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REPORT NO. P-1005

DATE 15 November 1933

SUBJECT

REPORT ON ENCLOSED SUBMARINE BATTERY STORAGE CELL PROBLEM.

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REPORT ON

Enclosed Submarine Battery Storage Cell Problem.

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
Washington, D.C.

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CATALYTIC DESTRUCTION OF ELECTROLYTIC GAS IN LEAD STORAGE CELLS.

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SECTION I.

Statement of Problem

The purpose of the work given in this report was to determine if it was practical to eliminate the hydrogen and oxygen gas generated at certain times in the lead storage cell through its recombination to water. This gas is produced by local action on the plates and in the charging process when excess current is passed through the cell. Its formation results in a loss of water from the cell, but, more important, its presence is a hazard through the possibility of its accumulation and subsequent change to water with explosive violance. The present method in submarine practice is to dilute and sweep away the gas with air. This has certain drawbacks which do not, however, come within the province of this report.

This recombination could take place in the individual cell or could be effected at some place in the present ventilating duct system. However, the main purpose of the work was to evolve a method for eliminating this duct system. The work was therefore limited to a study of methods for producing an individual completely-sealed, self-contained cell.

Although certain other methods have been proposed as discussed in Section V this report concerns itself only with the possible use of hot wires or catalysts for removing the gas. These appear to be the only methods which might be successful.

A general outline of the work is given in Section III.

SECTION II.

Historical Background

Studies by the U.S. Navy of the gases given off by storage cells reach back to 1914. These studies concerned themselves principally with the evolution of hydrogen and chlorine gases.

In that year a Board consisting of Naval Constructor W. McEntee and Surgeon E.W. Brown was convened to investigate: (a) air purification, and (b) the nature of the gases given off by submarine cells. They of course found hydrogen being evolved and gave its percentage as 60. Oxygen was reported as 32%. This Board, as far as can be determined, made no investigation as to the possibility of removing hydrogen from the submarine interior.

In 1917 Dr. E.W. Brown made a thorough study of battery gases on the L-1 and L-4. He was interested more in what gases were present rather than in how to eliminate them. His recommendations concerned charging rates, ventilation efficiency, and the upper safety limit for hydrogen in air mixtures.

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About the same time the British Navy designed a hydrogen eliminator for shipboard. This was developed to eliminate the "Blue Flame" hazard due to hydrogen accumulation on submarines. This device consisted of an electric lamp of 16 candle power filament and tubular in shape. Surrounding it and in contact with it was a layer of copper gauze about which was wound palladized asbestos. A "chimney" effect was also developed. These were only nominally successful and were never adopted for general use.

On 10 November, 1917, the Commander Submarine Force informed the Bureau of Construction and Repair that hydrogen eliminators were considered necessary for submarine use. On 23 November, 1917, the Bureau directed that experiments be conducted at the New York Navy Yard and that Professor Gibbs of the Bureau of Mines be detailed to the work. He was assisted by Lieut. E.F. DuBois (MC) USN.

On 27 November, 1917, the Bureau of Construction and Repair stated that unless the eliminators developed were extremely simple and reliable, a reasonable doubt existed as to whether their installation would be justified. Shortly after the start of the work Professor Gibbs was detailed to other work and Lt. DuBois took charge.

The following eliminators were tested:

1. British design. Layer of palladized asbestos around an ordinary electric light bulb.
2. An incandescent platinum wire in a porcelain tube, the tube being impregnated with palladium black.
3. Layer of palladized asbestos warmed by electrically heated plates.
4. Nichrome or platinum wire of proper resistance wound with asbestos impregnated with palladium black.
5. Hydrogen flame burning in an alundum tube (object to have hydrogen in surrounding air consumed in the intense heat of the flame).
6. Gas mantal. Material warmed electrolytically to be used as a catalyzer.
7. Resistance wire in sealed alundum tube, filling the rest of the tube with palladized asbestos and drawing through it a current of air.
8. Copper oxide warmed electrolytically.
9. Blowing air through incandescent platinum gauze heated by a 5 volt, 50 ampere current.
10. Copper wire.
11. Platinum wire.
12. Copper wire coated with copper oxide.
13. Copper-plated iron wire.

The eliminators tested narrowed down to the following:

1. Gibbs' Hydrogen Eliminator. Two alundum thimbles one within the other. Outer thimble is 4-1/8 in. long and 1-3/8 in. in diameter. Between the two thimbles is a platinum wire formed into a coil. A voltage of 25-30 volts produces red heat in

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the coil. His conclusions were that this eliminator is entirely unsuitable, expensive to construct and operate, and low in elimination rate.

2. Palladium Asbestos Eliminator. An electric lamp of 8-1/2 in. bulb and 10 candle power filament of standard Edison screw base. Surrounding and in contact with this is a double layer of copper gauze of forty mesh. Between the gauze layers is the active material consisting of palladized asbestos. Due to poisoning effects the copper screens were later eliminated. It was found that the catalyst would operate without the heat. Several of the lamps were used in an eliminator bank. It was found that these gave quite satisfactory service in general, although the life of the catalyst was a questionable quantity. Oil films and grease poisoned the active material.

At this stage of development the work was transferred to Lieut. E.R. Noyes (MC) USN. He developed an eliminator consisting of No. 8 asbestos cloth impregnated with palladium, four of these mats being mounted in a metal frame. These were quite active but after twenty-five uses became inactive. It is not known just what is meant by the word "uses". They could be restored by subsequent heating and washing. He considered that the use of this eliminator would be very dangerous in the ventilating ducts during a charge as in high hydrogen concentrations they would get very hot and would involve the same hazard as a spark. His last report on 3 September, 1919, seems to mark the termination of the work.

However, in his report of the above date Lieut. Noyes reported that the metal used by the Germans for their soda lime canisters in the air purification systems was catalytically active toward hydrogen under certain conditions. A full discussion of this metal is given in Section VII-B. It shall be designated as the Westphalian Canister Metal.

On 15 February, 1917, Professor M.T. Bogert, Chairman Chemistry Committee, National Research Council, submitted to Dr. W.C. Bray of the University of California, Chairman of the sub-committee on Inorganic Chemistry, the problem of developing satisfactory methods of absorbing hydrogen from storage cells. Dr. Bray, in cooperation with Professors Bisson and Randall, in the course of their investigations tried out the use of an apparatus known as the Standard Oxygen Purifying Apparatus manufactured by the Burdett Manufacturing Company of Chicago, Illinois. Platinized pumice stone was used to destroy the hydrogen. They reported that the apparatus was capable of keeping the hydrogen percentage on a submarine below a set limit of 3 or 4%.

The question of hydrogen elimination by catalytic action was not raised again until September, 1928, when the Submarine Board convened to investigate the question of submarine safety as a result of the S-51 and S-4 disasters. A general study of the storage cell and its use was undertaken by the Naval Research Laboratory. It was decided to study thoroughly the possible elimination of the hydrogen by converting it back to water by catalytic or other means.

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In the meanwhile Lieut. H.A. Guthrie, USN, submitted to the Bureau of Engineering an application for a patent covering the use of a catalyst in a completely-sealed, self-contained submarine cell. This patent will be discussed more in detail in Section VI-B and in the conclusions in Section VIII.

Active work was started by the author of this report in the summer of 1931.

SECTION III.

Outline of Work.

As stated in Section I the work given in this report concerns itself only with the elimination of the electrolytic gas within the individual cell.

The work has divided itself into the following parts:

A. Searth of the scientific literature.
B. Search of the patent literature.
C. Laboratory tests with catalysts.
D. Hot wire tests with small cells.
E. Catalytic tests with small cells.
F. Catalytic tests with large cells.

The use of absorbents or flames and sparks was not studied. Their use will be discussed further in Section V.

The bibliography lists the articles and publications pertinent to the particular problem. It does not include a bibliography of the mechanism of the hydrogen-oxygen reaction. All patents bearing on the subject are listed and discussed in Section VI-B.

The actual experimental work is given in Section VII.

Section IV is a discussion of the mechanism of the hydrogen-oxygen reaction. It is not presented as a complete statement of the mechanism of this reaction. The purpose of its inclusion is to give only such facts about the reaction that are pertinent to the general problem and which must be understood to properly interpret the experimental work.

The purpose of Section V, Possible Methods of Elimination and General Aspects of Each, is to set forth the main points in the suggested methods and to discuss at some length the limitations of certain of them. In it is also discussed the theory of catalytic action and in that sense parts of it might be considered as an extension of Section IV.

In Section XI are included certain tables which contain data pertinent to the problem.

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In the experimental work not all data is included as this would result in an extremely bulky report. Sufficient data are given to illustrate fully the results obtained and to justify the conclusions drawn.

Chronologically the work has divided itself as follows:

Laboratory tests with catalysts	- -	Summer, 1931
Catalytic tests with small cells	-	Summer, 1931
Catalytic tests with large cells	-	Summer, 1932
Catalytic tests with large cells	-	Summer, 1933

The above work was carried on at the Naval Research Laboratory. During the winters of 1931-32, and 1932-33, certain minor work on the catalytic tests on small cells was carried on in the Chemistry Laboratory of the University of North Carolina at Chapel Hill, N.C.

SECTION IV.

Mechanism of the Hydrogen-Oxygen Reaction.

As stated in Section III the purpose of this Section is not to give a thermodynamic and scientifically exact and complete discussion of the mechanism of the formation of water from hydrogen and oxygen. Its purpose is only to set forth that information necessary for a complete understanding of the results given in this report and the general conclusions drawn.

The equation for the reaction is expressed as follows:

$H_2(gas) + 1/2O_2\ (gas) = H_2O\ (gas) + 242$ kilojoules. (18°C, constant pressure).

In calories this heat of reaction is 57,825. At constant volume the value is somewhat less due to the expansion of the products when the reaction takes place under these conditions. The actual value is 57,542 calories. In a sealed cell the latter quantity would apply. This is the heat of reaction necessary to form 9 grams of water at 18°C from the component gases. For the heat of reaction at other temperatures an integral equation involving the specific heats of the reactants and products would be employed. The value does not change sufficiently in magnitude to make it advisable to use other than the above in calculations concerning this report. Tables I and II give the heat that would be evolved in the formation of the water produced from gases of various charging currents assuming that the entire current is producing water electrolysis. It should be pointed out that the values given in the above reaction are for the formation of gaseous water, not liquid water.

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With the subsequent condensation of the water vapor a further heat effect of 539 calories per gram must be considered. This is the latent heat of vaporization or evaporation. Table II gives this heat of vaporization for the water produced from the gases from various charging currents and also the heat of formation of the liquid water from these currents. This heat of vaporization may not necessarily be evolved at the point where formation of water takes place and therefore must be considered separately.

The reaction takes place to the right with what is thermodynamically known as a loss of free energy. In this report the looser and less exact term "energy" will be used. In other words, to reverse the reaction energy must be supplied to the water. That is what takes place when excess current is passed through the cell and electrolysis of water is produced. The charging current furnishes the energy. Now theoretically the hydrogen and oxygen should spontaneously form water when mixed in proper proportions. This brings into the discussion the question of the velocity of a reaction. It also introduces the idea of a "starting force".

Some reactions proceed very rapidly: the neutralization of an acid with a base, the precipitation of silver chloride in a solution of a soluble chloride and soluble silver salt. Others take place with measurable velocity: the reaction of an alcohol with an acid, the solution of a salt in water, etc. The velocity is a function of several variables: temperature, concentration of reactants and products, pressure, catalytic forces, etc. Mathematically the velocity of a reaction may be expressed by a differential equation, usually easy of integration, which in the case of the reaction in question would have the form:

$$\text{velocity} = dx/dt = K\ (C_{H_2} - x)\ (C_{O_2} - x/2)^{1/2}$$

when we are dealing with molecular hydrogen and oxygen. In this equation x is the concentration of water in mols per liter of mixture and C_{H_2} and C_{O_2} are the initial concentrations of hydrogen and oxygen. A similar equation would hold if partial pressures were used instead of concentrations. K is a constant for a given temperature, pressure, etc. In this reaction it is also a function of the catalytic forces and would therefore vary with the catalyst and with various conditions of the same catalyst. K increases very rapidly with temperature, another factor of importance in this reaction.

Looking at the reaction from a mechanistic standpoint to have a water molecule formed, one oxygen molecule must hit simultaneously with two hydrogen molecules. This would result in the formation of two molecules of water. In no other way could a single molecule of water be formed from the two gases when both remain the molecular state. However, and this is very important, a molecule of water could be formed from the collision of an atom of oxygen and a molecule of hydrogen, or an atom of oxygen and two atoms of hydrogen. The last type of combination might result from a simultaneous collision

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of the atoms or from a collision of one atom of hydrogen and one of oxygen with the formation of an unstable OH group which could later react with the additional hydrogen atom. In other words the mechanics of the formation will vary with the state of the oxygen and hydrogen, that is, whether it is in a molecular or atomic state.

It can be calculated that the actual number of collisions in a gaseous system is far in excess of the fruitful collisions, that is, the number of collisions which results in chemical reaction. In fact in a hydrogen-oxygen mixture we may have so few fruitful collisions that apparently no reaction whatsoever is taking place. What, then, are the conditions for fruitful collisions? This brings us to a consideration of active atoms and molecules as opposed to inactive ones, and takes us back to the idea of a starting force and a consideration of certain reasons why the value of the constant K increases rapidly with temperature.

At this point it would be well to consider the two general types of gaseous reactions:

Type I. This type may be considered as one in which the combination takes place with the same velocity as the reactants are formed. In this particular reaction it would be the state we would have in a cell in which water formation from the gases is proceeding with the same rate as the formation of the gases from electrolysis. This action may be localized at one point or in one space or perhaps may even fill the gas space.

Type II. In this type the steady state mentioned in Type I gives way to an explosion wave which sweeps through the entire gas space and destroys all accumulated gas.

The next point to consider is how the above may take place in the light of the idea of fruitful collisions and activated particles. To handle this subject without the use of detailed thermodynamic concepts is difficult. Statistically we assume an average energy content for a gaseous particle at a given temperature. Actually some have a much greater energy content than others. For simplification let us assume that the reactivity of a particle as being proportional to the energy content. How may the energy content of a given particle be increased? One method would be through the collision of gas particles, one particle receiving some of the energy of motion from the other. Another method would be through the addition of heat (raising the temperature). This is one reason for the increase of the constant K with temperature. Further the increase of temperature would increase the number of collisions and the velocity of the particles. This in turn would affect the accumulation of collision energy. Besides the absorption of heat energy, other forms might be absorbed: light energy, X-rays, etc. Light illumination in a hydrogen-chlorine mixture will result in explosion. These effects may not only increase the energy content of the molecules but may split them into smaller molecules or atoms which are much more highly reactive than the original molecules. Furthermore, in the water reaction these atoms may

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be produced by an initial reaction of the gas molecules on a specific type of surface. This leads to the subject of catalysis which will be discussed in a later section. The starting force would be the force which would initiate the reaction. Paper is heated with a match to cause it to start burning. Once started it burns of itself as long as sufficient oxygen is supplied, or its temperature not appreciably reduced. The hydrogen-oxygen reaction may be initiated by a spark, by a hot wire, by a general heating, or by the catalytic action of a given catalyst.

In Type I the resulting reaction is "steady". In Type II infinite velocity is reached, an explosion results. Type I may produce a flame and thus part of the energy appears as radiant energy.

Now if a reaction proceeds from a central point or points by virtue of a series of reactions we term such a reaction a "chain reaction". For instance, in the hydrogen-oxygen reaction, hydrogen molecules or oxygen molecules, or both, may be split by the catalyzer or by a hot wire or flame into highly reactive atoms. These atoms hit other molecules or atoms splitting them into atoms. This process may continue indefinitely until all gas is consumed or the active particles may become "deactivated" by a cool surface or area, by a collision with a very heavy article, or by other methods. In the first case we have a "long" chain or a "branching" chain. An explosion results. In the latter case we have a "short" chain with no explosion. Reactions of Type I may involve short chains. Reactions of Type II always involve long chains.

Another point in the hydrogen-oxygen reaction is the matter of pressure. Theoretically the reaction should result in volume contraction as the number of gas molecules is reduced from three to two. Expansion, however, takes place due to the heating effect which causes the gaseous products to greatly expand. The expansion due to the heat is of much greater magnitude than the contraction due to the reaction.

Lead has a high overvoltage that causes the existence, at least momentarily, of monatomic H_2 in the grid metal. The electrode reactions are:

$$H^+ + e = H$$

$$2H = H_2$$

The initial reaction is the faster one. The accumulation of this highly reactive monatomic hydrogen may be a factor in initiating explosion waves under conditions of high current density and high percentages of electrolytic gas. This is pure speculation on the part of the author.

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The matter of the effects of other gases on the hydrogen-oxygen reaction has received almost no attention. Other gaseous reactions are much affected, especially in the case of chain reactions, by the presence of other gas molecules. A study of this for the hydrogen-oxygen reaction should give very interesting results.

This discussion has been made as elementary as possible. The subject of catalytic action is being left for another Section. For a rigid and mathematical treatment of the subject the reader is referred to the various books and articles on the kinetics of gas reactions. It should be pointed out, however, that the work on this particular reaction is rather meager as compared with the work on other types of gaseous reactions.

Summarizing we see that the reaction is highly exothermic and quite complex in nature. It requires, usually, an initial starting force which probably starts action through the production of active particles. These active particles may be the molecular gas particles, atoms, or active groups. The active particles may be produced by rise in temperature, a spark, a flame, by a catalyst, etc. The reaction may be localized in a given space or on a surface. This localized action may continue through short reaction chains. Long chains may be produced in which case explosion results.

SECTION V.

Possible Methods of Elimination and General Aspects of Each.

A. Use of Absorbents.

Certain fundamental drawbacks eliminate the use of absorbents for removal of the electrolytic gas. An absorbent must be supplied for both the hydrogen and the oxygen or else ventilation must be supplied to remove the unabsorbed component. The number of absorbing agents for oxygen and hydrogen are limited. Some of these are liquids and consequently their use is impractical. The solids as a whole are relatively poor absorbents when considered in the light of the large quantities of gas formed. In other words, immense quantities would have to be used.

The only active absorbents of hydrogen are those substances which are most active in the catalytic production of water from oxygen and hydrogen. Their use, therefore, would result in catalytic rather than absorptive activity unless steps were taken to remove the oxygen before the gas is allowed to come in contact with the absorbent.

The absorptive properties of a substance in general decrease rapidly with rising temperature. In practice it is demanded in this particular problem that maximum absorption take plate at maximum temperature. Should the absorbent be saturated or nearly

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saturated at a lower temperature an increase of temperature would result in an evolution of gas rather than a further absorption.

Since the value of the absorbent would be lost when it became saturated, renewal would have to take place at frequent intervals depending, of course, on the quantity of absorbent used and the quantity of gas to be absorbed.

Should better absorbents for hydrogen be developed than those now available, it might be possible to eliminate the hydrogen through absorbents in the duct system as is done with carbon dioxide in the ventilating system of the submarine although at the best this use would be doubtful in a condition as critical as that existing in a battery duct system.

B. Flame and Spark Ignition.

Flame ignition merits little consideration. Such a method would involve either a constant or intermittent flame or spark. An intermittent flame would require rekindling. It is not seen how this could be effected in a closed submarine cell. For a constant flame gases from the cell would have to be used. External gases could not be used without steps being taken to remove the products. This is opposed to the idea of a completely sealed cell. The gases from a submarine cell under most conditions would be insufficient in quantity to maintain a flame even if a method could be developed to so handle them as to produce a flame. Should a flame be produced it would be extinguished with any minor explosions which take place within the cell.

