MASTER

HYDROGEN AND METHANE SYNTHESSES
THROUGH RADIATION CATALYSIS

Progress Report
for Period September 1, 1978 - August 1, 1979

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ABSTRACT

Results of the second contract year are described on production of hydrogen through water radiolysis at ^{60}Co gamma energies, in the presence of solid oxide catalysts. The intent of the research is an improved theoretical understanding of radiation-induced hydrogen generation within the framework of the electronic theory of catalysis.

Correlation of hydrogen yield with catalytic activity, based on prior work, was difficult to attain and an assessment of experimental parameters was made. Three sets of observations appear of some significance, however: (1) Antimony oxide (Sb_2O_3 , $E_g=3.3$) shows consistently a dramatic increase in catalytic performance which cannot be attributed solely to band gap values. (2) There appears to be a correlation between hydrogen yield and dielectric properties of the catalyst. (3) Gamma irradiation changes the constitutive electrical properties of oxide catalysts in a manner proportional to hydrogen yields.

Subsequent research will examine items 1, 2 and 3 more fully. It will also evaluate quantitatively the utility of the theoretical model.

PREFACE

Under the terms of this contract, the experimental research related to catalyst definition and radiation testing was to be performed in the Physics Department at the Colorado School of Mines, Golden, and that relating to thin film preparation and electrical property measurements, pre and post-irradiation, was to be done in the Electrical Engineering Department at Colorado State University, Fort Collins.

Dr. Jerome G. Morse, adjunct associate professor of Physics at CSM, was the principal investigator of this project. He was assisted during the project's second year by Dr. Agnes Wang, research associate, CSM. Dr. Joel B. DuBow, assistant professor of electrical engineering at CSU was co-investigator on the project. He was assisted by Dr. R. Rajeshwar, visiting assistant professor of electrical engineering, Dr. V. R. Pai Verneker, research associate and Mr. P. J. Singh, graduate student at CSU.

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INTRODUCTION

Research on alternative production sources of hydrogen, particularly from non-fossil sources, continues to enjoy world-wide interest. Its use as a chemical feedstock for synthetic fuels and other industrial products, and as potential fuel itself, provide the basis of this interest.

Water is usually used as the starting material. Much of the reported research centers on thermochemistry, or chemically-sequenced "water-splitting" at elevated temperatures, and is reported under laboratory investigation in the United States, Japan, Germany, Italy and France. Many investigators use nuclear heat as thermal input to the process examined⁽¹⁾.

Alternatively, radiant energy is also used to sever the O-H bond, producing hydrogen and oxygen. Earlier work involved irradiating water at gamma and x-ray frequencies, and accomplished the splitting of the water molecule, but at low yield. Within the last decade, the radiation emphasis shifted to the ultraviolet and visible spectral regions, often coupled with heterogeneous catalysis. By selectively altering the oxidation state of the catalyst through radiant energy absorption, energy could be transferred to the water molecule enabling severance of its O-H bonds.

More recently, hydrogen generation has been studied in electrochemical cell configurations^(2,3). The parallel between heterogeneous and electrochemical approaches to hydrogen generation is both striking and suggestive. This parallel suggests the applicability of the electronic theory of catalysis, which was one of the starting points of the present study. The connection between catalytic hydrogen generation and charge transfer in electrochemical cell configuration was explained extensively in an earlier report and publication arising from this research⁽⁴⁾. The data obtained in the present program on oxide catalysts suggests that the electrochemical and catalytic approaches to hydrogen generation may be driven by the same physical mechanism. This mechanism supports an electronic theory of catalysis, although the details of this model

explained in another publication arising from this work differs from that proposed by Krylov and that described in our original proposal⁽⁵⁾.

The program described here involves production of hydrogen from water using gamma radiation and heterogeneous catalysis as the driving forces. Basic to this process is the verification of the electronic theory of catalysis requiring knowledge of the electronic properties of the catalyst prior to the irradiation. These properties involve the electron affinity and work function of the solid materials, and the properties of the Helmholtz and Gouy interfacial layers at the surfaces of wide band gap insulators used.

Treatment of the theoretical basis of the research and the experimental approaches used were described in our first progress report⁽⁶⁾. What follows is a description of the work performed during the period September 1, 1978 - August 1, 1979.

- (i) Selection of Suitable Catalyst Materials
- (ii) Irradiation Experiments
- (iii) Effects of Radiation on the Catalyst
- (iv) Measurements of the Electrical Properties of the Catalyst Before and After Use as a Catalyst
- (v) Correlation of the Change in Electrical Properties with the Catalytic Activity
- (vi) Explanation of the Observed Correlation in Terms of the Electronic Theory of Catalysis.

I. SELECTION OF SUITABLE CATALYST MATERIAL

One critical parameter which governs the selection of the catalyst material is its bandgap. Selected catalysts should have bandgaps larger than the energy needed to break the O-H bond. In addition to the appropriate bandgap, the band bending at the catalyst-liquid interface must be large enough to effectively separate the radiation generated $e^- - h^+$ pairs. Electron affinity, carrier mobility and lifetime in the selected catalyst material determine the extent and effectiveness of carrier separation. Electron affinities and work functions of these catalyst materials exhibit wide uncertainty bands. Research to better establish these values would significantly assist theoretical modeling of the catalytic process. A number of oxide materials were selected with the above considerations in mind. A partial listing of the selected

oxides of their electrical properties is presented in Tables 1 and 2. The selected oxides catalysts were used in the powder form both for measurement of catalytic activity and dielectric characterization. Powders have the major advantage of large surface area. However, they suffer from difficulty in their characterization in that average particle sizes and packing fraction are crucial variables which are often not well characterized. In addition any interpretation of the results obtained for powders is complicated by the effects of grain boundaries. Pressed pellets of powder samples will be employed in the next phase of the program to overcome some of these difficulties.

II. IRRADIATION EXPERIMENTS

More than 150 experimental runs were performed during this reporting period. These runs included calibration gases; water alone and containing 26 solid catalysts individually. The experimental procedures used were generally identical to those reported previously except as noted below, and a tabulation of all relevant data is given in Appendix A. The experimental setup is shown as Figure 1.

Appendix B treats (1) a review of the relatively minor experimental design changes; (2) a discussion of calibration and equipment problems.

Analysis of Results

The 154 runs performed yielded data that can be grouped into six curve types listed below and shown as Figures 2-6.

- A. Hydrogen yield is approximately constant.
- B. Hydrogen yield decreases gradually.
- C. Hydrogen yield increases gradually.
- D. An anomaly appears, usually at the beginning of a run.
 - a. Large maximum (only with antimony oxide)
 - b. Significant minimum somewhere in the run.

