ELECTROLYTIC PRODUCTION OF HYDROGEN PEROXIDE

by

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INTRODUCTION

The chemical and electrochemical reactions involving hydrogen, oxygen, water and hydrogen peroxide have been studied extensively from kinetic and thermodynamic standpoints. The earlier workers have usually assumed that water is the primary product of the reaction between hydrogen and oxygen.

From the studies on the electrochemical reduction of oxygen, there is little doubt that hydrogen peroxide is an intermediate product with its subsequent decomposition to water and oxygen. The instability of hydrogen peroxide makes it difficult to study the production and chemistry of hydrogen peroxide, the reaction taking place in a hydrogen-oxygen cell and the corrosion mechanism. Attempts made to study the formation and decomposition of hydrogen peroxide have produced ambiguous results.

The purpose of the present investigation was to study the factors affecting the electrolytic formation and decomposition of hydrogen peroxide at different cathode materials.

II. LITERATURE REVIEW

A. Introduction

The electrolytic production of hydrogen peroxide from hydrogen and oxygen is important from various standpoints. It promotes better understanding of the production and chemistry of hydrogen peroxide, electrochemistry of hydrogen, oxygen and water, reactions of hydrogen, oxygen and water, and the mechanism of corrosion. Hence it would be well to consider the above topics as a background to the understanding of the present investigation.

B. Importance of Hydrogen Peroxide

General: Hydrogen peroxide in concentrations up to 35% is used as an insecticide, a bleaching agent, in medicine, and as a chemical agent. Hydrogen peroxide is now available in concentrations up to 90%. The higher strength is a new chemical of great potentialities in fields ranging from buzz bombs, rockets and submarines to commercial explosives and synthetic chemicals. It is in effect a new, self-contained source of energy.

As an Energy Source:[9] The value of high test hydrogen peroxide as an energy source lies in the fact that when proper catalysts are present it dissociates instantly into five thousand times its volume of steam and oxygen. This power system was used by Germans to drive various types of engines during the last world war. Some of the applications included

propulsion of submarines, naval and aviation torpedoes, assist take-off units, jet-propelled planes and missiles.

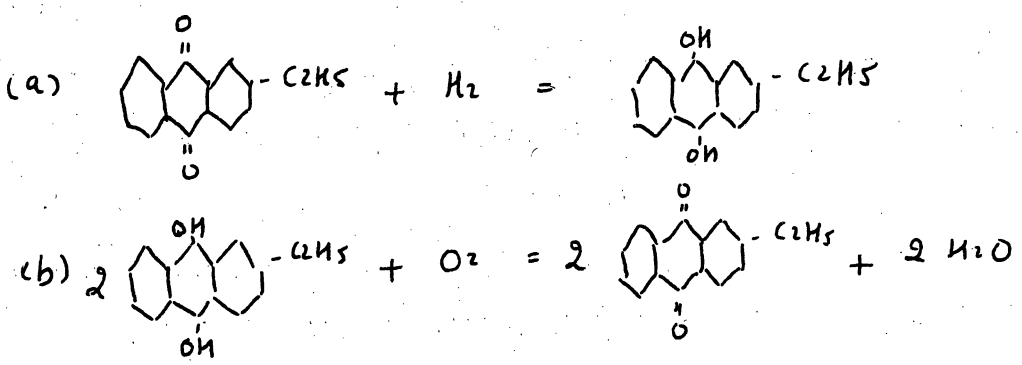
As a Fuel[9]: The oxygen from hydrogen peroxide is used to burn customary fuels such as a type of diesel fuel in the Walther engine for submarines, or special chemicals such as hydrazine hydrate. As a commercial explosive it is used as a fuel component with organic compounds. The ingredients - the peroxide and alcohol for example - may be shipped and stored separately, free from the customary hazards of explosives. They do not release any toxic nitrogenous gases.

Chemical Uses[9]: High test hydrogen peroxide is soluble in a number of organic media. It is almost free from water which makes it useful for bulk polymerization of monomers, treatment (e.g. bleaching) of water insoluble materials such as oils, fats and waxes, and as an oxidizing agent for organic reactions. It is valuable as a catalyst in the formation of some resins and as a reactant in forming soap-like synthetics.

C. Production of Hydrogen Peroxide

Chemical Methods: I. By the Action of Barium Peroxide on an Acid[24]: Finely ground barium peroxide prepared by heating anhydrous baryta to a dull red heat in a stream of oxygen is made into a thin paste with water and introduced very gently into the acid solution. The temperature should be kept at 10-15°C and the solution must be constantly agitated. When the solution is nearly neutralized, the liquid is decanted and further purified. Hydrogen peroxide concentration of 30-40% can be thus prepared.

Chemical Methods: II. From 2-Ethyl Anthraquinone[9]: A potentially promising method of hydrogen peroxide production, under serious investigation in Germany, utilized the following reactions:



Reaction (a) above was carried out at room temperature by passing hydrogen through 2-ethyl anthraquinone dissolved in a one to one mixture of thiophene free benzene and cyclohexanol containing Raney nickel. Only enough hydrogen was added to the aluminium vessel to reduce one half of the quinone to the hydroquinone. After filtering, the hydroquinone solution was placed in an enameled iron oxidizer where reaction (b) was carried out by bubbling oxygen through the solution at a temperature of 30-37°C. The hydrogen peroxide solution formed the bottom layer of the tank from which it was drawn off as a 20% solution into aluminium containers.

Electrolytic Method[9]: The electrolysis of ammonium acid sulphate in sulphuric acid solution yields ammonium persulphate which by metathesis with potassium bisulphate produces relatively more stable and insoluble potassium persulphate. The potassium persulphate is hydrolyzed with live steam and the resultant vapors are rectified under reduced pressure and condensed to yield an aqueous solution of hydrogen peroxide.

In a German plant producing high-test hydrogen peroxide, porcelain electrolytic cells were used. Each cell operated at 5.7 volts with a current efficiency of 85%. Ammonium thiocyanate (0.1 gm per litre) was placed in the electrolyte to increase the overvoltage. Platinum wire anodes supported by rubber-covered aluminium tubing and graphite rod cathodes wound with blue asbestos rope to serve as a diaphram were used. The electrodes were so arranged that each anode was surrounded by four cathodes. A forced air current above the cells maintained the hydrogen gas concentration below 5%.

The potassium persulphate formed was separated by a centrifuge and then steam distilled in a porcelain retort. The resultant vapors were rectified at a pressure of about 38 mm mercury to produce a 35% solution of hydrogen peroxide which served as stock for the preparation of concentrated hydrogen peroxide.

The reactions taking place are represented by the following reactions:

(a) $4NH_4HSO_4 + O_2 = 2(NH_4)_2S_2O_8 + 2H_2O$
(b) $(NH_4)2S_2O_8 + 2KHSO_4 = K_2S_2O_8 + 2NH_4HSO_4$
(c) $K_2S_2O_8 + 2H_2O = 2KHSO_4 + H_2O_2$

The concentration of 35% to 85% hydrogen peroxide represents the advance of German production. For this step, two similar units were placed. Each unit consisted of a steam-heated retort, a Raschig ring separator, a Raschig ring rectifying column, a surface condenser, a vacuum pump and a barometric condenser with trap. Porcelain was used except for the aluminium condensers and polished Krupp V14A stainless steel (18% Cr., 8% Ni., 5% Mo.) heating coils of the concentration retorts. Ammonium pyrophosphate was used as a stabilizer for H_2O_2.

The overall efficiency of the conversion from 35% to 80-90% hydrogen peroxide was 98%.

D. Storage of Hydrogen Peroxide

To improve the stability[28] of stored concentrated hydrogen peroxide attempts were made (a) to find stabilizers to add to the liquid such as phosphoric acid, acetanilide and sodium pyrophosphate, (b) to find new materials for containers. The materials used for containers include aluminium, tin, porcelain, glass and polyvinylchloride based plastics. Aluminium with its safety, low cost and ease of working is probably the most suitable construction material.

The theory of the stability of hydrogen peroxide in containers is not completely worked out. The stability of strong hydrogen peroxide appears to vary more or less directly with its purity and inversely with its heavy metal content.

E. Properties of Hydrogen Peroxide[18]

Physical: M.P. = -2°C, B.P. 84-85°C at 68 mm. mercury pressure. It is a syrupy acidic liquid, bluish green when viewed in bulk and transparent when viewed in less amounts.

Chemical: (a) When heated to about 100°C, it decomposes with explosive violence but is stable if absolutely pure.

(b) Acidic action: With alkalies, hydrogen peroxide acts acidic with the formation of peroxides. Thus, $Na_2CO_3 + H_2O_2 = Na_2O_2 + H_2O + CO_2$

F. Detection of Hydrogen Peroxide[24]

Quantitative Methods:

(a) Strongly acidify the solution with H_2SO_4 or HCl, then add a solution of potassium iodide free from iodate and determine the iodine liberated by means of sodium thiosulphate.

(b) By direct titration with potassium permanganate in presence of an acid. Thus $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$.

Qualitative Methods:

(a) Hydrogen peroxide gives a blue-green coloration with an alcoholic solution of guaiacol and sulphuric acid.

(b) Hydrogen peroxide gives an intense yellow color with a solution of quinine sulphate in concentrated sulphuric acid.

(c) An ammoniacal silver nitrate solution gives a characteristic gray opalescence with hydrogen peroxide.

(d) Solutions of titanic acid are turned red by hydrogen peroxide.

G. Stability of Hydrogen Peroxide Solutions

Spontaneous Decomposition of Hydrogen Peroxide[5]: Hydrogen peroxide solutions are very stable when pure. Table I shows the rate of decomposition of high purity 90% hydrogen peroxide. Nothing is mentioned about the containers.

TABLE I [5]

RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE

PURITY - 90%

Temperature	Time for 1% loss
25°C	1 year
66°C	1 week
100°C	24 hours

The above table indicates that the rate of spontaneous decomposition of pure hydrogen peroxide increases with increasing temperature.

(5) Bretschger, M. E. and Shanley, E. S. "Concentrated Hydrogen Peroxide" Trans. Electrochem. Soc. Preprint 92-36 (1947).

Catalytic Decomposition of Hydrogen Peroxide: Bretscher and Shanley[5] have found that certain metallic ions decompose hydrogen peroxide solutions catalytically. Certain metal ions, as soluble salts, were added in a mildly acid 6% commercial type hydrogen peroxide solution with the results shown in Table II.

The mechanism of the catalytic decomposition of hydrogen peroxide is explained by Murphy[2][20]. Hydrogen peroxide is decomposed catalytically according to

$$2H_2O_2 = 2H_2O + O_2 \qquad (a)$$

and not according to

$$H_2O_2 = H_2O + O \qquad (b)$$

If hydrogen peroxide decomposed according to the second reaction, it would be one of the most powerful oxidizing agents, because it would be setting free such a powerful oxidizing agent as the nascent oxygen. Experimentally, however, it is found that hydrogen peroxide is a weak oxidizing agent. The catalytic action by platinum is explained by Murphy[20] according to:

$$H_2O_2 + Pt = Pt(2H) + O_2$$
$$H_2O_2 + Pt(2H) = Pt + 2H_2O$$

in which Pt(2H) indicates an adsorption complex of hydrogen on metallic platinum.

The measured reaction was, therefore, predicted to be monomolecular. This was later confirmed by Weiss and Jaffe[27].

