B	113(119)	.098	.088	.928	.009	.4058	8.86	
C	110(116)	.090	.082	.927	.010	.3894	5.37	

TUBE 101 (Condition B)

PYREX

276A	215	.067	.057	.951	.013	.2806	4.11	592
B		.068	.058	.947	.014	.2771	5.03	
C		.068	.057	.948	.014	.2863	4.87	
290A	215	.041	.037	.978	.009	.3729	2.36	592
B		.036	.033	.982	.007	.4393	2.16	
C		.038	.033	.983	.008	.4351	2.01	

TUBE 101 (Condition C)

SOFT GLASS ROD (A = 204 cm²) ADDED TO TYPE 101

279A	215	.065	.049	.963	.011	.3816	11.6	204
B		.073	.061	.953	.015	.3152	19.3	
C		.065	.049	.960	.014	.3834	14.8	
296A	215	.042	.035	.980	.012	.2343	1.32	204
B		.039	.034	.987	.007	.3022	.98	
C		.037	.028	.991	.008	.2607		

TUBE 101 (Condition D)

SOFT GLASS ROD TREATED WITH 4N H_3PO_4

281A	215	.029	.025	.988	.008	.3178	1.42	4
B		.028	.026	.988	.009	.3031	1.28	
C		.029	.026	.986	.011	.3148	1.72	
298A	215	.063	.054	.966	.012	.3784	2.89	204
B		.065	.057	.960	.013	.3743	3.11	
C		.063	.055	.960	.013	.3897	2.26	

METALS

TUBE 37 (Condition A)

SHORT PYREX TUBE FOR METAL RODS 219 - 311

301A	150	.018	.017	.982	.009	.3810	1.67	162
B		.018	.017	.984	.008	.3818	1.47	
C		.018	.016	.983	.009	.3839	1.98	
302A	180	.064	.064	.931	.018	.3141	6.02	162
B		.068	.066	.930	.018	.3143	6.98	
C		.064	.062	.931	.013	.3062	4.48	

TUBE 37 Condition B)

SHORT PYREX TUBE FOR METAL RUN 312 - 336

318A	150	.039	.039	.983	.008	.3636	2.04	162
B		.039	.039	.985	.004	.3710	1.86	
C		.039	.038	.985	.004	.3655	2.38	
316A	150	.076	.073	.984	.006	.3080	6.06	162
B		.074	.072	.946	.006	.3196	4.32	
C		.073	.071	.948	.006	.3072	5.28	
328A	180	.136	.127	.986	.003	.3026	15.2	162
B		.135	.127	.987	.004	.3064	14.8	
C		.135	.126	.989	.003	.3161	14.0	

TUBE 37 (Condition B)
(Continued)

320A	180	.178	.171	.841	.006	.2869	12.1	162
B		.182	.173	.888	.006	.2951	15.0	
C		.188	.174	.837	.004	.2956	16.1	
306A	180	.199	.175	.825	.006	.3614	47.1	162
B		.196	.173	.828	.006	.3721	46.3	
C		.194	.172	.830	.006	.3748	46.8	
314A	180	.043	.040	.979	.008	.2580	4.63	162
B		.044	.043	.979	.008	.2821	5.71	
C		.044	.043	.979	.008	.2741	4.45	
317A	180	.074	.068	.950	.008	.3069	8.03	162
B		.072	.068	.948	.007	.3009	7.47	
C		.072	.068	.948	.008	.2999	8.14	
328A	180	.157	.140	.867	.004	.3075	23.2	162
B		.153	.139	.872	.004	.3088	23.9	
C		.148	.138	.872	.004	.3096	17.9	
324A	180	.188	.162	.840	.008	.2849	29.1	162
B		.184	.160	.838	.008	.2811	28.1	
C		.183	.163	.840	.008	.2106	24.9	

RUN	T_{ov}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	B	F	A	t
2S ALUMINUM									
CONDITION A ELECTROPOLISHED									
308A	150	.047	.040	.981	.011	.1096	106.8	12.3	
B		.046	.037	.985	.009	.1083	91.0		
C		.045	.037	.986	.010	.1020	76.2		
304A	180	.035	.029	.976	.008	.3034	128.1	12.3	
B		.034	.028	.975	.009	.2986	119.4		
C		.034	.031	.976	.010	.2966	109.1		
308A	150	.030	.025	.988	.009	.4100	120.6	12.3	
B		.032	.026	.981	.010	.4134	128.2		
C		.033	.030	.981	.009	.4061	110.1		
2S ALUMINUM									
CONDITION B PREHEATED									
306A	150	.029	.025	.986	.005	.3115	74.0	12.08	
B		.028	.026	.986	.006	.3199	88.6		
C		.030	.026	.986	.005	.3188	94.0		
2S ALUMINUM									
CONDITION C ANODIZED									
314A	180	.037	.034	.984	.009	.4248	56.3	12.14	
B		.037	.033	.984	.005	.4243	60.9		
C		.035	.031	.981	.008	.4381	68.5		
2S ALUMINUM									
CONDITION B PICKLED									
309A	180	.041	.037	.974	.006	.3675	53.8	12.07	
B		.039	.035	.976	.008	.3619	91.6		
C		.040	.036	.969	.006	.3590	62.4		
332A	150	.046	.039	.980	.004	.3804	134.0	12.07	
B		.046	.040	.980	.004	.3808	131.8		
C		.048	.038	.981	.005	.3813	128.0		
334A	180	.082	.075	.943	.006	.3446	97.3	12.07	
B		.077	.071	.948	.004	.3535	77.4		
C		.084	.076	.941	.006	.3480	109.0		
338A	180	.112	.[illegible]	.919	.006	.3267	286.0	12.07	
B		.108	.093	.930	.006	.3034	288.0		
C		.109	.091	.921	.006	.3289	318.0		
328A	150	.157	.138	.876	.009	.3366	478.0	12.07	
B		.151	.118	.885	.008	.3245	561.0		
C		.152	.122	.886	.009	.3258	510.0		
333A	180	.165	.151	.849	.017	.3621	557.0	12.07	
B		.166	.152	.849	.010	.3590	522.0		
C		.168	.153	.847	.009	.3585	468.0		
327A	150	.234	.178	.813	.010	.3598	1076.0	12.07	
B		.231	.181	.807	.017	.3517	880.0		
C		.230	.179	.813	.012	.3649	976.0		
335A	180	.042	.032	.945	.005	.3348	194.5	12.07	
B		.041	.031	.945	.006	.3384	208.2		
C		.041	.031	.947	.005	.3387	199.7		
326A	180	.073	.062	.912	.008	.3387	148.8	12.07	
B		.075	.065	.918	.007	.3380	186.5		
C		.069	.064	.907	.009	.3296	134.8		
324A	180	.127	.096	.905	.011	.3099	508.0	12.07	
B		.119	.089	.915	.010	.3019	487.0		
C		.117	.088	.915	.010	.3094	480.0		
329A	180	.137	.098	.887	.012	.3011	653.0	12.07	
B		.144	.103	.893	.010	.3028	680.0		
C		.138	.100	.894	.014	.3881	621.0		
330A	180	.191	.141	.843	.017	.3033	774.0	12.07	
B		.191	.138	.846	.016	.3037	782.0		
C		.200	.142	.840	.018	.3081	804.0		
325A	180	.245	.178	.810	.026	.3286	2084.0	12.07	
B		.228	.132	.823	.026	.3327	1860.0		
C		.237	.141	.813	.026	.3214	1838.0		

RUN	T_{ov}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	B	F	A	t
TANTALUM									
CONDITION A									
312A	150	.0280	.0253	1.006	.006	.3808	38.2	13.09	1
B		.0271	.0246	1.006	.006	.3620	33.8		
C		.0274	.0245	1.006	.006	.3881	42.8		
TANTALUM									
CONDITION B (TREATED WITH ZnO_2)									
313A	150	.0442	.0395	.990	.008	.4004	73.8	13.09	1
B		.0432	.0391	.991	.008	.3978	58.0		
C		.0427	.0391	.990	.008	.3996	42.8		
STAINLESS STEEL 303									
CONDITION A (ELECTROPOLISHED)									
298A	150	.0527	.0447	.976	.007	.3062	121.5	12.8	5
B		.0505	.0428	.978	.006	.3051	130.2		
C		.0505	.0418	.979	.007	.3028	145.8		
293A	150	.0446	.0419	.992	.008	.5430	39.9	12.5	1
B		.0434	.0395	.993	.008	.5305	17.6		
C		.0414	.0379	.996	.008	.5158	43.9		
294A	150	.0277	.0239	.999	.007	.2710	41.8	12.8	2
B		.0269	.0237	.998	.007	.2784	32.7		
C		.0270	.0237	.998	.007	.2761	38.1		
295A	180	.102	.0952	.986	.008	.5003	56.7	12.5	3
B		.102	.0918	.960	.008	.4993	115.8		
C		.1034	.0961	.935	.009	.4942	63.9		
296A	180	.1371	.1286	.902	.009	.4928	48.8	12.5	4
B		.1385	.1308	.900	.009	.4818	20		
C		.1468	.1380	.891	.008	.4992	92.6		
297A	150	.0827	.0756	.958	.006	.5038	101.4	12.5	5
B		.0863	.0794	.954	.006	.4986	79.8		
C		.0793	.0733	.960	.006	.5038	80.7		
298A	180	.0475	.0435	.992	.006	.5091	51.1	12.5	7
B		.0484	.0410	.994	.006	.5185	76.7		
C		.0827	.0488	.986	.006	.5151	56.7		
299A	150	.0608	.0543	.961	.010	.1260	17.3	12.5	8
B		.0586	.0528	.965	.010	.1191	13.75		
C		.0563	.0511	.965	.010	.1008	15.2		
300A	150	.0302	.0262	.971	.008	.3528	77.5	12.5	9
B		.029v	.0256	.971	.009	.3550	85.4		
C		.0289	.0256	.972	.009	.3471	51.1		
STAINLESS STEEL 303									
CONDITION B (PASSIVATED)									
314A	150	.0479	.0382	.990	.006	.4280	26.2	12.96	1
B		.0384	.0368	.992	.005	.4291	13.1		
C		.0384	.0360	.992	.005	.4291	22.4		
STAINLESS STEEL 416									
CONDITION A (ELECTROPOLISHED)									
290A	150	.030	.026	1.016	.006	.5131	105.5	14.99	1
B		.030	.025	1.013	.005	.5111	115.5		
C		.030	.026	1.013	.006	.5119	110.2		
291A	150	.027	.024	1.017	.004	.5078	70.2	12.98	2
B		.027	.024	1.018	.004	.51.7	74.0		
C		.027	.023	1.020	.004	.5042	92.5		
STAINLESS STEEL 304									
CONDITION A (ELECTROPOLISHED)									
287A	180	.038	.032	1.007	.007	.5129	138.4	12.0	1
B		.037	.031	1.008	.006	.5264	154.2		
C		.036	.030	1.009	.006	.5114	174.3		
288A	150	.036	.027	1.012	.006	.3756	146.8	12.0	1:18
B		.034	.028	1.011	.007	.3764	166.0		
C		.034	.026	1.013	.006	.3755	144.2		
289A	150	.047	.039	1.001	.006	.5164	236.2	12.0	2
B		.048	.040	.999	.006	.4977	208.2		
C		.047	.039	.999	.006	.5013	191.0		
STAINLESS STEEL 304									
CONDITION B (PICKLED)									
307A	150	.032	.030	.983	.006	.3637	22.2	12.6	
B		.035	.032	.980	.007	.3519	25.4		
C		.032	.029	.983	.006	.3742	17.65		
STAINLESS STEEL 304									
CONDITION C (PASSIVATED)									
304A	150	.0345	.028	.980	.006	.3521	28.8	12.6	
B		.0350	.032	.979	.009	.3677	44.6		
C		.0326	.030	.982	.008	.3564	19.65		

RUN	T_{ov}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	B	F	A	t
TIN									
CONDITION A									
310A	150	.0488	.0437	.956	.006	.3522	99.6	10.6	1
B		.0473	.0431	.962	.006	.3567	89.6		
C		.0469	.0436	.962	.006	.3598	57.5		
TIN									
CONDITION B (TREATED WITH ZnO_2)									
311A	150	.0469	.0438	.963	.006	.3642	56.4	9.78	1
B		.0467	.0436	.963	.006	.3657	34.4		
C		.0437	.0411	.965	.006	.3658	31.8		

RUN	T_{av}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	n	k	A	t

STAINLESS STEEL 416

CONDITION A (ELECTROPOLISHED)

AREA OF GLASS = 162 cm²
AREA OF METAL ROD = 12.98 cm²

206A	120	.001	.040	.955	.015	.5041	9.15	1.20	
B		.000	.039	.979	.015	.5135	9.43		
C		.040	.0394	.981	.015	.5082	8.97		
207A	120	.000	.030	.951	.013	.4892	17.49	2.50	
B		.002	.029	.959	.013	.4939	19.16		
208A	120	.036	.001	.993	.001	.5167	7.04	2.75	
B		.034	.030	.995	.001	.5179	6.43		
C		.034	.030	.990	.001	.5130	6.71		

STAINLESS STEEL 303

CONDITION A (ELECTROPOLISHED)

AREA OF GLASS = 162 cm²
AREA OF METAL ROD = 10.56 cm²

233A	120	.035	.034	.980	.010	.5169	9.992	1.00	
B		.0344	.033	.980	.010	.5182	10.78		
C		.034	.033	.980	.010	.5173	10.11		
234A	120	.030	.029	.981	.014	.5116	9.59	2.50	
B		.030	.029	.981	.014	.5090	9.68		
235A	120	.035	.023	.984	.017	.5105	5.09	5.00	
B		.035	.023	.976	.018	.5048	5.05		
C		.034	.023	.988	.017	.5042	4.99		

STAINLESS STEEL 304

CONDITION A (ELECTROPOLISHED)

AREA OF GLASS = 162 cm²
AREA OF METAL ROD = 12.6 cm²

227A	120	.033	.0423	.955	.018	.4834	10.33	1.5	
B		.0388	.0438	.961	.016	.4840	17.2		
C		.0403	.0435	.964	.016	.4839	16.6		
228A	120	.0348	.043	.959	.016	.4873	22.4	2.5	
B		.0348	.0445	.959	.016	.4855	24.4		
C		.0348	.0440	.960	.016	.4881	24.9		
229A	120	.0525	.0574	.940	.015	.4915	4.0	3.75	
B		.0524	.0574	.948	.016	.4917	3.8		
230A	120	.049	.024	.941	.009	.5169	11.8	5.0	
B		.049	.044	.957	.009	.5121	11.7		
C		.049	.043	.959	.009	.5148	11.7		
231A	120	.037	.030	.932	.008	.4843	13.7	6.25	
B		.037	.026	.934	.009	.4795	13.7		
C		.035	.030	.943	.009	.4773	13.0		
232A	120	.041	.0393	.971	.010	.5132	5.56	9.50	
B		.041	.039	.971	.010	.5067	5.62		
C		.0415	.04	.970	.010	.5118	5.04		

RUN	T_{av}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	n	k	A	t

STAINLESS STEEL 303

CONDITION B (PICKLED)

AREA OF GLASS = 162 cm²
AREA OF METAL ROD = 12.6

239A	120	.0748	.046	.965	.013	.5803	14.5	1.25	
B		.073	.044	.965	.014	.5684	14.6		
C		.071	.0435	.966	.014	.5645	13.3		
242A	120	.0680	.032	.982	.016	.5180	7.72	.50	
B		.069	.032	.980	.013	.5134	7.71		
C		.0695	.031	.980	.019	.5167	7.60		
241A	120	.076	.074	.984	.021	.5116	5.26	1.25	
B		.077	.073	.986	.022	.5201	5.24		
C		.076	.073	.987	.022	.5218	5.07		

STAINLESS STEEL 304

CONDITION C (PASSIVATED)

AREA OF GLASS = 162 cm²
AREA OF METAL ROD = 12.6 cm²

244A	120	.074	.050	.968	.013	.5047	12.41	1.25	
B		.074	.048	.968	.013	.4993	12.0		
C		.0720	.047	.970	.014	.5041	11.2		
247A	120	.0655	.037	.979	.016	.5003	7.77	2.50	
B		.064	.036	.980	.017	.5030	7.69		
C		.0635	.036	.981	.016	.5146	7.96		
246	120	.046	.0201	.984	.019	.5167	4.84	5.75	
B		.045	.020	.987	.019	.5193	4.71		
C		.045	.0205	.988	.018	.5219	4.12		

STAINLESS STEEL 304

SAMPLE 2
CONDITION A (ELECTROPOLISHED)

AREA OF GLASS = 170 cm²
AREA OF ROD = 41 cm²

2139	120	.060	.031	.944	.016	.3669	3.66	1
2A9	120	.060	.0395	.941	.018	.3679	3.88	2
221A	120	.047	.032	.959	.011	.3472	4.07	3
220C	120	.035	.025	.963	.019	.4029	4.07	4
218A	120	.110	.076	.909	.012	.4764	11.9	5
B		.116	.077	.909	.013	.4791	11.45	
C		.116	.073	.911	.014	.3619	11.88	
216A	120	.086	.042	.936	.014	.4121	7.66	7
B		.086	.039	.936	.015	.4127	8.40	
C		.085	.036	.934	.015	.1960	9.31	
215A	120	.084	.0485	.932	.017	.4745	16.9	8
B		.084	.046	.932	.015	.5014	17.0	
C		.083	.048	.931	.018	.5097	16.88	
214A	120	.060	.028	.946	.020	.1629	8.29	9
B		.062	.032	.954	.020	.1901	9.84	
C		.060	.030	.947	.023	.1748	9.21	

NONISOTHERMAL RUNS

RUN	T_{av}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	n	k	A	t

TUBE 107

76CA	460	.029	.013	.962	.042	.3905	17.6	592	300
B		.026	01	.954	.044	.2913	43.8		
451A	427	.028	.010	.958	.043	.2918	45.7	592	300
B	428	.028	.010	.953	.040	.2964	45.0		
C	425	.029	.011	.957	.044	.2909	23.2		
264A	47[illegible]	.032	.025	.958	.041	.2855	18.7	592	300
B		.0296	.025	.960	.039	.2873	18.2		
C		.031	.025	.957	.041	.2863	18.1		
273A	765	.035	.030	.957	.038	.2801	12.7	592	300
B	760	.038	.032	.955	.039	.2854	16.2		
C	765	.039	.030	.95[illegible]	.039	.2807	15.6		
264A	329	.0376	.033	.955	.037	.2824	10.3	592	300
B	331	.037	.033	.956	.035	.2868	10.6		
C	328	.038	.033	.956	.035	.2861	13.3		
265A	295	.039	.037	.954	.036	.2889	6.2	592	300
B		.039	.037	.956	.035	.2944	6.1		
C		.037	.035	.954	.035	.2837	6.1		
266A	250	.037	.0367	.954	.034	.2179	3.3	592	300
B		.0365	.036	.952	.038	.2102	3.8		
C		.037	.036	.954	.039	.2114	3.8		

TUBE 104

276A	490	.074	.0115	.933	.068	.2633	137.7	592	300
B		.0712	.0103	.938	.066	.2870	149.1		
C		.0722	.0113	.941	.064	.2926	138.5		
271A	460	.0652	.0106	.979	.025	.2949	36.5	592	300
B		.0648	.0104	.979	.028	.2810	32.2		
C		.0686	.0099	.977	.029	.2893	30.9		

RUN	T_{av}	$P_{H_2O_2}$ [1]	$P_{H_2O_2}$ [2]	P_{H_2O}	P_{O_2}	n	k	A	t

TUBE 108

262A	490	.0353	.001605	.947	.058	.2444	56.52	592	300
B		.036	.00163	.950	.053	.2492	59.47		
C		.0344	.00153	.952	.057	.2056	52.7		
263A	480	.0263	.00274	.911	.055	.2139	49.4	592	300
B		.0268	.00287	.957	.049	.2136	50.4		
C		.0267	.00265	.953	.053	.2005	45.1		
264A	470	.0321	.0081	.958	.051	.2800	56.5	592	300
B		.0302	.00828	.959	.049	.2605	55.8		
C		.0312	.0077	.961	.051	.2671	58.5		
268A	460	.0339	.0131	.947	.051	.2891	52.5	592	300
B		.0334	.0120	.947	.052	.2806	54.4		
C		.0331	.0123	.949	.048	.2938	55.2		
269A	440	.0391	.0226	.945	.046	.2872	41.3	592	300
B		.039	.022	.945	.047	.2944	41.7		
C		.0376	.0208	.943	.046	.2867	41.3		
267A	430	.0439	.0292	.945	.040	.2081	27.6	592	300
B		.0437	.0281	.940	.047	.1856	28.3		
C		.044	.026	.945	.044	.1862	33.9		
270A	360	.0519	.0321	.933	.036	.2974	10.7	592	300
B		.064	.053	.935	.033	.2779	8.8		
C		.0644	.0508	.935	.036	.2779	11.4		
269A	310	.072	.0728	.903	.022	.2148	1.9	592	300
B		.0736	.0732	.900	.029	.2002	1.1		
C		.0744	.0707	.919	.029	.2115	1.0		

was treated with acid, fused, treated with sodium hydroxide and finally coated with boric oxide. Tubes 8 and 9 prior to being coated were unaltered Pyrex surfaces. Condition A of tube 9 refers to its behaviour immediately after receiving the boric oxide coating. It was then exposed to the atmosphere for four days, which condition was designated condition B. Next a bundle of Pyrex rods, coated with a fused boric oxide coating, were added to tube 9 in order to change the surface to volume ratio. The area of the tube was 590 cm², that of rods plus tube was 1450 cm². The rate data in Figure 3 are based on the total area, indicating that the activity of the packing was slightly greater than that of the tube. After the tube was studied in this condition for a period of about one week, these rods were removed, which condition was designated as condition D.