Spark ignition offers a possible method particularly with small cells. It would involve the use of a spark plug or other sparking device in the gas space or in a space isolated from the gas space but still connected with it in such a way that the electrolytic gases could come in contact with the spark. Such a spark would have to be maintained by an outside current as it would hardly be feasible to use the voltage of the cell itself to operate it. Various reasons might cause the spark to fail. The acid spray would be very corrosive to any exposed metal parts. Whatever method of sparking might be used, a complicated electrical system would be necessary to maintain the sparks in all the cells of a storage bank. Methods would also have to be supplied to check up on possible failures in individual cells.

The use of sparks for destroying electrolytic gas has been patented. See Section VI-B. However, the drawbacks to the use of a spark appear to be too great to merit experimental work with their possible use on submarine batteries as the goal in view.

C. Hot Wire Ignition.

The idea of a hot wire for destroying the electrolytic gas has been patented. See Section VI-B.

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There are certain drawbacks to its use but it appeared to warrant further experimental work. A discussion, therefore, of its drawbacks will be left for the section on results and conclusions.

The mechanism of its action may be that of straight ignition through the production of a point of high temperature or it may be catalytic in nature. The desired action would be one in which the gas is destroyed as rapidly as it is produced. This would result in accumulation of high gas concentration which would be conducive to the production of explosions.

D. General Catalytic Destruction.

A catalyst may be defined as a substance which affects the velocity of a reaction but which itself is not changed in form or consumed by the process. It may enter into the reaction but in the end is recovered unchanged. Catalysts may speed up a reaction or retard it. In the latter case they are spoken of as catalytic poisons. An example of catalytic action is that of the conversion of carbon dioxide by the plant in the presence of sunlight and chlorophyll, the gree coloring matter of the leaf. The action of certain body fluids, particularly the secretions of certain glands, is catalytic.

The actual mechanism of catalytic action varies with different reactions. In a very general way, however, catalytic action may be divided into two subdivisions: contact catalysis and carrier catalysis. Carrier catalysis is rather well defined. Contact catalysis is not and in the end in a great many cases to term a catalytic action as "contact" is to little more than give it a name and admit a lack of knowledge of the true action. A discussion of each type will add materially to this report.

In carrier catalysis the catalyst enters chemically into the reaction. The catalytic action of copper in the hydrogen-oxygen reaction is an example of carrier catalysis. The consideration of this reaction is probably the best way to illustrate this type of action. The oxygen reacts with the copper to form copper oxide. The hydrogen then reacts with the copper oxide to form water and regenerate the copper. The reactions are as follows:

$$Cu + O = CuO$$

$$CuO + H_2 = Cu + H_2O$$

It is seen that the sum total action is merely the union of hydrogen and oxygen. Such a type of catalysis is quite common. On the whole the action is comparatively slow. Obviously the surface extent and the quantity of the catalyst is quite important for the more surface exposed the greater the amount of hydrogen and oxygen that can be catalyzed. The catalytic action of nickel in the production of water is this type of action.

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Contact catalysis is much less simple. The name is applied when the surface plays the main part in the action through the production of activated particles of various types or through the absorption and hence accumulation of the reacting particles on the catalyst surface or in the body of its mass. In some cases the action may be similar to carrier catalysis but the compound form is much less definite and its existence may be momentary. It may result only in an orientation on the catalyst surface, the orientation placing the particle so that its reactive part is exposed to collision with the other gas particles. The catalyst may absorb the reacting gas particles and the reaction then proceeds in the pores or on the surface. Perhaps the activation may proceed from the catalytic splitting of the molecule into atoms, as for example, the change of H_2 to H, through contact with the catalytic agent. The gas particle may be activated by having added to it by the catalyst the necessary increment of energy without any splitting effect. Resulting reactions from surface effects may take place only on the surface or may move outward from the surface by means of a chain mechanism as explained in Section IV. Different types of action may take place with the same catalyst at different temperatures and in different concentrations of the reacting gases. The action of platinum and palladium in effecting the destruction of electrolytic gas is an example of contact catalysis.

Catalysts in general are quite susceptible to being poisoned. These poisons are specific; that which poisons one catalyst may not poison another. Of the various groups of catalysts probably the metals of the platinum group are most easily poisoned.

It is thus seen that a catalyst furnishes a starting force for a chemical reaction. It may also be necessary to maintain the reaction once it is started. The quantity of catalyst required depends on the type of action.

The characteristics of the hydrogen-oxygen catalysis will be discussed more in detail in a later Section.

SECTION VI.

Prior Work on Problem

A. In U.S. Navy.

Section II, Historical Background of Work, included a fairly complete discussion of the prior work carried out by the U.S. Navy for the period 1914-1928. It does not seem necessary to repeat the discussion. Briefly, the purpose of the work as concerns this report was to develop a method of eliminating the hydrogen from the interior of the ship and from the ventilating ducts by catalytic means. No satisfactory devices were developed. It may be concluded in a very

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general way from the work that it is possible to construct hydrogen eliminators by the use of finely-divided platinum or palladium. However, their performance is entirely untrustworthy and their activity easily destroyed. The Naval authorities decided that their use was entirely unnecessary and so the work was dropped. It should be pointed out that no attempt was made to produce destruction of the hydrogen in the cell proper or to produce a completely-sealed cell. The matter of the Westphalian Canister Metal was brought up but no final conclusions as to its possible value were drawn.

The work on the NRL Hydrogen Detector developed by Dr. R.H. Canfield at the Naval Research Laboratory in connection with the general submarine battery studies has added greatly to our knowledge of the use of catalysts for the destruction of electrolytic gas. It would therefore be well to consider this instrument and some of the results of the experimental work in its development. Briefly, the operation consists in drawing ventilating gas over a palladium catalyst heated to about 100°C. The palladium will catalyze the hydrogen present and the resulting temperature rise is registered through thermocouple action on a meter calibrated to read hydrogen percentage. Palladium and platinum were found to be good catalysts and approximately equal in their activity. The catalyst for best performance must be maintained at the temperature noted above. Otherwise full catalysis does not take place. The life of the catalyst is quite uncertain. One lot may last for months. The next lot may last for only a few days. Different samples from the same lot may give different performances. In the detector this lack of activity is easily noted and remedied. The reverse would be true in a submarine cell. In the detector the catalyst is working under optimum conditions. The instrument is, of course, so constructed. The performance of the catalyst in the detector is what may be expected as the best possible performance in a submarine cell.

B. Patent Literature

A search of the patent literature shows eleven registered patents covering the destruction of electrolytic gas in storage cells. A brief description of each follows. The numbers used in this section refer to the number of the patent in the list given below. Unless otherwise noted the patent is registered in the U.S. Patent Office.

The patents divide themselves into two main classes. One class includes those patents which employ a hot wire, a flame, a spark, or some incandescent material to ignite the gas (1, 3, 4, 8 and 9). The other class includes those patents which employ a catalyst (1, 2, 3, 7, 10, and 11). Only platinum and palladium are mentioned as catalytic materials. These are employed in either the pure form or the form of the oxide.

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The patents on the whole do not go into detail as to the way the catalyst is to be employed (method of support, etc.). In no cases do they go into detail as to possible poisoning troubles. The question of material for cartridges, or other auxiliary devices is not discussed in detail.

In only two cases (10 and 11) are special means employed to produce cooling of the hot gases. In these cases the idea seems to be to cool for purposes of condensing the water rather than for preventing excessive temperatures.

Two patents (2 and 3) are mentioned as being of practical use in submarines.

The chief purpose in the minds of the inventors seems to be the replenishing of the electrolyte rather than the elimination of the hydrogen gas so as to prevent explosions. Certain (3, 4, 9 and 10) recognize the danger of the propagation of flames to the gas space with the subsequent possible explosions and employ wire gauze to prevent it.

List of Patents

1. U.S. No. 1,016,874. Thomas A. Edison, February 6, 1912.
This patent is based on the idea of the "use of heat" to cause recombination of electrolytic gas to form water. For this purpose either a hot wire or a catalyst of platinum oxide, finely-divided platinum, or platinum sponge is employed. The matter of protecting the catalyst from moisture is recognized. The matter of the possibility of an auxiliary gas space for the catalyst is recognized. The possible need of drying the gas by electrical heating before it is permitted to come in contact with the catalyst is discussed briefly. It is not thought that the author of the patent is at all clear in his ideas about recombination.

2. U.S. No. 1,116,893. Miller Reese Hutchison, November 10, 1914.
This patent covers a device described as a "combined separator, electrolyte replenisher, and flame extinguisher". The device is described in certain modified forms, but the essential feature is the passing of the electrolytic gas through water or an electrolyte solution. This is to remove entrained water, to prevent explosion propagation from cell to surrounding air, and also in case of an explosion the ultimate contracting of the hot gases is supposed to "pull" electrolyte into the cell to replenish the water lost through the electrolysis. The matter of the use of such a device in submarine battery service is discussed briefly. The idea of the Ripple Theory of battery explosions is given in a rudimentary form.

3. U.S. No. 1,324,797. Lewis W. Chubb, December 16, 1919.
This patent covers methods of consuming electrolytic gas before it reaches the surrounding atmosphere. This may take place in an

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individual cell or at a common point for a number of cells. Three methods for consuming the gas are given: use of catalytic material (platinum black, platinized asbestos, palladium black), use of flame, and the use of incandescent material such as incandescent wires or highly-heated fire clay or other refractory material. The use of wire gauze for the prevention of flame propagation is discussed. The matter of diluting the gas to prevent serious explosions is mentioned. It is interesting to note that the author of the patent states that a glow discharge arrangement, X-rays, or radium emanations may be employed for consuming the gases. The possible use of the patent in submarine cells is discussed.

4. British No. 214,177. John Ferreol Monnot, April 17, 1924. This patent covers the use of a capsule attached to the cell which effects recombination of electrolytic gases either by means of a glowing wire or a spark. In the case of the arc, the gas pressing against a diaphragm causes contact to be made in the firing circuit. Ball valves prevent the explosions from moving into the gas space in the cell proper. Platinum is recommended for the glowing wire.

5. Swiss No. 107,711. John Ferreol Monnot, November 17, 1924. Same as No. 4.

6. U.S. No. 1,557,602. John Ferreol Monnot, October 20, 1925. Same as No. 4.

7. U.S. No. 1,694,530. Dean W. Davis, December 11, 1928. This patent covers the use of a platinum wire catalyst so placed in the cell that, whatever the position of the cell, part of the wire will be exposed. This wire is so placed in series with the poles of the cell that it can be heated by the cell during a charge.

8. U.S. No. 1,733,334. Dean W. Davis, October 29, 1929. This patent covers a rather complicated device for burning the gases by means of a hot wire. The wire is heated by the cell itself and the circuit is completed by the raising of a diaphragm due to gas pressure. The method employs two cartridges but the hot wire is placed in the gas space above the electrolyte. A novel feature of this patent is the use of a rubber expansion bulb to take up the shock of an explosion.

9. U.S. No. 1,733,335. Dean W. Davis, October 29, 1929. This patent covers a small, compact cartridge which is screwed in the top of the cell. The cartridge contains a filament which can be heated by the power from the cell. The circuit is completed by the gas pressure against a moving diaphragm in the cartridge. The body of the cartridge is separated from the gas space by means of sponge rubber.

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10. British No. 303,799. Societe Anonyme des Etablissements Tecalemit, April 8, 1930.
This patent covers the use of a cartridge to be screwed into the cell top. This cartridge contains a platinum wire masked from the main gas space by wire gauze so as to prevent the action of combination from extending to the gas space and thus causing an explosion. The hot gases produced by the burning hydrogen are condensed and returned to the electrolyte through a porous plug. The cooling and condensation are helped by means of cooling gills on the cartridge.

11. British No. 339,824. Societe Anonyme des Etablissements Tecalemit, December 18, 1930.
This patent covers a small and compact, but highly complicated cartridge carrying catalytic material for the purpose of effecting the recombination of the gases. The battery gases are freed of entrained moisture before coming in contact with the catalyst. Cooling gills condense the vapor produced and the condensed water passes through porous material back into the cell. The catalyst employed is some form of platinum.

A patent application has been filed by Lieutenant H.A. Guthrie, USN, covering the use of a catalyst particularly for submarine cells. A rather complicated modified cell top is proposed. The catalyst is to be carried in a precipitated form in alundum or similar material. The temperature of the catalyst is prevented from becoming excessive by radiation through Pyrex vessels containing water. Calculations are given to show the efficiency of this heat loss. The need of proper ventilation or circulation of gases is recognized. Platinum or palladium is to be used as the catalyst. The catalyst is to be heated by electrical means so as to maintain proper activity.

C. General Scientific Literature.

Considerable experimental work is reported in the general scientific literature on the catalytic combustion of hydrogen. A complete bibliography is given in Section IX. This work in the main concerns itself with experiments whose purpose is to check up on the type of reaction rather than to develop a catalyst suitable for catalytic gas destruction. It is not worth while to more than summarize these articles. In general, metals of the platinum group are the only ones to show pronounced catalytic activity. Other catalysts are reported such as copper, nickel, silver, gold, etc. but their activity is entirely too low to make their use practical where any quantity of gas is involved. It is generally concluded that for rapid reaction high temperatures are necessary.

A bibliography of the mechanism of the hydrogen-oxygen reaction is not given as its inclusion would make the report entirely too bulky. Kinetics of Homogeneous Gas Reactions, by Louis S. Kassel, Chapter XII, gives a rather full discussion of the reaction.

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SECTION VII

A. Hot Wire Tests on Small Cells.

Apparatus. For the hot wire tests small seven plate KXH Exide cells of 80 ampere-hour capacity were employed. The regular glass jars were used but special modified tops were employed in connection with the hot wires. Plate 21 shows the Mark I KXH Modified Cell Top used in the first set of tests. Plates 22, 23 and 24 show the Mark II Modified Cell Top used with the second set of tests. Pressures were recorded by means of open top U-tube manometers. Temperatures were obtained from spirit thermometers placed in the cell top and caps. Various kinds of wire for the heating circuit were employed without noting any difference in results. For most of the work either platinum or palladium wire of 30 gauge was employed. This type of wire is not easily corroded and requires only a small amount of electrical energy for heating purposes. It is to be noted that with the Mark I Top the wire is approximately 2-1/2 inches long and is placed in the main gas space. In the Mark II Top the wire is about 1/2 inch long and is placed above the main gas space. About two amperes were required to produce redness in the type of wire employed.

Results and Conclusions. The hot wire will destroy the electrolyte gas as fast as it is produced for currents as high as 9 amperes in the type of cell employed. Pressures as high as 20 mm. of mercury were obtained although the average is much less than that amount as can be seen from an inspection of the data given at the end of this discussion. Excessive temperatures were not found and the temperature increase is limited to the immediate neighborhood of the heated wire.

Little difference was obtained in the performance obtained with the use of the two types of top. It may therefore be concluded that the position of the hot wire plays little part in the type of action secured.

The great difficulty with the use of the hot wire is the need for the maintenance of the heating current. Should a wire become cold great danger of explosion will result. With a cold wire, hydrogen will of course accumulate in the gas space even on an open circuit cell. Then when the wire is again brought to red heat an explosion will inevitably result. Even under proper operating conditions explosions are likely to occur without warning or explanation. A cell may be operating in a perfectly normal manner and suddenly will explode with great violence. It can be concluded that the use of a hot wire will result in numerous explosions.

Due to the extremely hazardous nature of the action with the hot wires it was decided that their use did not offer a likely method for eliminating electrolytic gas. It was therefore decided to abandon this phase of the study.

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Sets of typical data follow:

Test No. 1

Mark II Modified Cell Top. 1/2 inch palladium wire; cell fully charged and gassing.

Time	Temperature Cartridge	Cell	Pressure mm Mercury	Charge
1240	29.0	22.0	0	0-9
1246	29.0	22.0	5	9
1250	29.0	22.5	17	9
1252	29.0	22.5	13	9
1330	29.0	24.0	15	9
1400	30.0	25.25	20	9
1425	30.50	26.0	15	9
1450	31.0	27.0	8	9
1517	31.5	27.75	12	9
1545	32.0	29.0	10	9
1610	32.5	29.25	10	9-0
16105	32.50	29.25	4	0

Test No. 2

Same as Test 1 except that platinum wire was used instead of palladium.

0920	26.0	22.5	0	0-9
0930	26.75	23.0	3	9
1000	27.50	23.0	4	9
1030	28.0	23.25	4	9
1130	29.0	24.50	7	9
1300	38.50	26.0	11	9
1330	42.0	27.0	11	9
	hard gassing			
1345	45.50	27.0	24	9
1405	31.50	27.0	30	9
1415	31.0	27.5	33	9
1500	31.25	28.0	30	9
1545	32.0	29.0	32	9-0
1548	32.0	28.5	5	0
1600	32.0	28.5	4	0

Test No. 3

Same as Test No. 2.

1102	33.5	24.0	1	0-9
1105	33.5	24.0	1	9
1108	33.75	24.0	5	9
1110	36.5	24.0	8	9
1112	39.5	24.0	14	9
1112	explosion -- very violent			

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It should be explained that the above test numbers have no significance other than their order in this report.

B. Catalytic Experiments on Laboratory Scale.

The purpose of these experiments was to determine the type of action to be expected from certain catalytic materials and to check certain conclusions reached by an inspection of the literature. Only those materials which seemed to hold promise of success were employed.

For these studies the following laboratory apparatus was employed. The electrolyte gas was generated by a current of variable magnitude passing between platinum electrodes immersed in a solution of sodium hydroxide. This gas was passed through a drying tower filled with calcium chloride to free it from water vapor. The gas was then passed through a piece of tubing eighteen inches in length and three-quarters of an inch in diameter. This tube contained the catalyst and is designated as the catalytic chamber. This chamber was surrounded by heating elements. By regulating the current flowing through these elements various temperatures could be maintained in the catalytic chamber. From the catalytic chamber the gases passed through another drying tower of calcium chloride and through into an outlet tube the end of which opened under water so that the rate of bubbling gave an indication of gas flow. Also the pulling back of water into the outlet tube would indicate pressure decrease in the catalytic chamber, a condition which would be realized should the electrolytic gas accumulate and then suddenly be destroyed.

The results and discussions of the individual tests follow:

Palladium Sponge - Regular commercial palladium sponge was employed. This showed immediate catalytic action at room temperature. Three amperes of gas were easily handled. The water produced by the catalytic action condensed on the cold parts of the tube with the result that it gradually "drowned" the catalyst. This "drowning" resulted from water running down about the catalyst, not from water condensing on the catalyst. The activity gradually decreased. However, the activity was completely restored by heating the catalytic chamber.

Further tests were made by soaking the sponge prior to the test in water for various periods of time. The activity was always completely restored by heating.

The experiments show that sponge palladium is a very excellent catalyst for the purpose under consideration. It reacts completely at the current employed at room temperature. One may also conclude that palladium in a divided form on certain carriers (on alundum, porous tile, etc.) should likewise give excellent results.

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Palladium Gauze - A fine mesh gauze was employed. The catalytic action was not immediate. Upon being heated to around 300°C, catalytic action would set in. However, this action was usually accompanied by an explosion.

It may be concluded that palladium gauze is not immediately active at room temperature. At somewhat higher temperatures it is active but even with small quantities of gas the result is usually an explosion.