The curve types are noted in Table 3 which lists catalyst performance and also in Appendix A. With the exception of Da, (Sb_2O_3 runs) these types are not typical "water only" runs, or associated with certain oxides although types B and D_b were mostly from runs with solids. The appearance of the different curves could be explained by the different factors listed in

TABLE 1
COMPOUNDS WHICH DO NOT EXHIBIT SIGNIFICANT CHANGES
ON IRRADIATION (CLASS A)

Freq. (Hz)	unirr.	Capacitance (pF)		Resistance (ohms)	
		irr.	unirr.	irr.	
<u>TiO₂</u>					
10,000	7.26	7.37	2.0×10^{12}	1.5×10^{12}	
500,000	7.08	7.17	3.4×10^{13}	6.8×10^{13}	
<u>Nb₂O₅</u>					
10,000	13.1	11.9	2.1×10^{11}	3.4×10^{11}	
500,000	10.7	9.0	4.3×10^{12}	2.5×10^{12}	
<u>SiO₂</u>					
10,000	4.6	5.0	5.6×10^{14}	2.4×10^{14}	
500,000	4.6	5.1	2.8×10^{13}	2.6×10^{13}	
<u>MoO₃</u>					
10,000	10.0	9.6	6.2×10^{11}	6.0×10^{11}	
500,000	8.3	7.8	1.9×10^{12}	2.2×10^{12}	

TABLE 2
COMPOUNDS WHICH SHOW SIGNIFICANT
CHANGES ON IRRADIATION (CLASS B)

Freq. (Hz)	Capacitance (pF)		Resistance (ohms)	
	unirr.	irr.	unirr.	irr.
<u>SnO₂</u>				
10,000	25.6	11.5	1.6×10^{10}	12.3×10^{10}
500,000	9.4	5.9	3.2×10^{11}	12.3×10^{11}
<u>WO₃</u>				
10,000	62.6	12.0	4.7×10^{10}	399×10^{10}
500,000	49.9	12.0	1.7×10^{11}	280×10^{11}
<u>NiO</u>				
10,000	625.5	53.8	7.17×10^8	107×10^8
500,000	37.1	14.7	1.74×10^{10}	13×10^{10}
<u>SrTiO₃</u>				
10,000	16.2	12.4	3.6×10^{11}	47×10^{11}
500,000	14.9	12.3	6.3×10^{12}	29×10^{12}
<u>Sb₂O₃</u>				
10,000	6.9	7.1	3.5×10^{13}	1.5×10^{12}
500,000	7.0	6.5	1.7×10^{13}	9.2×10^{13}

Figure 1 — Experimental Setup

Figure 2. Curve Type A

Figure 3. Curve Type B

Figure 4. Curve Type C

Figure 5. Curve Type Da

Figure 6. Curve Type Db

TABLE 3 CATALYST PERFORMANCE

<u>Solid</u>	<u>Eg</u>	<u>Run No.</u>	<u>R.V.</u>	<u>Curve Type</u>	<u>Max.</u>	<u>Ave. of Longest Range</u>	<u>Notes</u>
V ₂ O ₅	2.3-2.5	28	8,9,10, or 11*	B	6,500	6,000	average base-line
V ₂ O ₅		32	8,9,10, or 11*	B	6,200	6,000	average base-line
V ₂ O ₅		128, 1977-1978	---		5,335.60	4,300	irradiated solids turned darker
WO ₃	2.8-2.9	33	*	B	6,900	6,400	
WO ₃	2.8-2.9	37	*	C	6,000	5,600	
WO ₃	2.8-2.9	82	6	C	5,100	4,800	
WO ₃	2.8-2.9	105	6	A	---	1,900	
In ₂ O ₃	2.8-3.8	27	*	C	5,800	5,600	
In ₂ O ₃	2.8-3.8	31	*	A	---	6,300	
In ₂ O ₃	2.8-2.8	134 1977-1978	---		4,742.80	4,000	
TeO ₂	3.0	112	8	B	3,000	2,700	
TeO ₂	3.0	152	8	B	3,500	2,700	
Dy ₂ O ₃	3.08 (593°K)	106	7	B	2,000	1,900	
Dy ₂ O ₃	3.08 (593°K)	111	7	Db	2,500	2,100	
Er ₂ O ₃	3.26 (653°K)	107	6	B	2,800	2,500	
Er ₂ O ₃	3.26 (653°K)	110	6	B	---	2,600	
Sb ₂ O ₃	3.3	12	*	Da	11,000	5,400	
Sb ₂ O ₃	3.3	16	*	Da	9,700	5,400	
Sb ₂ O ₃	3.3	18	*	Da	9,600	7,700	
Sb ₂ O ₃	3.3	123B	*	Da	4,900	2,600	average base-line value during this period is 2500 units

*Runs prior to #61 may have used Reaction Vessels 8, 9, 10 or 11 whose average baseline count is the 1st calibration period in 4940

<u>Solid</u>	<u>Eg</u>	<u>Run No.</u>	<u>R.V.</u>	<u>Curve Type</u>	<u>Max.</u>	<u>Ave. of Longest Range</u>	<u>Notes</u>
Sb_2O_3	3.3	127	7	Da	4,700	2,800	average baseline value during this period is 2500 units
Sb_2O_3	3.3	133 B	7	Da	4,900	2,900	average baseline value during this period is 2500 units
Sb_2O_3	3.3	147 B	7	Da	3,700	2,600	average baseline value during this period is 2500 units
Sb_2O_3	3.3	136 1977-1978	---		5,850.70	4,400	
TiO_2	3.3	11	*	B	7,400	7,200	
TiO_2	3.3	15	*	B	7,200	6,800	
TiO_2	3.3	131	2	E	5,200	3,100	average baseline value during this period is 2770
TiO_2	3.3	142	2	E	2,650	2,500	average baseline value during this period is 2770
TiO_2	3.3	120 1977-1978	---		5,091.71	4,600	
TiO_2	3.3	138 1977-1978	---		5,072.50	4,400	
ZnO	3.35	42	*	Db	5,000	4,300	
ZnO	3.35	45	*	Db	5,000	4,300	
Nb_2O_5	3.48	20	*	A	5,900	5,800	
Nb_2O_5	3.48	23	*	B	5,600	5,400	
MoO_3	3.66	26	*	A	6,500	6,400	
MoO_3	3.66	29	*	A	6,000	6,000	
MoO_3	3.66	121 1977-1978	---		4,589.40	4,300	
MoO_3	3.66	127 1977-1978	---		4,523.80	4,300	

<u>Solid</u>	<u>Eg</u>	<u>Run No.</u>	<u>R.V.</u>	<u>Curve Type</u>	<u>Max.</u>	<u>Ave. of Longest Range</u>	<u>Notes</u>
NiO	3.7	34	*	C	5,500	5,200	
NiO	3.7	38	*	F	5,800	5,200	
NiO	3.7	81	8	A	5,700	5,600	
SnO ₂	4.3	13	*	Db	5,100	4,800	
SnO ₂	4.3	17	*	C	6,800	6,200	
SnO ₂	4.3	19	*	C	7,000	6,800	
SnO ₂	4.3	22	*	C	5,000	4,800	
SnO ₂	4.3	122	8	B	3,600	3,000	average baseline counts during this period is 2560
SnO ₂	4.3	125B	8	A	---	2,700	average baseline counts during this period is 2560
SnO ₂	4.3	148 B	8	A	---	2,650	average baseline counts during this period is 2560
SnO ₂	4.3	130 1977-1978	--		6,643.60	4,600	
ZrO ₂	4.99	104	8	A	---	2,900	
ZrO ₂	4.99	108	8	C	2,750	2,500	
BaO	5.13	103	3	B	2,700	2,350	reacts with water
BaO	5.13	109	3	Db	2,350	1,850	
CeO ₂	5.5	77	3	B	4,700	4,000	
CeO ₂	5.5	83	3	db	4,700	4,000	
HfO ₂	5.55	78	4	A	4,000	3,800	
HfO ₂	5.55	84	4	B	3,700	3,600	
HfO ₂	5.55	131 1977-1978	---		6,221.90	6,000	
SrO	5.7	132B	11	A	---	2,500	some irradiated solid turned transparent