As the boric oxide surface continued to be exposed to hydrogen peroxide vapor there occurred an initial increase in surface activity, but after this initial aging, the activity remained constant. Thus, some 20 hours of exposure to H_2O_2 vapor elapsed between conditions B and D of tube 9, yet the activity is seen to be the same. Surfaces exposed to hydrogen peroxide vapor for but a short period, [tubes 7 (in condition F), 8 and 9 (in condition A), --all shown on Figure 3] have approximately equal activities.

The rate of decomposition of hydrogen peroxide vapor at 215°C on a fused silica (Vitreosil) surface, tube 27, which had been treated with an acid, and also on a Vycor surface, tube 11 (in condition A), can be seen on Figure 4. In Figure 5 are the results of a study of the decomposition on a soft glass surface. The soft glass surface studied was a rod which was placed coaxially in a Pyrex tube, tube 101, and rested on supports blown in this tube. (The data in Figure 5 are calculated for the area of soft glass exposed, after allowing for the extent of reaction on Pyrex). Eight different Pyrex surfaces were examined and the results are to be seen on Figure 6. Finally a lead glass surface, tube 20, was studied and the results are in Figure 7.

To summarize and compare the above results, the rates of decomposition observed on the various glass surfaces are tabulated below for a partial pressure of hydrogen peroxide of 0.04 atm. The temperature for all the studies was 215°C.

Table II

RATES OF DECOMPOSITION ON SEVERAL GLASSES

Temp. = 215°C.

Surface	Composition in Wt. % SiO_2	B_2O_3	Na_2O	K_2O	CaO	Al_2O_3	PbO	Rates of decomp. (mole/min cm^2) x 10^8 $P_{H_2O_2}$ = 0.04 atm.
Fused Silica	100							2
Boric Oxide		100						2.5-4
Vycor	96	4	0.02			0.04		2.7
Pyrex	80.5	12.9	3.8	0.4		2.2		3-6
Soft Glass	70		14	6.2	6.3	3.3		9
Lead Glass	68		10	6.0	1		15	43

Although there is considerable quantitative irreproducibility, it is evident that the activities of the different glasses rank as follows: Fused Silica $<$ Boric oxide $\approx$ Vycor $<$ Pyrex $<$ Soft Glass $\ll$ Lead glass.

The relationship in Table II between the compositions of these surfaces and their catalytic activity suggests that sodium, potassium, calcium, aluminum and especially lead atoms in the glass are active centers for the decomposition. Dowden (7) has suggested that for electron transfer reactions, the electrical properties of the material are informative as to a catalyst's activity. It is interesting that a ranking of these 5 glasses in order of increasing dielectric constant is the same as their ranking in order of increasing catalytic activity, although this may be fortuitous.

Ion Addition to Pyrex

To test further the hypothesis that the catalytic activity of a glass surface is a function of the sodium in the glass, two Pyrex tubes were soaked in 5% sodium hydroxide, which presumably reacts with the glass to form Si-O-Na bonds on the surface (35). The decomposition rate on these surfaces can be seen on Figure 8. Tube 7 was soaked for 16 hours (this is designated condition E) and tube 24, for 2 hours, (called condition A). It can be seen that this treatment of tube 7 increased its activity about threefold.

In addition to sodium, two other substances--silver and iron--were added to Pyrex by treating the glass for 20 hours with a 1N nitrate solution of these ions at 60°C. These ions may add to the surface by an exchange mechanism with existing ions in the glass (8,12) or they may be reduced to a lower oxidation state on the surface. In the latter case an ion may acquire an electron at a surface defect or else it could rearrange its electronic field as

it approaches the glass surface (36). For example, the electrons of the polar silver ion are repelled by the glass so that in the direction of the glass the silver behaves at Ag^{+}_{2}, whereas in the opposite direction the chemical properties of the surface resemble those of metallic silver.

The determination of the catalytic activity of a surface after the addition of ions gives no measure of the activities of individual sites since their number is unknown. Consequently to determine which of two elements on a surface is the more reactive, a Pyrex tube was first immersed in a solution of one of the species and the rate of decomposition measured; then the tube was immersed in the other species and the rate of decomposition again determined. This procedure was then repeated in the reverse order in a second Pyrex tube. In each case the tube was immersed in a 1N solution of the appropriate nitrate salt for 20 hours at 60°C.

On Figure 9 is shown a comparison of sodium and silver. Tube 12 was first treated with sodium nitrate, (designated as condition A) and then with silver nitrate, condition B. Tube 13 was treated first with silver nitrate, condition A, followed by the sodium nitrate treatment, condition B. The silver is seen to be more reactive than sodium. Because subsequent treatment with sodium nitrate of a surface previously treated with silver nitrate (tube 13) did not greatly lower the activity, it appears that the silver exists not as an ion on the surface, but rather in the reduced metallic state.

The effect of treating a Pyrex surface with sodium and ferric nitrates was compared in the same way, the results being shown on Figure 10. Pyrex tube 14 was first treated with ferric nitrate, (condition A), and then treated with sodium nitrate, (condition B). Tube 15 was given the reverse treatment. The results indicate that a iron active center is more reactive than a sodium center. Because the sodium did not significantly replace the iron, it appears likely that the iron was adsorbed in a reduced form, similar to that occurring with silver.

A comparison of silver and iron is shown in Figure 11. Tube 16 in condition A was a Pyrex tube treated with silver nitrate and condition B was this same tube after ferric nitrate treatment. Tube 17 was a Pyrex tube treated first with ferric nitrate and then with silver nitrate. These results indicate that silver active sites are more reactive than iron.

Summary

The presence of cations on a glass surface increases the catalytic activity for the heterogeneous decomposition of hydrogen peroxide vapor. The activities of these individual sites rank as follows:

$$Ag > Fe \gg Na > \text{Pure Pyrex}$$

The presence of lead in a glass greatly increased the catalytic nature of a glass. The activities of these substances for the decomposition rate of hydrogen peroxide vapor parallel their activities for the decomposition of the liquid. Thus, silver, lead and ferrous ions are excellent catalysts for the decomposition of liquid H_2O_2, whereas sodium ions are relatively poor.

Acid Treatment of Pyrex

The preceding results indicate that cations on a glass surface are active centers and that if these were removed, the resulting surface would be more inert. One method is by treatment with an acid (24), which replaces them with hydrogen ions by an ion exchange mechanism. However, the silica network is also attacked, thereby forming a surface resembling silica gel. Because of this double action, it is desirable to determine the effect of different types and concentrations of acids.

Figure 12 shows the activities of several Pyrex tubes which were treated with nitric acid. Tubes 18, 10 and 7 were soaked for 20 hours in concentrated (15.5N) nitric acid, while tubes 6 and 19 were treated with 2N nitric acid for the same period of time. All these tubes had been exposed to H_2O_2 vapor in the studies reported in Figure 6 before being subjected to acid treatment. The kind of treatment with HNO_3 is evidently less important than adventitious variation from sample to sample of Pyrex. Figure 13 shows the rates of decomposition observed on several Pyrex tubes which had been soaked for 20 hours in 4N phosphoric acid. In Figure 14 are the rates of decomposition on Pyrex surfaces previously treated with 4N hydrochloric or 4N sulfuric acids (tubes 33 and 34) or with 1% hydrofluoric acid for 20 hours.

Summary

In Table III are tabulated the rates of reaction at 215°C on the various acid treated tubes and also the rates of reaction on some of the untreated surfaces. It is concluded that acid treatment decreases the activity of the surfaces, and that 4N phosphoric acid and 2N nitric acid are the most satisfactory acid solutions with which to treat Pyrex.

Table III

SUMMARY OF ACID-TREATED PYREX SURFACES

T = 215°C

Tube	Rate of Decomposition x 10^6 (moles/min cm^2), at $P_{H_2O_2}$ = 0.04 atm. Treated	Untreated
2N HNO_3		
Tube 6 (in condition B)	1	5.2
Tube 19 (in condition B)	1.9	6.5
Conc. HNO_3		
Tube 18 (in condition B)	3.75	6.5
Tube 10 (in condition C)	3.75	
Tube 7 (in condition B)	1	2.5
4N H_3PO_4		
Tube 22 (in condition B)	1.75	3.5
Tube 25 (in condition A)	1.75	
Tube 26 (in condition A)	1.1	
Tube 101 (in condition A)	2.75	
4N H_2SO_4		
Tube 34	3.25	
4N HCl		
Tube 33	3.25	
1% HF		
Tube 35	2.3	

There is considerable irreproducibility of results, even where two tubes were taken from the same original stock of glass, and treated in exactly the same manner, as for example tubes 25 and 26, treated with H_3PO_4.

Acid Treatment of Various Types of Glasses

The effects of acid treatment of other glass surfaces are shown on Figures 15 and 16, and are summarized in Table IV. The Vycor was treated with 2N nitric acid for 20 hours; the fused silica, soft glass and lead glasses were treated with 4N phosphoric acid.

Table IV

EFFECT OF ACID TREATMENT ON VARIOUS TYPES OF GLASSES

T = 215°C

Surface	Rate of Decomposition x 10^6 (moles/min cm^2), at $P_{H_2O_2}$ = 0.04 atm Before Acid Treatment	After Acid Treatment
Fused Silica		2
Pyrex (tube 22)	3.7	1.75
Vycor	2.7	3
Soft Glass	9	2
Lead Glass	43	25

The above summary emphasizes the fact that as the cations are removed from the glass surfaces, the activities converge towards a common value which presumably is the activity of silica. The seeming slight increase in the catalytic activity of Vycor is within experimental accuracy. The activity of lead glass was not decreased as much as the others, presumably because all of the lead atoms, which are bound more securely to the silica network than are the other substances, were not entirely removed by the action of the acid.

Miscellaneous Treatments

Sodium Stannate - Sodium stannate ($Na_2SnO_3 \cdot 3H_2O$) stabilizes liquid hydrogen peroxide solutions by hydrolyzing to form colloidal hydrous stannic oxide ($SnO_2 \cdot xH_2O$)(30) which absorbs catalytic ions, either in solution or on vessel surfaces. A Pyrex surface, previously acid-treated, was soaked in a 200 p.p.m. sodium stannate solution for 20 hours. The results on Figure 17 indicate that this treatment slightly increased the tube activity.

Sulfur Dioxide - The sodium ions in glass have been reported to react with gaseous sulfur dioxide to form sulfate type structures (5,6). To see if this treatment would poison the active centers, gaseous sulfur dioxide at 200°C was passed for 20 hours through a Pyrex tube which had been previously treated with 5% sodium hydroxide solution, tube 24 (in condition A). On Figure 18 it can be seen that the activity of the surface was not appreciably changed by this treatment.

Hydrogen Peroxide Solution - The common procedure for passivating surfaces which are to be used in contact with hydrogen peroxide liquid is to soak them in a hydrogen peroxide solution. However an acid-treated Pyrex tube, tube 18 (in condition B) after soaking for 20 hours in a 50% hydrogen peroxide solution showed no lowering of surface activity (see Figure 19).

Metakaolin - When a glass surface is heated at 300°C in contact with a slip of metakaolin, the hydrogen ions in the clay presumably replace the sodium ions in the glass by an ion exchange mechanism (37). A Pyrex tube, tube 10 in condition A, was treated in this manner, but as seen on Figure 20, the activity was unaffected.

Fused Surfaces - When a glass is heated to a temperature approaching the annealing temperature, the surface of the glass becomes more plane as the mechanical and intrinsic defects on the surface are eliminated. Figure 21 shows that a fused Pyrex surface is quite inert, about 10 times less reactive than an acid-treated Pyrex surface. Tube 103 was heated uniformly in a constant temperature bath to 490°C and was then cooled to 400°C in a time period of about 4 hours. Tube 100, on the other hand, was heated in the bath to 460°C, the temperature of which was lowered over a period of two hours to 250°C. The lowest temperature studied in this tube was 250°C; consequently, the datum point on this plot was extrapolated to 215°C.

Numerous attempts were made to fuse a surface with a small flame because such a method would be of greater ease in practical use. Tube 6, (in condition B), an acid treated Pyrex tube, was heated with a torch until the yellow sodium flame appeared. The temperature of Pyrex at this point is just below the annealing point, which is about 500°C. The torch was played up and down the surface so that the tube was at this temperature for approximately one minute. The activity of the resulting surface, designated as tube 6 in condition C, is shown on Figure 22 to be unaffected. On Figure 23 is the result of treating a second tube, tube 7 in condition B, in a similar manner as tube 6 with the exception that the flame was passed through the tube, thereby heating directly the catalytic surface. This likewise did not decrease the activity. A third Pyrex tube, tube 101 in condition A, was heated in the same manner as tube 6, but for a duration of 2 to 3 minutes. As is seen on Figure 24, the activity was not lowered.

All of these attempts were unsucessful presumably because the glass surfaces were not heated and cooled uniformly. The defects which may have been removed, probably reappeared as the surface was cooled unevenly.

A Pyrex tube, tube 26, was heated to 430°C in a molten salt bath for half an hour. It is seen on Figure 24 that this did not decrease the rate of decomposition on the surface. The temperature and duration of heating were presumably insufficient to fuse the surface.

These results indicate that defects in a glass surface, which are electron donor sites (7, 25), are active sites for the decomposition of hydrogen peroxide vapor. When the defects are removed by fusing a surface, and the ions are removed by acid treatment, the activity of Pyrex is decreased by a factor of about 40.

Activation Energy

On many of the surfaces decomposition rates were measured over a moderate temperature range. On Figure 26 is plotted the logarithm of the observed decomposition rate as calculated for a partial pressure of hydrogen peroxide of 0.04 atm., against the reciprocal of the absolute temperature. Also listed are the activation energies corresponding to the slopes of the lines.

It is seen the activation energies are small; change in temperature from 180°C to 250°C, for example, increases the reaction rate by a factor of only 2 or 3. Although the rate of reaction at a given temperature varies by a factor of 100 or more from one surface to another, the activation energies are all nearly the same.

Multilayer Adsorption

At temperatures below 150°C, the decomposition rate was found to increase with a decrease in temperature, contrary to the usual expectation. The effect of temperature at a fixed value of the H_2O_2 partial pressure is shown on Figure 27, and Figure 28 shows the effect of H_2O_2 partial pressure at each of two temperatures studied, 110° and 120°C.

This effect is presumably caused by a very large increase in the amount of hydrogen peroxide adsorbed as the temperature is lowered in this range. As a guide, Figure 28 shows the partial pressure of H_2O_2 that would exist in equilibrium above a liquid containing H_2O_2 and H_2O at 110°C., and also at 120°C. The data at the higher partial pressure of H_2O_2 are scattered; indeed the runs made at 110°C. and partial pressures of 0.08 to 0.09 H_2O_2 are in the range for condensation to occur. However, the data at the lower H_2O_2 partial pressures, as compared on Figure 27, are unequivocal.

The adsorption of vapor from H_2O_2-H_2O vapor mixtures onto glass surfaces has been reported by Giguere (10), Baker and Ouellet (2), Mackenzie and Ritchie (17), and Tamres and Frost (33) and various tests have indicated that at least a portion of the vapor adsorbed was hydrogen peroxide. Some adsorption has been noted at temperatures as high as 175°C. (10), although, of course, the amount adsorbed would increase as a function of the ratio of total pressure to saturation pressure. For example, recent studies on adsorption of water vapor on glass at 30°C. showed that the thickness of the adsorbed layer ranged from 620Å at P/Po of 0.9976 to 37Å at P/Po of 0.505 (9).

Comparison of Vapor Decomposition Rate to Liquid Decomposition Rate

The decomposition of highly purified aqueous hydrogen peroxide solutions is believed to be exclusively a surface process in laboratory-sized vessels. Since the amount of adsorption from the vapor phase increases as the temperature is lowered, to a multilayer infinitely thick as the condensation temperature is reached, one might expect to find a smooth transition from vapor-phase decomposition rates to liquid-phase decomposition rates as the temperature is lowered. For a rough comparison, consider the case of a hydrogen peroxide vapor mixture containing 0.125 atm H_2O_2 and 0.875 atm. H_2O at 120°C., its saturation pressure.

As a basis for comparison one may take the data reported by Roth and Shanley (26) on the rate of decomposition of very highly purified 99% H_2O_2 liquid at 100°C. in small laboratory Pyrex flasks. They reported that their reaction was almost wholly heterogeneous. Using their temperature coefficient of 2.5 for each 10°C. temperature rise and estimating the surface--volume ratio of their vessles to be about 1 cm^{-1}, one would predict a decomposition rate in the liquid phase of about 2×10^{-6} moles/(min)(cm^2) at 120°C. This is to be compared to 7.5×10^{-6} moles/(min)(cm^2) which is the approximate value extrapolated from the present studies for vapor at 120°C. The comparison is remarkably close considering the possible variations in activities of Pyrex surfaces and other factors, and it suggests that there is no abrupt transition in the decomposition mechanism as one goes from the liquid to the vapor phase. Very highly purified liquid H_2O_2 samples in laboratory vessels show a decomposition rate which is independent of concentration (i.e. zero order) so that this factor does not enter into the above analysis. Approximately the same liquid phase rate would be calculated from the data reported by Schumb (30) on very pure samples but of slightly lower concentrations.