Platinum Gauze - Approximately the same results were obtained with platinum gauze as were obtained with palladium gauze. Perhaps the catalytic activity may be somewhat less.

Platinum - Palladium Gauze - Ammonia - Catalyst Alloy No. A-137. This alloy required a slight heating current for action to begin. However, once started, action was complete and persistent. The explosion hazard seems to be much less in this gauze than in either the platinum or palladium.

Platinized Asbestos - This gave very excellent results. Action was immediate and complete for five amperes of gas. Only the smallest amount of catalyst seems necessary. No explosions were obtained. Like the palladium sponge the catalyst was "drowned out" when water condensing on the colder parts of the tubes ran back over the active mass. It may be concluded that this material is an excellent catalyst. After wetting, its activity is restored by drying.

Iridium Powder - The finely-divided powder is active even in minute quantities. It is rendered inactive by wetting but its activity is completely restored by subsequent drying. The activity seems to center in certain localized areas which appear as small red hot points. Minor explosions occurred. It may be concluded that iridium is a most excellent catalyst but that it would probably have to be employed in some form other than the powder.

Ruthenium Powder - The finely-divided powder does not seem to be immediately active although action starts shortly after exposure to the gas. Again the action seems to be localized with red-hot points appearing in the catalytic mass. Explosions may occur after water formation and condensation has progressed to an advanced point. This may be considered an excellent catalyst except for its failure to give immediate action. Probably this difficulty would be overcome if the metal were employed in a different form.

Rhodium Powder - The action of this material is very similar in all respects to the action of ruthenium powder.

Gold Wire - A No. 26 gold wire spiral was employed. No activity was noted at room temperatures. At temperatures of around 400°C a slight activity may have taken place. It is useless catalytically for the purpose in hand.

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Copper Gauze - The results with this material are very interesting although they show the material to be of no value for the problem under discussion. A spiral of bright copper gauze was employed. With a gas-generating current and at room temperatures its activity was nil. Upon being heated to 300°C a superficial irridescent oxide film appeared. This gave way to a steely film and with the appearance of the latter, water formation set in. The characteristic color of copper again made its appearance and water formation continued in increasing magnitude. Further increase in current gave a larger gas loss from the outlet tube, this showing that the ability of the catalyst to handle gas volumes was limited. After stopping the current it was found that the surface of the gauze had become powdery. Of course, this course of events was to be anticipated. The catalytic activity of the copper is due to an intermediate compound formation. The oxygen oxidizes the copper to copper oxide. The hydrogen then reacts with the copper oxide to form water and copper. The extent of the surface of the catalyst determines the amount of gas that can be catalyzed. The tests show that very large surfaces are necessary for appreciable quantities of gas. They also show that the copper is subject to rapid disintegration due to the continuous exidations and reductions of the material.

Westphalian Canister Metal - It was found by Lieut. E.R. Noyes, (MC) USN, that the alloy which was employed to line the iron cans holding sodium hydroxide in the air purifying system of the German submarine U-117 was slightly active when warmed and quite reactive when moistened with sodium hydroxide and warmed. It was found that a concentration of 2.75% hydrogen could be eliminated in 35 minutes. This, of course, is quite insufficient for the purpose of complete elimination from submarine cells. This alloy seems to be principally lead and antimony with a trace of copper and possibly some arsenic according to the letter of Lieut. Noyes to Commanding Officer of the Naval Medical School under date of September 3rd. Subsequent analysis by Dr. Borgstrom of the Naval Research Laboratory showed the analysis to run as follows: lead, 92-95%; iron, .22-1.63%; tin, 4.15-2.57%; antimony, 1.52-2.84%, with traces of arsenic. In order to further test the possibility of this alloy for catalytic purposes the following series of alloys were made up, rolled into sheets of approximately one-sixteenth inch in thickness, and cut into narrow strips.

	Percent by weight		
Number	Lead	Tin	Antimony
1	98	2	0
2	98	0	2
3	95	5	0
4	95	0	5
5	90	10	0
6	90	0	10
7	90	5	5
8	95	2.5	2.5
9	98	1	1
10	97	1.5	1.5

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These were each introduced into the apparatus, both dry and moistened with sodium hydroxide, and both at room temperatures and higher temperatures. If catalytic activity was shown in any case it was too slight to be noticed. Certainly it can be concluded that the compositions studied show no appreciable catalytic activity.

Summary of Conclusions

An inspection of the various tests shows that palladium sponge and platinized asbestos offer the best possibilities for use in storage cells. It is also to be concluded that quite probably iridium, rhodium, and ruthenium would be very satisfactory in the sponge form or precipitated in asbestos or other carriers. Palladium and platinum would probably work quite satisfactorily in alundum, porous tile, or similar carrier. It should be pointed out that iridium, rhodium and ruthenium are quite rare and expensive as compared to platinum or palladium. The Pt-Pd ammonia catalyst is interesting and indicates that perhaps best results might be secured with the two in combination or perhaps with one or the other or both in combination with iridium, ruthenium, or rhodium.

The matter of the Westphalian canister metal should be further investigated although it seems certain it would never do as a complete catalyst for any appreciable volumes of electrolytic gas.

C. Catalytic Tests on Small Cells.

Apparatus - The catalytic tests on small cells were carried out with the elements from KXH seven plate cells of 80 ampere-hour capacity. For most of the work these elements were employed in the regular glass jar and set-up. For part of the work an experimental cell was employed. This consisted of a circular glass jar containing the acid and elements. This was covered with a Bakelite cap with a small opening leading through it into a glass chimney which in turn was covered with a Bakelite cap. See Plates 18 and 19. Temperatures were obtained from spirit thermometers and pressures were measured with open U-tube manometers. The catalytic materials employed were platinized asbestos, palladium sponge, and platinized alundum.

For the tests with platinized asbestos and palladium sponge the regular cell jar was employed in connection with the Mark II modified cell top and the KXH Catalyst Carrier. See Plates 23, 24, and 25. For the tests with the platinized alundum the Experimental Cell Mark I was employed. In the KXH Catalyst Carrier either wire gauze or alundum plates were used to support the catalyst. Only very small quantities were required. The size and position of the alundum plates in the experimental cell are shown in the illustrations.

Certain tests were made with a combined catalyst and hot wire.

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Discussion of Results and Conclusions - It was found that for currents as high as eight amperes the catalysts employed seemed to easily effect recombination of the gases. The temperature of the catalyst apparently was quite high as thermometer bulbs in close contact with the catalyst showed temperatures as high as 75°C. That this temperature is localized was determined by changing the height of the thermometer bulb in the cartridge. A further check was obtained when the catalyst was placed between alundum plates. In this last case no appreciable increase was noted in the region immediately above the upper plate. The gas space temperature would vary from one to five degrees above the room temperature, depending on the condition of the experiment (temperature of room, air currents, etc.). Pressures were variable. Values as high as 75 mm of mercury were obtained but the average was very much lower. On the whole the pressures seem to fall between the limits of 10-20 mm with the regular cells. With the experimental cells somewhat different pressure characteristics were found. The pressure effects can be noted from the data for the typical tests included at the end of this discussion. It is seen that in certain cases a maximum pressure was necessary before appreciable catalysis would take place. But when catalysis was once started, the pressure diminished rapidly.

Several explosions took place. In the use of the combined hot wire and catalyst the explosion hazard is as great as with the hot wire alone. Two explosions took place with the platinized alundum. Two took place with the platinized asbestos. It can be concluded that explosions are very apt to take place and that it is impossible to predict under just what set of conditions they will occur.

In reviewing the data it should be remembered that in practically all cases the cells were sealed with the gas space more or less filled with electrolytic gas. It is to be noted that in certain cases after the stopping of the charge the pressure became negative due to the additional hydrogen in the cell at the time of sealing.

No tests were made to test the life of the platinized asbestos or the palladium sponge. In all cases these were found quite dry and active after several hours use. In the case of the platinized alundum it was found that the catalyst would remain active for as long as six months. However, it should be noted that other samples of the catalyst prepared in exactly the same way would last only a few hours. However, in a general way the longer the catalyst remains in use the higher the initial pressure necessary to start active catalysis.

The purpose of the Experimental Cell Mark I was to place the catalyst away from the main cell space with the idea of preventing explosions. However, it did not produce the desired results.

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A series of typical tests follow:

TEST NO. 1

Platinized asbestos. Thermometer one inch over catalyst. Catalyst on copper gauze. Room temperature 20°C. Cell hard gassing.

Time	Current	Pressure (mm mercury)	Temperature Cartridge	Cell Top
1010	0	0	19.5°C	19.5°C
1010	4	0	19.5°C	19.5°C
1011	4	2	19.5°C	19.5°C
1015	4	17	19.75	19.5
1025	4	16	20.00	20.00
1040	4	13	20.50	20.50
1105	4	12	21.50	21.50
1125	4	13	22.00	22.00
1155	4	12	22.00	22.25
1215	4	12	21.75	22.25
1240	4	10	21.25	22.25
1500	4	10	22.25	23.50
1500	6	--	--	--
1510	6	13	22.00	23.50
1540	6	10	22.25	23.75
1555	6	10	22.25	23.75
1600	0	--	--	--
1601	0	2	22.25	23.75
1605	0	5	22.25	23.75
1700	0	2	20.00	22.25

TEST NO. 2

Platinized asbestos - Thermometer one inch over catalyst. Catalyst on copper gauze. Room temperature, approximately 21°C. Cell temperatures high from prior charges. Cell gassing hard.

Time	Current	Pressure (mm mercury)	Temperature Cartridge	Cell Top
1435	0	0	--	--
1435	4	2	24.	25.
1445	4	12	24.	25.
1455	4	14	24.	25.25
1520	4	22	24.25	25.50
1535	4	33	24.25	25.50
1545	4	13	24.25	25.75
1620	4	12	24.50	26.25
1700	4	12	24.50	26.50
1712	4	12	24.50	26.75
1712	0	-	--	--

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TEST NO. 3

Sponge Palladium between alundun plates.

Time	Current	Pressure (mm mercury)	Temperature Cartridge	Cell Top	Room
1255	0	--	--	--	--
1255	7	2	27°C	27	27.5
1315	7	5	27.5	27	28
1330	7	5	28	27	28
1345	7	5	28	28	28
1415	7	5	28.5	28.5	29
1500	7	6	29.25	29.25	29
1530	7	6	29.75	29.75	29.25
1600	7	7	30.00	30.00	29.50
1615	7	7	30.50	30.25	29.75
1615	0	--	--	--	--

TEST NO. 4

Platinized asbestos. Thermometer close over catalyst. Catalyst on copper gauze. Room temperature 25°C.

Time	Current	Pressure (mm mercury)	Temperature Cartridge	Cell Top
1302	0	0	24°C	24°C
1305	6	0	24	24
1307	6	20	24	24
1310	6	75	29.5	24.5
13105	6	13	30	24.5
1311	6	5	32	24.5
1313	6	3	34	24.5
1320	6	3	41.5	25.0
1330	6	3	49.0	25.5
1355	6	2	58.5	26.5
1405	6	2	60.0	27.5
1405	0	2	60.0	27.5
1410	0	-3	55.0	28.0
1420	0	-1	44.0	28.0

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TEST NO. 5

Platinized asbestos. Thermometer close over catalyst. Catalyst on copper gauze. Room temperature variable.

Time	Current	Pressure (mm mercury)	Temperature Cartridge	Cell Top	Room
0830	0	0	22°C	22°C	21°C
0835	9	0	22	22	21
0836	9	17	22	22	21
0840	9	35	22	22	21
0845	9	40	22	22	21
0850	9	33	22.5	22.5	21.5
0900	9	30	23.5	23	22
0910	9	0	55.5	24.5	22
0925	9	7	63.0	24.5	22
0940	9	20	68.0	28.0	22
1000	9	10	72.0	28.0	22.5
1015	9	2	73.0	28.5	23.5
1021	9	0	78.0	29.5	23.5
1022	9	-2	78.5	29.5	24.0
10235	9	+15	78.5	29.5	24.0
1024	9	10	73.5	29.5	24.0
1030	9	5	70.5	30.0	24.0
1035	9	8	72.0	30.0	24.25
1040	9	5	73.0	30.5	24.5
1050	9	2	74.5	30.5	24.5
1057	9	2	74	31.0	24.50
1100	9	+1	35.5	31.25	24.50
1101	9	-2	75.5	31.25	24.50
1103	9	+2	75.25	31.50	25.0
1107	9	2	75.25	31.50	25.0
1107	0	2	75.25	31.50	25.0
1108	0	-18	75.25	31.50	25.0
1110	0	-100	73.0	33.0	25.0
1113	0	-65	66.75	34.0	25.0

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TEST NO. 6

Platinized asbestos. Thermometer one inch over catalyst.
Catalyst on copper gauze. Room temperature approximately 25°C.

Time	Current	Pressure (mm mercury)	Temperature Cartridge	Cell Top
1042	9	33	29	24
1045	9	55	29	24
1100	9	33	29.5	24.5
1120	9	23	30.5	25.5
-	-	-	-	-
1247	0	0	31.5	26
1250	9	0	31.5	26
1300	9	25	32.0	26
1310	9	23	32.0	26.5
1320	9	23	34.0	26.5
-	-	-	-	-
1340	0	0	34.0	27.0
1341	9	0	34.0	27.0
1345	9	23	34.0	27.0
-	-	-	-	-
1410	0	0	29.00	24.50
1412	9	0	29.0	24.5
1413	9	7	29.0	24.5
1415	9	+24	32.0	24.5
1416	9	-210	37.0	26.0
1418	9	-25	35	25.5
1419	9	+18	33.50	25.0
1422	9	9	33.0	25.0
1435	9	8	30.0	25.0

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TEST NO. 7

Experimental Cell Mark I. Platinized alundum catalyst. Room temperature approximately 25°C. Temperature of catalyst recorded with thermometer bulb one inch over catalyst.

Time	Temperature	Pressure (mm mercury)	Current
1130	25.5°C	0	0-6
1620	30.0	20	6
1630	29.0	60	6
	slight gassing		
1645	28.0	105	6
1700	27.0	15	6
1715	27.0	13	6-0
	following day		
0845	23.5	9	0-5
0900	23.5	12	5
	medium gassing		
0950	24.0	12	5
1030	24.0	12	5
1300	24.0	12	5-0

TEST NO. 8

Same as Test No. 7 except that cell was sealed for period of six months. Cell was cycled on an average of once a month over the period.

Time	Temperature	Pressure (mm mercury)	Current
1445	25.0	40	0-5
1515	25.5	90	5
1520	25.5	125	5
1525	25.5	145	5
1526	25.5	10	5
1533	25.5	8	5-6
1540	25.5	5	6

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D. Catalytic Tests on Large Cells

The catalytic tests on large cells were made on two regular submarine cells. The various modified tops, caps, catalyst carriers, etc. employed are described in this report only where their use has added to the total results of the study. These are illustrated and described in the accompanying plates. The total extra parts employed in the use of the catalyst are termed collectively the "cap". The actual parts employed in the holding of the catalyst are termed the "catalyst carrier". The alundum discs used with the catalyst are termed "catalyst plates".

Gravity readings were made with either a Hay gravity meter or a regular hydrometer.

Temperature measurements were made with thermocouples composed of No. 32 copper and cupron wire. An ice-water bath in a thermos bottle served as a cold junction. Temperatures were obtained in a Leeds and Northrup thermocouple potentiometer by means of a calibration curve. In some cases as many as eight couples were employed at the same time, the individual readings being made by a suitable switch system.

Pressure changes were obtained from an open top U-tube manometer connected to the gas space through a one-way glass stopcock on the cell top or cap. Either mercury or water was used as the manometer fluid.

All thermocouple readings and pressure readings were made at a distance of eight feet from the cells. A brick wall and shatter-proof windows separated the observer from the cell.

The cell tops and parts were constantly checked for leaks by covering them with water or by the use of soap lather.

For the last half of the tests a lead-lined box was employed to hold the rubber jar. Suitable openings allowed the electrolyte to fill this lead box so that the jar merely acted as an insulator for the elements. This lead box was employed to cut down the effect of explosions which often shattered the regular jar.

All results of individual tests are not given as this would make the report entirely too bulky. A discussion of the general groups of tests will be given with data included only where it seems advisable to illustrate the results obtained and the conclusions drawn.

The large cell tests divide themselves into six main groups. The characteristics of the tests in these groups will be discussed under these six headings.

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These groups are as follows:

1. Tests with Cap Mark I and Cap Mark II and Catalyst Carrier Mark I.
2. Tests with Cap Mark III.
3. Tests with Cap Mark IV and Catalyst Carrier Mark II.
4. Tests with Caps Mark IV and V and Catalyst Carriers Mark III, IV and V.
5. Tests with Cap Mark VI and Catalyst Plate Mark I.
6. Tests with Cap Mark VII and Catalyst Plate Mark II.

Group 1. Apparatus: Mark I Modified Cell Top. Mark I and II Cap. Mark I Catalyst Carrier. Mark I Cooling Mechanism. See Plates 1, 2, 4, 5, 6 and 7. Catalyst: 1 gram of 5% platinized asbestos held loosely in place by platinum gauze of fine mesh. Electrolyte level about four inches of cell top.

Discussion and Results - Note that the Mark I Catalyst Carrier is characterized by being so constructed that the catalytic gas has access to the catalyst only through the holes in the catalyst carrier. Hence there is not a good access of gas to the catalyst and the circulation of the gases can not be expected to be very good. The tests conducted with the above divide themselves into two sub-divisions; viz. those conducted without the use of the cooling mechanism and those conducted with the cooling mechanism.

Division 1 - Preliminary tests showed that high temperatures will be obtained immediately over the catalyst. Since the couple recording these temperatures is 3/4 inch over the catalyst and separated from it by a wire gauze it is to be expected that the actual temperature of the catalyst is very much greater. A typical set of data is given. Note rapid dimunition of pressure when cell is first sealed thus indicating immediate catalysis. Note high temperatures which certainly create a dangerous source of explosion. After the test given below the Catalyst Carrier was examined and the bakelite surface in contact with the catalyst was very badly scorched. 140 amperes of gassing current was the highest charge with this set of tests. Comparatively low pressures were obtained. It was decided that the high local temperatures obtained were entirely too great to make this type of cap successful without some form of cooling.

Typical Test. Cell sealed at 936. Temperature of electrolyte 88-90°F during course of test.

Time	Temperature F Gas Space	Cap	Current	Voltage	Pressure (mm mercury)
0944	88	138	0	2.08	5
1000	88	145	0	2.08	1
1010	88	165	0	2.08	0
1035	88	187	0-50	2.10	0
1110	91	212	50	2.14	0
1130	91	201	50-140	2.18	0

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1150	95	226	140	2.24	2
1205	93	255	140	2.25	7
1235	93	270	140	2.25	5

explosion

Division 2 - The high local temperatures found in Division 1 indicated that studies should be made to see if these high temperatures could be eliminated by suitable cooling devices. For this purpose the Cooling Mechanism Mark I was developed. Cap II was used as the glass used in this cap is a much better conductor of heat than the bakelite of the Mark I Cap. The catalyst was the same.

Various methods of handling the cooling water were employed. In the first set of tests tap water was circulated through the mechanism at the rate of approximately 2 gallons per hour. With 100 amperes of current a temperature rise of approximately 2°F was obtained in the circulating water. In another set of tests ice water was employed in the cooling mechanism. In still another set water at ordinary temperatures was used. A typical set of data is given at the end of the discussion on Group 1.