<u>Solid</u>	<u>Eq</u>	<u>Run No.</u>	<u>R.V.</u>	<u>Curve Type</u>	<u>Max.</u>	<u>Ave. of Longest Range</u>	<u>Notes</u>
SrO	5.7	132 B	11	A	---	2,600	
GeO ₂	5.5-6	140	9	E	2,500	2,400	
GeO ₂	5.5-6	146	9	E	3,000	2,300	
Sc ₂ O ₃	5.4-6.2	135	8	A	---	2,550	
Y ₂ O ₃	5.6	79	11	A	---	4,000	
CaO	7.7	21	*	B	6,700	6,000	reacts with water
CaO	7.7	25	*	B	6,600	6,000	
Al ₂ O ₃ - 3H ₂ O	8.7-9.9	40	*	C	5,500	4,800	
Al ₂ O ₃ - 3H ₂ O	8.7-9.9	43	*	F	4,000	3,600	
SiO ₂	8.4-11	41	*	F	6,400	5,500	irradiated solid turned blue-purplish
SiO ₂	8.4-11	80	10	C	4,800	4,700	
SiO ₂	8.4-11	86	10	A	---	3,100	
SrTiO ₃	3.4	35	*	B	7,200	6,800	
SrTiO ₃	3.4	39	*	B	7,300	6,800	
SrRiO ₃	3.4	120	3	B	3,400	3,000	average baseline counts during this period is 2910
SrTiO ₃	3.4	124 B	3	B	3,200	2,800	average baseline counts during this period is 2910
SrTiO ₃	3.4	137 B	3	B	3,300	3,000	
SrTiO ₃	3.4	144	3	B	3,200	2,600	
BaTiO ₃	3.3	150	2	C	2,800	2,350	

Runs 1-97	1st calibration period September 1, 1978 - March 26, 1979
Runs 98-116	2nd calibration period April 12, 1979 - April 30, 1979
Runs 117-154	3rd calibration period May 1, 1979 - June 8, 1979

Appendix B, such as "channeling" causing the dip in Type D_b, with evaporation contribution to the decreasing yield, shown as Type B.

Table 3 lists runs with solid oxides according to $E_g^{(7)}$ values except SrTiO_3 and BaTiO_3 which are listed at the end of the table. (All are listed in Appendix A). As seen in Table 5 the runs fall into three calibration periods. In the second calibration period (runs 98-116) all the values are equivalent to about two thirds of those found in the first period (runs 1 to 97). The third period (runs 117 to 154) are about 1.3 times the second.

As explained in App. B, about 50 runs using oxides were made before the differences in effect are catalytic performance caused by the reaction vessels was found. Therefore, it was necessary to redo water "baseline" runs. The average integrated count value of the four reaction vessels (8, 9, 10, or 11) with water in the first calibration period (see Table 5, Appendix B) was 4940. This was used as basis for comparison. Later in the third calibration period, the oxides that gave large increases over water runs were singled out for verification by testing with pure water runs, before and after using the same reaction vessel, as noted in the tables. The tables list the counts as taken directly from the integrator, rather than the differences between oxide runs and "water-only" runs. This was done because of the small differences between them.

Most oxide runs gave small increases in hydrogen yield over "water-only" runs. In view of necessary recalibrations and reaction vessel differences, reproducibility was difficult to establish. However, large maxima were always observed for Sb_2O_3 . There were suggestions of maxima for SnO_2 and SrTiO_3 . Although not reproducible, the increase in hydrogen when Sb_2O_3 was tested, was large in comparison with "water-only" runs, for example as seen in the runs 126 and 127.

Instrumentation delays precluded the testing of solids such as: V_2O_5 , In_2O_3 , TeO_2 , ZrO_2 . Those oxides studied repeatedly during the last month of the reporting period, namely, SrTiO_3 , BaTiO_3 , Sb_2O_3 , SnO and TiO_2 should be retested.

Conclusions of Irradiation Section

As stated previously, G-values for hydrogen generation for the catalytic systems studies were not tabulated. This was due in part to uncertainties in data based on calibration gas measurements, apparently arising from possible inhomogenities in the basic calibration gas mixture itself. The

effect may be manifest in concentration variations as the gases diffused through the valving apparatus. The certainty of this assumption is based only on the experimental results obtained. Further, the additive nature of hydrogen yield was not found, although expected, when the calibration gas mixture was used as a transport gas through water under irradiation conditions.

Another contributor to experimental error is the possibility that hydrogen, either from the calibration gas or that generated in the irradiation experiment, has the opportunity to combine with N_2 forming ammonia, albeit in small yield. To eliminate this uncertainty, the next phase of experimentation should consider replacing nitrogen with argon.

The cause of yield increase with Sb_2O_3 needs further investigation. It is obviously not due to its E_g value alone, as other oxides with similar E_g values produced dissimilar results. Antimony oxide does have limited solubility in water, with the solution slightly alkaline⁽⁸⁾, but other solids used have the same characteristics. Also, pH value does not play a role in the hydrogen yield of radiolysis of water⁽⁹⁾. Further investigation of this material will be accomplished in the next phase of this project. The semiconductor characterization part of the program yielded results which indicate that the electron affinity plus the Fermi energy referred to the conduction band edge should equal the redox potential of the electrolyte solution (water, in this case). Thus understanding the water-oxide configuration will enable us to address the catalyst coal slurry systems as well as others of interest.

III. EFFECT OF RADIATION ON THE CATALYST

When subjected to gamma radiation the catalyst material will undergo some changes. These changes may be classified by the nature of their relaxation characteristics.

(i) The radiation may lead to ionization and excitation of the crystal lattice which disappears when the radiation is stopped.

(ii) The incident radiation may displace atoms and these effects may persist long after irradiation has stopped but can easily be thermally annealed.

(iii) Defects caused by chemical conversions induced by radiation in

the solid such as decomposition of salts etc.

In addition the radiation can lead to changes in the surface, e.g. imperfections, which may participate actively in adsorption and catalytic processes. The types of defects produced by radiation depends on the energy of the incident radiation. When gamma rays of energy larger than 1 Kev are incident on the solid, the electrons carry away a large fraction ($\sim 99\%$) of the incident energy as kinetic energy. The energized particles are able to knock out atoms from their sites in the lattice which can lead to Frenkel and/or Schottky defects. Even though the energy needed for lattice disruption is of the order of a few Kev, a very high energy electron is needed to supply the required energy to the lattice due to the large disparity in the masses.

The creation of radiation defects in the semiconductor is accompanied by changes in the equilibrium concentration of charge carriers, due to the carriers being trapped by defects or ionization. These charge carriers may be trapped by surface centers and recombine there in the vicinity of an adsorbed molecule, the energy released being thereby given to the molecule. If this energy is more than the bond energy of O-H bond, this bond may be broken leading to evolution of hydrogen.

Gamma irradiation induces defect levels in the oxide semiconductor catalysts⁽¹⁾. However, proper doping of the oxide can minimize the effect of these defects, especially on powder catalysts. Thus it may be possible to develop suitably doped long lived catalysts as well as regenerate catalysts after irradiation⁽²⁾. However, a separate study of the affect of gamma-irradiation or diffusion lengths in oxide semiconductor is necessary to answer given questions concerning oxide lifetimes and possible regeneration.