Roth and Shanley reported that in their studies at 30°C, a portion of the decomposition seemed to be occurring heterogeneously in the vapor phase, based on the effects noted on changing the ratio of immersed vessel surface to liquid volume by varying the

liquid content of a particular flask. The rate of decomposition on immersed surface was estimated by them to be about 3 times as great per unit area as that on surface exposed to the vapor.

Their observation and the above results reported here both show that in the conventional stability tests carried out routinely on liquid hydrogen peroxide samples, considerable error may be introduced by neglecting the possibility of heterogeneous vapor-phase decomposition. The error would of course be greater the greater the fraction of the surface exposed to vapor, but would presumably also increase with increase in H_2O_2 concentration and with temperature, both of which would increase the partial pressure of H_2O_2 in the vapor phase.

Polymers and Plastics

Because of the thermal properties of these organic substances, some were studied at 215°C while others were studied at 120°C.

High Temperature Polymers

Fluorolube A Pyrex tube was coated with Fluorolube GR grease, an addition polymer of trifluorovinyl chloride. The rate of decomposition at 215°C. is shown in Figure 29. (condition A). The activity of this surface was about half that of silica when the hydrogen peroxide partial pressure was 0.04 atm. This polymer is stable to approximately 300°C. but it melts in the vicinity of 100°C. In view of this low melting point, the permanency of this coating was tested by passing live steam for several hours over the outside of the vertical sealed tube. The activity of this tube, designated as condition B, was again determined. As is seen on Figure 29, the rate of decomposition increased indicating that the Fluorolube no longer coated the Pyrex tube. Another indication was the fact that although water will not wet a Fluorolube surface, it did wet Tube 21 in Condition B.

Teflon The decomposition on Teflon, a polymer of tetrafluoroethylene, was investigated at both 215°C and 120°C. The surface studied at 215°C was a rod placed coaxially in a Pyrex tube, tube 25 (in condition B); at 120°C it was a Teflon strip placed in a Pyrex tube, tube 25 (in condition D). The width of the strip was the same as the diameter of the tube. These results (Figures 30 and 32) show that the rate of decomposition of Teflon is about 10 times higher than on Pyrex at 215°C, but only about twice as high at 120°C. The small difference at 120°C probably is a result of the fact that multilayer adsorption occurs on glass, as discussed previously, whereas Teflon, which is not wetted by water, presumably would have low adsorptivity for H_2O_2.

Methyl Trichloro Silane Methyl trichloro silane bonds chemically to glass to form a stable coating which is not wetted by water. The rate of hydrogen peroxide vapor decomposition was measured on this surface, tube 28, and the results are given on Figure 31. The silane coating was apparently not attacked by the hydrogen peroxide vapor; the activity of the surface was slightly less than that of the untreated surface.

Low Temperature Polymers

Methyl methacrylate is one of the few polymers which will form a continuous stable film on glass (11). However, a film of this substance on a Pyrex tube was attacked by the hydrogen peroxide and was blistered and bleached. A strip of polyethylene placed in a Pyrex tube became very soft and was attacked badly by the hydrogen peroxide vapor. A strip of Koroseal, a polymer of vinyl chloride, placed in a Pyrex tube, show slight bleaching by H_2O_2 vapor.

The activities of several polymers at 120°C are shown in Figure 32.

Summary In the first column of Table V are summarized the rates of decomposition on the various polymeric surfaces when the hydrogen peroxide partial pressure was 0.04 atm. In the second column of Table V are tabulated the rates of decomposition of 90% hydrogen peroxide liquid on some of these surfaces at 66°C (3). There is seen to be a positive correlation between the catalytic activity of a surface for the rate of decomposition of hydrogen peroxide liquid and for the vapor. The polyethylene value was high for the decomposition of the vapor because at 120°C the plastic was in an almost molten state.

Teflon is the most satisfactory polymer for use with hydrogen peroxide vapor at moderately elevated temperatures since it is unattacked. However, because of the high cost of this material it may be more satisfactory to use Koroseal for short term usage. Fluorolube grease would be an inert stopcock grease and might in addition be used to coat metallic surfaces. Methyl trichloro silane and Fluorolube coatings, which are not wetted by water, might very substantially decrease the rate of decomposition of H_2O_2 vapor on Pyrex or other glass surfaces at temperatures near saturation where multi-layer adsorption is the important factor in causing increased decomposition rates.

Table V

RATES OF DECOMPOSITION ON POLYMERS

Surface	Rate of Decomposition of H_2O_2 vapor x 10^6 (moles/min cm^2) $P_{H_2O_2}$ = 0.04 atm.	Percentage of 90% H_2O_2 liquid decomposed/week at 66°C.
T = 120°C		
Pyrex	2	---
Teflon	5	2.6
Koroseal	14	18-29
Methyl methacrylate	5 (attacked)	---
Polyethylene	30 (attacked)	1.7
T = 215°C		
Pyrex, acid rinsed	about 2	---
Fluorolube GR grease	1	1.7
Teflon	24	2.6
Methyl Trichloro Silane on Pyrex	1	---

Metals

Only metals to which hydrogen peroxide is relatively inert were studied: stainless steels types 303, 304, and 416, 2S aluminum, tin and tantalum. In each case, a rod of the metal about 0.23 cm in diameter and 16-17 cm. long was placed coaxially in a Pyrex tube. The rate data reported were calculated from the difference between the rates of decomposition with and without the rod present, calculated per unit area of metal rod.

Stainless Steels

Electrolytically Polished The rates of decomposition of hydrogen peroxide vapor at 150°C on polished stainless steels 304, 303, and 416 are given on Figures 33, 34, and 35 respectively. The electrolytic polishing procedure, which is described by Uhlig (34), causes preferable anodic solution of high points on the surface of the metal so that eventually the surface is levelled to a microscopic plane.

On these electrolytically polished steels there was no observable effect of aging during the decomposition studies at 150°C. The elapsed time between runs 287 and 289 on Figure 33 was two hours;

the time between runs 273 and 298 on Figure 34 was six hours; and on Figure 35, the time between runs was only one hour. Prior to these determinations at 150°C, these surfaces had been studied at 120°C, which may have caused an initial aging. The catalytic activity of the surface of stainless steel 416 increased steadily with time during runs at 120°C, but the others were affected only slightly. It has been reported that all of the stainless steels are bronzed by 90% hydrogen peroxide liquids (3), although stainless steels types 303 and 304 are reported to have greater chemical resistance than type 416 because they contain nickel. Types 303 and 304 are nearly the same with the exception that type 303 is softer because traces of selenium are present.

Pickled and Passivated Surfaces The rates of decomposition of hydrogen peroxide vapor on pickled and passivated stainless steels 303 and 304 are presented on Figures 36 and 37. By comparison with Figure 34, it can be seen that these treatments greatly lowered the catalytic activities of these surfaces.

In the pickling operation the steel was immersed in a 15-20% by weight sulfuric acid solution with no inhibitor, for 45 minutes at 150-160°F. The sample was then immersed in a 8-10% by volume nitric acid solution containing 1 1/4 to 2% by volume hydrofluoric acid at 140-160°F. (27). With no inhibitor present, the pickling solution preferentially dissolves FeO and Fe, leaving a surface containing mainly Cr_2O_3 and NiO, with small amounts of Fe_2O_3 (7a,16a,32a).

In the passivation operation, the sample is first pickled and then treated with a 20-40% nitric acid solution for 30 minutes at 120-170°F. (27). The purpose of this treatment is to form a resistant oxidized film on the metal. Examination of Figure 37 indicated that the oxide film formed by nitric acid is no less reactive than that formed by hydrogen peroxide on a pickled surface.

Aluminum

Electropolished The activity of a electropolished aluminum sample is shown on Figure 38. The elapsed time between runs 304 and 305 was one hour; there was no evidence of aging during these studies. Aluminum is not chemically attacked by 90% hydrogen peroxide solutions (3).

After completion of an electropolishing process the metal reacts with the electrolyte which was a solution of sulfuric and phosphoric acids. The final surface therefore probably consisted of a mixture of oxides and phosphates.

Anodized A hard stable oxide coating is formed on aluminum by anodizing the sample (22). The rate of hydrogen peroxide decomposition can be seen on Figure 39.

Pickled An oxide film can also be formed on aluminum by pickling the sample in a solution containing 6 oz. of sodium hydroxide per gallon of water at 180°-200°C. Then the rod is immediately immersed for a few seconds in a solution containing one part HNO_3 and one part H_2O (21). The density of this film is probably different from that of an anodized surface. The rate of decomposition on this surface is shown on Figure 40.

Phosphated A phosphate film can be formed on aluminum by treating it with a phosphoric acid solution (18). The activity of this surface is shown on Figure 39.

Tin

The tin used in this work was essentially pure. The rates of decomposition of hydrogen peroxide vapor were determined on two samples, one of which was rinsed in carbon tetrachloride and water to remove the grease, and the other which was dipped in a 20% nitric acid solution for a split second. The rates of decomposition are on Figure 41. The acid attacked the tin violently and formed a visible oxide coating.

Tin is not attacked by 90% hydrogen peroxide liquid but it has the disadvantage as a material of construction in that it changes allotropic forms with changes in temperature (23).

Tantalum

The rates of hydrogen peroxide vapor decomposition at 150°C were determined on two samples of pure tantalum. One piece was degreased with carbon tetrachloride and water, while the other was treated with a 40% nitric acid solution for 30 minutes at 120°F. The results on Figure 42 indicate that the rates were equal on each.

The effect of aging of tantalum was not studied, but it might be expected to be slight since tantalum is one of the more inert metals to oxidation.

Summary

In the first column of Table VI are summarized the rates of decomposition at 150°C of hydrogen peroxide vapor on metallic surfaces when the partial pressure of hydrogen peroxide was 0.03 atm.

TABLE VI

DECOMPOSITION RATES ON METALLIC SURFACE AT 150°C

	Vapor: Rate of decomp. x 10^6 (moles/min cm^2) ($P_{H_2O_2}$ = 0.03 atm.)	Liquid: Percent of 90% H_2O_2 Decomposed/week 66°C
Stainless Steels		
303 Electropolished	40	50-60 (nitric Acid)
Pickled and Passivated	17	
304 Electropolished	125	
Pickled	20	
Pickled and Passivated	20	
416 Electropolished	115	
2S Aluminum		
Electropolished	110	
Phosphated	105	
Anodized	45	
Pickled	35	3
Tantalum		
Degreased	42	
Acid treated (nitric)	42	
Tin		6.4-28.7
Degreased	45	
Acid treated (nitric)	31	

In the second column of Table VI are the percentages of 90% hydrogen peroxide liquid which are decomposed per week at 66°C (3).

It is observed that pickled stainless steels types 303 and 304 and pickled aluminum surfaces have the most desirable properties for use with hydrogen peroxide vapor. It is possible, however, that with time, the stainless steel surfaces may age.

Other salient observations from this table are: (1) stainless steels becomes less reactive as the iron is preferentially removed from the surface; (2) oxide coatings on aluminum are less reactive than phosphated coatings; and (3) tantalum and tin surfaces are nearly as inert as the pickled stainless steel and aluminum surfaces. However, they are much more expensive than the latter materials.

Although the data available for comparative purposes are sparse, there is a general qualitative correlation between the activities for the decomposition of the liquid and vapor on these metallic surfaces.

Various metallic surfaces were studied at 120°C; however, these data scattered widely because of the masking effect of the

decomposition on Pyrex, which at 120°C varies greatly with slight temperature changes, presumably because of multilayer absorption effects.

Reaction Mechanism

Derivation of Rate Equation

In three reactors (two consisting of boric oxide surfaces on Pyrex, the third a pickled 2S aluminum surface), a sufficiently wide range of conditions was studied that the heterogeneous decomposition rates could be expressed mathematically as a function of temperature and composition. If the Langmuir adsorption model is assumed, i.e. that the reactants are adsorbed in a monolayer on various active sites on the catalytic surface from whence the reaction proceeds, equations can be derived for various reaction mechanisms with each of several rate-controlling steps. The following mechanisms were considered: (1) reaction between two adsorbed hydrogen peroxide molecules; (2) reaction between one adsorbed molecule of hydrogen peroxide and a molecule in the vapor phase; (3) reaction between adsorbed OH radicals, resulting from the dissociation of a hydrogen peroxide molecule, and a molecularly adsorbed hydrogen peroxide molecule; (4) reaction between adsorbed OH radicals and a hydrogen peroxide molecule in the vapor phase; and (5) uncatalysed reaction in the vapor phase. For each mechanism the following rate-controlling steps were considered: (1) rate of surface reaction controlling, (2) rate of adsorption of molecular hydrogen peroxide controlling, (3) rate of adsorption of OH radicals controlling; and (4) rate of desorption of water controlling. These various combinations provided fifteen different possible mathematical relationships (the same form may result from more than one postulated mechanism and rate-controlling step.)

The experimental results for the decomposition on the three surfaces all fitted an equation of the form:

$$-\frac{dn_{H_2O_2}}{A\,d\theta} = \frac{\alpha K_{H_2O_2} P^2_{H_2O_2}}{\left(1 + \sqrt{K_{H_2O_2} P_{H_2O_2}} + K_{H_2O} P_{H_2O}\right)^2} \qquad (1)$$

Of the fifteen derived relationships, only three acceptably fitted the data; equation (1) was arbitrarily chosen. The other two acceptable forms were with the bracketed term in the denominator raised to the first or third power instead of the second.

For a Pyrex tube coated with boric oxide with a surface-to-volume ratio of 1.75 cm^{-1}, tube 9 in conditions A, B, and D, the experimental data and the theoretical curves for the three temperatures studied can be seen on Figures 43, 44, and 45. The temperature dependent terms for equation (1) are:

$$K_{H_2O_2} = 7.34 \times 10^{7}\, e^{-11.3 \times 10^{3}/RT}$$

$$K_{H_2O} = 3.82 \times 10^{-3}\, e^{7.76 \times 10^{3}/RT}$$

$$\alpha K_{H_2O_2} = 1.1$$

The average deviations of the experimental data from the theoretical values are 7% at 180°C; 16% at 215°C; and 9% at 250°C.

In another boric oxide surface, tube 9 plus rods, with a surface to volume ratio of 5.6 cm^{-1}, the temperature dependent terms are:

$$K_{H_2O_2} = 9.18 \times 10^{5}\, e^{-6.36 \times 10^{3}/RT}$$

$$K_{H_2O} = 3.15 \times 10^{-6}\, e^{13.97 \times 10^{3}/RT}$$

$$\alpha K_{H_2O_2} = 1.05$$

The experimental data and theoretical curves are plotted on Figures 46, 47, and 48.

For the third surface, a pickled 2S aluminum surface, the experimental data and curves are on Figures 40 and 49. The terms for equation (1) were found to be:

$$K_{H_2O_2} = 2.72 \times 10^{-9}\, e^{7.4 \times 10^{3}/RT}$$

$$K_{H_2O} = 1.12 \times 10^{-11}\, e^{20.9 \times 10^{3}/RT}$$

$$\alpha K_{H_2O_2} = 0.111$$

Because of diffusional effects, there will be a slight difference between the interfacial partial pressures and the bulk partial pressures, which would be greater at the higher rates of reaction. This inaccuracy does not alter the general form of the equations, but would slightly affect the values of the temperature-dependent terms.

Reaction Mechanisms

The mechanisms corresponding to the three acceptable equations are:

1. Reaction of adsorbed OH radicals and molecularly adsorbed hydrogen peroxide

   a) Desorption of water controlling (denominator of equation (1) raised to first power)

   b) Surface reaction controlling (denominator of equation (1) raised to third power)

2. Reaction of adsorbed OH radicals and hydrogen peroxide in the gas phase with the rate of surface reaction controlling (equation (1)).

In all three cases a hydrogen peroxide molecule is visualized as being adsorbed on two adjacent sites and dissociating to form two adsorbed OH radicals. One of these radicals then reacts with a hydrogen peroxide molecule, either adsorbed or in the vapor phase, to form water and an OOH radical. The OOH radical then combines with the adjacent OH radical, perhaps with the aid of a third body, to form water and oxygen which are then desorbed to leave the original two adjacent unoccupied active sites. Since it has been hypothesized in this work that the active sites for decomposition are electron donor sites, it is possible that the OH and OOH exist as ions rather than radicals.

This reaction mechanism is also consistent with a first order reaction, which has been reported under different experimental conditions by other investigators (2,10). If the OOH radical were to react with another hydrogen peroxide molecule to form as products water, oxygen and an adsorbed OH radical, instead of reacting with an adjacent OH radical as proposed above, then the model would be a surface on which all active sites are occupied with either an OH radical or an OOH radical. The reaction rate would be proportional to the concentration of hydrogen peroxide molecules which react with these adsorbed radicals, which describes a first order reaction.

The model system considered here is quite possibly an over-simplification of the true nature of the processes occurring on catalytic surfaces, and therefore one must be somewhat skeptical of the conclusions as to the mechanism involved when they are based on a matching of the mathematical form of the rate equation found against those derived from various models. Yet the steps of this heterogeneous mechanism are consistent with the steps proposed for the homogeneous decomposition of the vapor (28) and for the reaction steps proposed for both the homogeneous and heterogeneous catalytic decomposition of the liquid (1). In studies of the heterogeneous decomposition of hydrogen peroxide liquid on

supported manganese oxide catalysts, Hooi and Selwood (13, 14) found that a minimum of two adjacent manganese ions is a necessary condition for the decomposition.

Homogeneous Decomposition

The homogeneous decomposition does not become appreciable until relatively high temperatures are reached and experimental problems then are quite difficult. The data collected under these conditions were not extensive, but they do provide some information concerning the magnitude and characteristics of the homogeneous reaction.

Variation of Surface to Volume Ratios

The surface to volume ratio of a boric oxide coated Pyrex tube, tube 9, was increased from 1.75 cm^{-1} to 5.6 cm^{-1} to determine if the homogeneous decomposition were appreciable in the temperature range from 180-250°C. This change was made by adding to the tube a bundle of boric oxide coated Pyrex rods which uniformly filled a cross section of the tube. A comparison of the rate of decomposition at 180°C can be made by comparing Figures 43 and 46; at 215°C, Figures 44 and 47; and at 250°C, Figures 45 and 48. The fact that the rate per unit area of surface is independent of the surface to volume ratio, within the accuracies of reproducing surface, shows that homogeneous reaction can not be detected at these temperatures.

High Temperature Studies

The rate of decomposition of hydrogen peroxide vapor in the temperature range from 215°C to 490°C was investigated in three Pyrex tubes, each of which previously had been treated with 4N phosphoric acid and each of which had a surface area of 590 cm^2 and a volume of 300 cm^3. The results are shown on Figure 50.