General Results and Conclusions - The use of the cooling mechanism did not entirely eliminate the high temperatures. In certain of the tests very high temperatures developed in spite of the cooling effects employed. In other tests the temperatures went over a maximum and once this maximum was passed, increasing current resulted in a cooling action. It was found out later that this type of action is typical of certain forms of catalysis of electrolytic gas. This will be explained in detail further in the report. At the time it was thought that this desirable type of action was due to the setting up of convection currents in the cap which resulted in proper access of the electrolytic gases to the catalyst. In the case where the temperature became increasingly high it was thought that proper movement of gases was not taking place. It was therefore decided to abandon the Mark I type of cap and to continue the tests with a cap which would permit greater circulation of gases.

In the typical test given below it should be noted that the pressures never assume an alarmingly high value. Note that for part of the tests 400 amperes of current were employed. The low cap thermocouple was a quarter of an inch over the catalyst. The high cap couple was one inch over the catalyst. It is seen that excessive temperatures were not obtained any appreciable distance from the catalyst.

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Typical Test - Group 1 - Division 2.

Cap in place and cooling mechanism filled with water at 80°F at 900.

Time	Temperature High Cap	Temperature Low Cap	Current	Voltage	Pressure, mm H_2O
0915	81	81	0-40	2.03	10
0950	81	81	40	2.08	12
1000	81	81	40-80	2.12	12
1015	81	81	80	2.18	28
1030	81	87	80	2.18	34
1055	81	91	80	2.20	36
1110	102	151	80	2.20	29
1127	104	208	80	2.20	26
		Cooling mechanism filled with ice-water.			
1130	92	201	80	2.20	35
1135	92	183	80	2.20	36
		Temperature varying through 25°F.			
1145	102	151	120	2.20	49
1202	79	111	120	2.20	60
1230	57	82	120	2.20	53
1300	53	74	120	2.22	58
1330	50	73	120	2.21	53
1350	50	72	120-200	2.21	48
1405	50	68	200	2.24	83
1420	48	68	200-300	2.24	110
1445	46	59	300-400	2.28	143
1505	47	57	400	2.28	135
1507	charge stopped.				

Group 2. - Apparatus: Mark I and II Modified Cell Top. Cap Mark III. See Plates 2, 8, 9 and 10. Catalyst: 2 grams of 5% platinized asbestos. One thermocouple immediately over catalyst channel, one in center of cap half-way of length. Electrolyte within two inches of cell top.

Purpose: To test characteristics of the Mark III Cap.

Discussion and Results - It is to be noted that this type of cap permits easy access of gases to the catalyst. It also permits ready radiation of heat to exterior of cap. A typical charge is given at the end of this discussion. Note the maximum found in both the pressure and temperature. Note that excessive temperatures or pressures were not obtained. 1,000 amperes were employed during part of the tests.

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The maxima are explained on the basis that in a typical test the localized reaction which sets in on the surface of the catalyst gives way after a time to a space reaction. This space reaction is characterized by lower temperatures and pressures. See Sections IV, V-D, and VIII-A.

One explosion was obtained in this set of tests. At the end of the test given below the cap was left in place but the tube connecting the gas space to the manometer was removed. That night at 2000 the residual gas exploded. The explosion was quite destructive. No reason can be definitely assigned to the explosion. Perhaps the catalyst became inactive from moisture, then the accumulation of the hydrogen due to the displacement of the air through the pressure tube became again active with a resulting explosion. Whatever the cause, the explosion illustrates the treacherous nature of the reaction.

In view of the explosion secured it was decided to continue the tests with a type of cap that would eliminate the gas space over the electrolyte. For this purpose the Mark IV Cap was developed. Results are given in Group 3.

Typical test - Cap Mark III - Catalyst, platinized asbestos. Cap in place at 1145.

Time	Temperature Center	Temperature Over Catalyst	Current	Voltage	Pressure mm, H_2O
1150	108	109	0-100	2.18	200
1154	108	113	100	2.18	307
1155	108	115	100	2.19	25
1205	122	129	100	2.19	83
1210	122	133	100-200	2.19	--
1215	127	131	200-300	2.22	117
1223	126	127	300-400	2.27	150
1225	122	122	400-500	2.30	153
1229	--	--	500-750	2.33	170
1235	113	109	750	2.33	160
1255	97	97	750	2.33	150
1315	95	95	750	2.34	105
1325	92	92	750	2.34	105
1400	93	93	750	2.34	84
1500	86	86	750	2.34	60
1510	88	90	750-1000	2.34	--
1513	90	90	1000	2.38	77
1520	--	--	1000-0	2.38	--
1523	90	90	0	--	10
1530	--	--	0-750	--	--
1535	95	95	750-100	--	30
1615	100	100	100-0	--	33

Group 3. Apparatus: Cap Mark IV and Catalyst Carrier Mark II. See Plates 11 and 12. Catalysts: 2 grams of 5% platinized asbestos and 5 grams of palladium sponge.

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Purpose - To test characteristics of the Mark IV Cap in connection with both a platinum and palladium catalyst. This cap gives a very limited gas space and also should give a ready access of gases to the catalyst.

Discussion and Results - Note that this cap is suspended in the top of the gas space and that the catalyst is covered at top and bottom by wire gauze. The results were of such a nature as to indicate that this type of carrier is wholly unsuited for the purpose. Neither the platinum nor the palladium gave results that were at all favorable. Explosions were frequent but since the gas space was much smaller, their effect was greatly minimized. Exceedingly high pressures were obtained. Temperatures, however, were not excessive. A typical set of data is given. It was decided that this type of carrier was unsuitable and that tests should be carried on this type of cap but with the Mark III type of carrier.

Typical Test

Cap in place at 1338. Catalyst temperature recorded from couple in catalytic mass. Cap temperature from couple just above catalyst.

Time	Temperature, Catalyst	Current	Pressure
1345	132	0-60	-45
1346	111	60	20
1402	92	60-200	310
1410	91	200-1	640
1415	91	0	590
1425	86	0	410
1427	86	0	25
1430	86	0	155
1431	explosion - very violent.		

Group 4. Apparatus: The results of the Group 3 tests showed that the type of cap employed in these tests was not capable of handling any large quantities of gas. The results of the tests of Group 2 showed that the type used in those tests was capable under favorable conditions of handling large gassing currents. It was therefore decided to continue the tests using modifications of the Mark III Cap as catalyst carriers and employing them with the Mark IV Cap. It was hoped in this way to secure proper access of the gas to the catalyst. The advantage of the small gas space is apparent for while a number of explosions were obtained they were not destructive in character.

The Mark IV and Mark V Caps were therefore employed in connection with Catalyst Carriers Mark III, IV and V. See Plates 11, 12, 13 and 14. This type of carrier should give a chimney action in connection with the movements of the gases within the cap.

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Both palladium sponge and platinum sponge were used as catalysts.

Results and Conclusions - As is seen by referring to the plates the carriers used employed from one to three channels for holding the catalyst and in one type a copper "shed" was added to prevent accumulated water from running back on the catalyst. Approximately equal performance was found with these three modifications although it may be concluded with reasonable certainty that the quantity of catalyst plays some part in the total amount of current that can be handled especially in the case of a "cold" catalyst, i.e. one that has not been subjected to smaller gassing currents. Approximately three grams of platinum sponge will catalyze the gas from 200 amperes of current when "cold". In other words, that quantity of current can be passed through the cell and the resulting gases will be catalyzed at once.

Palladium sponge did not give as good results as platinum sponge but too much weight should not be given to this as only one sample of palladium sponge was available and its past history was not known.

On the whole excellent results were obtained with this combination of parts. Currents as high as 500 amperes were catalyzed with apparent ease. No explosions were obtained. Most of the tests showed the typical data, i.e. the temperature passed over a maximum after which the current could be raised without further temperature increase. The pressure showed the same maximum. A typical set of data is given and a plot of the data is given on Plate 17. Note the pressure maximum. Also note the temperature maxima occurring with the initiation of the charge and later in two instances when the current was stopped for some minutes. Note that these successive maxima diminish in height. An explanation of this is included in the general conclusions.

In general it may be concluded from these tests that the catalyst carrier and cap should be so constructed that a "chimney" type of ventilation is produced.

Typical Data.
Platinum sponge catalyst. Mark III Catalyst Carrier.
Cap in place at 950.

Time	Temperature Cap	Temperature Catalyst	Current	Pressure
1005	82	84	0-100	3 mm
1015	85	95	100	3
1030	92	120	100	80
1032	92	125	100	6
1040	97	175	100	10
1100	97	129	100-200	8

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1110	97	123	200	22
1130	93	111	200-500	14
1133	93	107	500	35
1200	85	93	500-0	14
1210	85	85	0	3
1230	81	85	0-100	-3
1240	85	95	100	5
1250	86	100	100	6
1300	85	100	100-500	8
1305	85	99	500	12
1315	85	95	500	14
1330	85	92	500-0	15
1345	82	87	0	5
1350	--	--	0-500	5
1355	82	90	500	10
1410	82	91	500-0	11

Group 5 - Tests as outlined in the first four groups have employed platinum or palladium sponge or platinized asbestos. Such forms of catalysts are obviously impossible for use in submarine practice. Platinized alundum was therefore selected as a form which is adapted to the rough usage to be expected on shipboard. Alundum is a fused form of aluminum oxide and is chemically inert. At the same time it is quite porous. The platinized plates are formed by soaking the plates in a solution of platinum chloride and then subsequently heating them in an atmosphere of hydrogen. A dense black deposit of metallic platinum is thus secured in the pores of the plate.

It was further decided to place the catalyst in more than one position in the gas space. Instead of having just one plate a number of small plates were to be used. By having thermocouples on each plate it would then be possible to compare the activity of the various catalysts.

Apparatus - The Mark VI Cap was employed with the Mark I Catalyst Plate. Five of these caps were employed at one time, one in the center of the cell top over the center opening and the other four as shown in the sketch of the Mark III Modified Cell Top. See Plates 3 and 15. The catalyst plates were thus suspended a short distance below the cell top and about two inches above the electrolyte level. Thermocouples were placed at various positions in the cap and on the catalyst surfaces so that conditions in all parts of the apparatus could be followed.

Results and Conclusions - A large number of tests were conducted with this apparatus. Certain very definite conclusions could be drawn. The activity of the catalyst was not constant. One plate might start catalytic action at once and the activity might be confined to that one plate for thirty minutes. Then one or more of the

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other plates might become active. The first plate might then go inactive only to become active again at some later time. The plate active in one test might in the next test become inactive. In other words, the action was irregular and showed that a single plate could not be depended on for even partial activity. On an active plate, temperatures as high as 300°F were recorded.

The pressure effects were not excessive. They were of the same order of magnitude as obtained in the typical tests of Group 4. When the cell was first sealed very high negative pressures were obtained. This is to be expected from the position of the catalyst in the gas space.

The life of this type of catalyst was quite short. In some cases activity was never secured. In others the activity was of only a few minutes duration. This was thought to be due to the splashing of the electrolyte on the catalyst plate. To test this point out protective plates of bakelite were suspended a short distance under the catalyst plates in such a way that direct splashing of the plates would be prevented. This seemed to help to some slight extent but poisoning of the catalysts continued and inspection of the plates showed that they contained much acid which, of course, was the cause of the loss of activity.

The plates were, of course, most active when hottest.

Certain results were obtained as to the quantity of catalytic surface necessary for catalyzing the gas from various charging currents. As this data was further checked and amplified in the tests of Group 6, it is not thought worth while to consider them at this time. Certainly with the five plates as shown in the plates and with temperatures as obtained without artificial heating currents of only small magnitudes could be catalyzed. The platinized alundum does not have near the activity as the platinized asbestos or the platinum sponge.

It is not thought worth while to include data for any tests in this group.

Group 6 - Apparatus: It was decided that the alundum plate impregnated with platinum or palladium offered the only solution for a practical catalyst. The tests in Group 5 showed that to be sure of proper activity the catalyst must be kept in a warm condition. Moreover, it must be so placed that the gases can have ready access to it. Proper movement of gases is necessary. Accurate data are necessary to determine exact quantity of catalyst necessary for various charging currents. For further study on the above points, the Cap Mark VII and the Catalyst Plate Mark II were developed. See Plate 16. The heating unit on the back of the catalyst plate is covered by another alundum plate similar to the catalyst plate, all joints being carefully cemented with alundum cement so as to prevent ignition of the electrolytic gas by the red hot wires of the heater. This plate was prepared the same way as the Mark I Catalyst Plate.

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The temperature of the catalyst plate could, of course, be maintained at any fixed value by adjusting the current flowing through the heating unit.

Results and Conclusions - As this catalyst plate was heated by external current the results did not show the temperature maxima with the state of charge as in the typical tests of other groups. However, the pressure maxima were obtained. It seems therefore proper to conclude that the tests secured with this apparatus followed the general course of the typical tests of Group 4.

As the main purpose of the tests of this group was to get data on the necessary quantity of catalyst for various charging currents, few tests of long duration were made. It was determined that a plate of 16 square inches of surface area would catalyze the gas from a charging current of 100 amperes. In order to function properly the catalyst had to be maintained at a temperature of approximately 200°F. The purpose of this temperature was not only to keep the catalyst in active condition but to prevent water from condensing on the catalyst surface.

With the cap characteristics determined, the amount of catalyst necessary for various charging currents established, and the temperature characteristics known, it was thought that sufficient knowledge was at hand to design the type of cap which would be most promising for the destruction of electrolytic gas. The general conclusions and the general description of the cap recommended are given in the following Section.

Typical Test. Heating current 1.5 amperes. Cell sealed 0928.

Time	Temperature Catalyst surface	Temperature one inch under catalyst	Pressure, mm H_2O	Current
0935	112	121	70	0
0955	190	214	113	0
1015	--	--	83	0
1030	232	246	22	0-100
1040	235	246	-10	100
1100	256	266	195	100-50
1101	--	--	250	50
1102	--	--	18	50
1110	260	283	5	50
1135	265	305	70	50
1200	261	300	73	50
1230	261	303	67	50
1245	260	305	70	50-100
1250	260	305	100	100
1310	265	300	100	100
1340	260	300	40	100-0

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SECTION VIII

Results and Conclusions.

A. Conclusions for Catalytic Destruction in Large Cells.

Before considering the conclusions that can be drawn from the results of the experiments conducted, certain points in connection with the use of catalysts will be discussed.

1. Poisonous Properties of Catalyst - The only materials suitable for catalysts in storage cells are metals of the platinum group or their alloys. Platinum in minute quantities is very harmful to lead storage cells. Of course, to exercise this harmful effect it must be in a soluble form in the electrolyte. Experiments on the poisonous effects of other members of the platinum group have not been conducted but there is no reason to think that their effect will be other than that of platinum as all are very similar chemically, have a low overvoltage, and are noble in nature. The catalytic material is not in a soluble form and quite probably the rate of solution would be quite slow. On the other hand, as it went into solution it would be deposited on the plates and this is the factor that accounts for its poisonous properties. Consequently the results in the end would be the complete solution of the catalyst in contact with the electrolyte and the subsequent destruction of the plate through local action. Of course, in use the catalyst will be protected from the electrolyte. However, in the normal operation of a submarine it is altogether probable that the catalyst would at some time or other come completely or partially in contact with the electrolyte. This might or might not come to the attention of the electricians. Even should it be detected it might not be easy to recover the catalyst and if the pieces were small enough recovery would be impossible. In the event of an explosion the catalyst in part or completely might drop into the electrolyte. The only recourse then would be to drain the electrolyte and completely remove the catalyst by washing or other means from the plates.

2. Diffusibility of Hydrogen - The velocities of gas particles are in inverse ratio of the square of their molecular weights. In other words, since hydrogen has a molecular weight of 2 and oxygen one of 32 the ratio of their molecular weights would be 1/16 and the ratio of their velocities 1/4. The velocity of the hydrogen molecule is thus 4 times that of the oxygen whatever may be the temperature. Now the time ratio for given volumes of gases to diffuse or leak out through small openings is the inverse of the velocities. Consequently hydrogen would effuse out through a small opening in one-fourth the time it would take for a similar volume of oxygen to effuse out. The actual velocities will, of course, increase with temperature. Therefore, if small leaks are present in the cell top or the catalyst cap the leakage will result in a greater amount of hydrogen than oxygen. They should of course

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leak in the ratio of 2 to 1 if the proper ratio for combustion is to be maintained. Of course, this leakage is not only objectionable because it disturbs the proper balance in the cell gas space but it also allows hydrogen to accumulate without the cell unless steps are taken to remove it.

3. Necessary Ratio of Hydrogen and Oxygen - The basis of either the catalytic combustion or the hot wire ignition is the effecting of the reaction whereby two parts of hydrogen react with one part of oxygen. Should hydrogen and oxygen be produced in other than the above ratio, accumulation of gas will result. Pressure effects would be produced. These will be discussed further under (6). Theoretically the hydrogen and the oxygen will be produced in the proper proportions but actually this is not the case. The plates are not always in the same state of discharge or charge. Local action will be different on the various plates. Just how this ratio will vary from the desired magnitude is of course dependent on the particular cell and the state of that cell at a particular time. Certainly it can not be hoped in practice to obtain the proper ratio in many of the cells. Not only may the ratio vary due to improper gassing but it may also vary due to effusion of hydrogen through small openings in the cell top as discussed under (2).

4. Ventilation - One of the purposes of the air in the present type of ventilating system is to cool the cell through evaporation of water from the electrolyte. Cells must be cooled to prevent excess temperature and subsequent shortening of the life of the cell. The use of a catalyst assumes a completely-sealed cell. Consequently, the cooling by evaporation is eliminated. Either it must be proven that this cooling is unnecessary or other means of cooling must be supplied. Since the cooling produced must be effective in the electrolyte and elements, it is hard to see how a more effective system of cooling can be devised. Air could be circulated around the jars but either a much larger volume would be necessary or it would have to be cooled before use. Both would probably be necessary.

5. Control - The use of a catalyst or hot wire assumes a completely-sealed cell without connection between its gas space and those of the other cells. If heating of the catalyst is used, there would be electrical connections for this purpose in addition to those already on the cells. But since each cell is a self-contained unit a central system of control would be impossible. There is no way in which the action of the catalyst in any of the cells of a battery could be checked without checking on the individual cell. Certain methods of remote control suggest themselves but they do not appear at all practical. Pressure methods might be used. The gas space from each cell could be connected to a central manometer in such a way that individual pressure readings could be made. The pressure would thus be taken as a measure of the activity of the catalyst. This method would present many mechanical difficulties. Moreover, an inspection of the data shows that the pressure is a very poor criterion of the catalytic activity. Of course, very high pressures would indicate lack of activity but it would be hard to interpret

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other than excessive readings. An electrical set-up might be used to indicate composition of gas in the cell space but this would be quite complicated.

6. Pressure Effects - Several factors must be considered in this connection. Under (3) was discussed the necessity for the production of hydrogen and oxygen in the ratio of 2 to 1. If this is not the case excessive pressures will develop. This effect might be very slight and again it might be appreciable. It would, of course, vary from cell to cell but could likewise vary in an individual cell with its condition and the state of the charge or discharge. In any event, it would be a factor that would have to be reckoned with.

The pressure of a gas varies directly with the absolute temperature. The absolute temperature is obtained by adding 273 to the Centigrade temperature. Consequently a cell sealed at one temperature would show a greater pressure than one sealed at another temperature when subjected to the same external environment. If the temperature change is sufficient in magnitude, pressure trouble might be developed.