H. Production of Hydrogen Peroxide From Hydrogen and Oxygen

The water which collects about the anode during the electrolysis of water acidulated with sulphuric acid possesses oxidizing properties. By various workers[6][17] this is attributed to the presence of hydrogen

TABLE NO. II [5]

EFFECT OF CERTAIN METALLIC IONS ON HYDROGEN PEROXIDE SOLUTION

PURITY - 90%

Contaminant		% loss in 24 hours at 100°C.
None		2
Aluminium	10 mg per liter	2
Chromium	0.1 mg per liter	96
Copper	0.01 mg per liter	24
Copper	0.1 mg per liter	85
Iron	1.0 mg per liter	15
Tin	10 mg per liter	2
Zinc	10 mg per liter	10

(5) Bertschger, H. E. and Shanley, E. S. "Concentrated Hydrogen Peroxide" Trans. Electrochem. Soc. Preprint 92-36 (1947).

peroxide. However, the anodic oxidation of sulphuric acid yields persulphuric acid[9] which is an oxidizing agent. The presence of hydrogen peroxide at the anode is, therefore, doubtful.

Traube[25] found that hydrogen peroxide is formed at the cathode during the electrolysis of dilute sulphuric acid provided oxygen is bubbled about the cathode at the same time. He suggests platinum and mercury as the best electrode materials. From his results, Traube concluded that (a) hydrogen peroxide is an intermediate product in the electrolytic reduction of oxygen to water, (b) hydrogen peroxide is not formed at the anode by bubbling hydrogen over it, (c) hydrogen peroxide is always a product of the reduction of molecular oxygen and is never produced by the oxidation of water. F. Richarz[21], on the contrary, believes that hydrogen peroxide is also formed at the anode but in a different way. Richarz assumes that persulphuric acid is primarily formed during the electrolysis of sulphuric acid. Persulphuric acid then further reacts with water to form hydrogen peroxide.

Traube's[25] results were confirmed by Richarz and Lonnes[22]. They obtained 80% efficiency in the production of hydrogen peroxide at platinum cathode at 25°C and atmospheric pressure. It is worth mentioning that the work of Traube, Richarz and Lonnes was confined to noble metal electrodes as cathodes and sulphuric acid as electrolyte.

Fischer and Kronig[11] studied the factors affecting the yields of hydrogen peroxide at the cathode. Bubbling air and oxygen over the cathode in separate experiments, better results were obtained with oxygen. Increasing the temperature decreased the current efficiency. Better current

efficiency in the formation of hydrogen peroxide was obtained with more vigorous stirring. Acids (H_2SO_4, H_3PO_4, H_3BO_3) were found to be the best electrolytes. Best results were obtained with 0.1% sulphuric acid and phosphoric acid of corresponding concentrations. Mercury was found to be the best electrode material. Too long action in the electrolytic cell decreased the yield. Fischer and Kronig repeated the experiments in an apparatus in which the electrolyte could be saturated with oxygen under pressure and at the same time stirred vigorously. (The construction of the apparatus is not described.) Using an amalgamated gold cathode and platinum anode, a set of experiments were carried out using 1% sulphuric acid as electrolyte. Table No. III indicates the effect of pressure and current density on the current efficiency of formation of hydrogen peroxide. However, the solution could not be concentrated in the electrolytic cell above 2.7%. While the yield of hydrogen peroxide increased by increasing the pressure, the voltage necessary for electrolysis decreased. With electrolytes of high acid concentrations, the results were less favorable.

The formation of hydrogen peroxide from metals, sulphuric acid and oxygen without passing any current was also studied by Fischer and Kronig. The yields of hydrogen peroxide increased by increasing pressure. Using liquid zinc-amalgam, 2 grams of hydrogen peroxide per liter were obtained from 25 sq cm metal in 60 ml of 1% sulphuric acid after ten minutes under 25 atmospheres pressure of oxygen. The metals may be arranged in order of decreasing yields as follows: Zn-Hg, Hg, H-Pt, amalgamated zinc, Pb-Hg,

TABLE NO. III [11]

EFFECT OF PRESSURE ON REDUCTION OF

OXYGEN AT AMALGAMATED GOLD CATHODE

Pressure, atm.	Current density amps per sq cm	Current efficiency for first 10 minutes
0.2	0.075	0.1%
25	0.030	29%
25	0.012	100%
100	0.023	83%

(11) Fischer, F. and Kronig, _. "Reduction to Hydrogen Peroxide of Oxygen Dissolved under Pressure." Ber. 46, 698 (1913). Chem. Abstracts 7, 1851 (1913).

Cu, Cd, Zn, Cu-Zn and amalgamated copper.

Fischer and Kronig's[11] results indicate that the formation of hydrogen peroxide is the primary reaction between hydrogen and oxygen in an electrolytic cell at high pressures. Fischer could not account for the low current efficiency in the production of hydrogen peroxide when working under atmospheric pressures.

Berl[3] has developed a new process for the production of hydrogen peroxide at the cathode. It is based on the fact that gases and vapors that are adsorbed on activated carbon with highly developed internal surface areas, act as if they were compressed under very high pressure. Berl[3] prepared the activated carbon electrodes from the water-soluble acid sludge of the oil refineries. This sludge was first neutralized with a suitable alkali to form sulphates and certain salts of sulphonic acid. The resulting material was carbonized by heating it. Using electrodes made from this activated carbon as cathodes, oxygen was bubbled about the cathode where hydrogen was being evolved. Alkaline solutions of 2-5% hydrogen peroxide could be prepared by this method with a current efficiency of over 90%. It is remarkable that the yields of hydrogen peroxide were better in alkaline than in acid media, although it is well-known[19] that solutions of hydrogen peroxide are more stable in acid than in basic solutions.

Weiss and Jaffe[27] have studied the reduction of oxygen to hydrogen peroxide at air electrodes. The mechanism by which oxygen passes through air-depolarizing electrodes is shown to be diffusion and a method for obtaining the diffusion coefficient is described. They have shown that, in

an electrolytic cell, hydrogen peroxide is both reduced at the cathode electrochemically and decomposed catalytically. However, they report that in 5 normal sodium hydroxide solutions at graphite and mercury cathodes, with a current density of 0.01 amp per sq cm, no hydrogen peroxide is electrochemically reduced. In saturated ammonium chloride a considerable amount of hydrogen peroxide could be reduced at the same current density at graphite cathodes. Using specially manufactured carbon electrodes (details not known) to serve as cathodes, Weisz and Jaffe obtained quantitative yields of hydrogen peroxide in 5 N sodium hydroxide solutions with a cathode current density ranging from 0.0033 amp per sq cm to 0.0142 amp per sq cm. The formation of hydrogen peroxide was not tried at the anode.

It might be pointed out that the work of Berl[3], Weisz and Jaffe[27] was confined to the formation of hydrogen peroxide at activated carbon electrodes. The use of activated carbon electrodes is another way of bringing hydrogen and oxygen in contact at high pressures. Hence, their work suffers from the same limitation as that of Fischer and Kronig[11].

Mention may be made of the process for the cathodic oxidation[31] of methyl glucoside to methyl glucuronide. In this process hydrogen peroxide is first formed at the cathode through the reduction of molecular oxygen which further oxidizes methyl glucoside to methyl glucuronide. Mercury cathodes were used. The efficiency of the process was 20% at room temperature (not specified) and 11 atm pressure. The electrolytic apparatus was constructed of two one-liter glass mason jars fitted into an air-tight steel shell. Holes were drilled through the walls of the

jars for the introduction of various connections to the electrodes.

The Formation of Hydrogen Peroxide During Corrosion Reactions. Schonbein[23] was the first to propose the so-called "auto-oxidation" theory of atmospheric corrosion. According to this theory, an atom of a metal reacted with one of the atoms of an oxygen molecule of air, leaving the other oxygen atom in a nascent state. The nascent oxygen so produced was said to oxidize water forming hydrogen peroxide. In substantiation of his theory, Schonbein showed that in the slow oxidation of lead amalgam in dilute sulphuric acid, the amounts of lead sulphate and hydrogen peroxide produced were stoichiometrically equivalent. His results were verified by Van't Hoff[26] and by Jorissen[14].

Dunstan[10] and his co-workers found that hydrogen peroxide was produced during the exposure of zinc, silver, lead and mercury to very dilute sulphuric acid when oxygen was bubbled through the solution. They represented the typical corrosion reaction by the equation $Zn + O_2 + H_2O = ZnO + H_2O_2$ maintaining that hydrogen peroxide was formed by the oxidation of water simultaneously with the oxidation of the metal.

The demise of hydrogen peroxide theory of corrosion followed after the work of Dunstan. Churchill[8] reports that it was argued that if hydrogen peroxide was one of the products of corrosion, the addition of hydrogen peroxide to the corroding medium should retard the corrosion instead of accelerating it, as was actually the case.

Formation of Hydrogen Peroxide During the Corrosion of Aluminium: Churchill[8] has shown that hydrogen peroxide is formed during the corrosion of aluminium in the presence of excess of oxygen. The method of

test consisted of exposing a coil of aluminium wire to various solutions and aerating continuously during the test. He found that the yield of hydrogen peroxide was considerable in case of 1.0 N sulphuric acid. Hydrogen peroxide was detected in distilled water, 1.0 N potassium chloride and 0.01 N potassium hydroxide but not in 1.0 N potassium nitrate.

Churchill[8] has shown that the production of hydrogen peroxide by an aluminium surface is a cathodic reaction. For this purpose, two small pieces of aluminium sheet were joined by a strip of filter paper which had been moistened with sulphuric acid. A current was passed through the cell so formed. Treatment of the filter paper with titanium sulphate solution showed a distinct test for hydrogen peroxide in the area adjacent to the cathode. Elsewhere the paper remained colorless.

I. Hydrogen-Oxygen Cell

The electrolytic reaction between hydrogen and oxygen is realized in what is known as a "hydrogen-oxygen cell." A hydrogen-oxygen cell is simply an electrolytic cell with inert electrodes like Pt dipping into an aqueous acid or alkali electrolyte. Oxygen and hydrogen are bubbled around the anode and the cathode respectively so that both gaseous oxygen and hydrogen are in equilibrium with their respective ions in the electrolyte.

The results of Traube[25], Richarz and Lonnes[22], Fischer and Kronig[11], Berl[3] and Weisz and Jaffe[27] as discussed previously indicate that the formation of hydrogen peroxide from hydrogen and oxygen takes place almost quantitatively at high pressures. Thus, it seems

probable that the formation of hydrogen peroxide is the main reaction taking place in the oxygen-hydrogen cell.

The measurement of the potential of hydrogen-oxygen cell throws more light on the reaction taking place in the hydrogen-oxygen cell. Lewis[16] measured the potential of an oxygen electrode in normal hydroxyl ions. From this data, he calculated the potential of hydrogen-oxygen cell to be 1.16. Assuming the reaction taking place in the hydrogen-oxygen cell to be $H_2 + \frac{1}{2}O_2 = H_2O$ and not $H_2 + O_2 = H_2O_2$, he calculated theoretically the potential of hydrogen-oxygen cell from the dissociation pressure of water at 25°C. The value he obtained was 1.27 volts. The potential of hydrogen-oxygen cell has been measured by Bose[4], Kremann-Muller[15] and various others. They obtained a value ranging from 1.06 to 1.1 volts, but never near about 1.27 volts. This indicates that the reaction taking place in the hydrogen-oxygen cell may not be $H_2 + \frac{1}{2}O_2 = H_2O$ as assumed by Lewis. On the other hand, if the reaction taking place in the hydrogen-oxygen cell is assumed to be $H_2 + O_2 = H_2O_2$, the theoretical value obtained checks closely with the experimental value, viz. 1.16 volts.