IV. MEASUREMENT OF THE ELECTRICAL PROPERTIES OF THE CATALYST BEFORE AND AFTER USE

A study of the change in the dielectric properties of the selected catalysts on gamma ray irradiation was carried out using the Dynamic Dielectric Analysis (DDA) technique⁽⁶⁾. This technique, the associated problems and their solutions has been described in a previous report. One major problem encountered is the strong dependence of the dielectric properties on the packing fraction. Use of pressed powder pellets should lead to

elimination of this problem because pellets with very high packing fractions (>90%) can be made.

The dielectric properties were investigated with a view to obtain a correlation between the changes in the dielectric properties of these materials upon irradiation and their effectiveness as catalysts in the radiation assisted decomposition of water. The change in the dielectric properties of the different catalyst materials (oxides) investigated can be classified as:

a) compounds which do not exhibit significant change in dielectric properties on gamma ray irradiation (class A - Table 1),

b) compounds which show significant change in dielectric properties upon gamma ray irradiation (class B - Table 2).

The term "significant" denotes a change in capacitance and resistance values of at least a factor of four and an order of magnitude respectively. Statistical variations in the results obtained for several runs were taken into account to determine whether the observed changes on gamma irradiation are "real". These results are shown in Tables 1 and 2. Upon examination of the data for all compounds that show significant radiation effects, it is seen that the capacitance value decreases and the resistance value increases upon irradiation. Increased defect incorporation into the oxide lattice structure upon gamma ray irradiation presumably accounts for these changes.

V. CORRELATION OF THE CHANGES IN ELECTRICAL PROPERTIES WITH THE CATALYTIC ACTIVITY

The results obtained from dielectric measurements on powder samples are complicated by their strong dependence on packing fraction and the effects of grain boundaries etc., which do not permit unequivocal assignment of the observed changes to a particular mechanism or mode. In spite of the above difficulties, certain correlations become apparent upon critical examination of the experimental results.

A correlation between the catalytic activity as determined by the experiments performed at Colorado School of Mines and the changes in the dielectric properties measured at Colorado State University is shown in Figure 7. This correlation is at best one of the first order. This

Figure 7. Correlation of Relative Changes in Capacitance, C, (Dielectric Constant) and Resistance, R, (Resistivity) with Changes in Relative Hydrogen Yield, H.

correlation is based on data on a limited number of oxides and runs per oxide. The catalytic activity of a number of oxides which belong to class B is not available at present. One would expect from the dielectric data, that materials such as NiO , SrTiO_3 , and WO_3 would also exhibit good catalytic activity. It is significant that materials such as TiO_2 and MoO_3 , which have been found to exhibit poor activity in the gamma ray assisted splitting of water, also show insignificant changes in their dielectric properties upon irradiation (see Table 1). These results indicate a relationship between the changes in the dielectric properties of the catalyst and its catalytic activity. A conclusive correlation between the dielectric and catalytic properties of the oxide catalysts must await further experiments.

VI. EXPLANATION OF THE OBSERVED CORRELATION IN TERMS OF THE ELECTRONIC THEORY OF CATALYSIS

Heterogeneous catalysis encompasses the phenomenon of enhancement of the rates of chemical conversions in fluids by the presence of solid surfaces which are called catalysts. The key step for many catalytic processes is the surface diffusion of chemisorbed reactants and subsequent surface reaction. The electronic approach to the understanding of catalysis in solids seeks a relationship between the catalytic activity and the bulk electronic properties of the solid. However, uniquely surface properties such as surface state density, surface potential and band bending may make this correlation with purely bulk properties difficult. This is explained in more detail in the theoretical model described in an earlier project report⁽⁶⁾. Measurements of electrical conductivity have established that the chemisorption of gases and vapors on semiconductors is accompanied by electron transfer from the semiconductor to the chemisorbed gas or vice versa, or by localization of the charge carriers of the semiconductor between the gas and the semiconductor surface. The direction of this change is an indication of the direction of electron transfer.

The model proposed for the gamma ray assisted decomposition of water in the presence of a catalyst is based on dipolar interaction between the adsorbed molecules and the oxide lattice leading to the formation of a chemisorbed layer $\text{MO} \cdots \begin{array}{c} \text{H} \\ \diagup \\ \text{H} \end{array} \text{O}$ groups in the oxide/water interfacial region (i.e. Helmholtz layer). Gamma ray irradiation produces electrons which are excited into the conduction band of the oxide. These electrons, upon subsequent recombination with the valence band holes, can emit photons of

energy equal to the bandgap of the catalyst material. The bandgap must theoretically exceed the O-H bond dissociation energy for hydrogen evolution to take place. The O-H bond dissociation energy is ~ 5.0 eV as calculated from the heat of dissociation of H_2O . The overall mechanism is shown in Figure 8.

The electrostatic aspects are illustrated in Figure 9. Various reaction mechanisms are shown in Figure 10.

Another experimental result that lends support to the proposed model is that the hydrogen yield is maximized when the energy gap of the catalyst used equals the bond energy of the bond to be broken.

Figure 8. Physical Model of Tunneling-Limited Charge Transfer at the Oxide-Electrolyte Interface.

Activated Complex

(b)

Figure 9. (a) Free Carrier Generation Using Gamma Rays and Subsequent Radiative and Non-Radiative Transitions in Ionized Water.
 (b) Physical Model of Activated Charge Transfer Complex Formation at the Surface of Oxide Catalysts.

Figure 10. Possible Reaction Mechanisms

SUMMARY AND CONCLUSIONS

During this contract period a detailed but preliminary investigation was made concerning the radiation induced synthesis of hydrogen using oxide catalysts. The gamma radiation utilized simulates an environment of neutron-shielded reactor wastes. Success in this effort would allow for a useful outlet for the spent fuel from nuclear reactors during the initial temporary storage phase.

The primary accomplishments of this contract period were an improved theoretical understanding of the radiation induced hydrogen generation, developing a data base on oxide semiconductors useful for hydrogen generation, and a correlation of hydrogen yield with changes in the dielectric constitutive parameters of these oxides. A technique was developed to ascertain the temperature dependent dielectric properties of the oxides in solid as well as in powder form.

Efforts were concentrated on the generation of hydrogen to the temporary exclusion of methane synthesis for a number of reasons. A body of literature in this area and understanding of the materials problems is available. More importantly, it was felt that focusing efforts on understanding the hydrogen problem, and obtaining an understanding of this problem, would enable the understanding obtained for this simpler system to be applied to other radiation-initiated reactions. Finally, with recent renewed interest in hydrogen generation, it was felt that a comparison of radiation-induced hydrogen generation with ultraviolet and visible induced hydrogen generation would be most useful.

Setting up high sensitivity radiation-induced hydrogen yield experiments, developing automated dielectric analysis measurement apparatus for powders and films, and understanding the device aspects of hydrogen generation occupied the bulk of the past program. Preliminary data were obtained concerning hydrogen yield and changes induced in the oxide semiconductor catalyst under irradiation. The theoretical understanding obtained in this work was applied to selection of oxides and will be further expanded and utilized in subsequent contract periods. Preliminary results demonstrate that oxide semiconductors can catalyze the decomposition of water in a gamma radiation environment. Moreover, gamma radiation does change the constitutive electrical properties of these oxides in a manner proportional to hydrogen yields.

Data concerning hydrogen yield under irradiation conditions were hampered by the trade off between absolute hydrogen yield and interpretation of changes in oxide properties. Solid oxide films or pellets provide more consistent changes and interpretation of changes of electrical properties under irradiation. However, the surface area of these films and pellets is much smaller than powder samples so that hydrogen yields are correspondingly reduced. This small surface area has made precision acquisition of radiation induced yields difficult. The use of tracer gases in the calibration mixture would have helped this. Similarly, lack of precise knowledge of certain key properties such as work function or electron affinity made it difficult to fit the theory to the model. It might have been useful to fabricate test structures which would assist in elucidating some of these critical properties.