The temperature of a gas space might change for various reasons: heating of gas space due to catalysis, heating of gas space due to radiation when cell temperature increases due to charge, change of temperature of environment of cell, change of geographical location of boat, etc.

While in general these pressure effects would probably be small they add to the complications of the system and would tend to destroy the use of pressure as a means of checking on the activity of the catalyst.

Another factor that would influence the pressure is the matter of the change of the electrolyte level. This effect would, of course, be a function of the size of the gas space as well as the height to which the electrolyte rises. Halving the gas space would double the effect of a particular height of rise assuming the temperature remains constant.

Of course, if the catalyst stops functioning the pressure rise would in a short time become enormous depending on the amount of gassing current. See Table III for the pressures that would be developed in a normal gas space.

7. Psychological Factors - The psychology of the use of a catalyst is a factor which at first might not appear to be important. The use of the present ventilating system is far from fool-proof but on the whole it is simple in operation and easy to understand. The use of the catalyst introduces an element of mystery, uncertainty, and lack of dependability. Catalytic action of the time that must

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be employed for this reaction is not at all thoroughly understood by those scientists most skilled in the particular field of catalysis. Its use by the average sailor would be accompanied by either complete mistrust or supreme confidence, either of which in the end might prove equally disastrous. Explicit rules would have to be made for the use of a catalyst and unless these were obeyed to the letter, trouble would surely result. Explosions of even a minor nature would destroy the confidence of the electrician. A period during which no explosions occurred would develop carelessness in handling of the cells and an explosion might then result with worse effects than usual. Of course, it may appear that the above discussion will hold in part or in whole for certain other instruments or methods now used on shipboard. However, it is believed that the reader after a few moments thought will see that the above is much more applicable to such a dangerous process as the destruction of electrolytic gas.

Conclusions and Results of Experimental Work

8. Possible Catalytic Materials - The catalysts which may be used for the destruction of electrolytic gas are platinum, palladium, iridium, rhodium, etc. or their alloys. Platinum and palladium are the only ones obtained in commercial proportions. They are about equal in catalytic activity as far as this reaction is concerned. Such substances as nickel, gold, copper, etc. are catalytic but their action is entirely too weak for them to be used for hydrogen destruction.

9. Condition of Catalyst

(a) State of subdivision - The condition of the catalyst from the standpoint of subdivision determines its activity. Catalysts in the form of the sheetmetal, wire, gauze, etc. are much less active than those in a finely-divided state such as platinum precipitated in asbestos or pumice, palladized asbestos or pumice, platinum powder, etc.

(b) Dryness - The catalyst must be perfectly dry to properly function. A complete wetting will entirely destroy its activity which, however, will be restored with subsequent drying.

(c) Temperature - The catalyst to exert its maximum activity must, other things being equal, have a temperature of about 200°F. If the catalyst is properly functioning this temperature, or one greater, will be produced from the heat of the reaction provided sufficient electrolytic gas is being generated. If the heat is insufficient to maintain this temperature, water may condense on the catalyst thus either destroying or greatly reducing its activity.

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10. Effect of Electrolyte on Catalyst - Electrolyte coming in contact with the catalyst will, of course, destroy its activity through wetting. In addition the action of the electrolyte tends to cut down the future activity of the catalyst and after several contacts with the electrolyte the activity can not be restored by subsequent drying. Its effect is quite poisonous.

11. Preparation of Catalyst - Fundamentally the catalytic mass is easily repaired. Several methods are available. Where solid carriers such as alundum or pumice are employed the best method is to soak the carrier in the chloride solution of the catalyst and then reduce the salt by means of hydrogen gas at 100°C. The difficulty lies in the fact that certain lots may show an unexplainably low activity. In other words, the activity is not reproducible. This has given some difficulty with the NRL Hydrogen Detectors but with these low activity detected and remedied.

12. Life of Catalyst - Work with the NRL Hydrogen Detector shows that the life of a catalyst of the type employed is difficult to determine. In this detector the conditions for long life are most ideal while in a submarine cell just the reverse is true. With the detector some catalysts have functioned for months. Others have lasted less than a week. If electrolyte spray comes in contact with the catalyst most assuredly the life will be greatly shortened. See (10). The life of the catalyst in the cells in a given battery will probably vary so that the use of a pilot cell to check catalytic activity on the whole would be impossible. There would be nothing standard about the activity of the catalysts in the various cells.

In the work carried on by the author, platinum precipitated in alundum has retained sufficient activity to catalyze small gas volumes for as long as six months. On the other hand, similar catalysts have lasted only a few hours.

13. Form of Catalyst - While the highest activity is secured with the catalyst impregnated in asbestos or in the form of powder the use of such forms is impossible. Asbestos easily mats when subjected to even slight moisture. Powder forms would easily get into the electrolyte if the cell was subjected to very much agitation. The same would be true to a lesser degree with the impregnated asbestos. It can be concluded that the only practical form is one in which the catalyst is precipitated in a plate of porous material with sufficient body to prevent powdering or loss of surface if subjected to normal submarine use. Alundum seems to answer this purpose. It is a very porous and highly unreactive form of aluminum oxide. However, impregnated alundum does not have the activity of the impregnated asbestos or the powder.

14. Quantity of Catalyst - Gas from currents as high as 1,000 amperes have been catalyzed with minute quantities of platinum in

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asbestos. As stated in (13) the activity of the platinized alundum is much less than some other forms consequently more would be required. Under favorable conditions a plate 16 square inches in area will catalyze the current from a charging current of 100 amperes. These plates contain approximately a gram of platinum. It should be pointed out that it is not a question of total quantity of catalyst but rather the amount of surface exposed to the gas that determines the total amount of catalyst.

In this connection it should be pointed out that the activity of the catalyst seems to vary from place to place on its surface. In other words, there are centers of activity. Moreover, these centers may shift during a period of catalysis. This phenomenon has been noted by other investigators in the field of catalysis. These centers of activity may get very hot and in certain cases in the catalytic studies on a laboratory scale incandescense was noted. These points of high heat may function as sparks and cause explosions if high concentrations of hydrogen should accumulate. Heating the catalyst will help prevent this localized action but will not necessarily prevent them. The state of the catalyst is also a factor in the quantity of gas catalyzed. A "cold" catalyst will handle far less gas than the same quantity of a hot one.

15. Nature of Catalytic Action - The catalytic action of copper, nickel, silver, etc. is of the carrier type as discussed in Section IV. Since only the platinum metals are applicable to the reaction in question only the mechanism of their action will be discussed.

In Section IV it was shown that contact catalysis can result in either a surface action or a space action depending upon whether or not reaction chains of considerable length develop.

A normal or typical charge with the more active forms of the catalysts is characterized by an increasing temperature and pressure as the charge proceeds. After an interval of time depending upon the rate of gassing, the temperature around the catalyst passes over a maximum and then falls in value. At the same time the pressure passes over a maximum. The charging current may now be increased with only a slight, or momentary, increase in temperature and pressure. Should the charge be stopped and the cell allowed to stand on open circuit and then the charge restarted the maxima are again secured but they are not as great as previously. The same would be true of maxima should the charge again be stopped and restarted. This is illustrated in the graphs on Plate 17. This type of action was found in a much less pronounced form in the catalytic tests with alundum carriers in small cells.

The above is explained as follows. The initiation of the reaction takes place on the surface of the catalyst or in its pores. The result is a number of points of high localized activity which may give way to a reaction in the space surrounding this localized activity through the formation of activated particles as explained in Section IV. The highly localized action gives rise to high local

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heat and high pressures as the electrolytic gas accumulates in the main gas space. After this local action proceeds for a time, it may give rise to chain reactions as previously explained which pass into the gas space. Should the chains branch greatly, major explosions will take place depending of course upon the quantity of accumulated gas. If the accumulation is not too great the result may be only a flame action. If this flame action continues the electrolytic gas would then react throughout the gas space, or perhaps more exactly over the surface of the electrolyte. This would result in a drop in the highly localized temperatures and a drop in pressure due to the removal of the accumulated gas. While the space action goes on, the catalyst probably plays little part in the reaction. It will of course be necessary to initiate and reinitiate the action. The explanation of the fact that successive maxima decrease in value is explained on the basis that a number of activated particles remain for a time after the stopping of the charge.

When external heating is used the temperature maximum cannot be detected as is to be expected. The space reaction is best secured in those cases where the catalytic mass is in close proximity to the gas space. In other words, its development is related to the type of cap and carrier employed as well as to the type and condition of the catalyst.

16. Temperature Characteristics - Table II gives the heat that will be evolved from gassing currents of various magnitudes. Of course, if this heat is not removed increasingly high temperatures will result. An examination of the results will show something of what may be expected in practice. In general high temperatures are obtained in the local surface action and relatively low temperatures with the space reaction. This is to be expected for the space reaction distributes the heat over a greater area and over an area from which it is more easily radiated. However, since local action is necessary to start the space reaction, if it does start, local heat action becomes very important. It is to be noted at this time that the experiments with the large cells were made under the most favorable conditions for the loss of heat. The cells were in a well-ventilated shed and most of the time water was kept over the cell top for the purpose of detecting leaks.

In caps such as the Mark I in which gas movement and ventilation in general is at a minimum, high temperatures result. In caps of the Mark III type excessive temperatures are less likely to result. However, even in this type points of very high temperature are secured as noted in the experimental work. It therefore follows that the type of cap and carrier plays a big part in the temperature situation. It is a very safe and conservative conclusion to say that temperatures of around 300-400°F can be expected on the catalytic surface if much gas is being catalyzed. Such high temperatures are a source of danger. Of course, higher temperatures which can very easily occur are as dangerous

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as a spark. Of course, these high temperatures will not be secured during the time that the space reaction is taking place as is seen from the data plotted in Plate 17.

17. Pressure Characteristics - Pressure changes are hard to predict and difficult to interpret due to the numerous factors which may produce them. Expansion of electrolyte will result in pressure change. The magnitude of the change depends on the amount of expansion and also on the size of the cell space. Temperature changes of course produce pressure changes, the pressure being directly proportional to the absolute temperature of the gas, other things being equal. Failure to completely catalyze the gas will result in pressure increase. If no catalysis takes place or if catalysis is partial, excessive pressures will soon develop as is seen from Table III. The pressures to be expected during a normal charge with the Mark VII cap would be about 10 inches of water.

Small gas waves due to flame action may during a charge produce negative pressures. The pressures may then again build up to six or eight inches of water before another flame sweeps out the gas.

With the space reaction, as is seen in Plate 17, the pressure is comparatively small. Also note the pressure maxima in this Plate.

Of course, in a very general way the pressure is a fair indication of the extent of the catalysis. With a cold catalyst there seems to be a minimum pressure which must be built up before catalysis becomes complete.

It can be concluded that only small pressures will develop as long as the catalyst functions properly but should the action be other than complete, extremely high pressures will soon develop.

18. Characteristics of Caps and Carriers - An inspection of the results shows that the type of cap and carrier play a very important part in the type and extent of the action secured. With types of caps and carriers such as Cap Mark I and Catalysis Carrier Mark II in which gas circulation is at a minimum, very high temperatures and comparatively high pressures will be developed as noted above. Certainly the caps and carriers should be so arranged that electrolytic gas can have ready access to the catalyst surface and at the same time the hot gas should pass away from the catalyst and thus not blanket its surface. The hot vaporized water produced should then come in contact with a cooling surface and be returned to the electrolyte. If gas volumes are large, the catalyst should be as nearly in the gas space as possible so as to burn the gas as fast as produced and hence eliminate the possibility of accumulation in dangerous concentration and quantities. The desired space reaction only takes place when proper circulation of gases is allowed for.

19. Explosive Hazards - The process of catalytic destruction is accompanied by a large element of danger and treachery. In the

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large cell experiments five major explosions took place. It should be emphasized that steps were taken to prevent explosions as far as possible, i.e. if a test was going in such a manner that an explosion seemed inevitable the test was stopped. Of course, this would be impossible under service conditions.

Lack of circulation seems to favor the occurrence of explosions. This is to be expected as it is the type of condition that produces high local heating.

One explosion will be described in detail as it illustrates the treachery and unreliability of the action. After a very successful test with the Mark III cap, the charge was secured and the cell left with the cap in place but the pressure tube disconnected and open to the atmosphere through a small hole about 1/4 inch in diameter. Four hours later a violent explosion took place. No doubt the electrolytic gas accumulated due to the gassing of the cell on open circuit and the forcing out of the air through the pressure tube. The catalyst was in a very reactive condition during the charge. Therefore, it was to be expected that the hydrogen would be catalyzed and therefore not allowed to accumulate. Perhaps the catalyst may have lost its activity due to wetting after the dimunition of the gassing. Then as the hydrogen accumulated, it regained its activity, perhaps rather suddenly, became incandescent, and due to the large amount of hydrogen an explosion resulted.

B. Conclusions for Hot Wire Ignition.

Hot wires of platinum, nichrome, or other metals may be employed for burning the electrolytic gas from the cell space in storage cells. However, the method offers little promise of value.

The requirement of a heating current is a serious drawback and the presence in the gas space of bare metallic wires which will be subject to corrosion from acid spray are fundamental drawbacks. Moreover, explosions are frequent. At any time, if the gassing current is heavy, even in small cells of the 80 ampere-hour type, explosions may take place due probable to the setting up of reaction chains as explained in Section IV. Should the wire become cold and the hydrogen gas accumulate the turning on of the heating current will inevitably result in an explosion.

Of course, it may be argued that it is not necessary to heat the wire to dull red heat but this merely changes the action to a catalytic one and therefore changes it to that classification.

Cells might be constructed in which periodic heating and explosion took place, the pressure of the accumulated gas making a connection in the heating circuit. Certainly that type of action could not be used on a submarine cell and would be of very questionable value on small cells.

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C. Conclusions for Catalytic Destruction in Small Cells.

The conclusions listed for large cells apply in general to small cells. Since small cells are usually used individually or if in battery the individual cells are easy of access the mechanical difficulties of control are much less. Also since the amount of gas generated at any one time is far smaller than in the large cells, the danger of excessive temperatures is much less and the need of cooling the catalyst thus reduced. The difficulty of cooling the catalyst would also be much less and could probably be handled without the need of other than ordinary exposed surfaces. The catalyst must, of course, remain in active condition or be fairly easily restored to active condition. As seen in the tests on small cells, this activity can be developed if the cell will withstand sufficiently high pressures to allow the time factor necessary for the restoration of the activity. Of course, if external heating is used the catalyst will, other things being favorable, remain in an active condition. With fairly stationary cells more active forms of catalysts can be used than the alundum plates and this would increase the efficiency of the process. However, on shipboard undoubtedly the plate forms would be necessary. The explosive hazard is much less in small cells than in large cells. The destruction from an explosion would also be much less. However, the explosion hazard does exist as was demonstrated from the explosions obtained from the experimental tests.

Since on the whole the danger of hydrogen gas in the handling and operation of small cells is far less than in large cells and in general practice gives little trouble, the chief value of the catalyst would be in the prevention of water loss. However, from a labor standpoint there would be no saving as the care and attention necessary to see that the catalysts remained active would far exceed the labor of watering cells.

The author does not see how the use of catalysts in small cells could prove either economical or efficient. Certainly far more attention would be necessary than is required in present methods of operation. The performance of the catalyst, while much better than in the large cells, is still far from trustworthy. The explosion hazard would always be present. Leaks would undoubtedly develop from time to time resulting in the unexpected and unsuspected presence of hydrogen around the cells. Such accumulation would be far more dangerous than under present conditions as the caution followed around the ordinary battery would probably not be considered necessary by the operator when a catalyst is employed.

D. General Recommendations for Use of Catalyst in Large Cells.

From an inspection of the results of the experimental work and the general conclusions the following points must be included in the design for the most successful type of cap and carrier to be used:

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1. Catalyst must be platinum or palladium.
2. Catalyst must be in a precipitated form on a firm carrier such as alundum plate.
3. To remain catalytically active the catalyst must be heated to 200°F. This must be effected by an electrically-heated device on the catalyst plate.
4. The catalyst must be placed in the actual gas space.
5. The catalyst must be so arranged as to produce a chimney effect so that the hot gases will pass upward thus removing them from the environment of the catalyst and at the same time permitting the generated electrolytic gas access to its surface.
6. A cooling surface must be placed above the catalyst to assist in the chimney action described in the preceding paragraph by condensing the water from the hot gases and at the same time to keep down excessive temperatures around the catalyst.
7. Allowing an overage factor of 100% a cell employing a finishing rate of 500 amperes must have available a total surface of catalyst of 160 sq. inches.
8. The cap carrying the catalyst must be easily detached from the cell.
9. All joints on cell top and cap must be absolutely airtight. No leakage can be permitted.
10. A safety device must be incorporated so that if excess pressure should develop the cell top will open without shattering of any parts.

With the above in mind certain general recommendations are made for a cap and carrier. The catalyst plates are 6 in number and are arranged as shown in Plate 20.

Note that plates are arranged at an angle so that a chimney effect is produced. Heating units are placed on the back of each plate. Condensation and cooling takes place on the top of the carrier and cap. This is effected by circulating cold air over the top of the cell. The engineering details of this cap are not included. In these details will be: method of fastening cap to cell top with gas-tight joint, electrical connections to heating units, supporting units for catalyst plates and heating units, etc. The cap must be easily replaced. It is assumed that in case of trouble an entire unit will be used for replacement. Material for the cap is not specified.

It is believed that this cap has certain features superior to that proposed in the patent of Lieut. Guthrie. A better circulation of gases will be secured. Condensation will take place above the catalyst plates and the returning water will have no chance to come in contact with the catalyst as it drops back on the covered heating units. If the units are too hot this water dropping back will again be vaporized, thus acting as a heat remover from the over-hot carrier and heating unit. The condensing surface will have greater cooling efficiency. The design is much simpler and it can more easily be replaced on the cell top. It admits of a

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greater expanse of catalytic surface and a surface better exposed to the electrolytic gases.

Of course, the catalyst must be protected from acid spray and to accomplish this a baffle arrangement must be placed over the electrolyte. Such a device is shown in the plate. It consists of two or more sets of staggered plates so arranged that there is no direct path from the electrolyte surface into the gas space.

E. Conclusions as to Advantages, Disadvantages, and Practicability of Catalytic Destruction in Large Cells.

The following discussion is an attempt by the author to present as he sees them the advantages and disadvantages of the use of a catalyst in submarine cells. Part of the discussion will of necessity be repetition. Personal opinion will, of course, enter into this discussion but as far as possible conclusions will be limited to results as obtained in the experimental work.

1. Advantages: These advantages are based on perfect performance of the catalyst:

(a) Elimination of the necessity of watering cells.
(b) Elimination of ventilating system. This has nothing to do with the uses of the present ventilating system other than that of sweeping out the hydrogen gas from the cell space.
(c) Elimination of danger of hydrogen accumulation in cell tops, ventilating ducts, etc.

2. Disadvantages: From the standpoint of practicability the following disadvantages stand out:

(a) Elimination of cooling effects produced by ventilation over electrolyte. The need for keeping the cell cool is recognized in battery practice. The most efficient way on the whole of cooling a liquid is to do so by having evaporation take place from its surface. It is this evaporation which produces a great part of the cooling in an ordinary charging cycle. Other cooling is of course effected by direct radiation to the moving stream of ventilating gas. Remove this ventilation and you remove the two main cooling effects in charging procedure. This would introduce the need of some other method of handling cell temperatures. If air is used much greater volumes would have to be supplied or the air would have to be cooled before being passed over and around the cell jars. Quite probably both would be necessary.