Two facts show quite clearly that a transition from heterogeneous to homogeneous decomposition occurred in the temperature range of 400 to 450°C; (1) the sharp increase in decomposition rate with temperature and (2) the fact that different tubes showed different decomposition rates in the lower (heterogeneous) temperature region but the same results in the higher temperature region. The data in the heterogeneous range were obtained at H_2O_2 partial pressures of 0.025 to 0.038 atmosphere, those in the homogeneous range from 0.006 to 0.029 atmospheres. To put the results on a comparable basis, the rates of decomposition were recalculated for a H_2O_2 partial pressure of 0.02 atmosphere, assuming that in the homogeneous range the rate is proportional to the 3/2 power of the H_2O_2 concentration, and in the heterogeneous range that the concentration effect is the same as that found at lower temperatures.

Analysis of the data in the homogeneous range is made difficult by two factors: (1) the rate is so rapid under these conditions that a large fraction of the H_2O_2 entering the reactor decomposed therein, so that for data analysis it must be treated as an "integral reactor", (2) the temperatures reported are an average of the bath temperature and that of the vapor entering the reactor. This is a satisfactory measure of reaction temperature when reaction takes place exclusively on the tube wall. However in the homogeneous range the exothermicity of the reaction may cause the vapor to be appreciably hotter than the tube walls. To estimate this factor, the temperature variation of the vapor as a function of tube length was calculated for various inlet H_2O_2 concentrations, assuming the heat transfer coefficient to be 3.5 BTU/(hr.)(°F.)(ft.^{2}), the latter being based on the Reynolds number, with allowance for entering turbulence. It was concluded that for only one set of runs (Runs 270A, B &C, at 460°C and P_{av} = 0.029) was this factor an appreciable source of error and that here the vapor temperature was about 10°C. higher than the wall temperature. For plotting on Fig. 51, (discussed below) the observed values were therefore corrected using the Arrhenius equation with an activation energy of 55 kcal.

To analyze data from an integral reactor requires knowledge of the order of the reaction to determine the correct manner in which to average inlet and exit H_2O_2 concentrations. Therefore, it is necessary to assume a reaction order in order to analyze the data, after which the assumption may be checked by examining a set of data obtained at one temperature. Assuming the reaction rate to be proportional to the 3/2 power of the H_2O_2 partial pressure,

$$-\frac{dn_{H_2O_2}}{Vd\theta} = k p_{H_2O_2}^{3/2} \qquad (2)$$

where the average value of $p_{H_2O_2}$ is given by:

$$p_{H_2O_2} = \left[\frac{p_{in}^{1/2} p_{out} + p_{out}^{1/2} p_{in}}{2}\right]^{2/3} \qquad (3)$$

the homogeneous rate data obtained at somewhat differing average partial pressures may be recalculated to a common basis of a H_2O_2 partial pressure of 0.02, yielding the curve in Figure 50 for the homogeneous reaction. The slope of this curve correspond to an activation energy of about 55 kcal/gm.mole.

To check the assumption of a 3/2 order reaction, data obtained at 460°C. and several concentrations were plotted as on Figure 51. The slope corresponds to a 3/2 order reaction. Further evidence for a 3/2 order reaction comes from the data of Miss Huang (15) which were obtained in the same type of apparatus, differing principally in that the reaction temperature was determined from 5 thermocouple wells placed equidistantly along the reaction tube. A group of 9 runs at temperatures between 466°C and 489°C. and at mean H_2O_2 partial pressures of from 0.001 to 0.035 atmosphere were available for evaluation. The rate data were converted to the common basis of 475°C. using the Arrhenius equation and an activation energy of 55,000 kcal. Although the data scatter somewhat, the results, shown on Figure 52, clearly correspond to a 3/2 order expression rather than a first or a second order. The data of Miss Huang when recalculated to 475°C and 0.02 partial pressure of H_2O_2 and allowing for the difference in reactor volumes correspond to a rate of homogeneous reaction about 30% less than that shown in Figure 50.

Only one other study of the homogeneous reaction that is more than fragmentary has been reported. McLane (19) obtained data at average concentrations of 0.002 atmosphere pressure of H_2O_2 and below at temperatures of 470-540°C in boric acid-coated Pyrex. His rate reportedly followed a first-order expression and in the lowest surface-volume ratio vessel studied, ($S/V = 3$ cm^{-1}) he reported an activation energy of 50,000 calories.

There are several important differences between his experimental conditions and those in the present study. The H_2O_2 concentrations here were one to two orders of magnitude greater; the surface-volume ratio of the present vessel was about 2 cm^{-1}, compared to 3 cm^{-1} of McLane, and the flow pattern here approximated slug flow whereas that of McLane appeared to be close to that of a completely mixed reactor. The present rate data are about twice those reported by McLane if the rate is taken to be proportional to the 3/2 power, or about ten times those of McLane if the reaction were assumed to follow a first order expression. This most probably reflects an increase in chain length of the reaction as the surface-volume ratio is lowered and the H_2O_2 concentration is raised.

The most probable initiating s ·p in the reaction is

$$H_2O_2 + M \longrightarrow 2OH . \qquad (4)$$

The energy required for this reaction is about 53 kcal/g.mole whereas about 90 kcal/g.mole would be needed for the only alternate initiating step, formation of H and OOH.

Chain propagation is most probably by

$$OH + H_2O_2 \longrightarrow OOH + H_2O \qquad (5)$$

and

$$OOH + H_2O_2 \longrightarrow H_2O + O_2 + OH \qquad (6)$$

both of which are exothermic whereas all chain branching steps are endothermic. Chain breaking can occur by absorption of radicals on the walls or by 3-body comustion reactions of OH or OOH, thus

$$2OH + M \longrightarrow H_2O_2 \qquad (7a)$$

$$OH + HO_2 + M \longrightarrow O_2 + H_2O_2 \qquad (7b)$$

$$2HO_2 + M \longrightarrow H_2O_2 + O_2 \qquad (7c)$$

If the rates of reactions 4,5, 6 and (7a) are formulated in terms of the appropriate rate constants and reactant concentrations, and the rate of production and destruction of each of the free radicals is equated, one can derive the following expression:

$$-\frac{dn_{H_2O_2}}{Vd\theta} = 2k_5\sqrt{\frac{2k_4}{k_7}}\left(\frac{1}{RT372}\right)^{3/2} P_{H_2O_2} \qquad (8)$$

A 3/2 order expression is also obtained if one of the other free radical combination reactions is chosen instead of (7a). However, if 3 body free radical combination reactions are regarded as negligible and chain stopping is assumed to occur by adsorption on walls, the mathematical formulation leads instead to a second order expression. The fact that the decomposition rate in fact followed a 3/2-order expression suggests that the 3 body free radical recombinations were the chain stopping mechanism here and not wall reactions.

The existence of long chains here is indicated by a comparison of the observed decomposition rate with the number of collisions of hydrogen peroxide molecules in which the energy is greater than 55,000 calories/g.mole.

The measured decomposition rate at 460°C. and H_2O_2 partial pressure of 0.02 atmospheres corresponds to about 1.8×10^{17} molecules decomposing per cc per min. Assuming that the fraction of collisions having activation energies greater than 55,000 equals $e^{-E/RT}$, the number of such collisions is about 1.1×10^{12} per cm^3 per sec. Even allowing for the possibility that the activation energy may be shared between more than 2 "squared terms" and therefore that the fraction of effective collisions may be somewhat greater than

$e^{-E/RT}$, it appears that long chains are involved here, perhaps of the order of magnitude of 10^6.

LITERATURE CITATIONS

(1) "Advances in Catalysis" Vol. IV, Academic Press, New York, N. Y., 1952.

(2) Baker, B. E., and Ouellet, C., Can. J. Research, 23B, 167 (1945).

(3) Buffalo Electrochemical Company, "Engineering Materials for Use with 90% Hydrogen Peroxide," Buffalo New York, 1950.

(4) Cook, G. A., U. S. Patents 2,368,640 and 2,368,806, Feb. 6, 1945.

(5) Coward, J. N. and Turner, W. E. S., J. Soc. Glass Tech., T22, 309 (1938)

(6) Douglas, R. W., and Isard, J. O., J. Soc. Glass Tech., 33, 289 (1949).

(7) Dowden, D. A., J. Chem. Soc. (London), I, 242 (1950).

(7a) Evans, U. R., "Metallic Corrosion, Passivity and Protection", E. Arnold & Co., London, England, 1946.

(8) Fitzgerald, J. V., Glass Ind., 30, 259 (1947).

(9) Garbatski, U. and Folman, M., J. Chem. Phys, 22, 2086 (1954).

(10) Giguere, P. A., Can. J. Research, 25B, 135 (1947).

(11) Hedvall, J. A., Jagitsch, R., and Olsen, G., Zeits. f. Phys. Chem., 196, 23 (1950).

(12) Hensley, J. W., Long, A. O., and Willard, J. E., Ind. Eng. Chem., 41, 1415 (1949).

(13) Hooi, J. and Selwood, P. W., J. Am. Chem. Soc., 72, 4333 (1950).

(14) Hooi, J. and Selwood, P. W., J. Am. Chem. Soc., 74, 1750 (1952).

(15) Huang, Y. M., S. M. Thesis in Chemical Engineering, M.I.T., 1955.

(16) Kondrat'eva, E., and Kondrat'ev, V. N., J. Phys. Chem. (USSR), 19, 178 (1945).

(16a) Kubraschewski, O., and Hopkins, B. E., "Oxidation of Metals and Alloys", Academic Press, Inc., New York, 1953.

(17) MacKenzie, R. C., and Ritchie, M., Proc. Roy. Soc., (London), A185, 207 (1946).

(18) Manual 43, Materials and Methods, 28, 83 (1948).

(19) McLane, C. K., J. Chem. Phys., 17, 379 (1949).

(20) Metal Finishing, 18th Annual Ed., Guidebook, 182 (1949).
(21) Ibid, 200 (1949).
(22) Metal Finishing, 20th Annual Ed., Guidebood, 428 (1951).
(23) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. VII, Longmoors, Green and Co., London, England, 1940.
(24) Morey, G. W., "Properties of Glass," ACS No. 77, Reinhold Publishing Co., New York, 1938.
(25) Rees, A. L. G., "Chemistry of the Defect Solid State", London Methuen, Wiley & Co., New York, 1954.
(26) Roth, E. M. and Shanley, E. S., Ind. Eng. Chem., 45, 2343 (1953)
(27) Rustless Iron and Steel Corp., "Heat Treatment of Stainless Steels", Baltimore, Md., 1944.
(28) Satterfield, C. N. Kavanagh, G. M., and Resnick, H., Ind. Eng. Chem., 43, 2507 (1951)
(29) Satterfield, C. N., Ceccotti, P. J., and Feldbrugge, A. H. R., Ind. Eng. Chem., 47, 1040 (1955)
(30) Schumb, W. C., Satterfield, C. N., and Wentworth, R. L., "Hydrogen Peroxide", A. C. S. Monograph No. 128, Reinhold Publishing Corp., 1955.
(31) Selwood, P. W., in "Catalysis" Vol. I, edited by P. H. Emmett, Reinhold Publishing Corp., New York, 1954.
(32) Sherwood, T. K. and Pigford, R. L., "Absorption and Extraction" McGraw-Hill Book Co., Inc., New York, 1952.
(32a) Speller, F. M., "Corrosion, Causes and Prevention", McGraw Hill, New York, 1951.
(33) Tamres, M. and Frost, A. A., J. Am. Chem. Soc., 72, 5340 (1950).
(34) Uhlig, H. H., Trans. Electrochemical Soc., 78, 265 (1940).
(35) Von Greffchen, W. and Berger, E., Glas. Tech. Ber., 16, 296 (1938).
(36) Weyl, W. A., Trans. New York Aca. Sci., II, 12, No. 8, 245 (1950).
(37) Williams, H. S. and Weyl, W. A., Glass Ind., 26, 324 (1945).

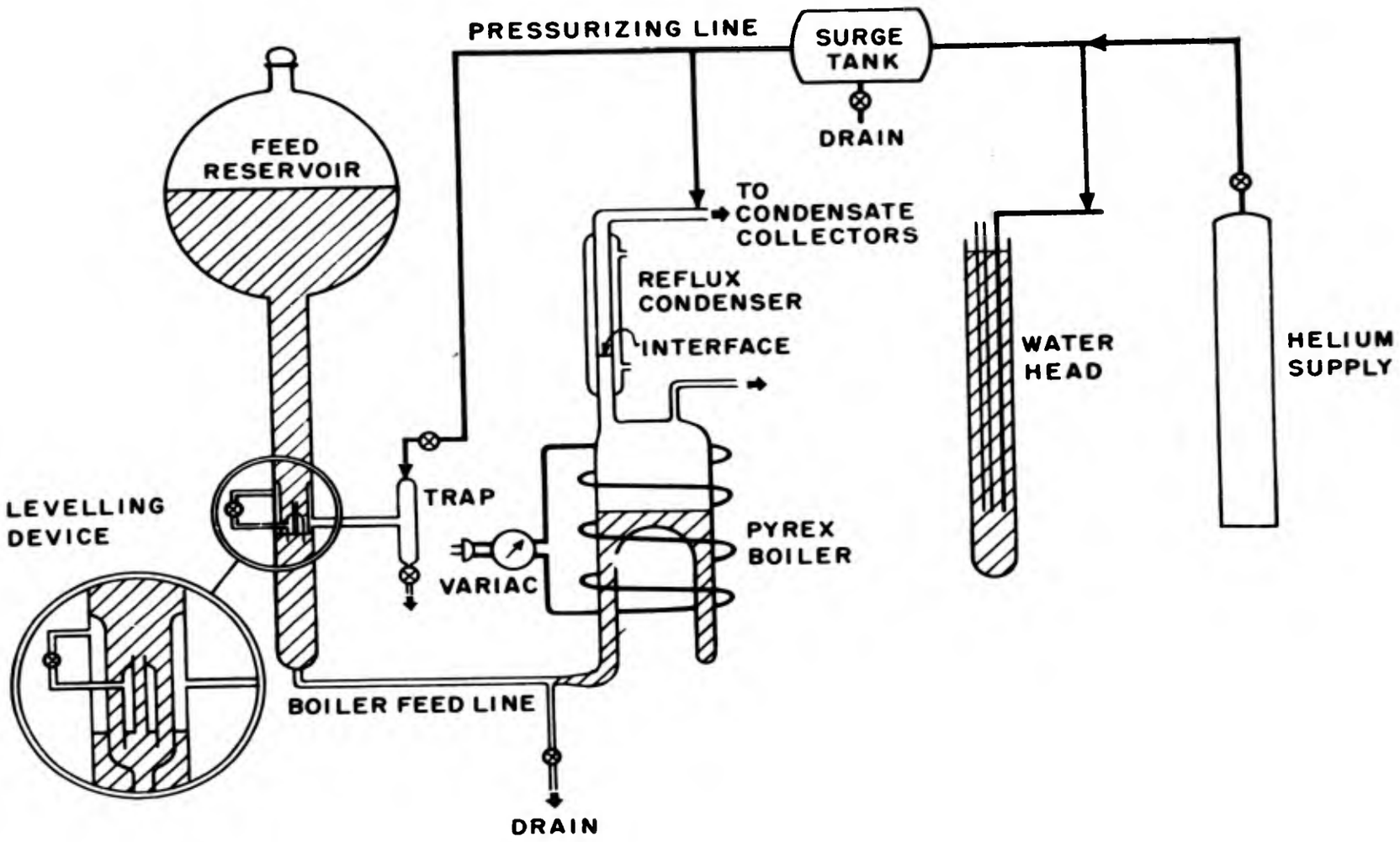

FIG. 1 – HYDROGEN PEROXIDE VAPORIZATION SYSTEM

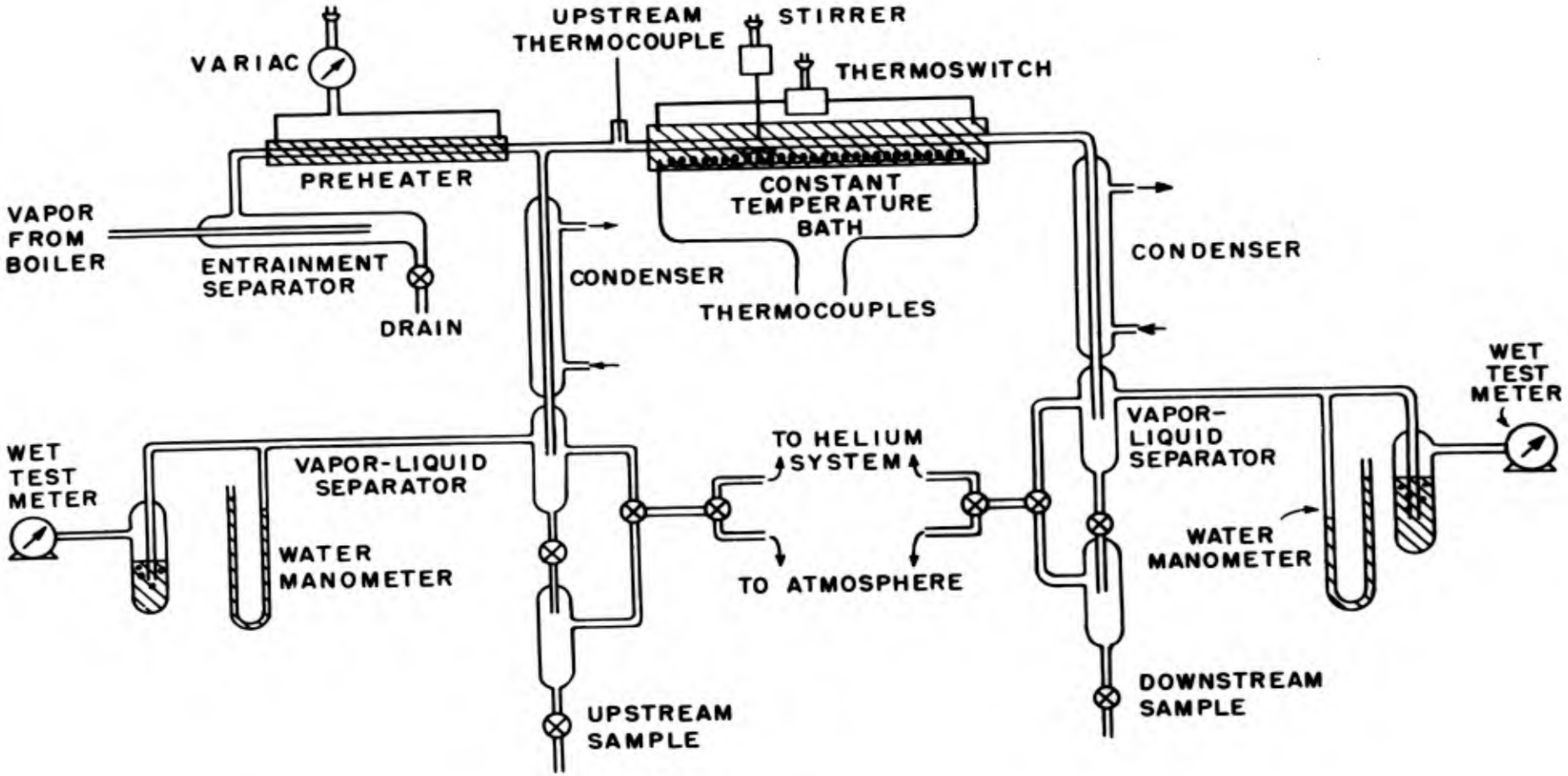

FIG. 2 - DECOMPOSITION APPARATUS (SHOWN WITHOUT INSULATION)