Bancroft and Murphy[2][20] have forwarded another argument in favor of the formation of hydrogen peroxide in the hydrogen-oxygen cell. The decomposition voltage curve for sodium peroxide between platinum electrodes is of the same type as that for copper sulphate between copper electrodes, an approximately straight line starting from the origin. They say that this means that the reactions at the two electrodes are the same in fact but opposite in sign.

If the anode process were the evolution of monatomic oxygen, with the later combination of monatomic to diatomic oxygen, we would expect the ordinary type of curve, with a decomposition potential. However, this is not the case. The product of the primary electrode reaction must be the one involved. This can be shown as follows:

$$O_2^{-2} = O_2 + 2e$$

At the cathode, which is already an oxygen electrode, the process must be

$$O_2 + 2e = O_2^{-2}$$

It cannot be:

$$H + e = H$$
$$4H + O_2 = 2H_2O.$$

Further, Bancroft and Murphy[2] have shown that the oxidation-reduction potential of hydrogen peroxide solutions is very near a value of 1.16 in an acid solution of unit hydrogen ion activity. This checks closely with the value found experimentally for the hydrogen-oxygen cell. They concluded, from a study of the electrochemistry of hydrogen peroxide, that the reaction for the hydrogen-oxygen cell is:

$$H_2 + O_2 = H_2O_2$$
$$2H_2O_2 = 2H_2O + O_2$$

and is not:

$$2H_2 + O_2 = 2H_2O.$$

Commercial application of hydrogen-oxygen cell[19]. The theoretical principles of the hydrogen-oxygen cell have been utilized for generation of battery power. The possibility of utilizing atmospheric oxygen for primary battery depolarization has long been recognized and has engaged the research activities of electrochemists for many years. The air-depolarized

cell comprises a caustic alkali electrolyte, an anode of amalgamated zinc and a carbon cathode capable of utilizing atmospheric oxygen. The air-depolarizing cathode is preferably of non-graphitic carbon, with powdered charcoal as one of the constituents, agglomerated with a suitable binder and baked. It must be sufficiently porous and gas-permeable to permit adequate access of air and occlusion of oxygen. Yet it should be close-grained enough to offer resistance to electrolyte penetration.

The operating voltage of a fresh cell is 1.1 to 1.2. The battery is rated at 600 amp hr. The normal discharge rate of the battery is 0.50 to 0.65 ampere when used for radio work in unwired houses. Under these conditions, the battery requires the utilization of the oxygen of 9 to 12 cc of air per minute.

III. EXPERIMENTAL

A. Purpose of Investigation

The purpose of the present investigation was to study the factors affecting the electrolytic formation and decomposition of hydrogen peroxide at different cathode materials.

B. Plan of Investigation

The investigation was carried out as follows:

Review of Literature. A literature search was made to obtain information on the production of hydrogen peroxide by various methods, stability of hydrogen peroxide solutions, potentials given to hydrogen-oxygen cell, hydrogen peroxide theory of corrosion and chemistry of hydrogen peroxide in general. The literature search covered Chemical Abstracts, Transactions of Electrochemical Society, Journal of the American Chemical Society and reference books on electrochemistry. Original articles were consulted wherever possible.

Construction of Equipment. An experimental electrolytic cell, a vacuum tube voltmeter (see Appendix 1) and an apparatus for generating oxygen were constructed. Apparatus for measuring current cell voltage, cathode potential and temperature was assembled. A device for stirring the electrolyte was provided.

Plan of Experimental Procedure. Aqueous solution of hydrogen peroxide was prepared in distilled water and its change in concentration was studied at various metal surfaces at 24°C without agitation of the solution. The metals used were platinum, zinc, nickel, lead and copper. Also the change in concentration of hydrogen peroxide solution was studied without contact with any of the metals.

Change in concentration of hydrogen peroxide solutions in the electrolytes to be investigated was studied in the porous cup of the experimental cell at mercury, magnesium alloy F-S-1, zinc, graphite, aluminium and lead surfaces. The solution was analyzed at various time intervals. The surface area of the metal dipping into the electrolyte was kept constant by introducing fresh electrolyte everytime a definite amount of electrolyte was removed from the cell for analysis.

The change in concentration of hydrogen peroxide solutions due to combined electrolytic and catalytic effects was studied at different cathodes at 29.5°C described in the previous paragraph in the porous cup of the experimental cell. The electrolyte was agitated except in special experiments. Platinum was used as the anode. The following conditions were varied:

a) Electrode material

b) Current density

c) Agitation

d) Nature of electrolytes

e) Effect of introducing sodium and potassium ions.

The change in concentration of hydrogen peroxide solutions due to combined electrolytic and catalytic effects was studied as in the previous paragraph, but this time electrolytic oxygen from the generator was bubbled at the cathode.

The normality of hydrogen peroxide solution-time curves were determined for all cases.

C. Materials

The following materials were used in this investigation:

Copper. Sheet, 0.025 in. thick. Composition and source unknown. Believed to be electrolytic copper. Used as cathode.

Nickel. Carbon free, sheet, 0.025 in. thick, less than 0.2 percent carbon. Cat. No. 13-107. Fisher Scientific Co., Pittsburgh, Pa. Used as cathode.

Lead. Sheet, 0.102 in. thick. Composition and source unknown. Used as cathode.

Zinc. Sheet, 0.062 in. thick. Obtained from Department of Metallurgy, Virginia Polytechnic Institute, Blacksburg, Va. 99.9% pure. Source unknown. Used as cathode.

Porous Cup. Porcelain, size 5, Cat. No. 700, Coors Porcelain Co., Golden Colorado.

Tin Foil. Thickness 0.002 in. thick. Source and composition unknown. Used as cathode.

Platinum Foil. 0.003 in. thick. Cat. No. 13-755. Fisher Scientific Co., Pittsburgh, Pa. Used as anode and cathode.

Platinum Wire. B and S gage No. 24. Cat. No. 13-765. Fisher Scientific Co., Pittsburgh, Pa. Used for suspending the electrodes in oxygen gas generator and for connecting mercury cathode to the electrical circuit.

Graphite. Cylindrical rod, non-porous. Obtained from Department of Metallurgy, Virginia Polytechnic Institute, Blacksburg, Va. 99.5% pure. Source unknown. Used as cathode.

Mercury. Quicksilver Producers Association Inc., San Francisco, Cal. Composition unknown. Used as cathode.

Aluminium. Sheet, B & S gage 22. Besby & Co., Chicago, Ill. 99% pure. Used as cathode.

Tygon Paint. Corrosion resistant plastic. Plastics and Synthetics Division, U. S. Stoneware, Akron, Ohio. Used for making air-tight connections.

Sodium Hydroxide. Lot No. C344, B & A quality. General Chemical Co., New York, N. Y. Used as electrolyte.

Acid Hydrochloric. Tech., 22° Be, Baker Chemical Co., Phillipsburg, N. J. Used for acidifying the electrolyte and cleaning the electrodes.

Hydrogen Peroxide. U.S.P., 3% solution. Mallinckrodt Chemical Works, New York, N. Y. Used as electrolyte.

Nitric Acid. C.P., Lot No. E209027. General Chemical Co., New York, N. Y. Used for cleaning the cathode.

Oxalic Acid. C.P., Lot No. 122143, Crystalline. J. T. Baker Chemical Co., Phillipsburg, N. J. Used to standardize potassium permanganate.

Potassium Chloride. C.P., Lot No. 73046. J. T. Baker Chemical Co., Phillipsburg, N. J. Used as electrolyte.

Activated Carbon. Grade S-51. Darco Corp., 60 E. 42nd St., New York, N. Y. Used to make an activated carbon electrode.

Potassium Permanganate. C.P., Lot 40857. Merck & Co., Rahway, N.J. Used for analysing hydrogen peroxide solutions.

Potassium Iodide. C.P., Lot No. 474160. Cat. No. P-257, Fisher Scientific Co., Pittsburgh, Pa. Used for making qualitative test for hydrogen peroxide.

Ammonium Chloride. C.P., Lot No. 123141. J. T. Baker Chemical Co., Phillipsburg, N. J. Used as electrolyte.

Potassium Hydroxide. U.S.P., Code 2117, General Chemical Co., New York, N. Y. Used as electrolyte.

Buffer. Concentrated buffer solution. pH of 7.0 at 25°C when diluted twenty-five fold with distilled water. National Technical Laboratories, South Pasadena, Calif. Used to standardize the pH meter.

Solder. Kester Radio Solder. Kester Solder Co., Chicago, Ill. Used to solder test clips and connectors to the electric wires.

Test Clips. Standard, small radio test clips. Obtained from Frank's Radio Shop, Blacksburg, Va. Used as test clips.

Connectors. U shape, small connectors. Obtained from Frank's Radio Shop, Blacksburg, Va. Used as connectors.

Electrical Wires. Crescent wire. Insp. cord T-277. Standard. Brown's Store, Blacksburg, Va. Used in connecting various electrical meters in circuit.

D. Equipment

The following equipment was used in this investigation:

pH Meter. Beckman, model H, range 0-7, 7-14, graduation 0.1 pH. Calomel electrode, No. 4970. Glass electrode, industrial model. Fisher Scientific Co., Pittsburgh, Pa. Used to measure the pH.

Thermometer. Range -10 to 250°C, graduation 1.0°C. No. .06516. Brothcom, New York, N. Y. Used to measure the temperature of the electrolyte.

Vacuum Tube Voltmeter. (Appendix I) Range 0-5, 0-15 volts. 2½" scale with thirty graduation marks. Built at Virginia Polytechnic Institute, Blacksburg, Va. by H. B. Greever. Used to read cathode potential.

Calomel Electrode. No. 8970-TA for Beckman pH meter. Fisher Scientific Co., Pittsburgh, Pa. Used as reference electrode.

Milliammeter. Model 283, multi scale. Range 0-1, 0-5, 0-10, 0-25, 0-50, 0-100, 0-250, 0-500 and 0-1000 ma, graduations 0.02, 0.1, 0.5, 2.0, 5.0, 10.0 and 20.0 ma respectively. Two inch scale with fifty graduation marks. Simpson Electric Co., Chicago, Ill. Used to measure current.

Milliammeter. Westinghouse, d-c. U.S.N. type CAY-22063. Range 0-200. 2½" scale with 40 graduation marks. Used to measure current.

Rheostat. 19.6 ohms, 4 amps. Sliding contact type. Rex Rheostat Co., Baldwin, N. J. Used to control current.

Rheostat. 430 ohms, 1 amp. Sliding contact type. Rex Rheostat Co., Baldwin, N. J. Used to control current.

Rheostat. 56 ohms, 2.8 amps. Heater type. Rex Rheostat Co., Baldwin, N. J. Used to control current.

Rheostat. 13 ohms, 6 amps. No. 91859. Central Scientific Co., Chicago, Ill. Used to control current.

Ammeter. D.C., model 301, range 0-1.5, 0-3, 0-30. Graduations 0.02, 0.1 and 1.0 respectively. Weston Electric Institute Corporation, Newark, N. J. Used to measure current.

Motor Controller. 600 volts, 16 ohms, maximum amps 5. Cutler-Hammer Inc., Milwaukee, Wis. Used to control current from motor generator.

Motor Generator. 4 hp, 220 a-c volts, 13 amps, 60 cycles, 500 watts. 28.5 d-c volts, 500 watts, 17 amps. Model 213-F. D. W. Onan and Sons, Minneapolis, Minn. Used to charge storage batteries.

Hot Plate. 120 volts, 600 watts. Gilma Mfg. Corporation, Louisa, Va. Used for heating purposes.

Swich. Single-pole, single throw. Source unknown. Used to open or close the circuit.

Balance. Pan type, graduation 0.1 g. accurate up to 0.1 milligram. Fisher Scientific Co., Pittsburgh, Pa. Used for weighing purposes.