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(b) General Mechanical and Engineering Difficulties. The necessity of an absolutely gas-tight cell has been discussed. The trouble that is to be expected from hydrogen effusion due to the small size of the molecule and its high velocity has been discussed. Grave engineering difficulties would be experienced in making a catalyst cap and cell top that would be absolutely tight and that would stay tight over a period of time.

The development of the heating system for the catalyst plates would be difficult. Energy for maintaining their temperature would be necessary. This might prove a very vital factor in war operations and would, of course, be quite vital during a period of extended submersion. The electrical hookup would prove complicated. Means would have to be developed to check on the individual units to see that each was functioning properly. The introduction of a heating unit within the cell, while not presenting any particularly difficult features, would have to conform to rigid specifications to keep the gases from coming in contact with exposed incandescent wires. Everything considered, the installation of the heating system appears to present grave difficulties.

A cooling system must be developed to keep to a minimum excess temperature around the catalyst. Means must also be supplied to keep down cell temperatures in the electrolyte and plates. Since hydrogen leakage will undoubtedly occur from time to time ventilation should be supplied to keep down accumulation of explosive concentrations. Hence the need of an extensive ventilating system is obvious. The most efficient way to cool the catalyst would be through circulating water or through refrigerating coils. If circulating water is used it in turn would have to be cooled or fresh water supplied. Evaporation could not be employed unless steps were taken to prevent the vapor from accumulating in the ship's interior. These methods might be used to keep down the cell temperature but of course would not take care of possible hydrogen accumulation. Therefore, circulating air appears as the only feasible method. This would involve a ventilating system much more complicated than the present one employed as the air would undoubtedly have to be refrigerated, larger volumes employed, and entrance effected near the bottoms of the jars so as to produce sufficient radiating surface to keep down cell temperatures.

(c) Lack of Reliability. The mechanism of the hydrogen-oxygen reaction is quite complicated and varies under different conditions and from time to time under the same conditions. The life of the catalyst and its activity are uncertain. The catalyst is very sensitive to moisture, acid spray, oil fumes, etc. Consequently, it can not be predicted what will take place in a single cell much less in the 120 cells making up a submarine battery. It is not seen

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It is not seen how in practice a given battery would require other than constant attention and constant replacement of catalysts. A check on the performance of the catalysts in the NRL Hydrogen Detectors will add to what may be expected in a battery. Consider 120 hydrogen detectors and you have somewhat of a picture of a battery under the best of operating conditions.

(d) Explosion Hazard. Catalytic action often is localized resulting in points of high temperature and even incandescence. The introduction of a catalyst may therefore under certain conditions be equivalent to introducing a spark from the standpoint of the explosion hazard. Of course, if a catalyst functions properly at all times, explosive mixtures should not accumulate. From the work with catalysts it is impossible to predict just when an explosion will take place and to decide just how it could have been avoided. The same is true to a much less extent in the operation of the present ventilating system. To use a catalyst is to extend the danger in the present system and to introduce that which can easily prove to be the factor in the starting of an explosion. The explosions would probably be limited to individual cells. However, it is not seen how explosions could be tolerated from the standpoint of destruction to property and the effect on the morale of the crew.

SECTION IX

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SECTION X

Table I

Hydrogen produced by various charging currents.

1. Current-Amperes.
2. Time-Minutes.
3. Hydrogen-Grams.
4. Water-Grams.
5. Water-Pounds.

1	2	3	4	5
50	30	.932	8.39	.5
50	60	1.86	16.74	.018
100	30	1.86	16.74	.037
100	60	3.73	33.57	.074
200	30	3.75	33.75	.074
200	60	7.50	67.50	.148
300	30	5.58	50.22	.110
300	60	11.16	100.44	.221
500	30	9.36	84.24	.186
500	60	18.72	168.48	.371

Table II

Heat Produced by Hydrogen Combustion.
(18°C)

1. Grams of Hydrogen.
2. Heat of Combustion to Gaseous Water-Calories.
3. Heat of Vaporization of Water Formed-Calories.
4. Heat of Combustion to Liquid Water-Calories.
5. Heat of Combustion to Liquid Water-BTU.

1	2	3	4	5
.01	287.7	48.5	336.	1.33
.1	2,877.0	485.	3,362.	13.34
1.	28,771.	4,850.	33,621.	133.40
10.	287,710.	48,500.	336,210.	1,334.0

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Table III

Pressures Developed from Various Charging Currents in a Completely Sealed Cell.

1. Current.
2. Time-Minutes.
3. Pressure, cm of water.
4. Pressure, atmospheres.
5. Pressure-lbs. per sq. inch.
6. Hydrogen Percentage.

1	2	3	4	5	6
50	15	750	.72	11	22.0
50	30	1498	1.45	21	41.0
100	15	1498	1.45	21	41.0
100	30	2977	2.9	42	50.0
200	15	2977	2.9	42	50.0
200	30	5954	5.8	84	57.0
500	15	7442	7.2	106	58.0
500	30	14,883	14.4	212	62.0

The above calculations are based on the assumption that at the time of sealing the cell the gas space is completely filled with air at atmospheric pressure. The size of the gas space is assumed to be 16.2 liters.

PLATES

Plate No.

1. Modified Cell Top Mark I.
2. Modified Cell Top Mark I.
2. Modified Cell Top Mark II.
3. Modified Cell Top Mark III.
4. Cap Mark I.
5. Cap Mark I.
6. Catalyst Carrier Mark I.
7. Cap Mark II.
7. Cooling Mechanism Mark I.
8. Cap Mark III.
9. Cap Mark III.
10. Cap Mark III.
11. Cap Mark IV, Catalyst Carrier Mark II.
12. Cap Mark IV, Catalyst Carrier Mark II.
13. Cap Mark V, Catalyst Carrier Mark III.
14. Cap Mark V, Catalyst Carrier Mark III.
14. Catalyst Carrier Mark IV,
14. Catalyst Carrier Mark V.
15. Cap Mark VI, Catalyst Plate Mark I.
16. Cap Mark VII, Catalyst Plate Mark II.

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17. Test Curves, Test 22.
18. Experimental Cell Mark I.
19. Experimental Cell Mark I.
20. Proposed Catalyst Cap.
21. Mark I Modified KXH Cell Top.
22. Mark II Modified KXH Cell Top, Mark I KXH Catalyst Carrier.
23. Mark II Modified KXH Cell Top.
24. Mark II Modified KXH Cell Top.
25. Mark I KXH Catalyst Carrier.

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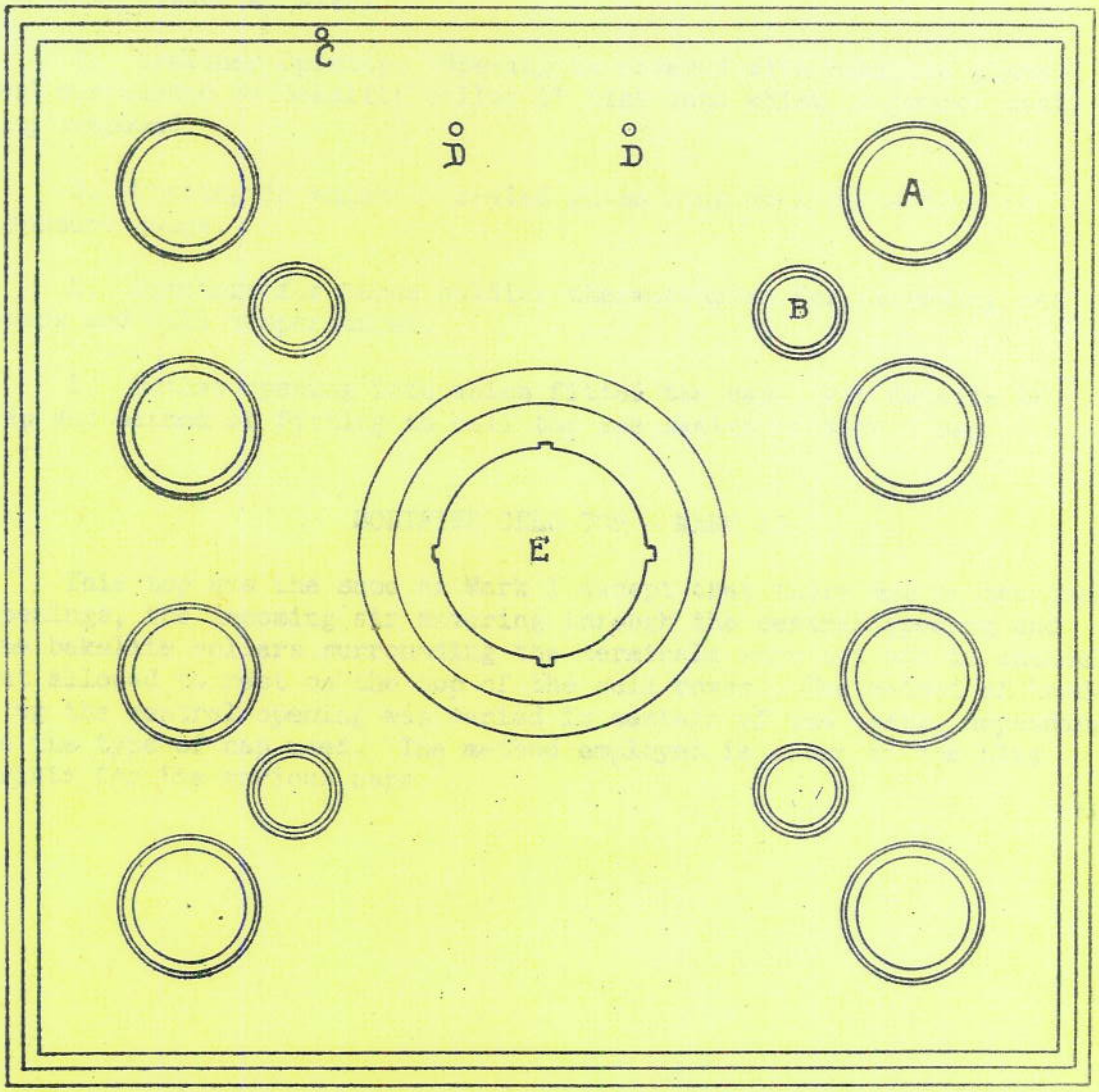
MODIFIED CELL TOP - MARK I



TOP VIEW - ONE-THIRD ACTUAL SIZE.

PLATE 1

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MODIFIED CELL TOP - MARK I.

A. Terminal Openings. Note channel around openings for holding Bakelite collar which in turn is filled with sealing compound. Bakelite collar 2" high.

B. Breather Opening. Opening is covered with bakelite plate and surrounded by bakelite collar 1" high into which is poured sealing compound.

C. Opening in which is sealed glass stop cock connecting to pressure gauge.

D. Openings for tubes holding thermocouples for recording gas space and cell temperatures.

E. Outlet opening into which fitted the cap. For details of cap and method of fitting to cell top see sketch of Mark I cap.

MODIFIED CELL TOP - MARK II.

This top was the same as Mark I except that there were no breather openings, the incoming air entering through the central opening and the bakelite collars surrounding the terminals were not set in channels but allowed to rest on the top of the cell cover. The method of handling the central opening was varied in certain of the tests, depending on the type of cap used. The method employed is shown in the blue prints for the various caps.

Plate 2

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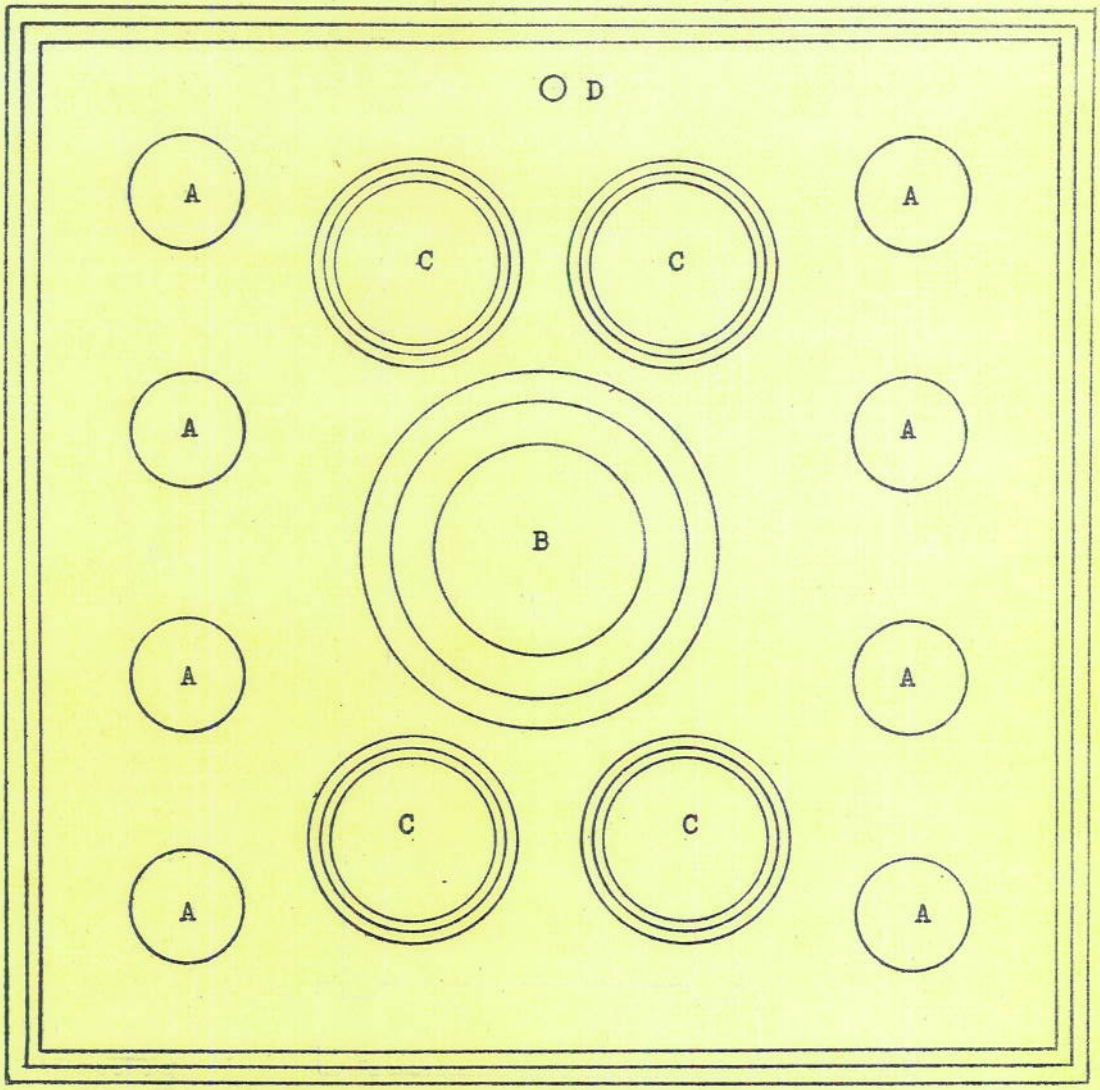
MODIFIED CELL TOP MARK III



Top View - 1/3 Actual Size.

A - Terminal Openings.
B - Central Opening, to be closed with Bakelite.
piece with hole same size as C.
C - Holes for Cap Mark VI.
D - Pressure Opening.

PLATE 3

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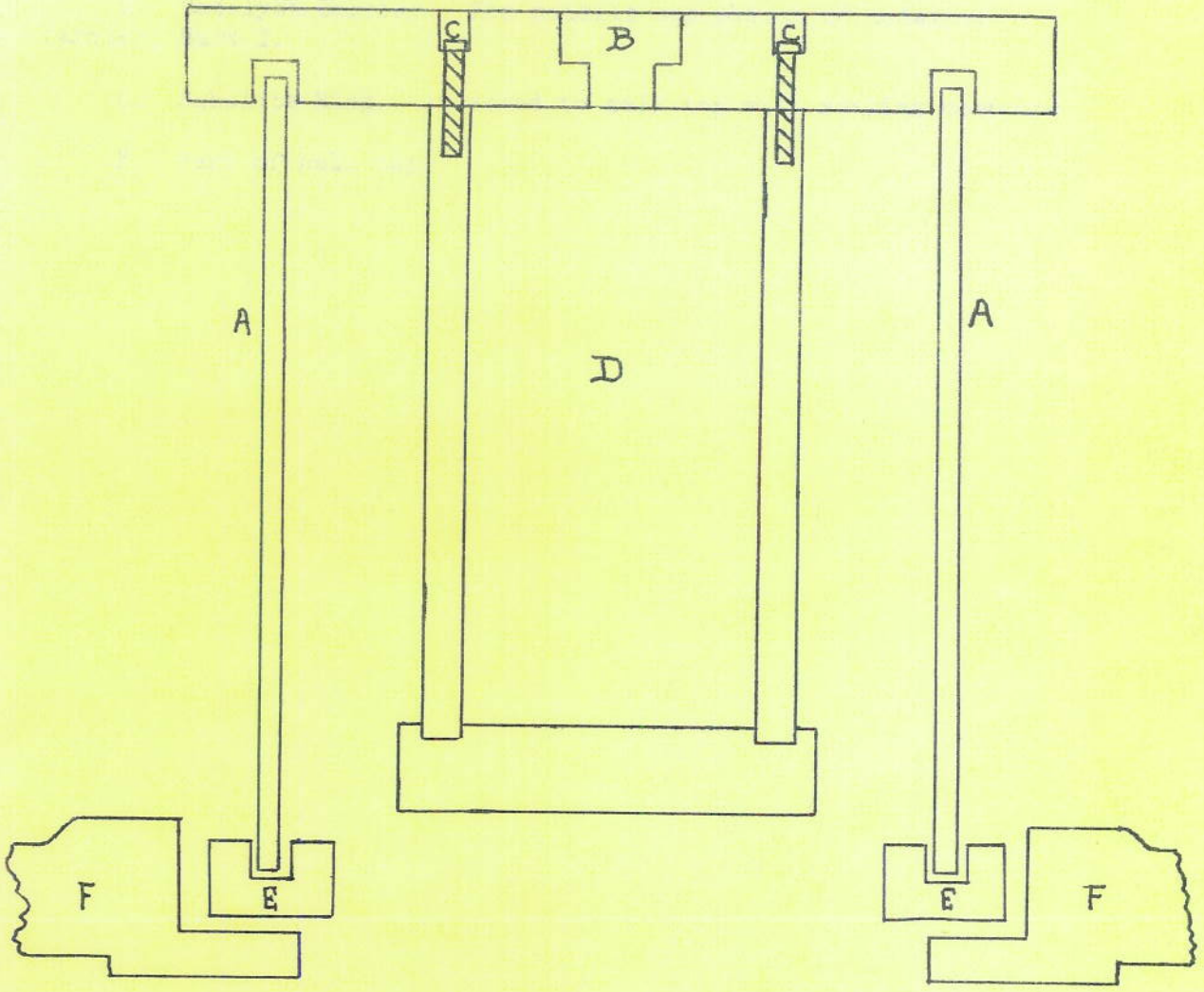
CAP - MARK I.



CROSS SECTION — ACTUAL SIZE

PLATE 4

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CAP - MARK I.