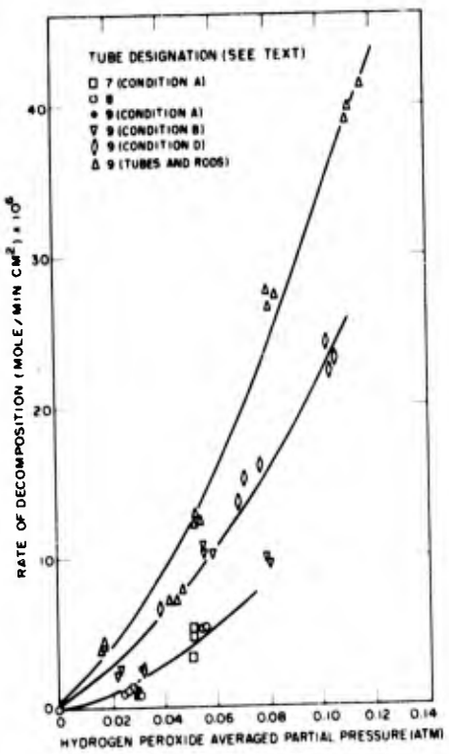

FIG 3 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON BORIC OXIDE SURFACES (T = 215°C)

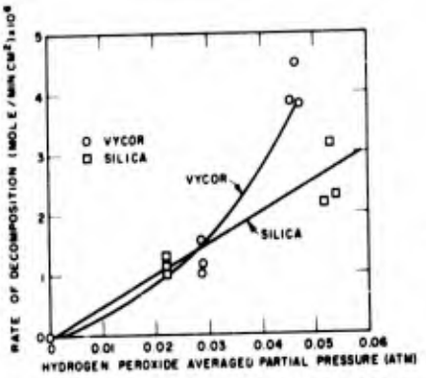

FIG 4 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON SILICA AND VYCOR SURFACES (T = 215°C)

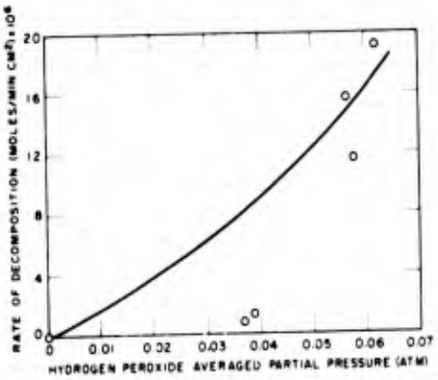

FIG 5 - DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON SOFT GLASS SURFACE (T = 215°C)

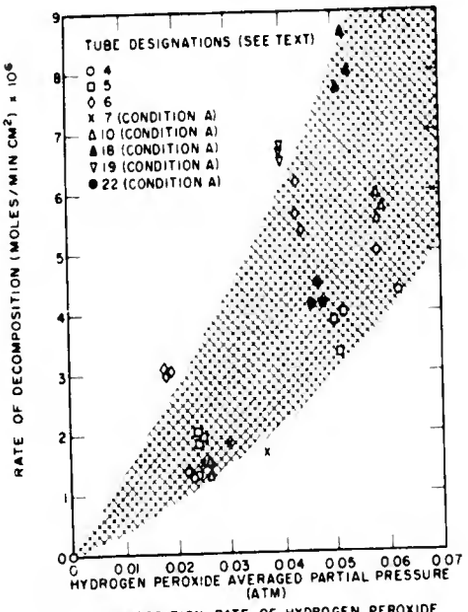

FIG 6 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PYREX SURFACES (T = 215°C)

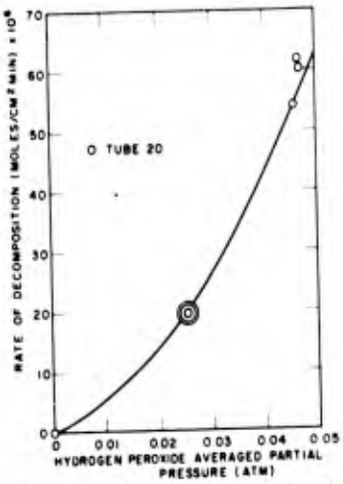

FIG. 7 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A LEAD GLASS SURFACE (T = 215°C)

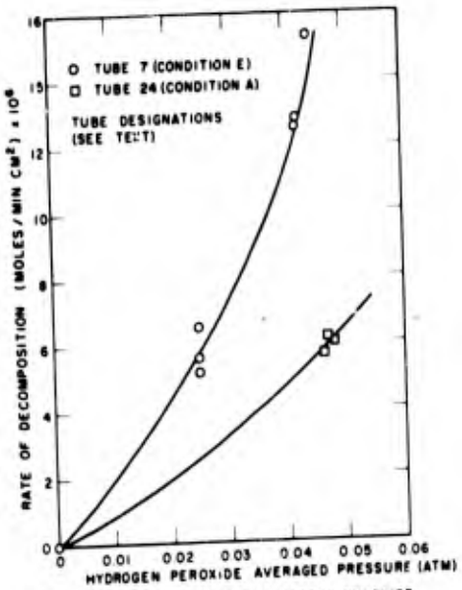

FIG 8 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR OF PYREX SURFACES TREATED WITH 5% SODIUM HYDROXIDE SOLUTIONS (T=215°C)

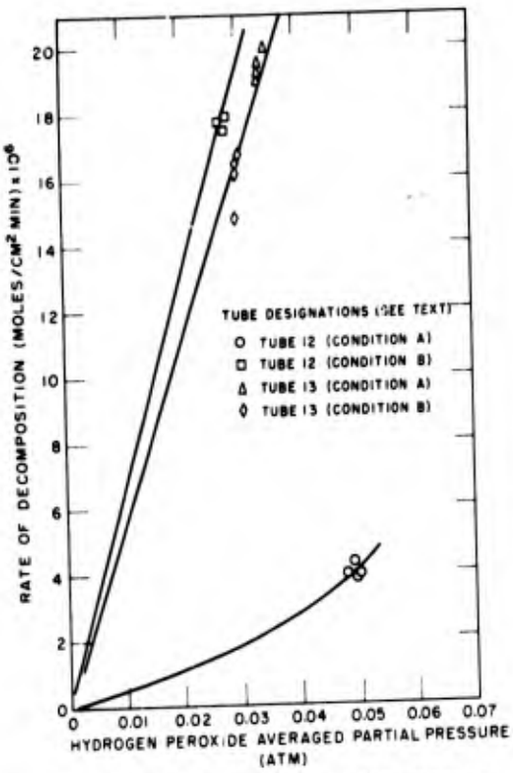

FIG 9 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PYREX SURFACES TREATED WITH SODIUM AND SILVER NITRATES. (T=215°C)

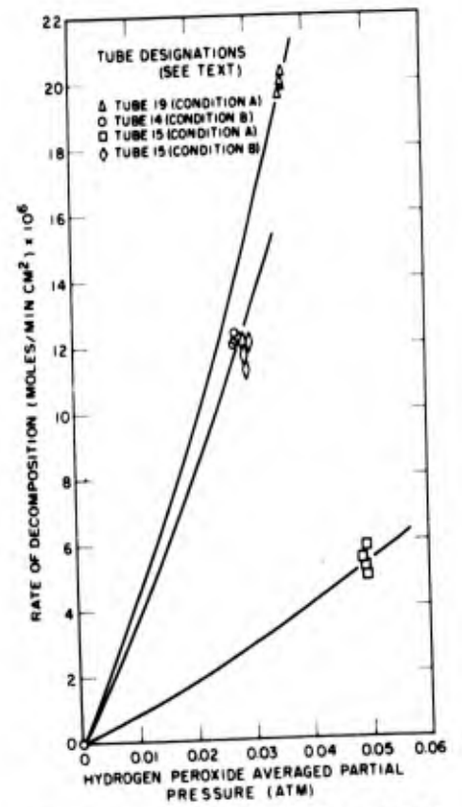

FIG 10 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PYREX SURFACES TREATED WITH SODIUM AND FERRIC NITRATES (T = 215°C)

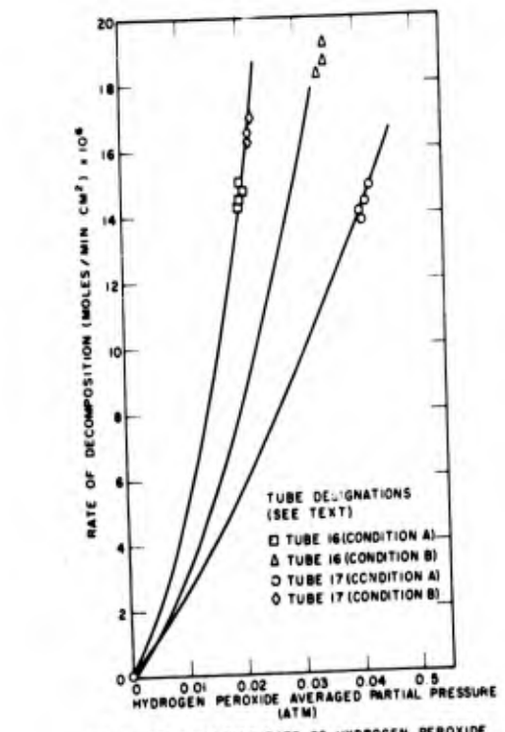

FIG 11 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PYREX SURFACES TREATED WITH SILVER AND FERRIC NITRATES (T=215°C)

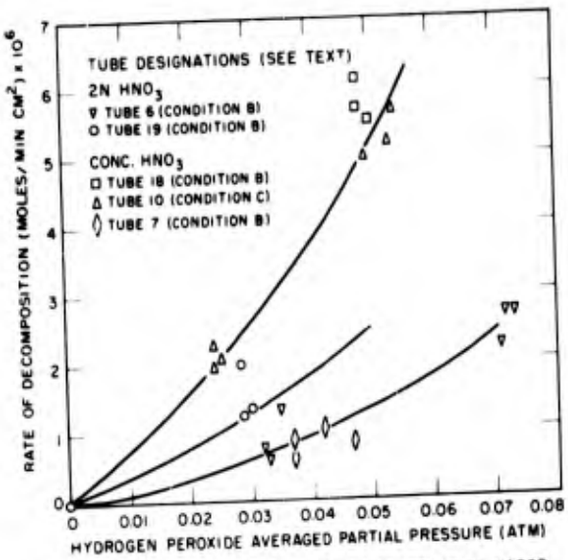

FIG 12 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PYREX SURFACES TREATED WITH NITRIC ACID (T=215°C)

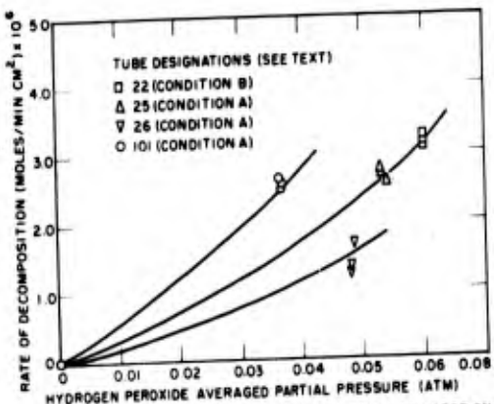

FIG 13 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PYREX SURFACES TREATED WITH 4N PHOSPHORIC ACID (T=215°C)

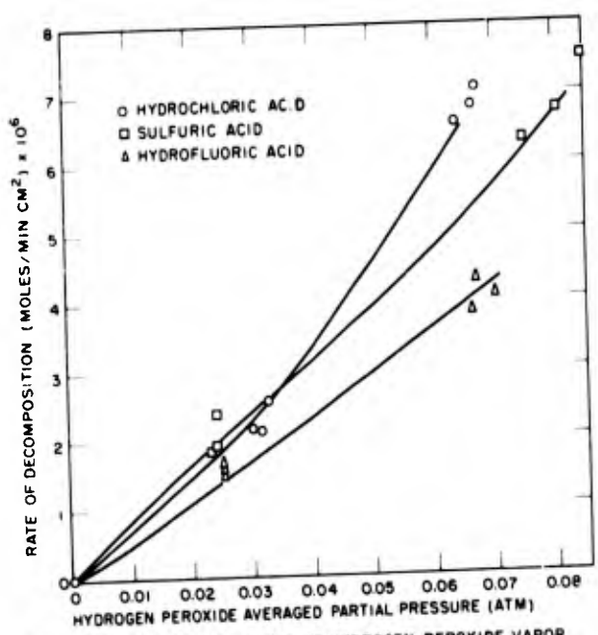

FIG 14 DECOMPOSITION RATES OF HYDROGEN PEROXIDE VAPOR ON PYREX SURFACES TREATED WITH VARIOUS ACIDS (T = 215°C)

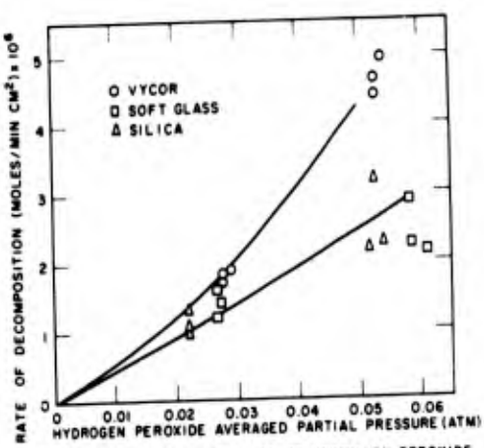

FIG 15 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON VARIOUS ACID RINSED GLASS SURFACES (T = 215°C)

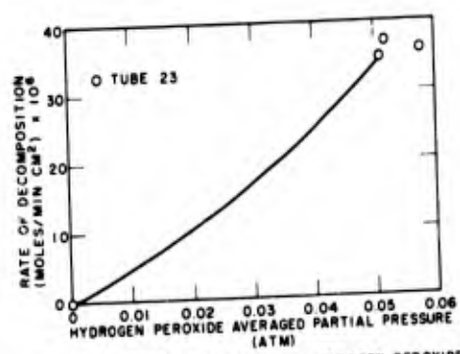

FIG 16 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A LEAD GLASS SURFACE TREATED WITH 4N PHOSPHORIC ACID (T = 215°C)

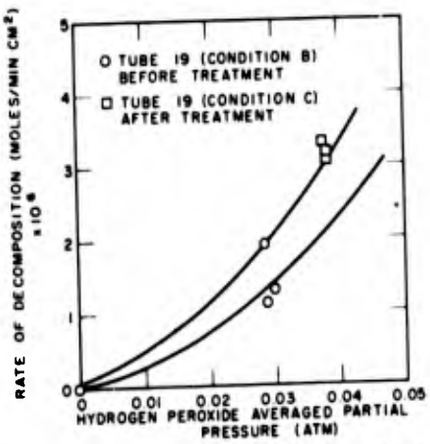

FIG 17 EFFECT OF TREATING A PYREX SURFACE WITH 200 PPM SODIUM STANNATE SOLUTION ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR (T=215°C)

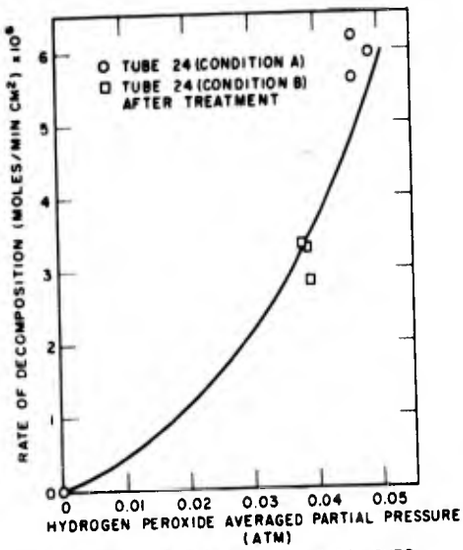

FIG 18 EFFECT OF PASSING GASEOUS SO_2 OVER PYREX SURFACE ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR (T = 215°C)

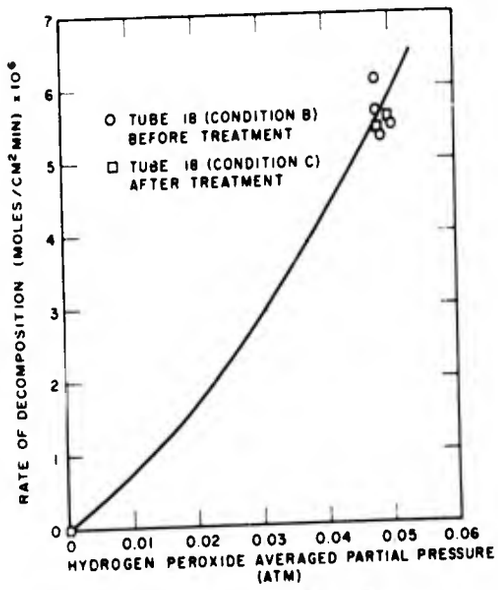

FIG 19 EFFECT OF TREATING A PYREX SURFACE WITH HYDROGEN PEROXIDE LIQUID ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR (T=215°C)

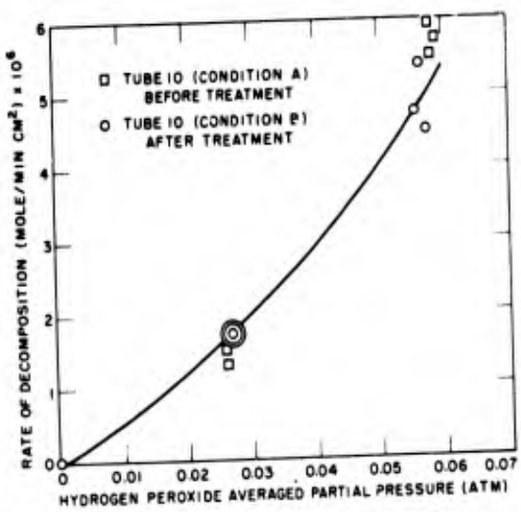

FIG 20 EFFECT OF TREATING A PYREX SURFACE WITH A METAKAOLIN SLIP ON THE DECOMPOSITION RATE HYDROGEN PEROXIDE VAPOR (T = 215° C)

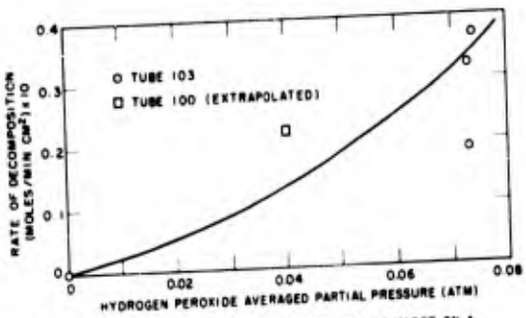

FIG 21 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A FUSED-ACID TREATED PYREX SURFACE (T = 215°C)

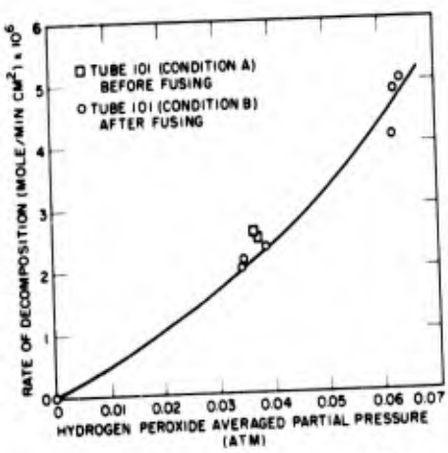

FIG 24 EFFECT OF FUSING A PYREX SURFACE WITH A FLAME ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR (T = 215°C)

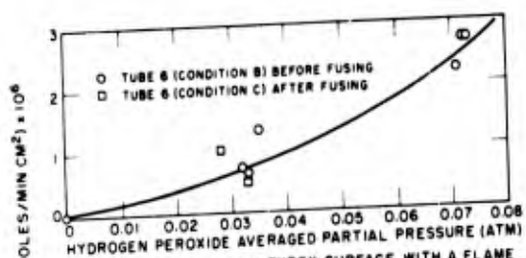

FIG. 22 EFFECT OF FUSING A PYREX SURFACE WITH A FLAME ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR (T = 215°C)

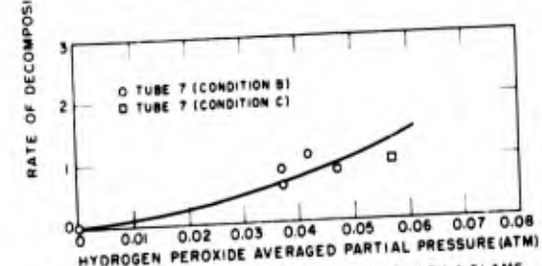

FIG. 23 EFFECT OF FUSING A PYREX SURFACE WITH A FLAME ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR (T = 215°C).