Subsequent work will attempt to quantify the results obtained in the early contract period as well as compare various visible, ultraviolet, and radiation induced hydrogen yields. Finally, work is needed to quantitatively evaluate the utility of the theoretical model by obtaining work function, energy gap, and transport properties of the substrates. The preliminary framework needs to be evaluated to properly assess the utility of radiation-induced hydrogen generation or production of other useful materials by using gamma radiation.

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TABLE 4

APPENDIX A

Data Summary

Water: Ricca (unless otherwise stated)

Flow Rate: 50 ml/min unless otherwise stated

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
1	A	--	#1	---	---	2,580	physics water flow rate 60 ml/min
2	D _b	--	#1	3,300 (hrs. 5-10)	2,900 (hrs. 0-4)	3,100	chemistry water 60 ml/min
3	A	--	#1	not long --- ---	enough --- ---	5,200 6,200	60 ml/min 50 ml/min 40 ml/min
3 ¹	A	--	#1	---	---	6,000	44 ml/min
4	A	--	#1	not long 5,900 (hrs. 6-11)	enough --- ---	5,700	chemistry water 40 ml/min 50 ml/min
5	Da	--	#1	12,000 (hrs. 0-5)	---	5,300	physics water 50 ml/min
5 ¹	B	--	#1	8,000	---	7,500	40 ml/min
6	E	--	#1	7,600 (hrs. 17-22)	6,500 (hrs. 0-5)	7,200	physics water low calibra- tion gas into water
7	A	--	--	---	---	800	low calibra- tion gas only
8	A	--	#1	---	---	5,200	physics water
9	A	--	#1	---	---	5,500	chemistry water
10	a	--	#1	---	---	4,800	
1	B	TiO ₂	--	7,400 (hrs. 3-7)	6,500 (hrs. 18-22)	7,200	
12	Da	Sb ₂ O ₃	--	11,000 (hrs. 10-15)	4,700 (hrs. 20-23)	5,400	

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
13	Db	SnO ₂	--	5,100 (hrs. 0-5)	---	4,800	
14	Db	--	#1	5,800 (hrs. 10-15)	5,500 (hrs. 19-23)	5,700	flowrate: 60 ml/min
15	B	TiO ₂	--	7,200 (hrs. 2-6)	6,300 (hrs. 16-22)	6,800	
16	Da	Sb ₂ O ₃	--	9,700 (hrs. 0-5)	---	5,400	
17	C	SnO ₂	--	6,800 (hrs. 18-23)	5,700 (hrs. 7-10)	6,200	
18	Da	Sb ₂ O ₃	--	9,600 (hrs. 0-5)	---	7,700	
19	C	SnO ₂	--	7,000 (hrs. 17-22)	6,000 (hrs. 0-4)	6,800	
20	A	Nb ₂ O ₅	--	5,900 (hrs. 4-7)	---	5,800	
21	B	CaO	--	6,700 (hrs. 0-5)	5,300 (hrs. 19-23)	6,000	
22	C	SnO ₂	--	5,000 (hrs. 7-22)	4,300 (hrs. 0-4)	4,800	
23	C	Nb ₂ O ₅	--	5,600 (hrs. 18-23)	5,000 (hrs. 1-5)	5,400	
24	B	--	#1	5,700 (hrs. 0-5)	5,500 (hrs. 15-20)	5,600	
25	B	CaO	--	6,600 (hrs. 1-6)	5,600 (hrs. 17-22)	6,000	
26	A	MoO ₃	--	6,500 (hrs. 0-5)	---	6,400	
27	C	In ₂ O ₃	--	5,800 (hrs. 18-23)	5,200 (hrs. 3-7)	5,600	
28	B	V ₂ O ₅	--	6,500 (hrs. 0-5)	5,500 (hrs. 19-23)	6,000	
29	A	MoO ₃	--	---	---	6,000	
0	Db	--	#1	7,300 (hrs. 1-5)	5,800 (hrs. 20-24)	6,500	

<u>No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
31	A	In ₂ O ₃	--	---	---	6,300	
32	B	V ₂ O ₅	--	6,200 (hrs. 0-5)	5,500 (hrs. 16-20)	6,000	
33	B	WO ₃	--	6,900 (hrs. 0-5)	6,000 (hrs. 18-22)	6,400	
34	C	NiO	--	5,500 (hrs. 19-24)	3,900 (hrs. 0-4)	5,200	
35	B	SrTiO ₃	--	7,200 (hrs. 1-6)	6,300 (hrs. 18-22)	6,800	
36	B	--	#1	6,900 (hrs. 1-5)	6,600 (hrs. 19-23)	6,800	
37	C	WO ₃	--	6,000 (hrs. 0-5)	4,500 (hrs. 0-4)	6,600	
38	F	NiO	--	5,800 (hrs. 1-5)	4,200 (hrs. 10-15)	5,200	
39	B	SrTiO ₃	--	7,300 (hrs. 1-6)	6,500 (hrs. 19-23)	6,800	
40	C	AL ₂ O ₃ ·3H ₂ O	--	5,500 (hrs. 18-22)	3,700 (hrs. 1-5)	4,800	
41	F	SiO ₂	--	6,400 (hrs. 1-6)	4,000 (hrs. 11-12)	5,500	
42	Db	ZnO	--	5,000 (hrs. 1-6)	3,600 (hrs. 18-22)	4,300	
43	F	AL ₂ O ₃ ·3H ₂ O	--	4,000 (hrs. 16-21)	3,000 (hrs. 6-10)	3,600	
44	Db	--	#1	6,700 (hrs. 0-5)	5,770 (hrs. 20-24)	6,200	
45	Db	ZnO	--	5,000 (hrs. 1-6)	3,700 (hrs. 18-22)	4,300	
46	A	--	--	---	---	17,000- 18,400	calibration gas 496 ppm H ₂
47	A	--	--	---	---	17,400	calibration gas leaked after this run
48	--	--	#1	---	---	---	≠

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
49	A	--	#1	---	---	7,500	≠
50	E	--	#1	---	---	5,400	
51	F	--	#2	6,300 (hrs. 20-24)	3,200 (hrs. 3-4)	6,000	
52	E	--	#1	---	---	6,400	
53		SiO ₂	--				≠
54	A	--	#2	---	---	4,000	
55	A	--	#2	---	---	4,400	erratic
56	C	--	#1	---	---	7,200	erratic
57	A	--	#1	---	---	7,200	
58	F	--	--	---	---	16,800	(calibration gas 550 ppm H ₂ in N ₂)
59	A	--	#1	---	---	22,800	calibration gas 550ppm H ₂ into water
60	C	--	#2	---	---	18,800	high calibration gas in water
61	A	--	--	---	---	14,000	
62	F	--	#3	---	3,100 (hrs. 5-6)	4,100	
63	Db	--	#4	4,000 (hrs. 2-3)	2,700 (hrs. 13-14)	3,400	
64	F	--	#5	---	3,800 (hrs. 1-3)	6,500	
65	F	--	#6	---	2,300 (hrs. 4-5)	4,000	
66	F	--	#7	---	3,000 (hrs. 8-9)	3,800	
67	B	--	#8	---	---	4,200	
68	B	--	#5	6,300 (hrs. 1-5)	5,400 (hrs. 20-23)	5,800	
69		--	#1	irregular			≠