Soldering Iron. Solder Master, 100 watts, 110-120 volts a-c. Leigh Co. Used to solder test-clips and connectors to the wire leads.

Oven. Model 70. 400 watts, 115 volts, a-c, d-c. Electric Hotpack Co., Inc., Fox Chase, Pa. Used to dry the electrodes.

Battery. Exide, N.A.F. part no. 1062-17A, 12 volts, 17 ampere-hours at 5 hour rate. The Electric Storage Battery Co., Philadelphia, Pa. Used as source of current.

Battery. Delco, Model 1724 A N, 24 volts, 17 amp. hr. Delco-Remy Division, General Motors Corp., Anderson, Indiana. Used as a source of current.

Battery. Goodyear, 6 volts, type A-115, group I. Used as a source of current.

Stop-Clock. Accuracy 0.5 second. Eastman Kodak Co., Rochester, N. Y. Used to record time.

Stirrer. Cenco, Cat. No. 18805, variable speed, 115 volts a-c, 60 cycles, 0-68 amps. No. 1331481. Central Scientific Co., Chicago, Ill. The blade was made by bending a 8 in. long, 3/16 in. diameter glass rod at one end. Used to stir the electrolyte.

Circuit-tester. Low voltage, Q.M.C. Model 1-42, Serial No. C.6846. The Electric Heat Control Co., Cleveland, Ohio. War Surplus. Used as voltmeter to record the experimental cell voltage and to calibrate the vacuum tube voltmeter.

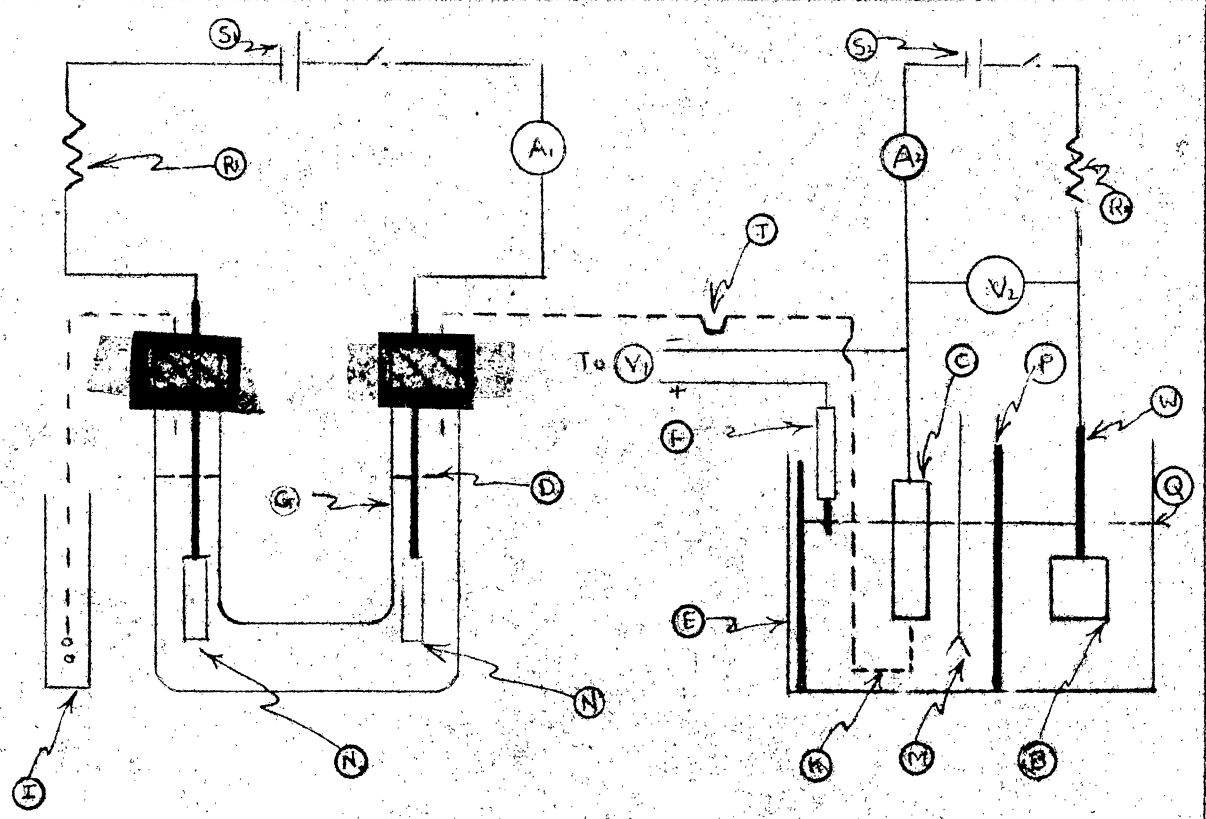
Glassware. Miscellaneous such as beakers, flasks, pipettes, etc. used for preparing and handling solutions. Glass and rubber tubing for transporting oxygen and for making capillary.

E. Method of Procedure

General. In order to determine the factors affecting the formation and decomposition of hydrogen peroxide in the experimental cell, it was necessary to know the total current passing through the cell, the total voltage drop across the cell and the cathode potential.

Construction of Equipment. (All letter references refer to figures 1, 2 and 3 on pages 30, 31 and 32). The equipment used for this investigation consisted of two separate electrical circuits. Circuit I was set up for generating oxygen gas electrolytically (figure 1). The apparatus consisted of a U-shaped tube (G) about 7" high and 3/4" diameter. The tube was half-filled with a 20% solution of sodium hydroxide (D). Two nickel electrodes (N) (3½"x¼") were suspended vertically in the U-tube, one in each arm, by means of two platinum wires (W) of 24 gage sealed through glass tubing. The two electrodes served as cathode and anode. The electrolytic cell so formed was connected in series with a 24-volt storage battery (S1). An ammeter (A1) and a 19.6 ohm rheostat (R1) were also connected in series to measure and control the current. On passing the current, oxygen was evolved at the anode. It was passed through a glass-tubing and a glass wool trap (T) and bubbled over at the cathode (C) of the electrolytic cell (E).

Circuit II consisted of the experimental cell (E) connected in series with a milliammeter (A_2), a rheostat (R_2) and a 12 or 6 volt battery (S_2). A 600 ml glass beaker was used as the electrolytic cell. A porous cup (P) 3-3/4" in height and 2" in diameter was used to serve as the cathode com-



Legend

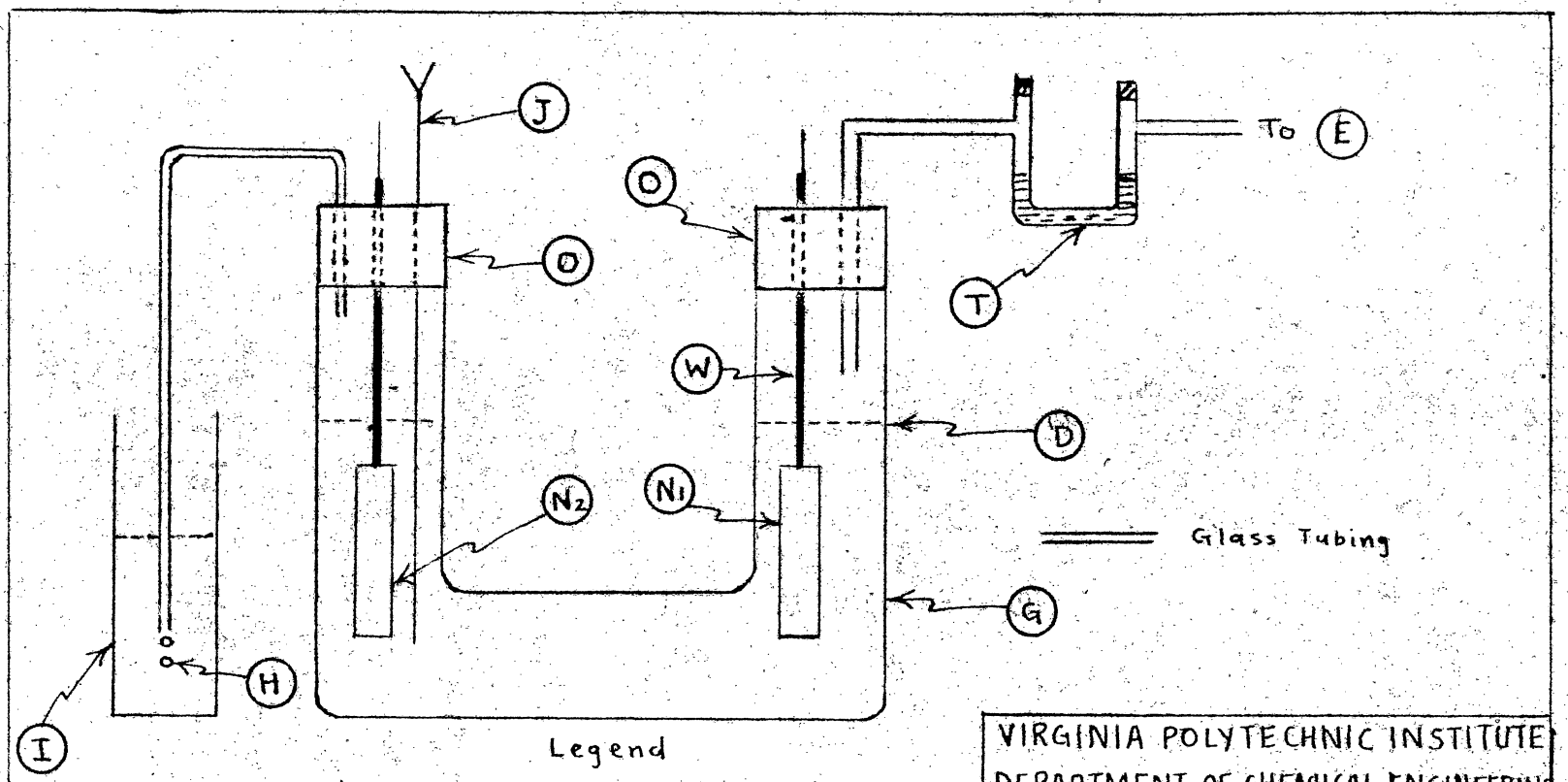
All Stoppers – Rubber
——————— Electrical Wiring
- - - - - - - Glass Tubing
A, A2 Ammeters
B Platinum Foil
C Cathode
D 20% Sodium Hydroxide
E Electrolytic Cell
F Saturated Calomel Electrode
G Hydrogen and Oxygen gas generator
I Glass Cylinder filled with water
K Capillary Tube
M Mechanical Stirrer
N Nickel Electrodes
P Porous Cup
Q Electrolyte Level
W Glass-protected Platinum wire
R1 R2 Rheostats
S1 S2 Storage Batteries
T Glass-wool Trap
V1 Vacuum Tube Voltmeter
V2 Voltmeter of Circuit-Tester