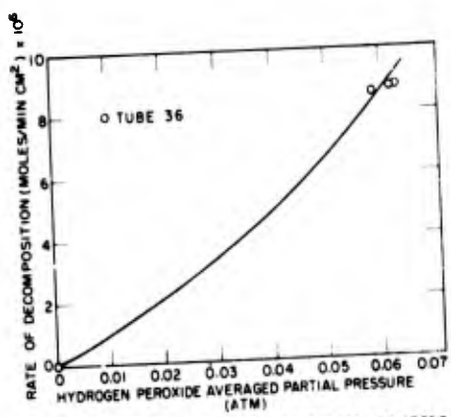

FIG 25 EFFECT OF FUSING A PYREX SURFACE AT 430°C ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR (T = 215°C)

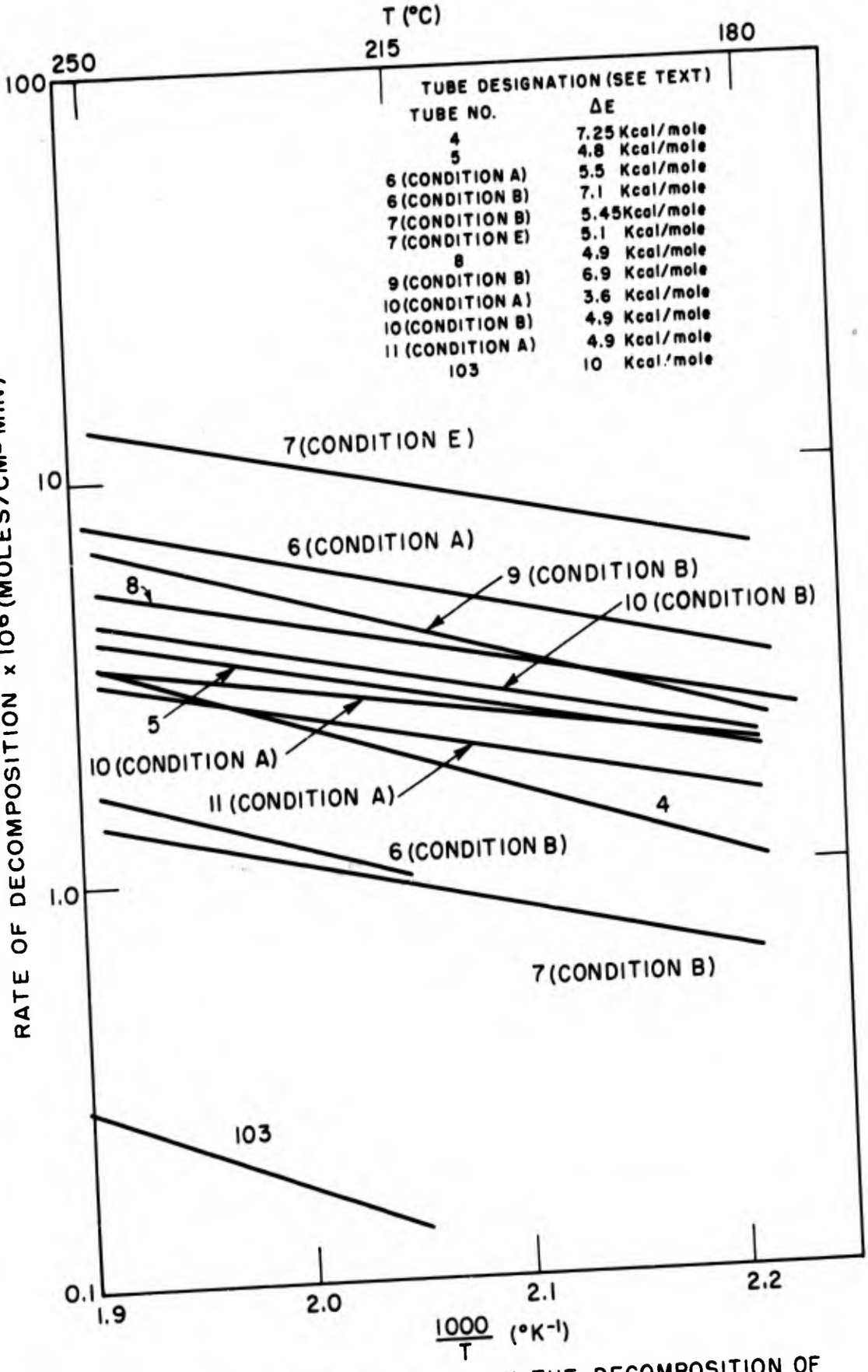

FIG. 26 EFFECT OF TEMPERATURE ON THE DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR ($P_{H_2O_2}$ = 0.04 ATM)

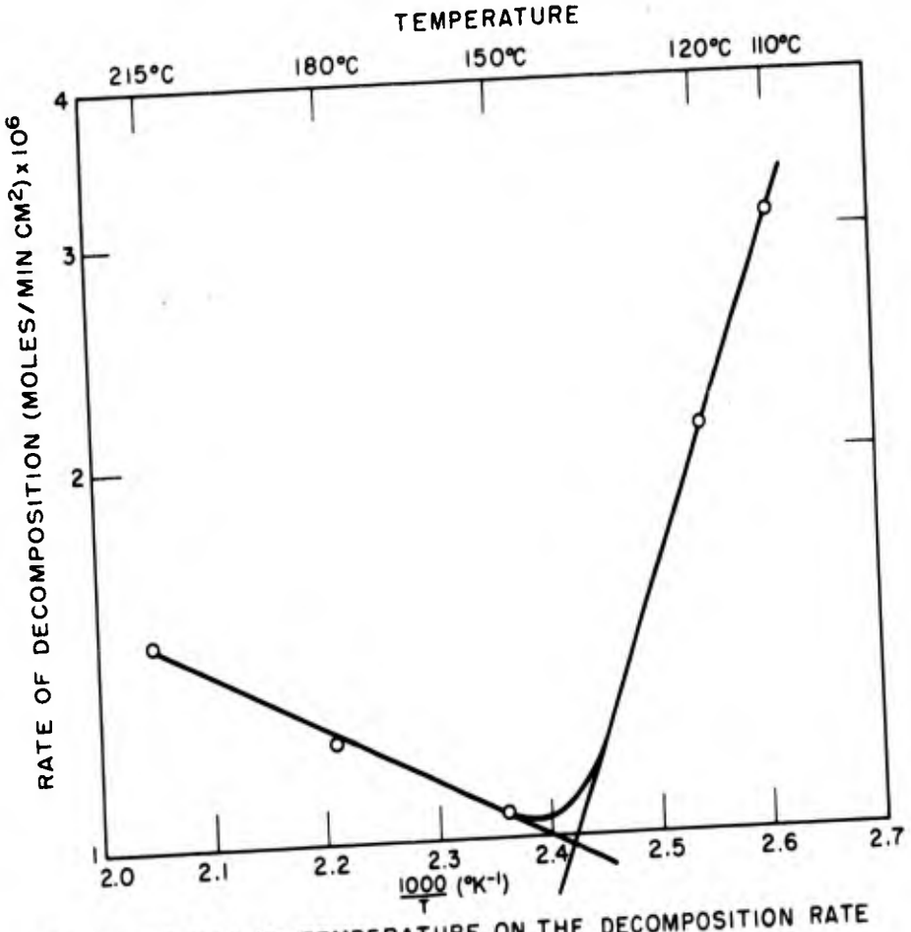

FIG. 27 EFFECT OF TEMPERATURE ON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ($P_{H_2O_2}$ = 0.02 ATM)

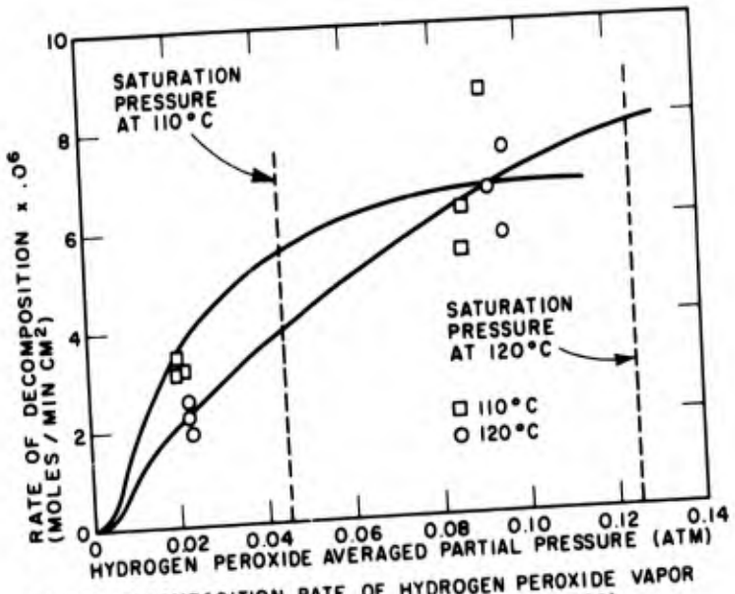

FIG. 28 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A PYREX SURFACE (T = 110°C AND 120°C)

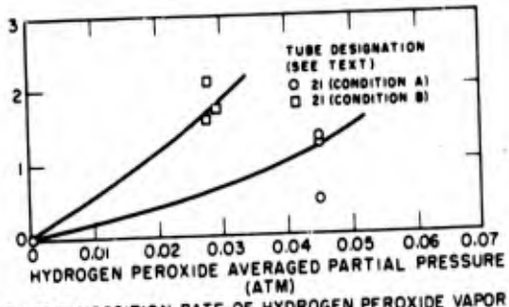

FIG. 29 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A PYREX SURFACE COATED WITH FLUOROLUBE GREASE (T = 215°C)

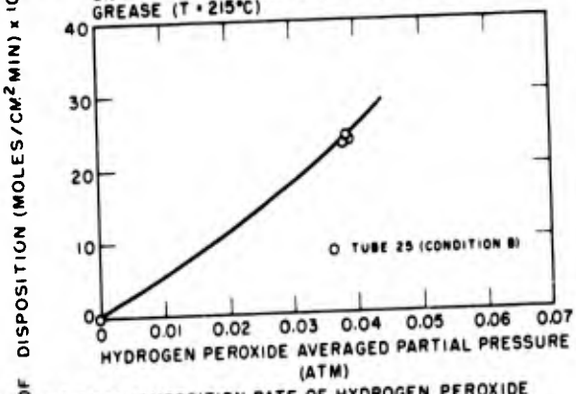

FIG. 30 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A TEFLON SURFACE (T = 215°C)

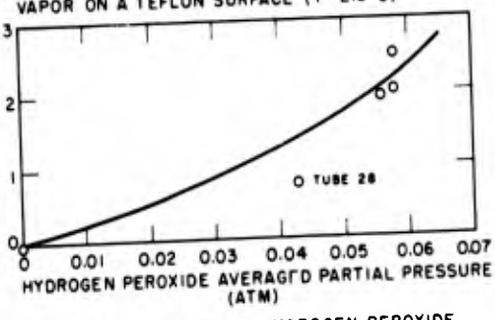

FIG. 31 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A PYREX SURFACE COATED WITH METHYL TRICHLORO SILANE (T = 215°C)

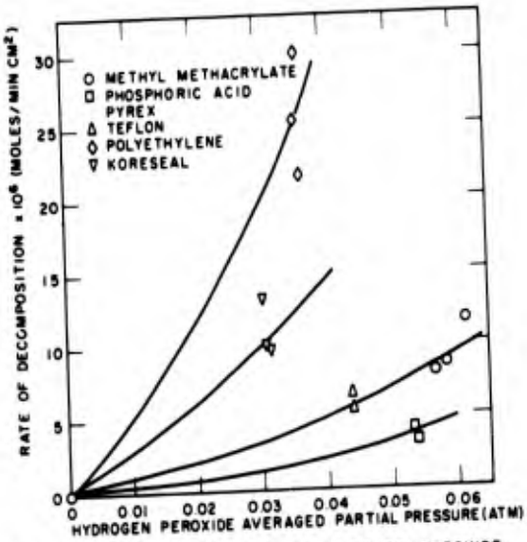

FIG 32 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON VARIOUS PLASTIC SURFACES (T=120°C)

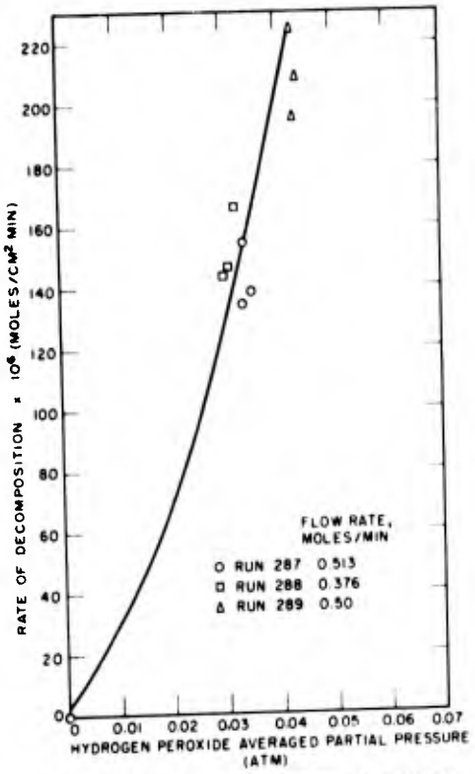

FIG. 33- DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON AN ELECTROPOLISHED STAINLESS STEEL 304 SURFACE (T = 150°C)

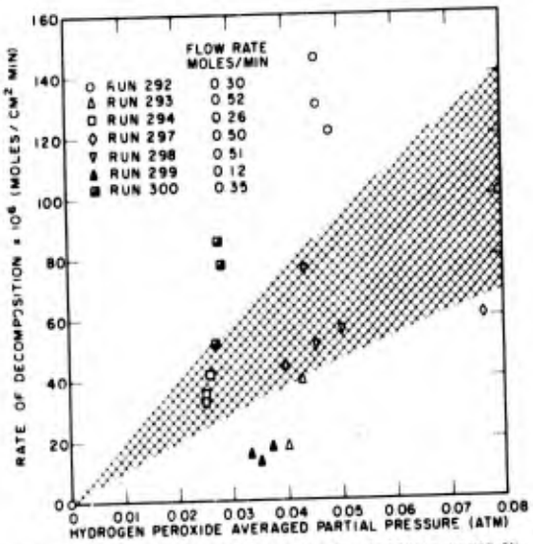

FIG. 34 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON AN ELECTROPOLISHED STAINLESS STEEL 304 SURFACE (T = 150°C)

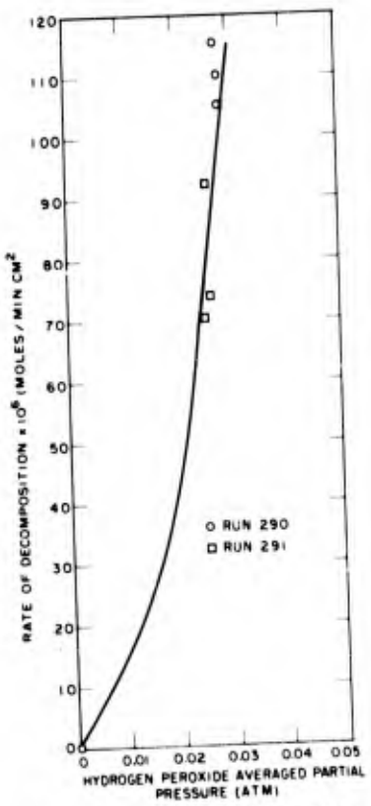

FIG. 35 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON AN ELECTRO - POLISHED STAINLESS STEEL 416 SURFACE (T = 150°C)

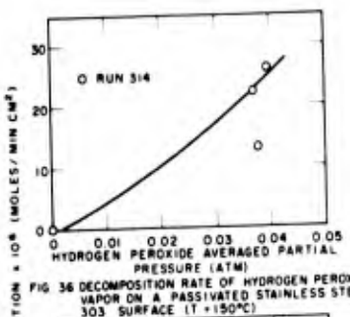

FIG. 36 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A PASSIVATED STAINLESS STEEL 303 SURFACE (T = 150°C)

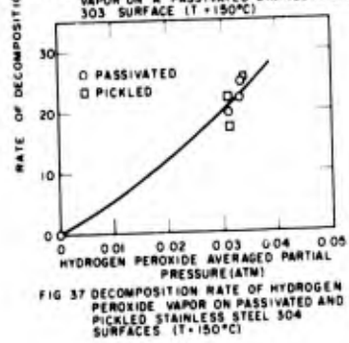

FIG. 37 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PASSIVATED AND PICKLED STAINLESS STEEL 304 SURFACES (T = 150°C)

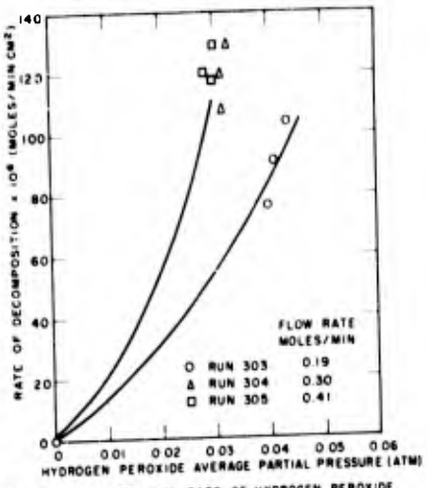

FIG 38 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON ELECTROPOLISHED 2S ALUMINUM SURFACE (T = 150°C)