A. Bakelite Chimney. Set in grooves in top and in bottom ring. These grooves filled with sealing compound.

B. Thermocouple Opening.

C. Countersunk holes for screws holding catalyst carrier in place.

D. Catalyst Carrier. For details see sketch of catalyst carrier, Mark I.

E. Bakelite Ring. Attached to cell top with sealing compound.

F. Part of cell top.

Plate 5

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CAP - MARK II

In the Mark II Cap the bakelite chimney in the Mark I Cap was replaced by a chimney of Pyrex glass of the same dimensions. The same top was employed except that in certain of the tests two thermocouples were employed in the catalyst carrier thus necessitating an enlarging of the couple opening in the top so as to carry the two couples. Glass is a much better conductor of heat than bakelite and hence there is a better heat interchange between the carrier and the external environment in this cap than in the Mark I.

COOLING MECHANISM - MARK I.

This mechanism consisted of a collar of 1/8" bakelite 10" in diameter and 6" high, which was placed around the cap. This mechanism was sealed to the cell top through insertion in the sealing compound held in a channel cut in the cell top. Two rubber faucets were placed in this collar, one at the top and one at the bottom. By means of these water could be circulated through the mechanism. The circulation method was used in certain tests. In others the faucets were closed and the water or the water-ice mixture held in the mechanism without circulation. Of course in the tests employing ice, constant replenishing of the ice was necessary.

Plate 7

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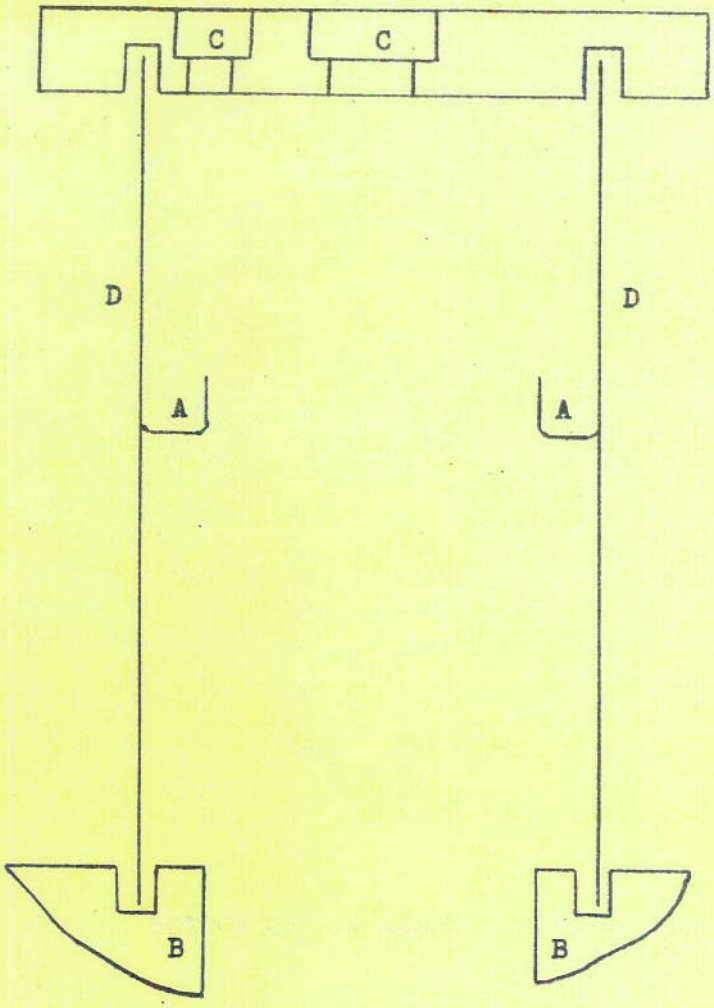
CAP - MARK III



CROSS SECTION - ACTUAL SIZE

PLATE 8

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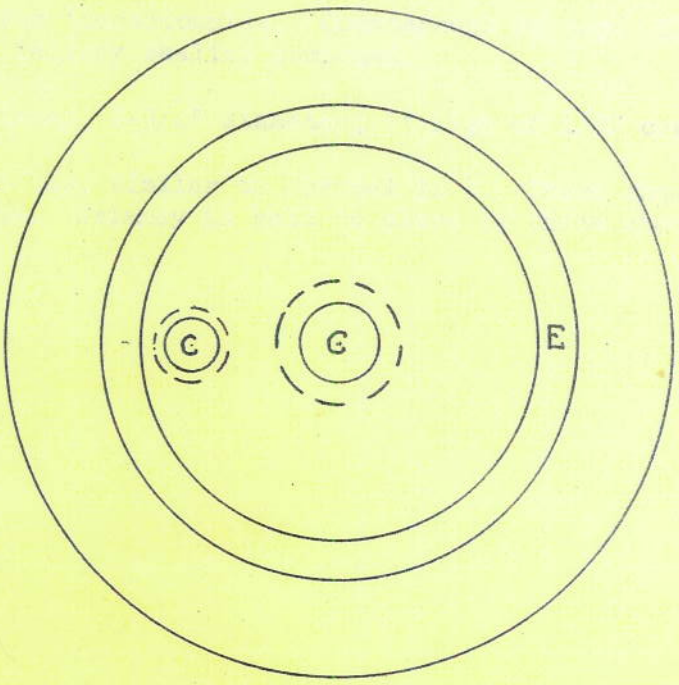
CAP - MARK III



BOTTOM OF CAP COVER - ACTUAL SIZE

PLATE 9

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CAP - MARK III.

A. Catalyst Channel. Made of 1/32 copper, 3/8" wide, 3/8" high, brazed to chimney. Completely encircles chimney.

B. Part of bakelite plate covering opening in center of cell top.

C. Openings for thermocouples. Countersunk in top. Thermocouples held in place with battery sealing compound.

D. Copper chimney, 2-3/4" diameter, 5" high of 1/32 copper.

E. Channel in top, similar to channel in B. These channels are 1/4" deep, 1/4" wide. Chimney is held in place in these channels with sealing compound.

Plate 10

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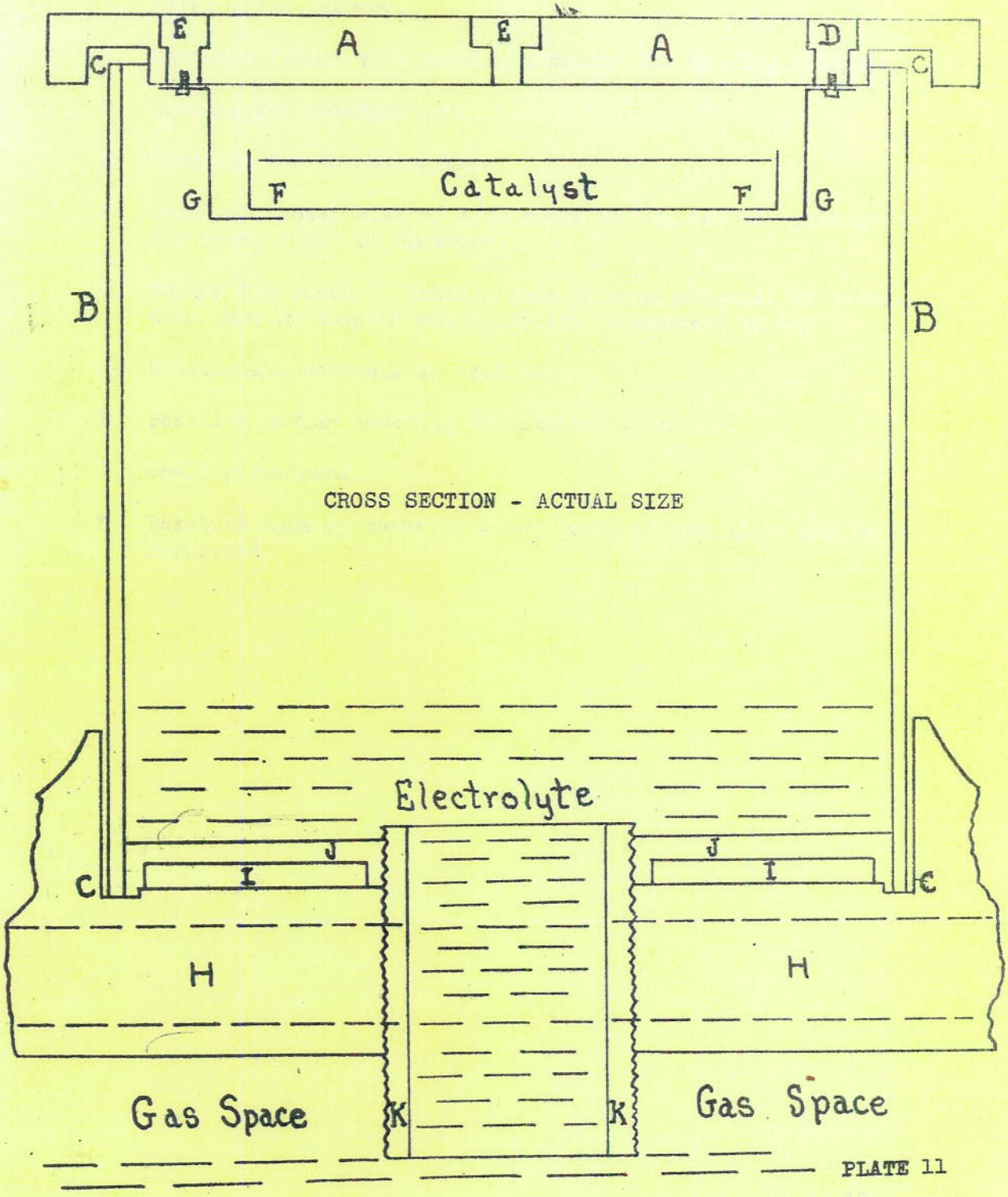
CAP. MARK IV and CATALYST CARRIER MARK II.



CROSS SECTION - ACTUAL SIZE

PLATE 11

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CAP - MARK IV and CATALYST CARRIER MARK II.

A. Bakelite top.

B. Pyrex glass chimney.

C. Channels filled with sealing compound for holding chimney.

D. Opening for pressure tube.

E. Openings for thermocouples.

F. Catalyst basket made of 1/32 brass having twelve openings to the inch, 3/64" in diameter.

G. Holder for catalyst basket, made of same material as basket. Note tabs by means of which carrier is screwed to top.

H. Ventilation channels in cell top.

I. Bakelite collar covering ventilation openings.

J. Sealing compound.

K. Bakelite tube by means of which depth of gas space may be regulated.

Plate 12

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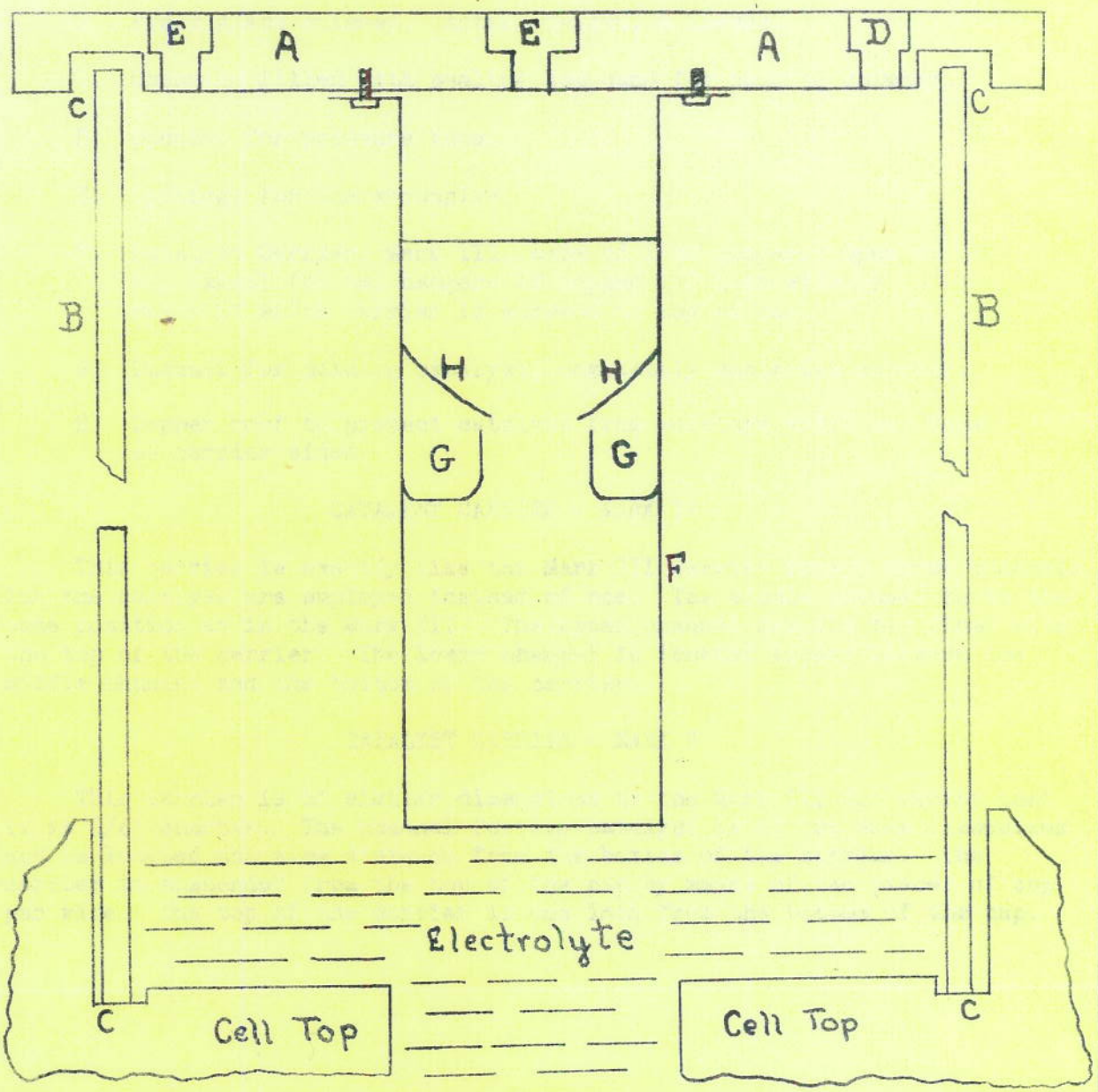
CAP. MARK V and CATALYST CARRIER, MARK III.



CROSS SECTION, ACTUAL SIZE.

PLATE 13

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CAP - MARK V and CATALYST CARRIER MARK III

A. Bakelite top.

B. Pyrex glass chimney. Actual height, 8 inches.

C. Channels filled with sealing compound for holding chimney.

D. Opening for pressure tube.

E. Openings for thermocouples.

F. Catalyst Carrier, Mark III, made of 1/32 copper. Open at top except for two hangers of copper 1/2 inch wide by means of which carrier is screwed to top of cap.

G. Channel for holding catalyst, completely encircles carrier.

H. Copper roof to protect catalyst from moisture which may form on carrier sides.

CATALYST CARRIER - MARK IV

This carrier is exactly like the Mark III carrier except three channels for the catalyst are employed instead of one. The middle channel is in the same position as in the Mark III. The upper channel has its top flush with the top of the carrier. The lower channel is located midway between the middle channel and the bottom of the carrier.

CATALYST CARRIER - MARK V

This carrier is of similar dimensions to the Mark III cap except that it is 3/4" shorter. The channel for the catalyst is of the same dimensions and is located the same distance from the bottom of the carrier. The carrier is suspended from the top of the cap by means of two pieces of copper wire. The top of the carrier is one inch from the bottom of the cap.

Plate 14

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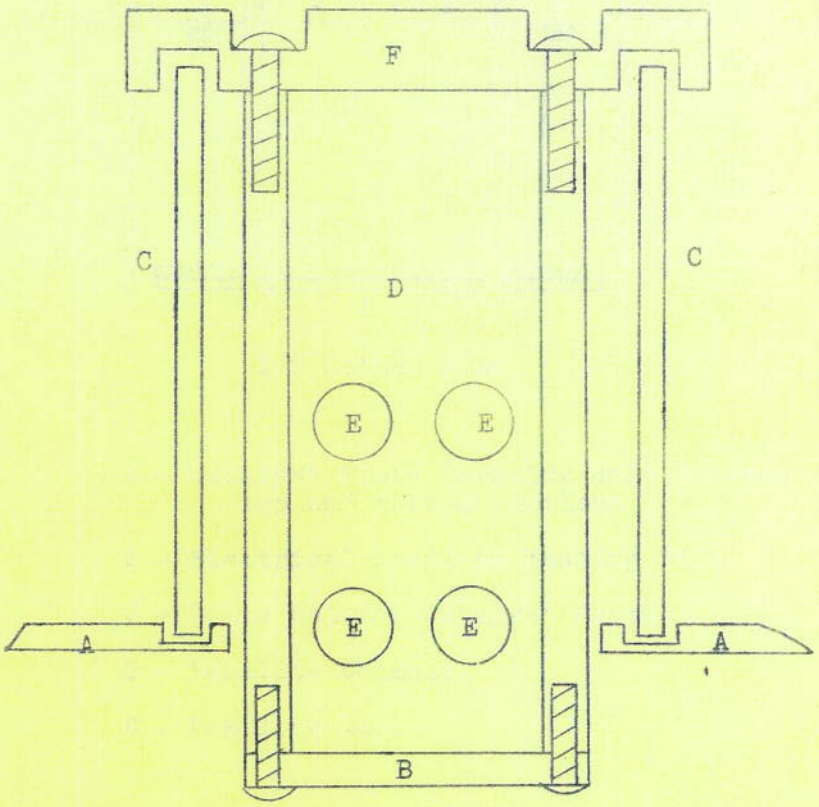
CAP MARK VI AND CATALYST PLATE, MARK I.



Actual Size.

A - Cell Top
B - Catalyst Plate.
C - Bakelite Chimney.
D - Bakelite Tube.
E - Ventilation Openings.
F - Bakelite Top.
(Openings for thermo-couples not shown.)

PLATE 15

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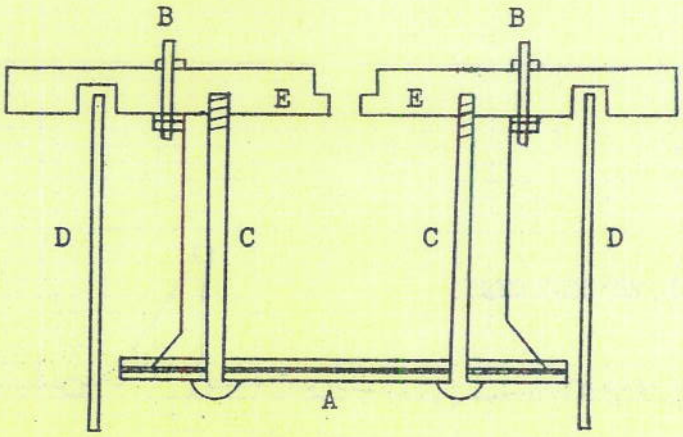
CAP MARK VII AND CATALYST PLATE, MARK II.



1/2 Actual Size

A - Catalyst Plate (heating unit between top and bottom sections.)

B - Electrical Leads to Heating Unit.

C - Bolts Holding Catalyst Plate.

D - Bakelite Chimney.

E - Bakelite Top.