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
70	C	--	#8	---	---	4,400	
71	E	--	#9	6,600 (hrs. 15-19)	beginning	6,300	
72	--	--	#10	---	---	---	#
73	A	--	--	---	---	14,400	Calibration gas 550ppm
74	B	--	#9	5,200 (hrs. 1-6)	---	4,800	
75	B	--	#10	5,600 (hrs. 1-6)	---	5,000	
76	A	--	--	---	---	14,600	Calibration gas 550ppm H ₂ in N ₂
77	B	CeO ₂	#1	4,700 (hrs. 1-7)	3,700 (hrs. 18-22)	4,000	
78	A	HfO ₂	#4	3,000 (hrs. 10-24)	3,400 (hrs. 7-11)	3,800	
79	A	Y ₂ O ₃	#11	---	---	4,000	
80	C	SiO ₂	#10	4,800 (hrs. 18-23)	4,300 (hrs. 1-5)	4,700	
81	A	NiO	#8	5,700 (hrs. 18-23)	5,300 (hrs. 1-5)	5,600	
82	C	NO ₃	#6	5,100 (hrs. 1-5)	---	4,800	
83	Db	CeO ₂	#3	4,700 (hrs. 1-7)	3,100 (hrs. 16-20)	4,000	
84	B	HfO ₂	#4	3,700 (hrs. 0-4)	---	3,600	
85	A	--	--	---	---	600	calibration gas 45.7ppm H ₂ in N ₂
86	A	SiO ₂	#10	---	---	3,100	erratic
87	C	NO ₃	#6	---	---	3,600	erratic
88	--	Y ₂ O ₃	#3	---	---	---	erratic
89	A	--	#8	---	---	6,400	curve smooth (too high)

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
90	A	NO ₃	#6	---	---	---	erratic
91	C	--	#3	---	---	6,400	curve smooth (too high)
92	A	--	--	---	---	3,600	too high
93	A	--	--	---	---	16,000	high
94	A	--	--	---	---	13,000 - 14,000	erratic after column was baked
95	--	--	#1	---	---	---	erratic after baking column
96	A	--	#3	---	---	8,000	high slow flow rate
97	--	--	#1	---	---	---	erratic
98	A	none	#3	---	---	1,750	
99	A	none	#3	---	---	6,500	high calibration gas only
100	A	none	#3	---	---	8,800	high calibration gas into water
101	A	none	#3	---	---	2,450	
102	C	none	#8	---	---	2,100	
103	B	BaO	#3	2,700 (hrs. 0-5)	2,100 (hrs. 15-20)	2,350	sloping down
104	A	ZrO ₂	#8	---	---	2,900	
105	A	NO ₃	#6	---	---	1,900	some scattering
106	B	Dy ₂ O ₃	#7	2,000 (hrs. 0-5)	1,700 (hrs. 15-20)	1,900	some scattering
107	B	T ₂ r ₂ O ₃	#6	2,800 (hrs. 0-5)	2,250 (hrs. 19-23)	2,500	
108	C	ZrO ₂	#8	2,750 (hrs. 15-20)	2,150 (hrs. 0-5)	2,500	sloping up

From run 87 to 97 the thermister had abnormal performance.

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
09	Db	BaO	#3	2,350 (hrs. 1-6)	1,850 (hrs. 19-23)	1,850	sloping down
110	B	Er ₂ O ₃	#6	---	---	2,600	flow interrupted
111	Db	Dy ₂ O ₃	#7	2,550 (hrs. 0-5)	2,000 (hrs. 18-22)	2,400	sloping down
112	B	TeO ₂	#8	3,000 (hrs. 0-5)	2,350 (hrs. 14-18)	2,700	sloping down
113	H-	none	#1	---	---	irregular	flow ≠ interrupted
114	B	none	#7	---	---	2,000	some scatterin
115	A	none	#2	2,500 (hrs. 15-20)	2,300 (hrs. 1-5)	2,500	
116	--	none	#6	scattering			≠
117	A	none	none	---	---	8,500	high cali- bration gas (low cali- bration gas used also)
118	F	none	#3	2,900 (hrs. 1-2)	500	irregular	goes through a big dip ≠
119	A	none	#3	---	---	3,200	
120	B	SrTiO ₃	#3	3,400 (hrs. 0-5)	2,600 (hrs. 19-23)	3,000	
121	A	none	#8	---	---	2,600	
122	B	SnO ₂	#8	3,600 (hrs. 0-4)	2,700 (hrs. 18-22)	3,000	(high calib- ration gas)
123 A	A	none	#7	---	---	2,500	
123 B	B	Sb ₂ O ₃	#5	4,900 (hrs. 0-5)	2,350 (hrs. 19-23)	2,600	
124 A	A	none	#3	---	---	3,150	
124 B	B	SrTiO ₃	#3	3,200 (hrs. 0-4)	2,600 (hrs. 19-23)	2,800	
125 A	A	none	#8	---	---	2,600	
125 B	A	SnO ₂	#8	---	---	2,700	

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
126	B	none	#7	2,800 (hrs. 0-5)	2,450 (hrs. 19-23)	2,700	
127	Da	Sb ₂ O ₃	#7	4,700 (hrs. 0-5)	2,750 (hrs. 19-23)	2,800	
128	A	none	#2	---	---	2,850	
129	F	none	#3	3,000 (hrs. 19-23)	2,000 (hrs. 7-10)	2,800	through a dip
130	F	SrTiO ₃	#3	3,400 (hrs. 0-2)	600 (hrs. 3-6)	---	sloping down at beginning (high & low calibration gas)
131	E	TiO ₂ (A)	#2	5,200 (hrs. 0-1)	2,000 (hrs. 15-25)	3,100	through a dip after max at beginning
132 A	E	none	#11	---	---	700	irregular
132 B	A	SrO	#11	---	---	2,500	
133 A	A	none	#7	---	---	2,450	
133 B	Da	Sb ₂ O ₃	#7	4,900 (hrs. 0-5)	2,900 (hrs. 18-22)	2,900	sloping down
134	C	none	#8	2,800 (hrs. 18-22)	2,500 (hrs. 2-6)	2,600	
135	A	Sc ₂ O ₃	#8	---	---	2,550	
136	E	--	#9	2,600 (hrs. 12-16)	1,500 (hrs. 1-3)	2,450	through a dip at beginning
137 A	A	none	#3	---	---	2,700	
137 B	B	SrTiO ₃	#3	3,300 (hrs. 0-4)	2,850 (hrs. 18-22)	3,000	
138	A	none	#11	---	---	2,750	(high + calibration gas)
139	A	SrO	#11	---	---	2,600	
140	E	GeO ₂	#9	2,500 (hrs. 0-1.5)	1,000 (hrs. .5-5)	2,400	sloping down rapidly at beginning
141	E	none	#2	2,900 (hrs. 19-23)	2,100 (hrs. 1-3)	2,700	through a dip at beginning