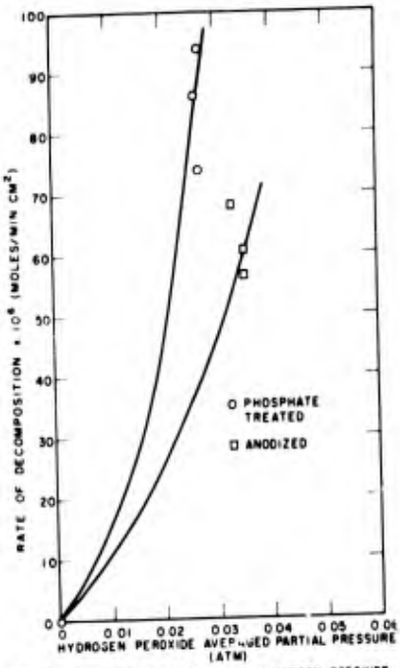

FIG 39 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PHOSPHATED AND ANODIZED 2S ALUMINUM SURFACES (T = 150°C)

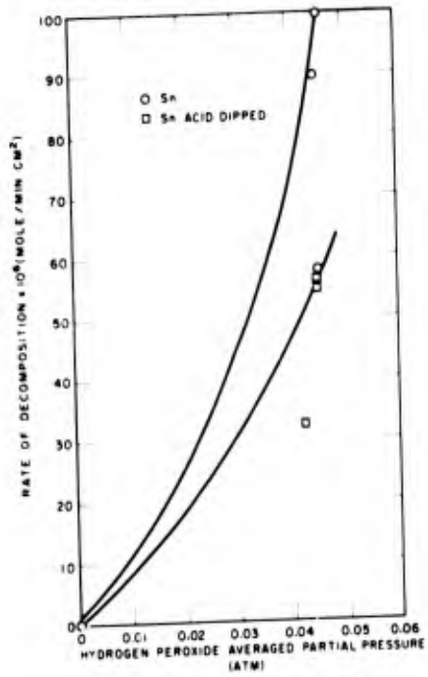

FIG 41 DECOMPOSITION RATES OF HYDROGEN PEROXIDE VAPOR ON TIN SURFACES (T = 150°C)

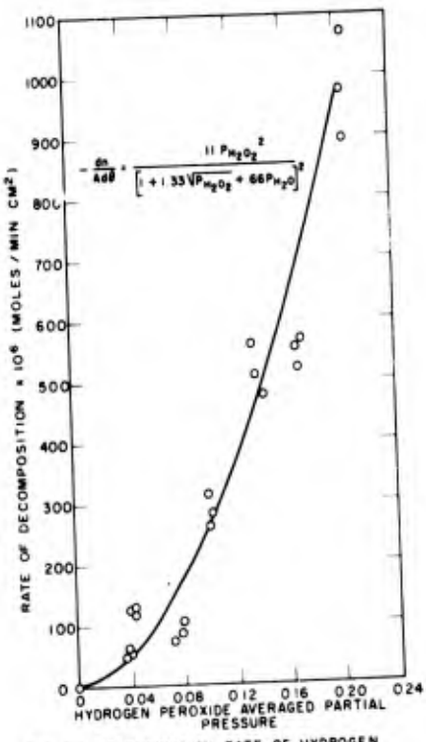

FIG 40 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON A PICKLED 2S ALUMINUM SURFACE (T = 150°C)

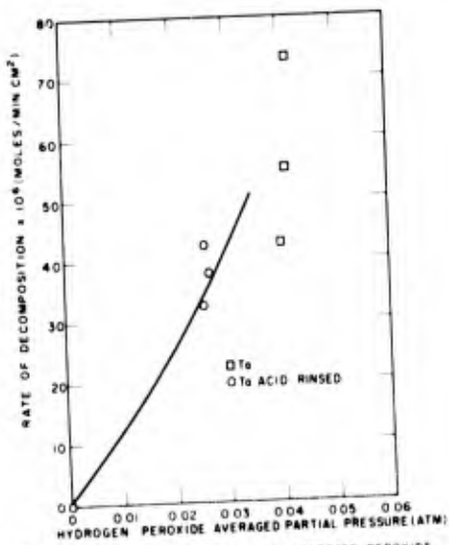

FIG 42 DECOMPOSITION RATES OF HYDROGEN PEROXIDE VAPOR ON TANTALUM SURFACES (T = 150°C)

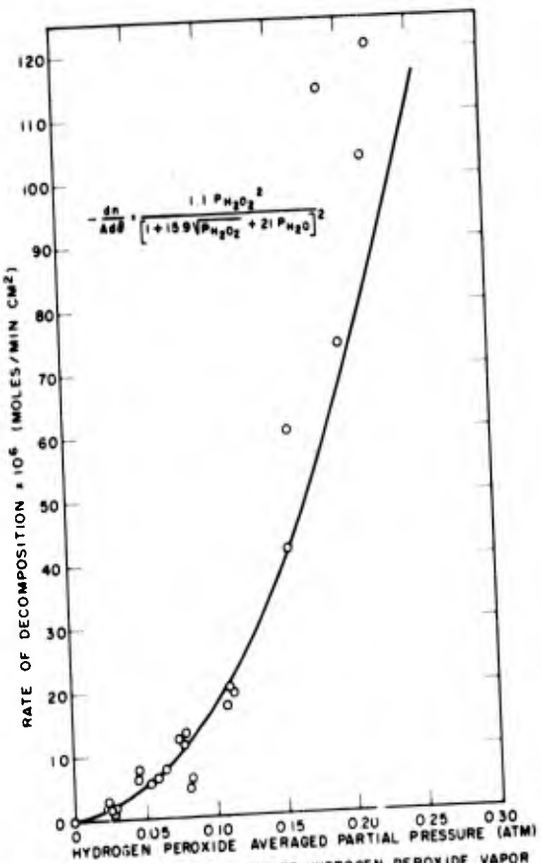

FIG 43 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON BORIC OXIDE SURFACE (TUBE 9) (T=180°C)

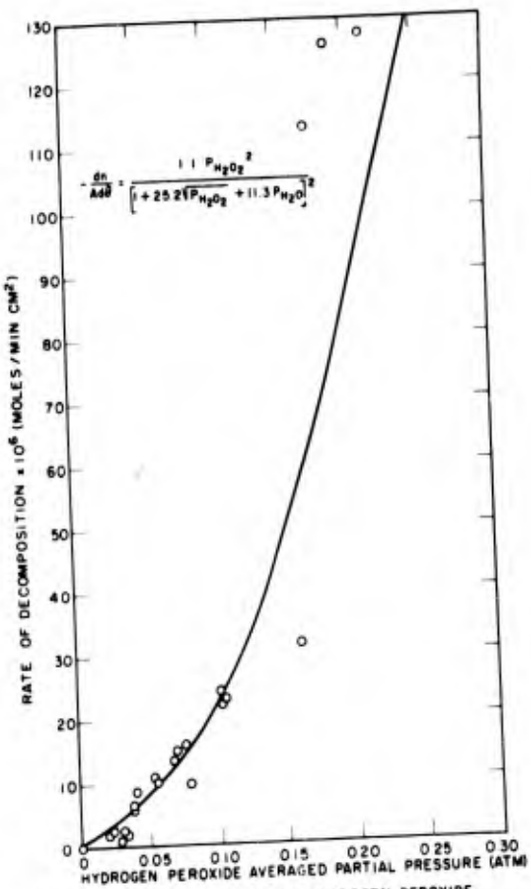

FIG 44 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON BORIC OXIDE SURFACE (TUBE 9)(T=215°)

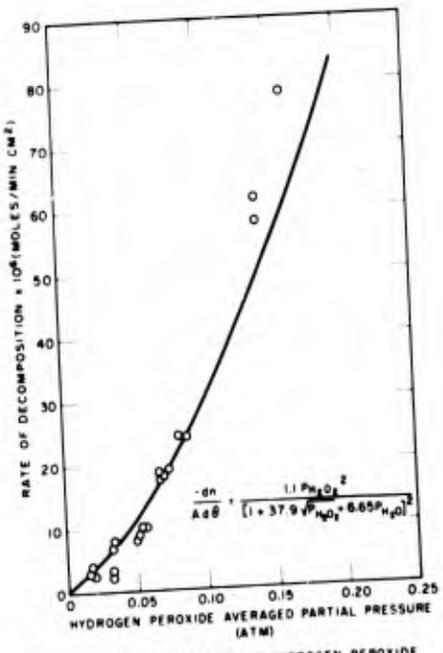

FIG 45 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON BORIC OXIDE SURFACE (TUBE 9)(T=250°C)

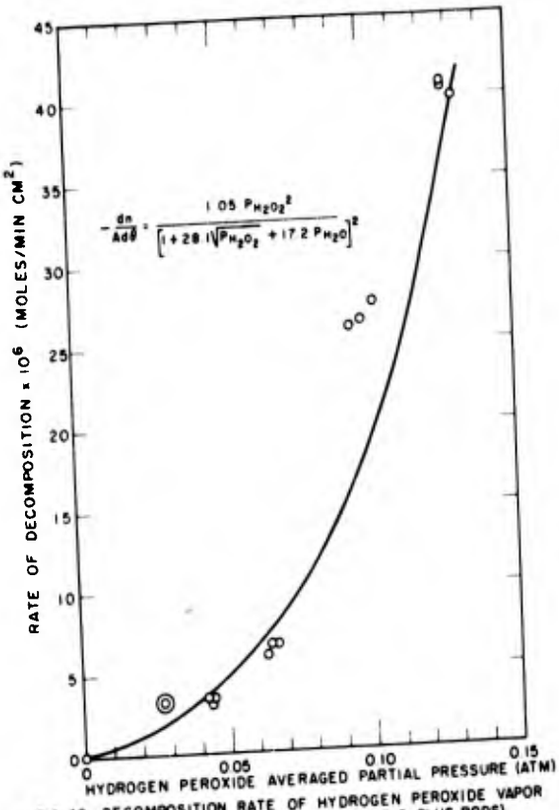

FIG 46 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON BORIC OXIDE SURFACE (TUBE 9 PLUS RODS) (T = 180°C)

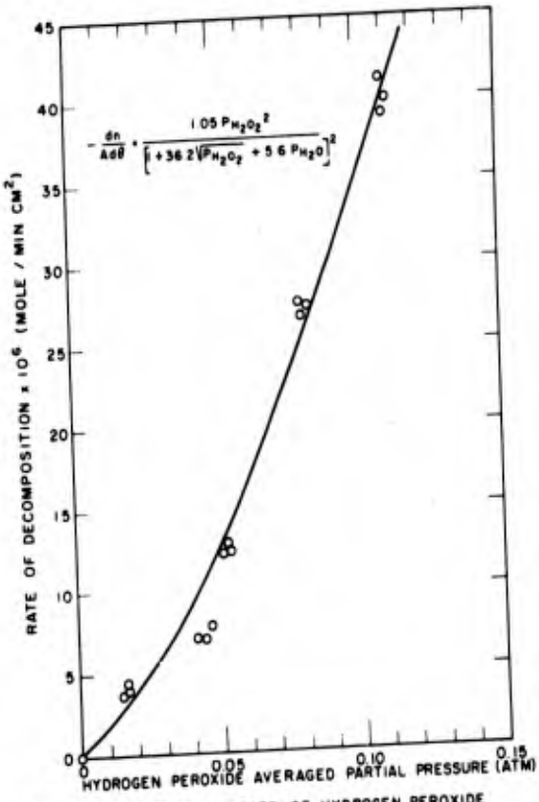

FIG 47 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON BORIC OXIDE SURFACES (TUBE 9 PLUS RODS) (T = 215°C)

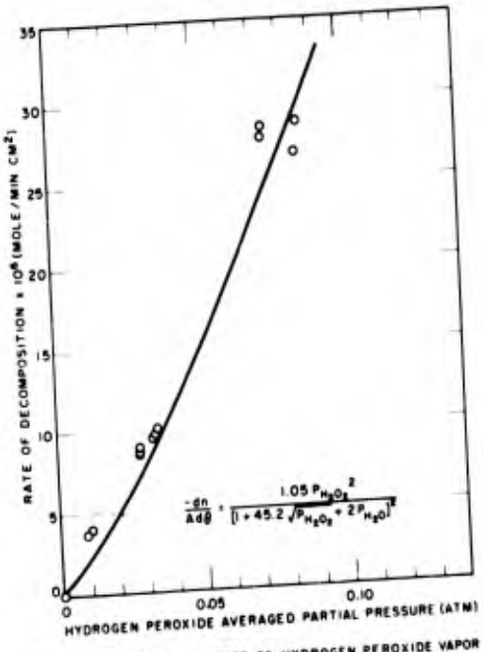

FIG 48 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON BORIC OXIDE SURFACE (TUBE 9 PLUS RODS) (T = 250°C)

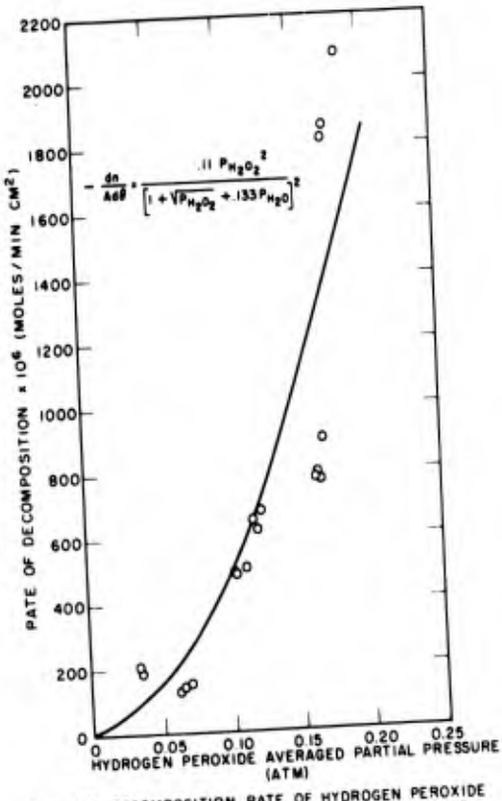

FIG 49 DECOMPOSITION RATE OF HYDROGEN PEROXIDE VAPOR ON PICKLED 25 ALUMINUM SURFACE (T = 180°C)

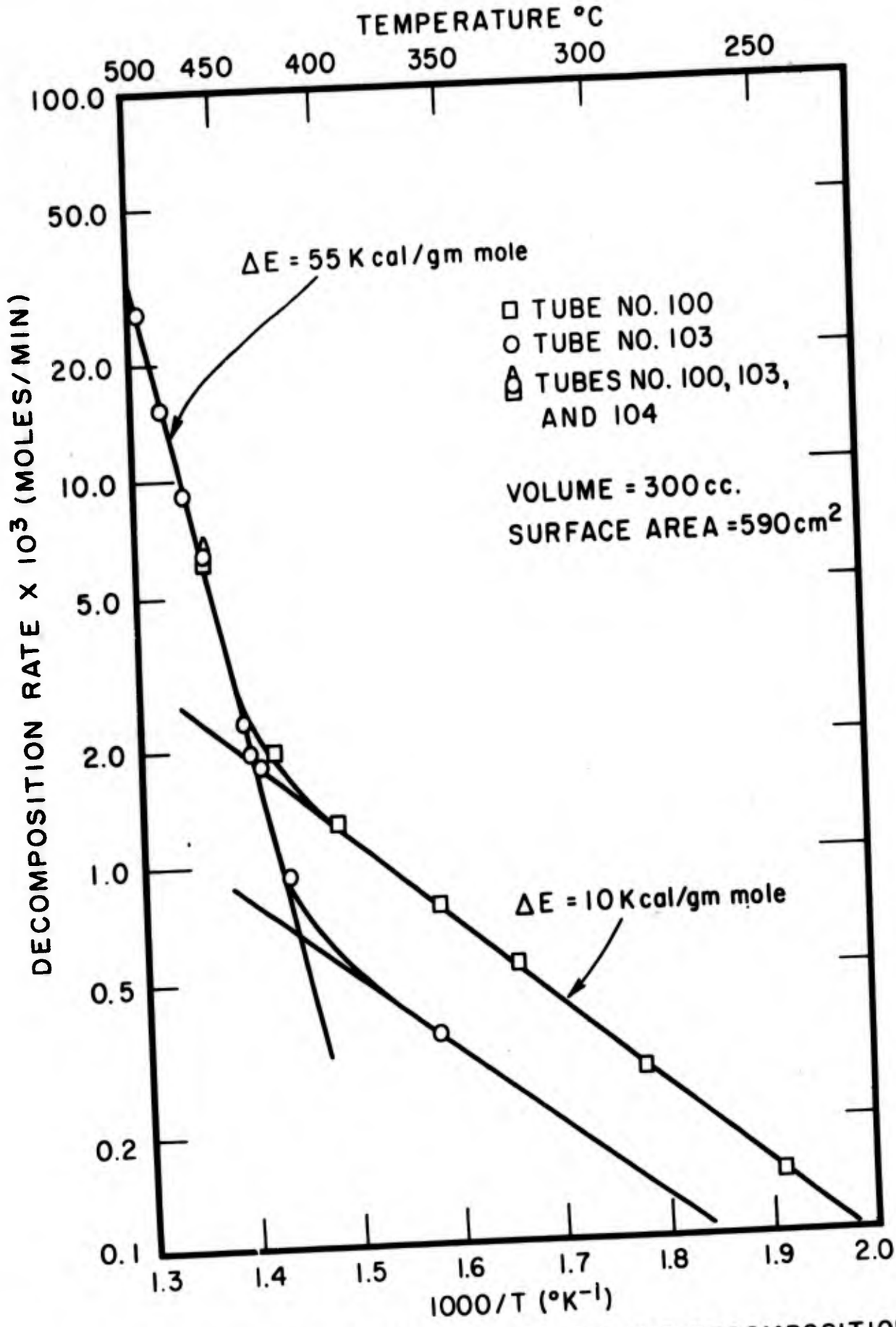

FIG. 50 – EFFECT OF TEMPERATURE ON THE DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR. ($p_{H_2O_2}$ = 0.02 ATM.)