PLATE 16

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TEST 22 SEPT. 13,1932

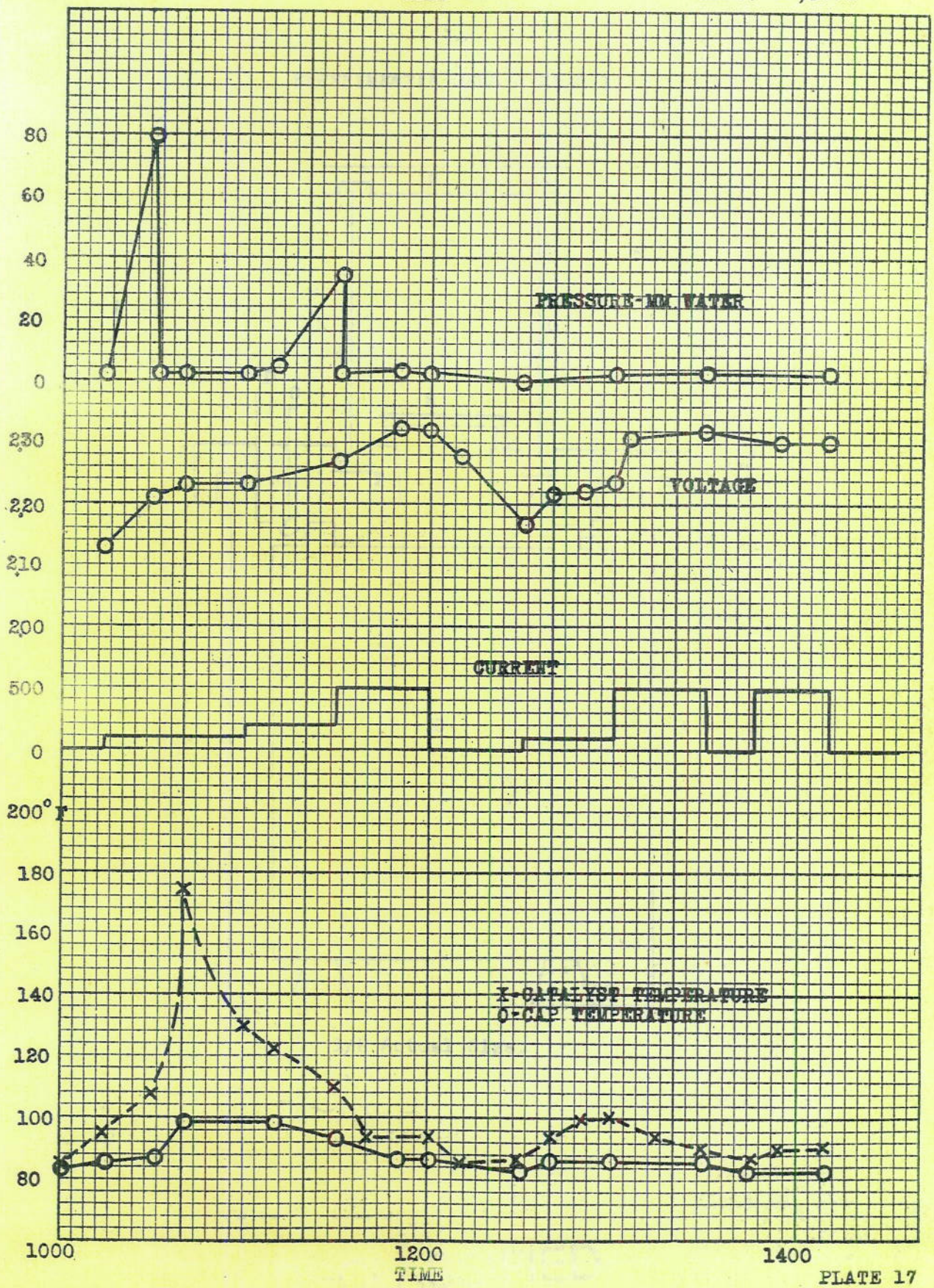

PLATE 17

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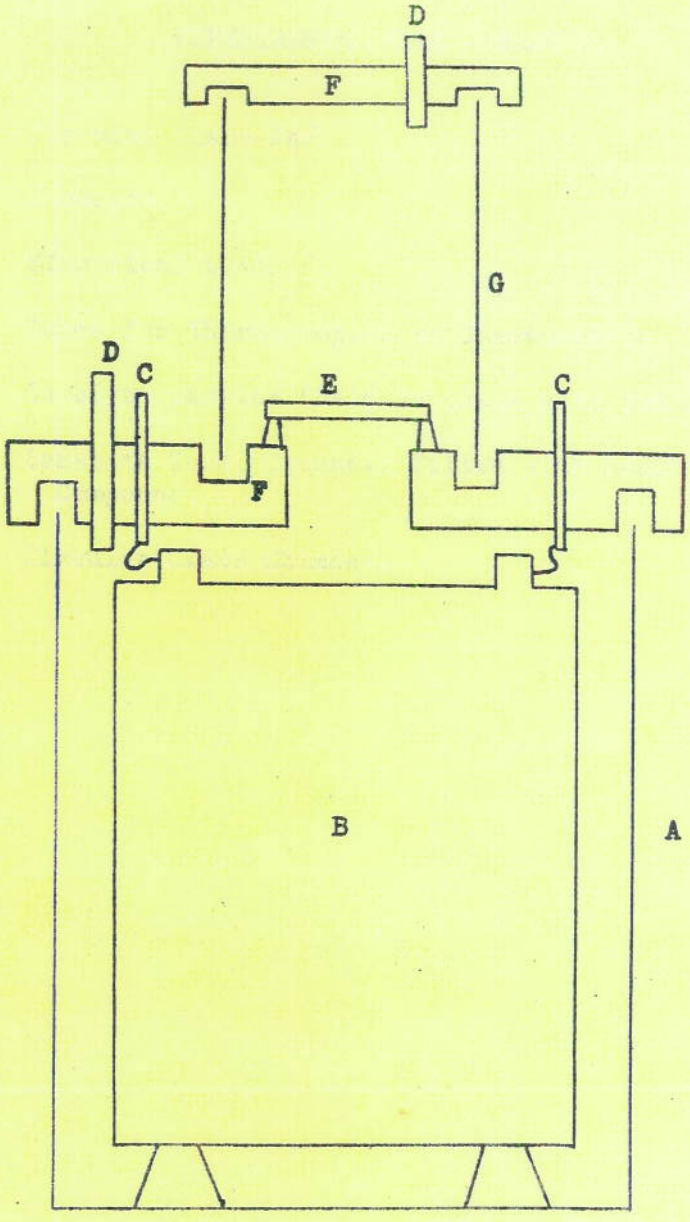
EXPERIMENTAL CELL - MARK I.



1/2 Actual Size.

PLATE 18

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EXPERIMENTAL CELL - MARK I.

A. Circular Glass Jar.

B. Elements.

C. Electrical Leads.

D. Tubes for Thermocouples or Thermometers.

E. Catalyst Carrier (held in place with small cork).

F. Bakelite Tops, Channels filled with Sealing Compound.

G. Circular Glass Chimney.

Plate 19

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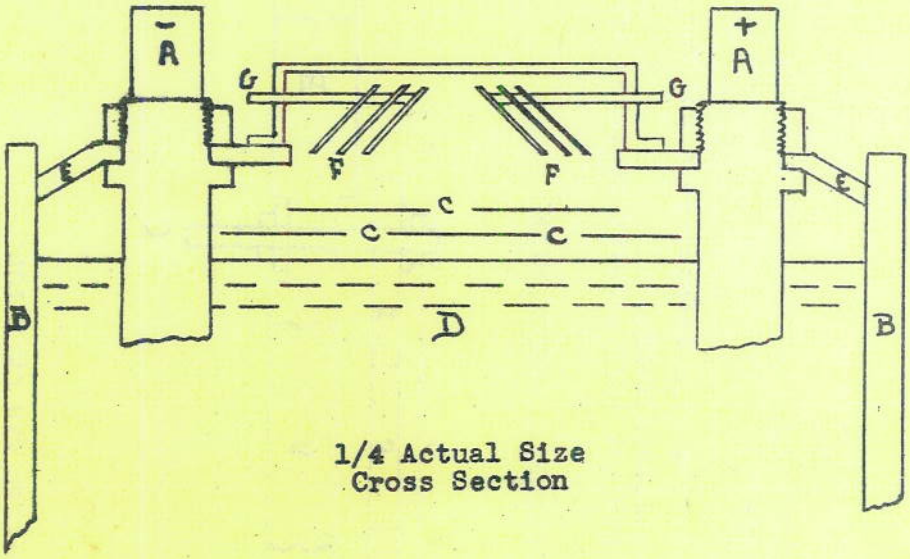
PROPOSED CATALYST CAP AND CARRIER
FOR SUBMARINE CELL.



1/4 Actual Size
Cross Section

A - Cell Terminals.
B - Cell Jar.
C - Baffle Plates.
D - Electrolyte.
E - Cell Top.
F - Catalyst Plates.
G - Support Rods, for Catalyst Plates.

PLATE 20

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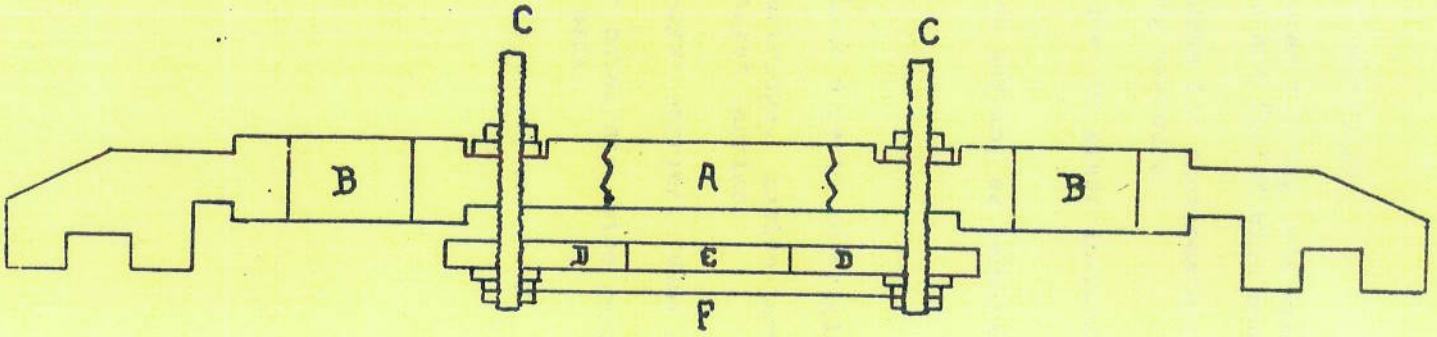
MARK I MODIFIED KXH CELL TOP.



CROSS SECTION - ACTUAL SIZE.

A - Opening for cell top. Cap for this opening contains glass stopcock connecting to pressure gauges.

B - Openings for terminals. Sealed with regular lead nut and sealing compound.

C - Brass terminals for hot wire.

D - Bakelite Plate.

E - Circular opening in bakelite plate D.

F - Hot wire.

PLATE 21

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MARK II MODIFIED KXH CELL TOP AND MARK I KXH CATALYST CARRIER.

A. Opening for cartridge.

B. Bakelite tubes fitting into openings for cell terminals. These tubes are filled with sealing compound.

C. Bakelite tubes for thermometers. Thermometers held in place with sealing compound.

D. Bakelite tube for glass stopcock which connects to pressure manometer.

E. Brass screws serving as terminals for heating current for hot wire.

F. Hot wire.

G. Bakelite plate screwed to original cell top.

H. Bakelite cartridge. Inside threaded in those tests using the Mark I catalyst carrier.

I. Mark I catalyst carrier. Made of bakelite.

J. Support for catalyst: wire gauze, alundum, etc., according to test being made.

Plate 22

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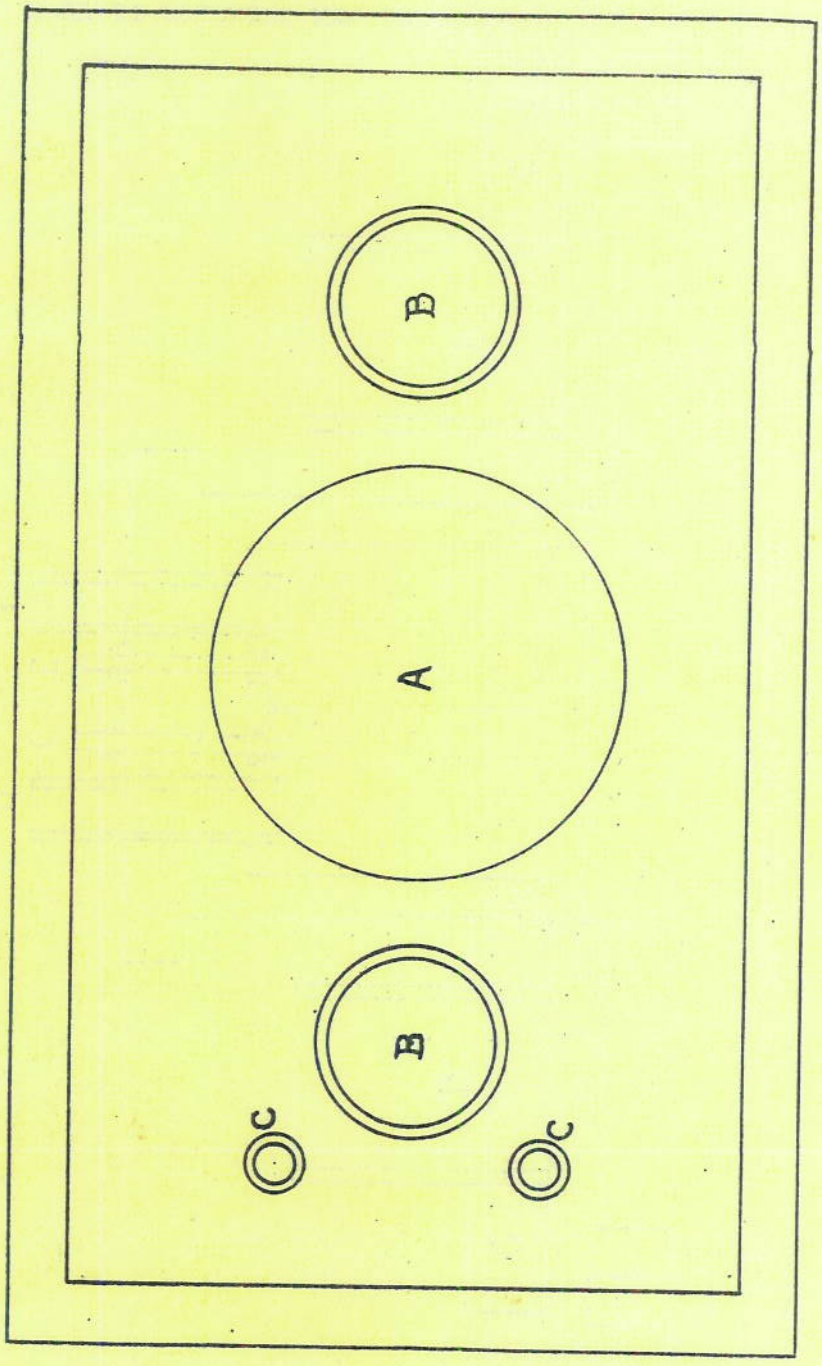
MARK II MODIFIED KXH CELL TOP



TOP VIEW - ACTUAL SIZE

PLATE 23

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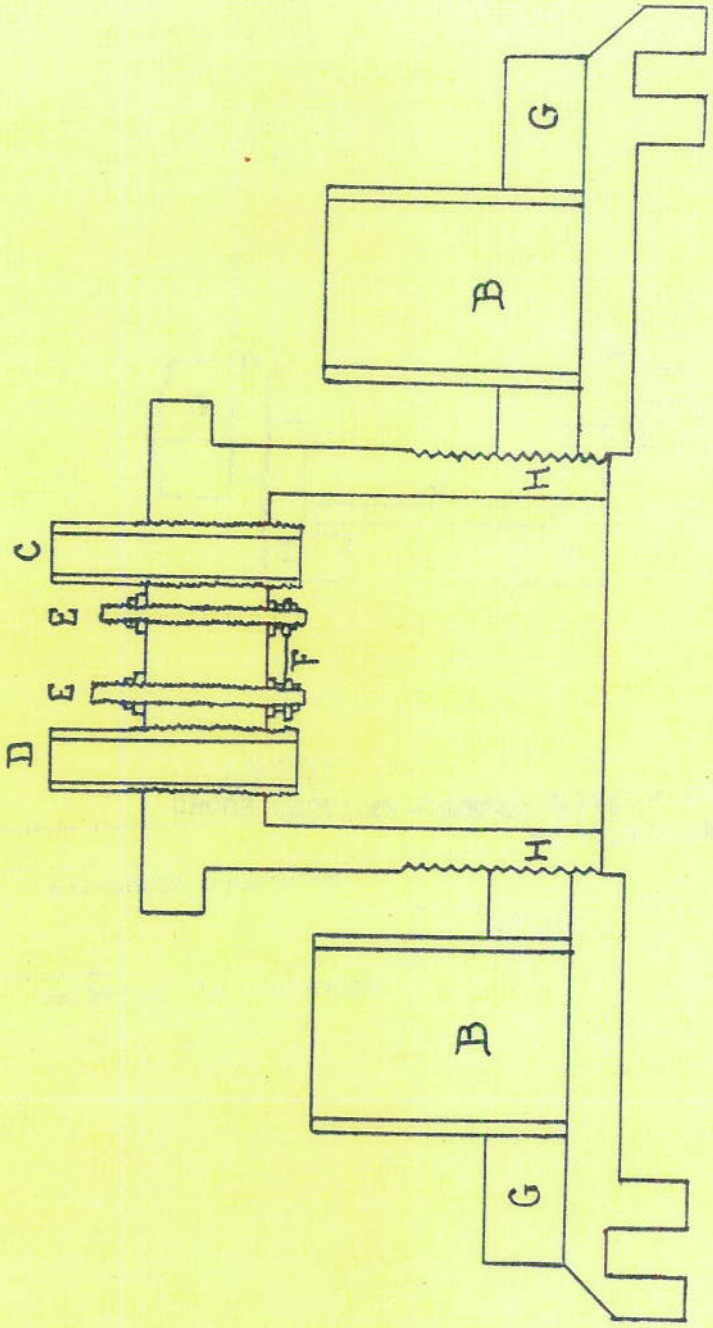
MARK II MODIFIED KXH CELL TOP



CROSS SECTION - ACTUAL SIZE

PLATE 24

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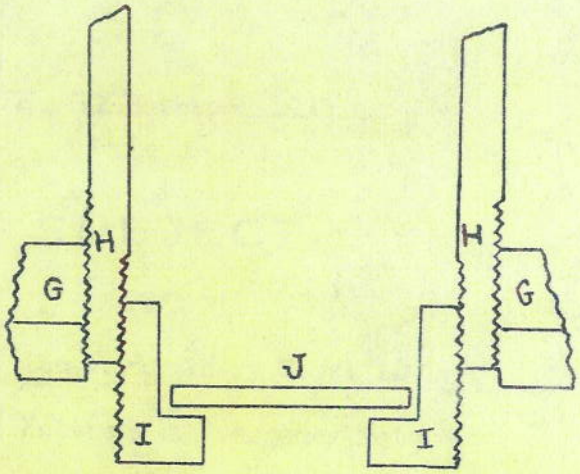
MARK I KXH CATALYST CARRIER



CROSS SECTION - ACTUAL SIZE

PLATE 25

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