<u>Run No.</u>	<u>Curve Type</u>	<u>Solid</u>	<u>R.V.*</u>	<u>Max.</u>	<u>Min.</u>	<u>Ave. of Longest Range</u>	<u>Note</u>
142	E	TiO ₂	#2	2,650 (hrs. 16-20)	2,150 (hrs. 1-4)	2,500	
143	E	none	#3	2,700 (hrs. 18-22)	1,750 (hrs. 1-3)	2,600	dip at beginning
144	B	SrTiO ₃	#3	3,200 (hrs. 0-4)	2,200 (hrs. 18-22)	2,600	
145	C	none	#9	2,200 (hrs. 15-20)	800 (hrs. 1-5)	2,150	
146	E	GeO ₂	#9	3,000 (hrs. 0-.15)	1,600 (hrs. 2-3)	2,300	dip in the beginning
147 A	A	none	#7	---	---	2,300	
147 B	Da	Sb ₂ O ₃	#7	3,700 (hrs. 0-4)	2,500 (hrs. 13-16)	---	sloping down (high calibration gas)
148 A	A	none	#8	---	---	2,350	
148 B	A	SnO ₂	#8	---	---	2,650	
149	E	none	#2	2,800 (hrs. 18-22)	2,100 (hrs. 1-3)	2,750	
150	C	BaTiO ₃	#2	2,800 (hrs. 16-20)	2,150	2,350	
151	E	none	#8	---	---	2,700	
152	B	TeO ₂	#8	3,500 (hrs. 0-5)	2,300 (hrs. 19-23)	2,700	sloping down
153 A	A	none	#3	---	---	8,500	high calibration gas
153 B	F	none	#3	through a big dip		11,100	high calibration gas in water
154	--	Sb ₂ O ₃	#7	0	0	0	no water

*Reaction Vessel ≠ considered bad runs

Runs 1-97: First calibration period. From start to 3/26/79

Runs 98-116: Second calibration period 4/12/79 - 4/30/79 approximately 2/3 efficiency as 1st period

Runs 117-154: Third calibration period. 5/1/79 - 6/8/79 approximately 1 1/3 efficiency as 2nd period.

APPENDIX B

1. Review of experimental design changes.

The experimental design and procedures used followed closely that of the first report with some minor changes.

a. Water: Three kinds of water were tested (runs 1-10). De-ionized water was obtained from the same source as that used in the first report (about 2 megohms resistivity); doubly distilled water from the CSM Physics Department; reagent grade water from the Ricca Company (Ricca Chemical Company, Arlington, Texas, 76011). "Water, de-ionized, Reagent grade, specially purified to be free from organic and inorganic impurities, suitable for APHA, AOHA, and ACS tests, atomic absorption analysis, etc. For laboratory use only." Lot No. H032). The differences observed using the three water sources seemed to contribute smaller variations in the hydrogen production than some other factors. To eliminate this variable, all runs starting with No. 11 used Ricca water.

b. Large samples: To obtain the relatively larger quantities of irradiated solids needed for dielectric properties measurements, standard reaction vessels were loaded with approximately 2-3 grams of catalyst in 100 ml. of water. Nitrogen flowed through suspended solids via the porous frit, as before, during radiation exposure. The outlet gas from the reaction vessel exited directly into the atmosphere after passing through the flow meter. Hydrogen output was not measured. The flow rate was measured only at the beginning and the end of the runs (50 ml/min.).

c. Experimental runs: A procedural change was the addition of solid to the reaction vessel at the outset rather than after the flow rate was adjusted. Thus the flow rate and the flushing out of air from the system needed to be done only once.

d. Water evaporation reduction: It had been planned to put a washing bottle in the N_2 line before the carrier gas entered the reaction vessel in the gamma-cell, to compensate for evaporation. This was not done as it was found later than evaporation was less of a problem than feared earlier (about 10 percent maximum).

2. Calibration and equipment problems.

a. The calibration gas: As stated in the first report, two calibration gases were used: The low calibration gas contained 45.7 ppm hydrogen in nitrogen; and high calibration gas contained 550 ppm hydrogen in nitrogen. Both were used for a number of runs dry to calibrate the GC and then bubbled through water in the reaction vessel housed in the gamma-cell. Both were used periodically for brief periods to check the instrument and the system. (Note: A run is defined when the reaction vessel and its contents were irradiated for approximately 24 hours, and each run was assigned a number.) During the year it became evident that the calibration gases could be relied on for this purpose only and not to be used to calculate the G-value. This was discussed earlier.

Tabulation of data obtained in the high and low calibration gas runs is shown in Table 5.

The large change in values found after April 12, 1979 and May, 1, 1979 are due to replacement of thermistors in the GC, and retightening of loose electrical connectors, resulting in three sets of calibration data.

Rapid loss of counts between runs 58 (1/8/79) and 61 (1/11/79) may indicate that hydrogen in the calibration gas separated from nitrogen (gas diffusion) rather than remaining uniformly distributed in the gas mixture. Thus, the calibration value listed in the earlier report represents the integrated hydrogen values of the high and low calibration gases during that particular period of time. Hence the absolute value of hydrogen production, or the G-value based on those calibration runs becomes less certain because of variations in absolute hydrogen values. In view of this uncertainty, this report discusses only the difference between the hydrogen production as represented by the counts from the integrator, of the runs in the presence of solids and those in their absence.

The calibration gases were also used weekly to check instrument reproducibility, and with greater frequency during the period when the thermistor indicated degraded GC performance (runs 92, 93, and 94 and numerous short periods between February 20 and April 12, 1979). We define reproducibility in terms of retention time of the gas in the column and integrated counts.

b. Flow rate: Nitrogen flow was set at the beginning of a run and

TABLE 5
CALIBRATION GAS RUNS

High Calibration Gas (550 ppmH₂ in N₂)

<u>Run No.</u>	<u>Counts</u>	<u>Notes</u>
58*	16,400-18,000	Erratic
59*	av. 22,500	Erratic through water in R.V. #1
60*	18,800	Through water in R.V. #2
61*	14,000	
73*	14,200	
76*	14,600	After baking column at 120°C
93*	16,000	#93 and #94 are during time thermister failed
94*	13,000-14,000	After baking column at 350°C, the calibration gas was used extensively to check instrument
99**	6,500	
100**	8,800	Through water in R.V. #3
117**	8,500	After runs #122, 130, 137 and 146, all av. 8, v0
153 A***	8,500	
B***	11,000	Through water in R.V. #3

Low Calibration Gas (45.8 ppm H₂ in N₂)

<u>Run No.</u>	<u>Date</u>	<u>Counts</u>	<u>Notes</u>
6*	9/27/78	7,200	Through water in R.V. #1
7*	9/28/78	800	Used weekly to check instrument
85*	2/12/79	600	Erratic
92*	2/23/79	3,600	The instrument was in disorder. Used extensively before 4/12/79. 325-350 between 4/12/79 and 5/1/79 #117 After 5/2/79 av. 447; dropped to av. to 378 later.

Comparison with Prior Runs (1977-1978)

102	769.4
103	894.0
112	797.0

- * 1st Calibration period 9/78 - 8/79
- ** 2nd Calibration period 4/12/79 - 4/30/79
- *** 3rd Calibration period 5/1/79 - 6/8/79

checked at the end, usually about 24 hours later. On occasion a change in flow was noted at the end of a run. This could be attributed to variation in the flow controller devices: two stage gas regulator, needle valve, micrometer and a buffering effect of the gas-liquid-solid system in the reactor vessel. It could also be due to the variation of the barometric pressure during the day. Variations in flow rate do not normally exceed ± 2.5 ml/min. (The flow meters are graduated in 5 ml/min. divisions; a reading such as 48 or 52 is an interpolated value) representing only a $\pm 5\%$ variation in the flow rate. This is not enough to account for occasional large variations in the baseline data on changing reaction vessels.