VIRGINIA POLYTECHNIC INSTITUTE
DEPARTMENT OF CHEMICAL ENGINEERING
BLACKSBURG, VIRGINIA

ELECTRICAL HOOK-UP FOR PRODUCTION OF
HYDROGEN PEROXIDE

SCALE: NONE
DRAWN BY: H.J.J.
CHECKED BY:
APPROVED BY: NFM DATE: 8-18-48

FIGURE 1



Legend

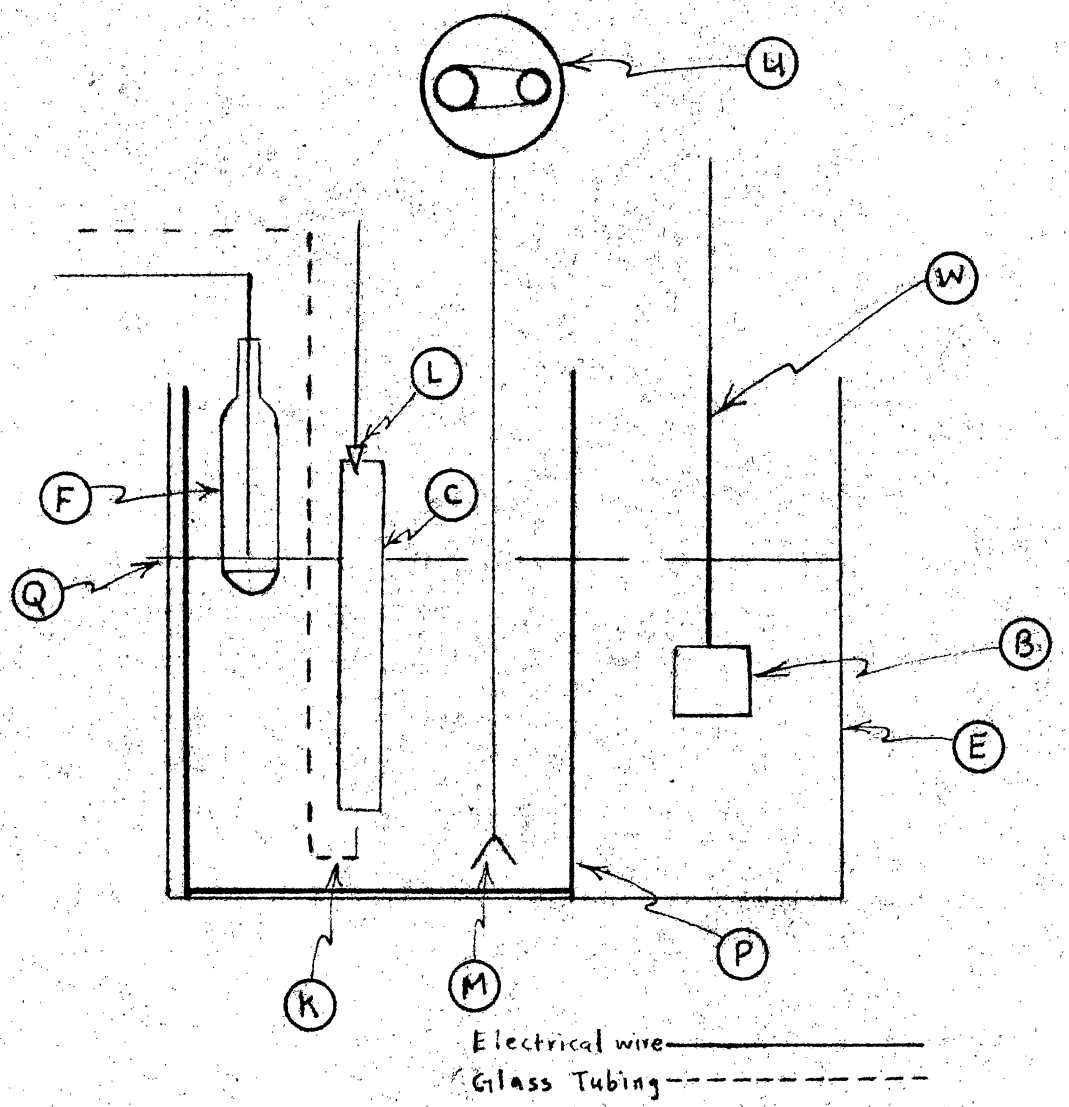
D 20 Percent Sodium hydroxide
E Experimental Cell (not shown)
G Oxygen and Hydrogen Gas Generator
H Hydrogen Gas Bubbles
I Glass Cylinder with water
J Glass Funnel
N_1 N_2 Nickel Electrodes
O Rubber Stoppers
T Glass-wool Trap
W Platinum wire - glass covered

VIRGINIA POLYTECHNIC INSTITUTE
DEPARTMENT OF CHEMICAL ENGINEERING
Blacksburg, Virginia

Oxygen Gas Generator for Production of

HYDROGEN PEROXIDE

Drawn by: Scale: None
Checked by: Figure 2
Approved by: NFM Date: 8-19-48



B Platinum Foil Anode
C Cathode
E Electrolytic Cell
F Saturated Calomel Electrode
K Capillary Tube
L Test-Clip
M Stirring Rod
P Porous Cup
Q Electrolyte Level
U Motor for Stirrer
W Glass-covered Platinum wire

VIRGINIA POLYTECHNIC INSTITUTE
DEPARTMENT OF CHEMICAL ENGINEERING
BLACKSBURG, VIRGINIA

ELECTROLYTIC CELL FOR THE PRODUCTION OF
HYDROGEN PEROXIDE

DRAWN BY: H.J.J.
CHECKED BY:
APPROVED BY: NFM DATE: 8-18-48

FIGURE 3

partment and to separate the catholyte from the anolyte. Anode was always platinum foil (W) unless stated otherwise. Different cathodes were used in the investigation. The anode and the cathode were suspended in the electrolyte by means of test-clips. The electrolyte was stirred continuously with a mechanical stirrer (M). The tip of the saturated calomel electrode (F) was put as near the cathode as possible in the electrolyte. The saturated calomel electrode and the cathode were connected to the vacuum tube voltmeter (V_1) in order to measure the cathode potential. The cell-voltage was measured by the voltmeter of the circuit tester (V_2) connected in parallel to the experimental cell. The temperature of the electrolyte was recorded by means of a thermometer. A capillary (K) was drawn out to bubble the oxygen gas over to the cathode (C). To use mercury as the cathode material, it was placed in the porous cup and the electrical connection was made by means of a glass-covered platinum wire slightly uncovered at the lower end and completely dipped in mercury. The upper end of the platinum wire served as a terminal for electrical connection. Oxygen was bubbled through the mercury.

<u>Preparation of Electrodes</u>. Before each run, all but mercury cathodes were dipped in concentrated hydrochloric acid, washed with distilled water and wiped off with filter-paper. The electrodes were then heated in an oven which was hereafter always kept at a constant temperature of 60-65°C. The platinum anode was dipped in concentrated nitric acid for several minutes, washed with distilled water, wiped with a filter-paper and heated in the oven for about ten minutes.

Preparation of Activated Carbon Electrode. Rod graphite was cleaned with acetone, washed with distilled water and wiped off with filter-paper. Activated carbon was suspended in acetone. Ethyl cellulose, weighing about 10% of activated carbon used, was added to the suspension and dissolved by agitation. This suspension was applied by pouring on the graphite surface. The electrode was then dried in the oven for about two hours till all the acetone evaporated.

Preparation of Electrolytes. The chemicals were weighed on a pan balance, accuracy ± 0.1 gm, and dissolved in proper amounts of distilled water. The acid or base normality of all the electrolytes used was determined by titration with a standard acid or alkaly previously prepared.

Bubbling Oxygen Over the Cathode. The rate of bubbling oxygen over the cathode was always kept at three or four times that required theoretically for the formation of hydrogen peroxide. The rate of oxygen formed in the generator was calculated from the current flowing. The electrolyte level in the gas generator was kept constant by adjusting the rate of bubbling of hydrogen in a cylinder filled with water. Uniform bubbles were produced in the experimental cell by adjusting the height of the capillary tube dipping into the electrolyte. Bubbles directly hit the cathode.

Standardization of the pH Meter. Beckman pH meter was standardized and used by following the instructions supplied.

Standardization of the Vacuum Tube Voltmeter. (See Appendix I) The vacuum tube voltmeter was standardized and used according to the instructions given in Appendix I.

Preliminary Attempts for the Electrolytic Formation of Hydrogen Peroxide. The formation of hydrogen peroxide was studied at zinc, nickel, tin, copper and platinum cathodes. Before the run, the cathode material was thoroughly cleaned with hydrochloric acid and washed with distilled water. Oxygen was bubbled over at the cathode by means of a fine capillary tube so that uniform bubbles hit right on to the surface of the cathode. Catholytes used in the porous cup of the experimental cell were 0.11 N phosphoric acid, 0.1 N potassium chloride and 1.5 N potassium hydroxide. The volume of the catholyte in the porous cup at start was 100 ml. Every fifteen minutes, 10 ml of the catholyte was pipetted out and titrated with 0.01 N potassium permanganate. Everytime, when 10 ml of catholyte were withdrawn for analysis, 10 ml of fresh electrolyte containing no hydrogen peroxide were introduced. Qualitative tests for hydrogen peroxide were also performed in case of all the metals mentioned above by means of adding a potassium iodide and starch solution to one ml of the catholyte solution. A blue coloration of the potassium iodide and starch solution indicated the presence of hydrogen peroxide.

Catalytic Decomposition of Hydrogen Peroxide. The change in concentration of hydrogen peroxide in aqueous solutions was studied in presence of copper, zinc, lead, nickel and platinum. These metals were kept in

200 ml of 0.884 N solution of hydrogen peroxide prepared in distilled water. Every hour 10 ml of the sample were pipetted out and titrated with standard potassium permanganate. A table of percentage change in concentration of hydrogen peroxide with time was prepared.

Formation of Hydrogen Peroxide at Activated Carbon Electrode. 125 ml of 1.5 M potassium hydroxide were placed in the porous cup of the experimental cell and were electrolyzed at an activated carbon cathode, oxygen being bubbled at the same time. 15.07 sq cm of cathode area was used at a current density of 0.009 amp per sq cm at 29.5°C. 10 ml of catholyte were analysed every fifteen minutes by titration with 0.01 N potassium permanganate.

Catalytic Decomposition of Hydrogen Peroxide in Cell. The change in concentration of hydrogen peroxide solutions was investigated in presence of zinc, lead, mercury, magnesium alloy FS-1 and graphite in the porous cup of the experimental cell. For this purpose, 100 ml of the hydrogen peroxide solution were kept in the porous cup in contact with different, but known, surface areas of the metals to be investigated. Every five or ten minutes, 10 ml of the sample were pipetted out and 10 ml of fresh electrolyte containing no hydrogen peroxide were introduced. The sample was acidified with hydrochloric acid and titrated against 0.01 N potassium permanganate solution.

Electrolytic and Catalytic Effects on Hydrogen Peroxide. In these experiments, the change in concentration of hydrogen peroxide solution was studied due to both catalytic and electrochemical effects at the cathode. For this purpose, 100 ml. of hydrogen peroxide solution were poured into

the porous cup in contact with known surface area of the metal to be investigated and current was passed. The current was measured by means of a milliammeter. The cell-voltage was measured by means of a circuit tester and the cathode potential against saturated calomel electrode was determined by means of a vacuum tube voltmeter. The concentration of hydrogen peroxide in the porous cup was determined every five or ten minutes by titration with 0.01 N potassium permanganate. Every time 10 ml of electrolyte was withdrawn for analysis, 10 ml of fresh electrolyte containing no hydrogen peroxide were introduced. The effects of varying the following conditions were studied:

(a) Current density

(b) Nature of electrolyte

(c) Agitation

(d) Cathode material

Current density was varied by keeping the cathode area constant and varying the current. The current density used ranged from 0.004 to 0.015 amp per sq cm. Electrolytes used were 5 N sodium hydroxide, 1.5 N potassium hydroxide, 0.1018 N sodium and potassium hydroxide, saturated ammonium chloride and 0.042 N phosphoric acid at 29.5°C. The cathode materials used were carbon, lead, mercury, magnesium alloy F-S-1, zinc and aluminium. The electrolyte was stirred by means of a mechanical stirrer at about 75 rpm.