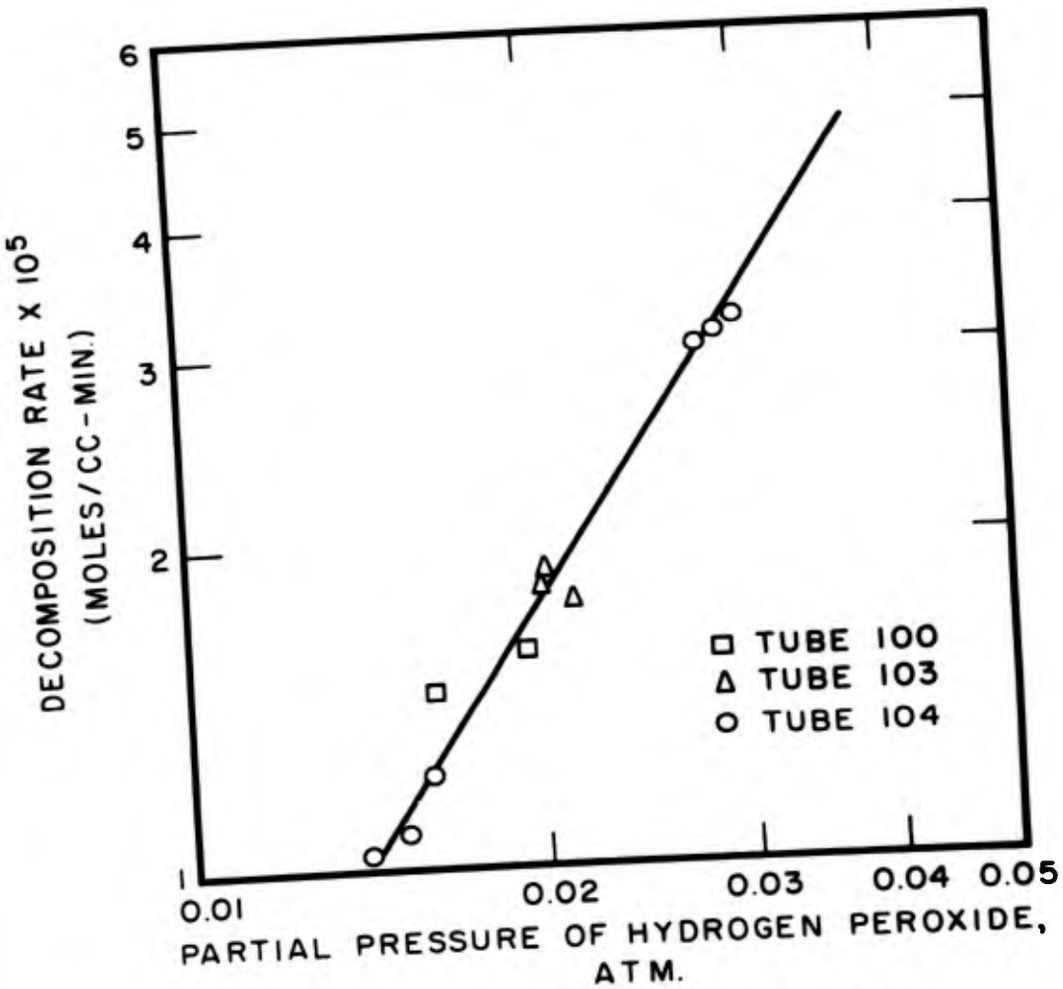

FIG. 51 - EFFECT OF CONCENTRATION ON THE HOMOGENEOUS DECOMPOSITION RATE OF HYDROGEN PEROXIDE. T = 460°C

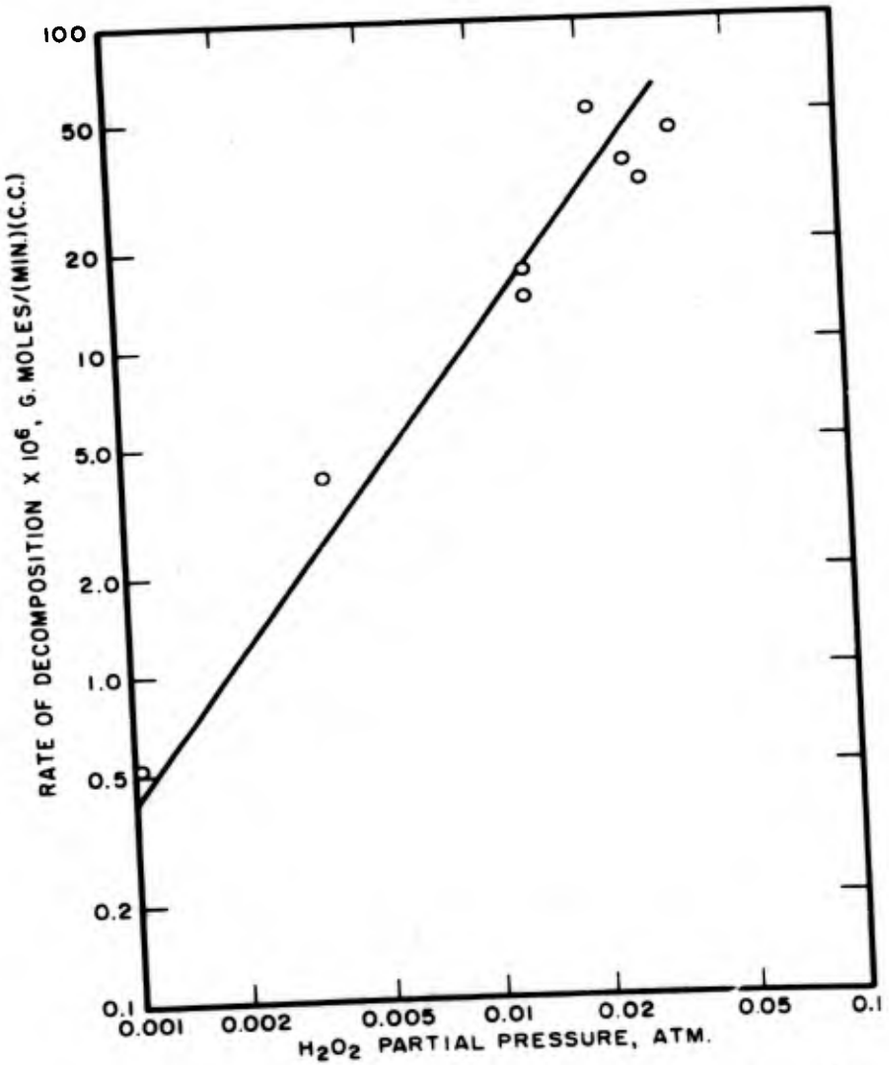

FIG. 52 - EFFECT OF CONCENTRATION ON THE HOMOGENEOUS DECOMPOSITION RATE OF H_2O_2 (FROM HUANG), T=475°C

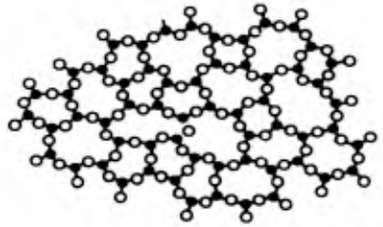

FIG. A1 - TWO DIMENSIONAL REPRESENTATION OF BORIC OXIDE GLASS

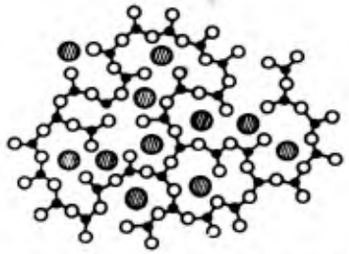

FIG. A2 - SCHEMATIC REPRESENTATION IN TWO DIMENSIONS OF THE STRUCTURE OF SODA-SILICA GLASS

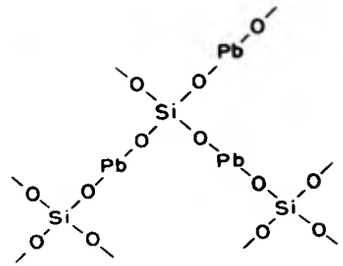

FIG. A3 - REPRESENTATION OF LEAD GLASS

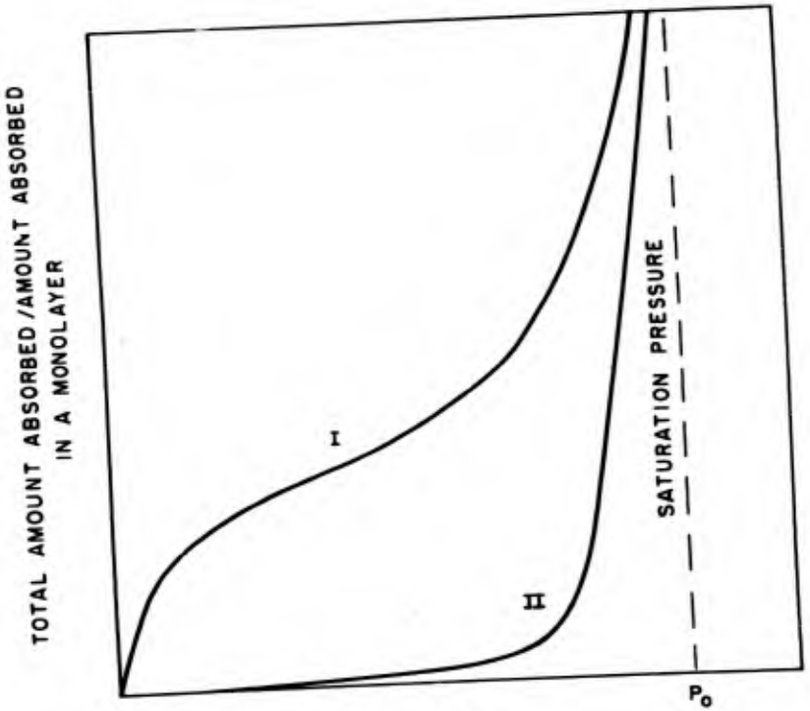

FIG. A4 MULTILAYER ABSORPTION ISOTHERM

DISTRIBUTION LIST
CONTRACT N5ori 07819
STABILITY AND REACTION STUDIES OF HYDROGEN PEROXIDE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

Addressee	Transmitted Via	Number of Copies
Committee on Guided Missiles **Office of the Secretary of Defense (R&D)** **Room 3D-125, The Pentagon** **Washington 25, D. C.**		1
Chief of Staff, U. S. Air Force The Pentagon Washington 25, D. C. Attn: DCS/D, AFDRD-AC-2 DCS/D, AFOP-00		1 1
Commanding General Air Material Command Wright-Patterson Air Force Base Dayton, Ohio Attn: MCREXP WCLPR-4		2 2
Chief, Bureau of Aeronautics Department of the Navy Washington 25, D. C. Attn: TD-4 SI-572		1
Chief, Bureau of Ordnance Department of the Navy Washington 25, D. C. Attn: Re6a Re9 Re3d		3 1 1
Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 541 Code 430 Code 520 Code 533 Code 549		1 1 1 1 1
U. S. Naval Air Rocket Test Station Lake Denmark Dover, New Jersey Attn: Dr. T. Shinemardt		1
Commander Naval Air Material Center Philadelphia 12, Pennsylvania		1
Commander U. S. Naval Air Missile Test Center Point Mugu, California		1
Commander U. S. Naval Ordnance Test Station Inyokern, California P. O. China Lake, California Attn: Reports Unit Code 4012		1 1
Director National Advisory Committe for Aeronautics 1724 F Street, NW Washington 25, D. C. Attn: Mr. C. H. Helms		2
Director U. S. Naval Research Laboratory Office of Naval Research, Anacostia Washington 25, D. C. Attn: Code 3260 Code 2000		1 6(if class if. only 1)
Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 429		3 (if classif. 13)
Commanding Officer Frankford Arsenal Philadelphia 37, Pennsylvania Attn: Fire Control Division		1
Superintendent U. S. Naval Postgraduate School Monterey, California Attn: Librarian		1
Department of the Army Office, Chief of Ordnance The Pentagon Washington 25, D. C. Attn: ORDTU		1
Commander Naval Ordnance Laboratory, White Oak Silver Spring 19, Maryland Attn: The Library, Room 10333		1
Commanding General AAA and GM Center Fort Bliss, Texas		1
Chief of Naval Operations Department of the Navy Washington 25, D. C. Attn: Op-51		1

Addressee	Transmitted Via	Number of Copies
Chief, Research and Engineering Division Office, Chief of Chemical Corps. Army Chemical Center, Maryland		1
Commanding Officer USS Norton Sound (AVM-1) c/o Fleet Post Office San Francisco, California		1
Commanding General White Sands Proving Ground Las Cruces, New Mexico		1
Technical Library Atomic Energy Commission 1901 Constitution Avenue Washington 25, D. C. Attn: Mr. P. M. Fry		1
Commandant of the Marine Corps Headquarters, U. S. Marine Corps. Washington 25, D. C. Attn: G-4 (Ordnance)		1
Commander Operational Development Force U. S. Naval Base Norfolk 11, Virginia		1
Office, Asst. Chief of Staff (G-4) Research & Development Division Department of the Army The Pentagon Washington 25, D. C.		1
Head of Ordnance and Gunnery U. S. Naval Academy Annapolis, Maryland		1
Commanding Officer U. S. Naval Underwater Ordnance Station Newport, Rhode Island		2
Naval Inspector of Ordnance Electric Boat Company Groton, Connecticut		1
Director U. S. Naval Engineering Experiment Station Annapolis, Maryland		1
Director Office of Naval Research Branch Office 150 Causeway Street Boston 14, Massachusetts		2
Director Office of Naval Research Branch Office 346 Broadway New York 13, New York		1
Director Office of Naval Research Branch Office 1000 Geary Street San Francisco 9, California		1
Director Office of Naval Research Branch Office 1030 Green Street Pasadena 1, California		1
Director Office of Naval Research Branch Office Tenth Floor The John Crerar Library Building 86 East Randolph Street Chicago 1, Illinois		1
Officer-in-Charge Office of Naval Research Navy No. 100 Fleet Post Office New York, New York		2
Commanding General Air Research & Development Command P. O. Box 1395 Baltimore 3, Maryland Attn: RDRPC		1
Dr. Martin Kilpatrick Department of Chemistry Illinois Institute of Technology 3300 Federal Street Chicago 16, Illinois		
State Engineering Experimental Station Georgia Institute of Technology Atlanta, Georgia		

If Classified Via:

Director
Office of Naval Research Branch Office
Tenth Floor
The John Crerar Library Building
86 E. Randolph St.
Chicago 1, Ill. — 1

Bureau of Ships (Code 620)
Department of the Navy
Washington 25, D. C. — 1

Addressee	Transmitted Via (If Classified Via)	Number of Copies
Applied Physics Laboratory Johns Hopkins University Silver Spring, Maryland Attn: Dr. Dwight E. Gray	Naval Inspector of Ordnance Applied Physics Lab. Johns Hopkins University 8621 Georgia Avenue Silver Spring, Maryland	1
Bell Aircraft Corporation Niagara Falls, New York Attn: Mr. R. B. Foster	U. S. Air Force Plant Representative Niagara Falls, New York	1
Consolidated-Vultee Aircraft Corp. San Diego 12, Calif. Attn: Mr. J. V. Naish	Bureau of Aeronautics Representative Consolidated-Vultee Aircraft Corp. San Diego 12, Calif.	1
Douglas Aircraft 3000 Ocean Blvd. Santa Monica, Calif. Attn: Mr. E. F. Burton	District Chief Los Angeles Ordnance District 35 No. Raymond Ave. Pasadena 1, Calif.	1
Rand Corporation 1500 Fourth Street Santa Monica, Calif. Attn: Mr. F. R. Collbohm	Chief, Los Angeles AFFFO 155 West Washington Blvd. Los Angeles 54, Calif	1
General Electric Company Project HERMES Schenectady, New York Attn: Mr. C. K. Bauer	Resident Ordnance Officer Project HERMES Campbell Avenue Plant General Electric Company Schenectady 5, New York	1
Glenn L. Martin Company Baltimore 3, Maryland Attn: Mrs. Lucille Walper	Bureau of Aeronautics Representative Glenn L. Martin Company Baltimore 3, Maryland	
California Institute of Technology Jet Propulsion Laboratory Pasadena, California	Distric Chief Los Angeles Ordnance District 35 North Raymond Avenue Pasadena 1, California	1
North American Aviation, Inc. 12214 Lakewood Blvd. Downey, California Attn: Group 95-17	Air Force Plant Rep. WEAPT North American Aviation Inc. Los Angeles International Airport Los Angeles 45, California	1
Princeton University Princeton, New Jersey Attn: Project SQUID	Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York	1
University of Michigan Aeronautical Research Center Willow Run Airport Ypsilanti, Michigan Attn: Mr. L. R. Blasdel	Commanding Officer Central Air Procurement Division West Warren & Lonyo Avenues Detroit 32, Michigan	1
Aerojet-General Corporation Azusa, California Attn: Dr. D. L. Armstrong	Bureau of Aeronautics Representative Aerojet-General Corp. Azusa, California	1
Battelle Memorial Institute 505 King Avenue Columbus 1, Ohio Attn: Dr. B. D. Thomas	Air Regional Representative Dayton Regional Office Central Air Procurement Agst. U. S. Bldg., Dayton 1, Ohio	1
Bethlehem Steel Corporation Shipbuilding Division Quincy 69, Massachusetts Attn: Mr. B. Fox	Supervisor of Shipbuilding, USN Bethlehem Steel Corp. Quincy 69, Massachusetts	1
Experiment Incorporated Richmond, Virginia Attn: Dr. J. W. Mullen, II	Naval Inspector of Ordnance Applied Physics Laboratory Johns Hopkins University 8621 Georgia Avenue Silver Spring, Maryland	1
Detroit Controls Company Research Division Redwood City, California	Asst. Inspector of Naval Material 533 Middlefield Rd. Redwood City, California	1
Fairchild Engine and Airplane Corp. Fairchild Engine Division Farmingdale, Long Island, New York Attn: Mr. E. M. Lester	Bureau of Aeronautics Rep. Fairchild Engine & Airplane Corp. Farmingdale, Long Island, New York	1
Purdue University Lafayette, Indiana Attn: Dr. M. J. Zucrow	Office of Naval Research Branch Office The John Crerar Library Bldg. 10th Floor, 86 E. Randolph Street Chicago 1, Illinois	1
Reaction Motors, Inc. Stickle Avenue & Elm Street Rockaway, New Jersey	Bureau of Aeronautics Rep. Reaction Motors, Inc. Stickle Avenue & Elm St. Rockaway, New Jersey	1
United States Rubber Company General Laboratories Passaic, New Jersey Attn: Mr. C. E. Hurdis	Inspector of Naval Material Naval Industrial Reserve Shipyard Bldg. 13, Port Newark Newark 3, New Jersey	1

Addressee	Transmitted Via (If Classified Via)	Number of Copies
Electrochemical Department Technical Division E. I. duPont de Nemours & Co. Inc. Niagara Falls, New York Attn: Dr. D. Campbell	Inspector of Naval Material Room 505-508 Post Office Building Buffalo 3, New York	1
Buffalo Electro-Chemical Co. Buffalo 7, New York Attn: Dr. N. S. Davis	Inspector of Naval Material Room 505-508 Post Office Building Buffalo 3, New York	1
Walter Kidde and Co., Inc. Belleville, New Jersey Attn: Project MX-922 Contract AF(33-038)3897	Inspector of Naval Material Naval Industrial Reserve Shipyard Bldg. 13, Port Newark Newark 3, New Jersey	1
Redel Incorporated 401 East Juliana Street Anaheim, California	Inspector of Naval Material 1206 South Street Los Angeles 15, California	1
Armed Services Technical Information Agency Documents Service Center Knott Building Dayton 2, Ohio		5 (Uncl. only)
Office of Technical Services Department of Commerce Washington 25, D. C.		1 (Uncl. only)
Thompson Products, Inc. Staff Research and Development 2196 Clarkwood Cleveland 3, Ohio Attn: A. O. Kresse	Bureau of Aeronautics Thompson Products, Inc. Cleveland 3, Ohio	1
Commanding General Redstone Arsenal Huntsville, Alabama Attn: Technical Library		1
Hayden Library M.I.T. Room 14S-226 Attention: Miss Bartlett Special Collections Librarian		2 (Uncl. only)