Hydrogen yield, measured in integrated counts, is sensitive to changes in flow rate. Run #3, for example, showed at 50 ml/min, 5200; at 40 ml/min, it was 6200, indicating the importance of proper flow control. The addition of a needle valve to the calibration gas tank regulator greatly facilitated the adjusting of calibration gas flow rate.

c. Reaction Vessel (Figure 11): Before January, 1979 only one reaction vessel was used to do the "water only" (baseline) runs, and use of this reaction vessel was limited to this purpose. When the baseline with this reaction vessel kept rising, and with the realization that the transport gas actually went through a "scrubbing action" to transport the hydrogen produced in the reaction vessel, thus creating a different bubble pattern, other reaction vessels were tested. It was found that different vessels indeed make a difference for the hydrogen measured. For example, five new reaction vessels (before using them for solids) were used to irradiate water in consecutive runs, 62 to 66; the counts were, 4100, 3400, 6500, 3800 respectively. When the reaction vessel producing the high count, approximately 6500 counts, was tested again (run 68), it gave the same result. Probably the frit texture of this particular reaction vessel made the best bubble size or pattern for scrubbing; the reverse may be true of the reaction vessel with the 3400 count. Later, those vessels giving especially high or low counts were used only for larger samples used in dielectric measurements. The more "dependable" ones were used for our experimental runs. Even so, on occasion the counts would change in the middle of a water-only experiment, noted in run 129 (type F) where a large minimum resulted, which later "bounced back" to the starting level. This effect can be magnified when

Figure 11. Radiation Vessel

solids are used. This may be attributed to the creation of a channel in the suspended solid causing more rapid passage of the transport gas, thus minimizing the gas-liquid contact and the amount of hydrogen carried out. It is suspected that the count rate became normal only after the channel broke up.

With the same vessel the baseline also varied from time to time, perhaps indicating a change in the flow pattern. This change may be attributed to frit clogging through capturing small particles, despite careful efforts to remove them after each run by dissolving the solids or back-flushing.

Sixty one runs had been made before these differences in reaction vessels were noted. In the last series of runs, (#117 to #154) each run containing solids was performed between two "water only" runs using the same vessel to isolate this effect. By then it became evident that the difference in the baseline from each vessel was significant when compared with the slight increase of hydrogen production in the presence of the solids. Comparative data on reaction vessel performance are given in Table 6.

d. The column: It was feared that moisture may escape from the indicating Drierite tube, enter the molecular sieve column in the GC and thus reduce column performance. Although the data did not show a decay of the column, the irregular nature of the baseline data suggested baking the column to remove any moisture that might exist. This was done between 1/29/79 and 1/30/79 at 120°C for 24 hours with nitrogen flowing through it at a higher rate than usual (20 ml/min.) The condition of the column was tested following baking. Satisfactory performance was noted in calibration runs #73 (prior to baking -- 14,200) and #76 (after baking -- 14,600).

Later when the system continued to show irregular performance, the column was baked in an oven external to the instrument at 325°C for three hours, at the suggestion of the Carle Instrument Company. Tests on the GC showed that this did not correct the problem. When the thermistors were changed on April 12, 1979, the column was also replaced as a safety measure.

e. The thermister: The original thermister with the instrument apparently degraded before Run 88 (2/19/79) at which time the counts suddenly became irregular and the values from both the high and low calibration gases became erratic. Attempts were made, including baking the column; noted earlier, and changing carrier gas flow rate to change retention time thus avoiding a large negative peak. These failed to correct the situation. Conditions were back to normal after new thermisters were installed. A new set of calibration data resulted.

f. Physical properties of the solids: The solid catalysts used had varying particle sizes and different specific gravities. Particle size differences may have altered slightly their water solubilities. Since this series of runs focused primarily on the screening of solids, efforts were not made to compensate for these factors. This is another area that should be evaluated in the third year of the project.

The lack of uniformity in particle sizes caused differences in particle suspension in water during a run. This may have intensified the channeling problem and reduced solid-liquid-gas contact. One possible way to eliminate this would be to include some device to stir the solid during irradiation, thus providing a maximum of three phase contact.

TABLE 6 COMPARATIVE REACTION VESSEL DATA

Water: Ricca
Flow Rate: 50 ml/min.

<u>R.V.</u>	<u>Run</u>	<u>Max.</u>	<u>Ave. of Longest Range</u>	<u>Curve Type</u>	<u>Notes</u>
#1	10	---	4,800	A	used for water only in 1977-1978 and till run #59
	24	5,700	5,700	B	
	30	7,300	6,500	Db	
	36	6,900	6,800	B	
	44	6,700	6,200	Db	
	49	---	7,500	A	
	50	---	5,400	E	
	52	---	6,400	E	
	56	---	7,200	C	
	57	---	7,200	A	
	59	---	22,800	A	
					high calibration gas into water in -cell
#2	51	6,300	6,000	F	high calibration gas in -cell
	54	---	4,000	A	
	55	---	4,400	A	
	60	---	18,800	C	
	115	2,500	2,500	A	
	128	---	2,850	A	
	141	2,900	2,700	E	
	149	2,800	2,750	E	
#3	62	---	4,100	F	Used for TiO_2 + BaTiO_3 after run #128
	98	---	1,750	A	
	100	---	8,800	A	
					high calibration gas into water in -cell

<u>R.V.</u>	<u>Run</u>	<u>Max.</u>	<u>Ave. of Longest Range</u>	<u>Curve Type</u>	<u>Notes</u>
#3	101	---	2,450	A	
	119	---	3,200	A	used for SrTiO_3
	124 A	---	2,150	A	
	137 A	---	2,700	A	
	143	2,700	2,600	E	
#4	63	4,000	3,400	Db	
#5	64	---	6,500	F	
	68	6,300	5,800	B	
#6	65	---	4,000	F	
#7	66	---	3,800	F	
	114	---	2,000	B	
	123A	---	2,500	A	used for Sb_2O_3 after run 123
	126	2,800	2,700	B	
	133A	---	2,450		
#8	147A	---	2,300	A	
	67	---	4,200	B	
	121	---	2,600	A	used for SnO_2 and TeO_2 after run 121
	125A	---	2,600	A	
	133A	---	2,450	A	
	148A	---	2,350	A	
	151	---	2,750	E	
	71	6,600	6,300	E	
#9	74	5,200	4,800	B	
	136	2,600	2,450	E	
	145	2,200	2,150	C	

<u>R.V.</u>	<u>Run</u>	<u>Max.</u>	<u>Ave. of Longest Range</u>	<u>Curve Type</u>	<u>Notes</u>
#10	75	5,600	5,000	B	
#11	70	---	4,400	C	
	138	---	2,750	A	

ABSTRACT

Results of the second contract year are described on production of hydrogen through water radiolysis at ^{60}Co gamma energies, in the presence of solid oxide catalysts. The intent of the research is an improved theoretical understanding of radiation-induced hydrogen generation within the framework of the electronic theory of catalysis.

Correlation of hydrogen yield with catalytic activity, based on prior work, was difficult to attain and an assessment of experimental parameters was made. Three sets of observations appear of some significance, however: (1) Antimony oxide (Sb_2O_3 , $E_g=3.3$) shows consistently a dramatic increase in catalytic performance which cannot be attributed solely to band gap values. (2) There appears to be a correlation between hydrogen yield and dielectric properties of the catalyst. (3) Gamma irradiation changes the constitutive electrical properties of oxide catalysts in a manner proportional to hydrogen yields.

Subsequent research will examine items 1, 2 and 3 more fully. It will also evaluate quantitatively the utility of the theoretical model.