<u>Reduction of Oxygen at Cathode.</u> The change in concentration of hydrogen peroxide in the porous cup was determined every five or ten minutes due to both catalytic and electrochemical effects but oxygen was

bubbled at the cathode. The same conditions, electrolytes and cathodes were used as in the previous experiments.

F. Data and Results

In this section the data and results of all experimental work are presented in tabular and graphical form.

The general temperature prevailing in the experimental cell was 29.5 $\pm 1.5^{\circ}C$. The electrolyte was agitated and the experiments were conducted at atmospheric pressure.

Qualitative tests for the presence of hydrogen peroxide were obtained with potassium iodide and starch solution at a current density of 0.002 amperes per sq cm at zinc, lead and copper electrodes at $24^{\circ}C$ in 0.15 normal phosphoric acid. But the amount of hydrogen peroxide formed was not enough to permit quantitative study.

Table IV represents the percent decomposition of hydrogen peroxide solution in distilled water at definite time intervals at $24^{\circ}C$ in presence of zinc, copper, platinum, lead and nickel.

Table V compares the catalytic decomposition of hydrogen peroxide in the presence of zinc, lead, mercury, aluminium, carbon and alloy F-S-1 in the porous cup of the electrolytic cell. Acidic, neutral and basic solutions were used as electrolytes.

Table VI gives the data for the combined electrolytic and catalytic decomposition of hydrogen peroxide solutions in the porous cup (used as diaphram) of the electrolytic cell. Current density, nature of the electrolyte, agitation and cathode material were varied.

Table VII represents the combined electrolytic and catalytic decomposition of hydrogen peroxide solutions with oxygen bubbled over at the cathode. Conditions varied were the same as in case of Table VI.

TABLE IV

Catalytic Decomposition of Hydrogen Peroxide at Differant Surfaces in Aqueous Media.

Volume of Solution at Start = 200 ml
Concentration of H_2O_2 at start = 0·977 N
Area of each surface = 8 sq cm. Temperature = 24°C

Surface	% Hydrogen Peroxide Decomposed ρ			
	Time in Hours			
	0	1	2	3
Pb	0	3.318	7·2	9·4
Pt	0	2·21	3·33	3·33
Cu	0	1·66	3·32	4·97
Zn	0	1·075	1·175	2·762
Ni	0	1·075	1·075	1·075
Blank *	0	0·7	0·85	1·00

ρ Based on Original Concentration

* Concentration of Solution at Start = 0·91N

TABLE V

Catalytic Decomposition of Hydrogen Peroxide at Vario Surfaces in Experimental Cell.

Solvent Stirred Temperature 29C

Solution	Volume of Solution at start ml	Material	Area of surface of the Material Sq cm	Normality of Hydrogen Peroxide Solutions x 10^4										
				Time in Min										
				0	5	10	15	20	25	35	45	55	65	75
0.1018N NaOH	100	Mg	18.84	73.14	71.4	69.9	69.69	68.9	68.5	68				
	100	Al	18.84		82.15	69.6	60.4	52.6	47.5	44	41.15	35.9		
	100	Pb	18.84	75.79	61.1	43.2	37.2	30.7	29.2	2				
	100	Zn	18.84	80.5	78.8	77.2	75.6	75.2						
	100	Hg	18.84	75.79	71.79	65.5	65.5	63.2	61.3					
0.1010N KOH	–	–	–	–	–	–	–	–	–					
	100	Mg	18.84	67.3	63.4	59.5	59.3	55.5	54.8					
0.042N H_3PO_4	100	Hg	18.84	79.5	78.9	78.6	78.5	78.4	78.4					
Saturated NHqcl	60	Hg	13.80	75.3		71.6	71.6		71.4	71.0				
	50	Hg #	13.80	62.7	62.3	61.7	61.3	61.0	61.0					
5M NaOH	100	Hg	18.84	–	–	–	–	–	–					
	100	Hg	18.84	60.4	57.4	52.2	55.9	55.7	54.6	5				
	100	Hg	18.84	–	–	–	–	–	–	–				
	125	Graphite	15.072	85.1		72.4		62.3		5		47.2	40.8	

Unstirred

TABLE VI

Electrolytic and Catalytic Decomposition of Hydrogen Peroxide at Various Cathodes. No Oxygen bubbled.

Temp. = 29.5 ± 1.5°C Anode - Platinum Electrolyte Stirred

Catholyte	Volume of electrolyte at Start ml	Cathode Material	Normality of Hydrogen Peroxide Solutions x 10^4 Time in Minutes												Cell-Voltage (volts)	Cathode Potential (Volts) ρ	Current ma	Cathode Current Density amp per sq cm	% Current Efficiency of Electrochemical Reduction
			0	5	10	15	20	25	30	35	45	55	65	75					
0.1018 N NaOH	100	Mg	75.79	69.5	64.13	61.2	57.5	53.6	53.2						5.4	2.35	168	0.0089	7.27
	100	Al	61.00	52.5	45.9	41.4	37.7	34.8							4.85	2.0	168	0.0089	1.91
	100	Pb	82.6	62.3	44.4	37.4	30.9	29.7	26.7						5.0	2.16	168	0.0089	0.95
	100	Zn	71.02	58.5	49.8	43.3		34.0							5.2	2.4	168	0.0089	5.70
	100	Hg	73.9	67.7	62.4	59.8	53.6	50.0							5.25	2.66	168	0.0089	4.6
0.1010 N KOH	100	Mg	78.4	73.5	69.0	64.3	61.9	59.7							—	—	—	0.0089	7.27
0.042 N H_3PO_4	100	Hg	67.8	53.4	40.7	34.6	30.3								—	—	168	0.0089	0.0
Saturated	60	Hg		77.4	70.8	63.0	55.2	45.6							9.95	2.83	168	0.0089	21.6
NH4Cl	50	Hg #	66.8	61.0	57.0	53.2	42.3								2.42	0.68	68	0.00493	14.18
5 M	100	Hg	76.5	70.0	66.7	60.8	55.3	54.6	51.9						—	—	68	0.00493	9.18
NaOH	100	Hg	59.9	49.97	44.8	40.3	36.09	34.87							3.0	1.88	76	0.00403	5.08
	100	Hg	75.4	61.9	53.6	47.9	44.4								3.1	1.96	168	0.0089	10.90
	125	Graphite	99.21			69.53		60.1			44.4	39.8			3.3	2.06	270	0.0143	5.35
															2.9	1.7	150.7	0.010	0.0

ρ Referred to Saturated Calomel Electrode # Unstirred

TABLE VII

Electrolytic and Catalytic Decomposition of Hydrogen Peroxide With oxygen Bubbled at Various Cathodes.

Electrolyte Stirred Temperature = 29.5°±1.5°C Anode - Platinum

Catholyte	Volume of electrolyte at start ml	Cathode Material	Normality of Hydrogen Peroxide Solutions x10⁴ — Time in Minutes												Cell - Voltage (Volts)	Cathode Potential (Volts) ρ	Current ma	Cathode Current Density amp per sq cm	% Current Efficiency of H_2O_2 formation
			0	5	10	15	20	25	30	35	45	55	65	75					
0.1018 N NaOH	100	Mg	73.14	71.4	69.9	69.6	68.9	68.5	68.3						5.4	2.55	168	0.0089	8.05
	100	Al	45.0	37.3	32.9	29.9	27.6	25.8							4.85	2.0	168	0.0089	0.0
	100	Pb	64.6	48.3	41.2	34.18	29.4	27.0	25.2						5.0	2.16	168	0.0089	2.96
	100	Zn			56.0	50.4	45.0	40.4		37.6					5.2	2.4	168	0.0089	4.20
	100	Hg	73.6	64.8	57.1	53.12	50.8	47.8							5.25	2.66	168		0.0
	100	Mg *	66.0	61.1	56.7	53.8	51.9	49.1							–	–	–	0.0089	0.0
0.1010 N KOH	100	Mg	77.5	75.1	72.85	72.6	71.7								6.4	–	168	0.0089	6.12
0.042 N H_3PO_4	100	Hg	68.37	53.4	42.3	34.8	31.1	27.8							9.95	2.83	168	0.0089	0.0
Saturated NH_4Cl	60	Hg	76.25	68.5	62.2	55.8	45.6								2.42	0.68	68	0.00493	2.4
	50	Hg #	87.25	77.6	69.4	62.6	55.4								–	–	68	0.00493	-1.9
5M NaOH	100	Hg	66.78	62.3	56.2	51.6	50.8	47.1							3.0	1.88	76	0.00403	0.0
	100	Hg	60.95	54.65	50.64	47.35	44.7								3.1	1.96	168	0.0089	5.35
	100	Hg	75.79	62.4	54.4	42.3	44.8								3.3	2.06	270	0.0143	6.0
	125	Graphite	85.15	–	–	64.05	58.4			46.28	38.8	34.15			2.9	1.7	1150.7	0.010	0.0
1.5 M KOH	115	Activated C	0.0	3.15	3.47		3.97		4.42			5.41	5.44				162.0	0.0091	4.125

* Nitrogen bubbled instead of Oxygen # Unstirred ρ Referred to saturated calomel electrode

Figure 4 represents the formation of hydrogen peroxide in 1.5 normal potassium hydroxide at activated carbon electrode.

Figure 5 represents catalytic, electrolytic and catalytic, and electrolytic and catalytic decomposition of hydrogen peroxide with oxygen bubbled over graphite cathode in 5 normal sodium hydroxide. The same slope of all the three curves indicates that hydrogen peroxide is decomposed only catalytically.

Figure 6 represents the behavior of hydrogen peroxide solutions in different electrolytes at mercury cathode. Curves No. 2, with steeper slope than those numbered 1 represent the catalytic and electrolytic reduction of hydrogen peroxide when no oxygen was bubbled at the cathode. Curves No. 3 represent the electrolytic and catalytic decomposition of hydrogen peroxide when oxygen was bubbled at the cathode. Different point notations were used to distinguish data for the curves. The curves on Figure 6 are grouped together to illustrate the effect of strong alkali, weak alkali and acid solutions. Figure 8 illustrates the effect in neutral solutions. This data was not included in Figure 7 because a different current density was used and Figure 6 would have been too crowded.

Figure 7 represents the effect of current density on the behavior of hydrogen peroxide solution at a mercury cathode in 5 N sodium hydroxide.

Figure 8 represents the effect of stirring ammonium chloride used as an electrolyte, on the decomposition of hydrogen peroxide at mercury cathode. This curve should be compared with Figure 6 for study of the effect of acidity on behavior of hydrogen peroxide solution.

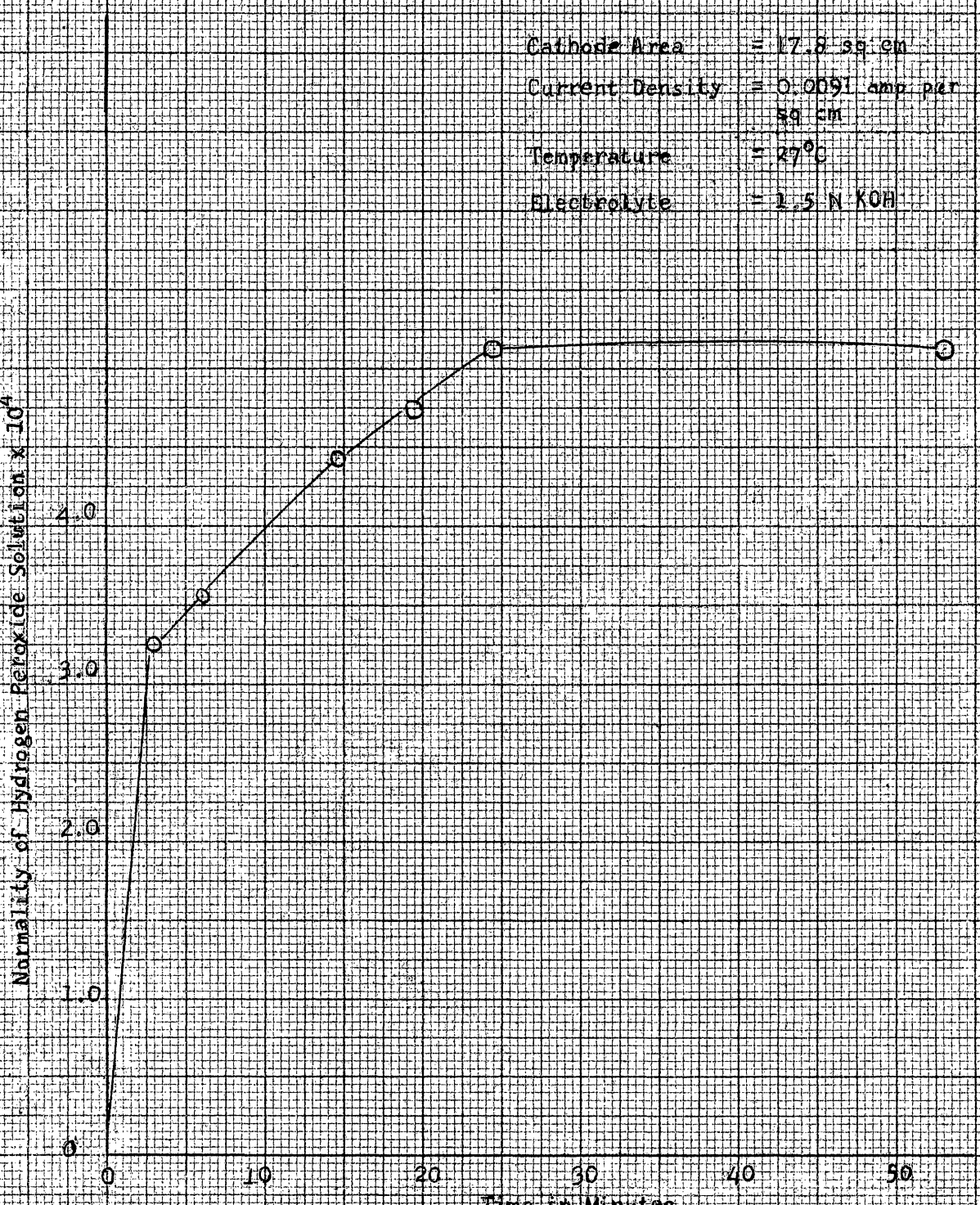


Figure 4

Formation of Hydrogen Peroxide at Activated Carbon Electrode.

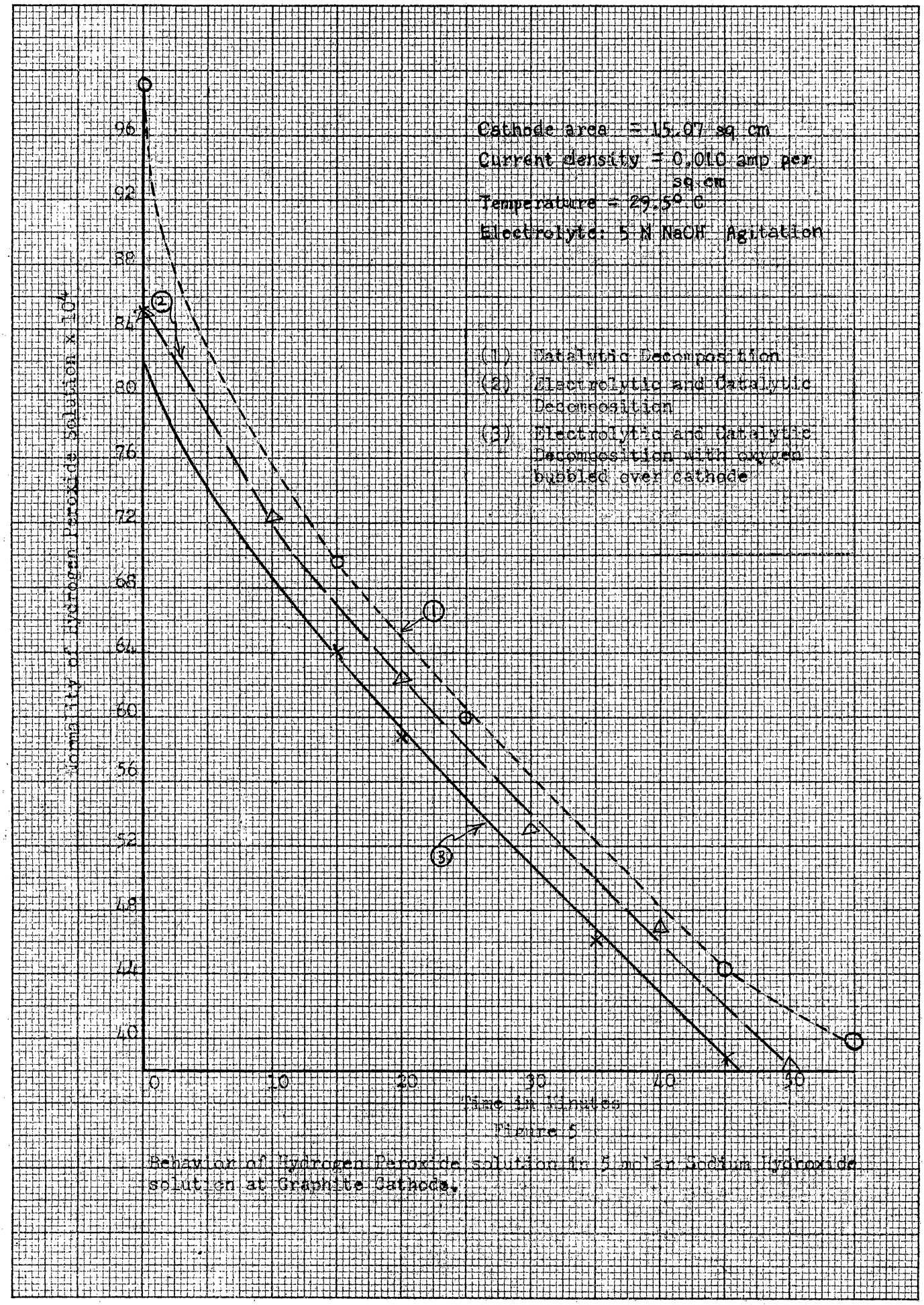


Figure 5

Behavior of Hydrogen Peroxide solution in 5 molar Sodium Hydroxide solution at Graphite Cathode.

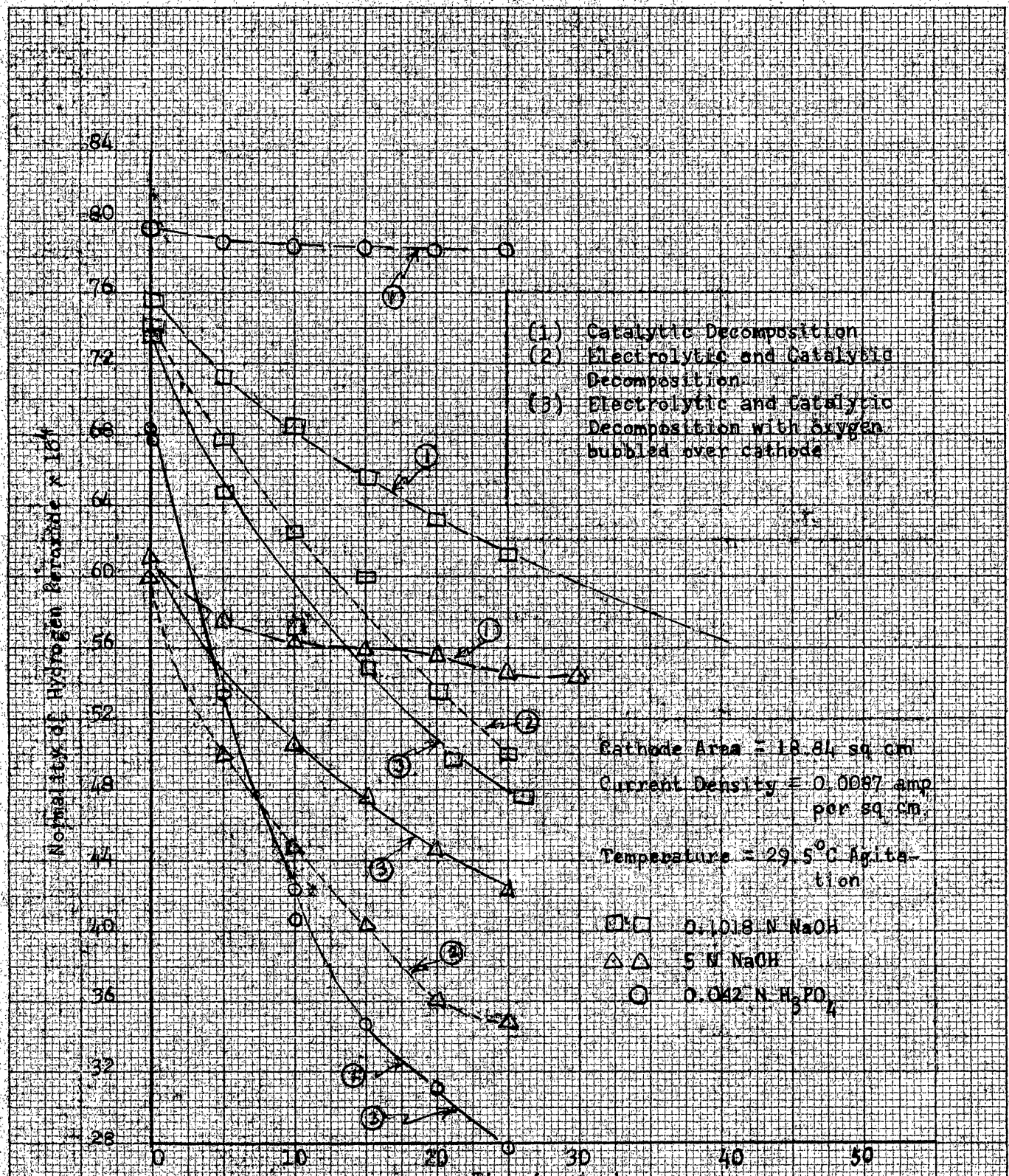


Figure 6

Behavior of Hydrogen Peroxide solution in various Electrolytes at Mercury Cathode

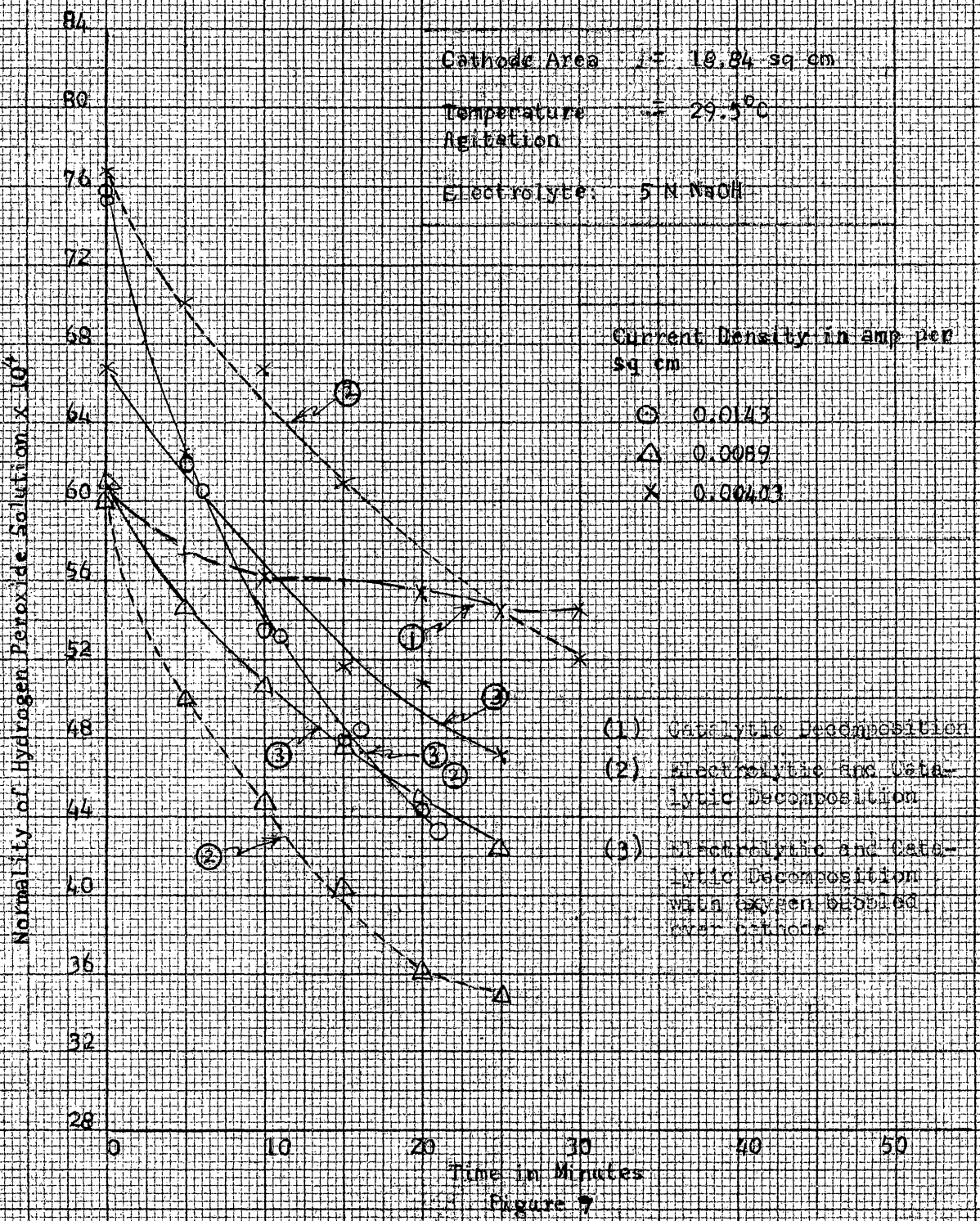


Figure 7

Behavior of Hydrogen Peroxide in 5 Molar Sodium Hydroxide Solution at Mercury Cathode at Various Current Densities

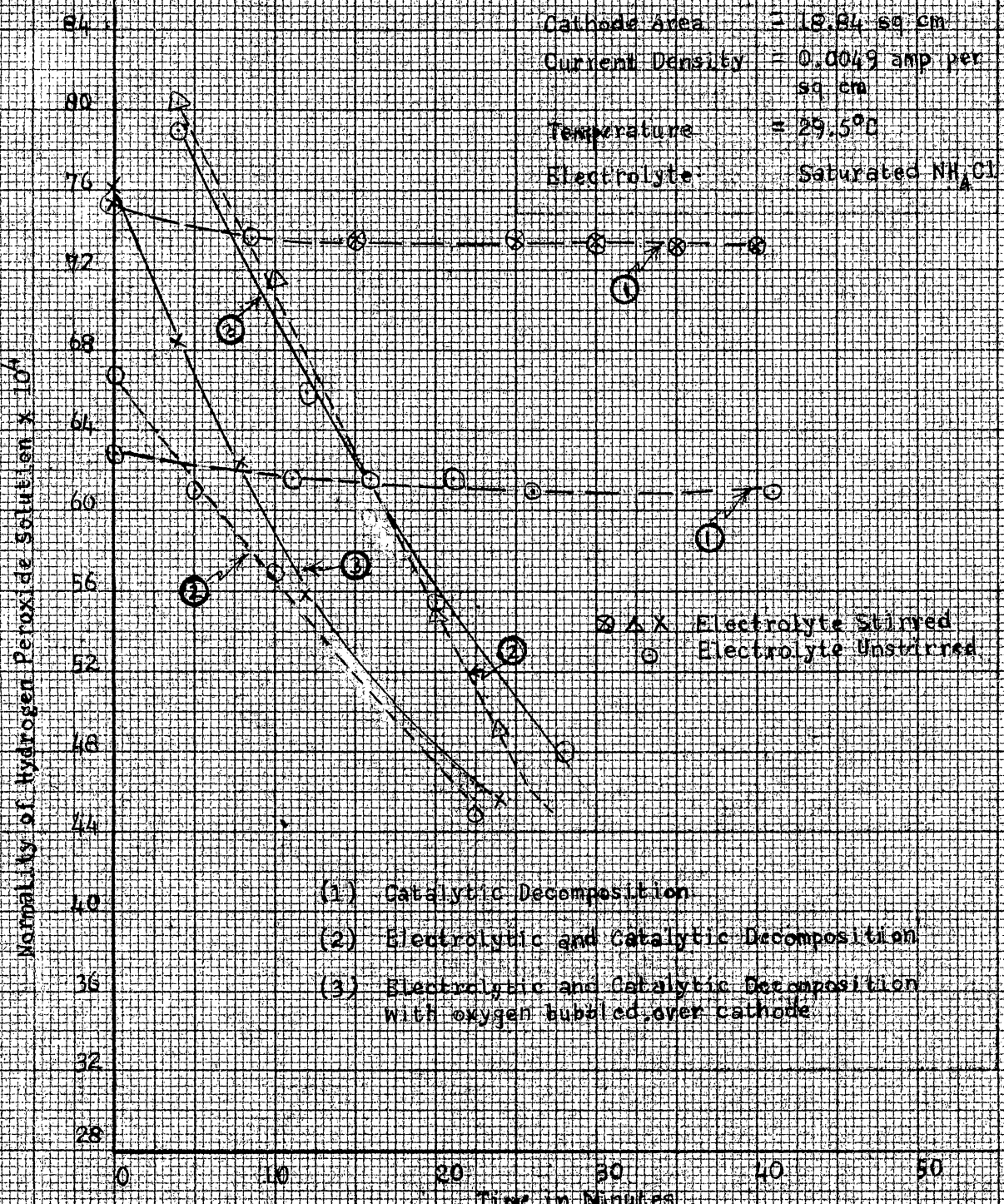


Figure 6

Effect of Stirring in the Behavior of Hydrogen Peroxide in Saturated Ammonium Chloride Solution at Mercury Cathode.

Figure 9 represents the effect of the presence of sodium and potassium hydroxide at the same concentration, on the catalytic and electrolytic decomposition of hydrogen peroxide at Magnesium alloy F-S-1 cathode. No hydrogen was evolved when this alloy was immersed in 0.1 N alkali.

Figures 10, 11, 12 represent the catalytic and electrolytic decomposition of hydrogen peroxide at zinc, aluminium and lead cathodes respectively in 0.1018 N sodium hydroxide. Aluminium reacts with 0.1 N alkali with hydrogen evolution.

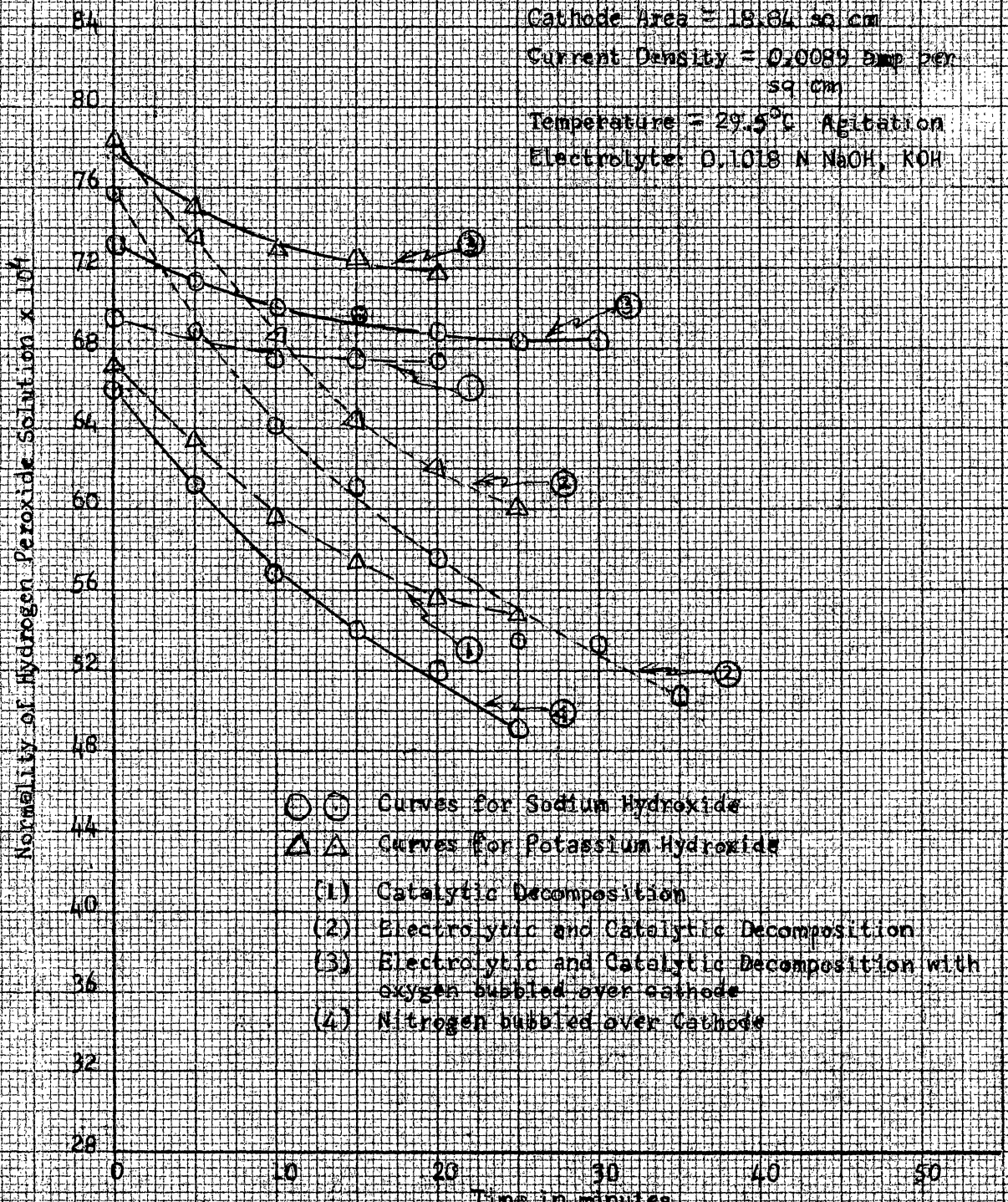


Figure 9

Behavior of Hydrogen Peroxide solution at Magnesium alloy FS-1 Cathode in presence of Sodium and Potassium Ions.

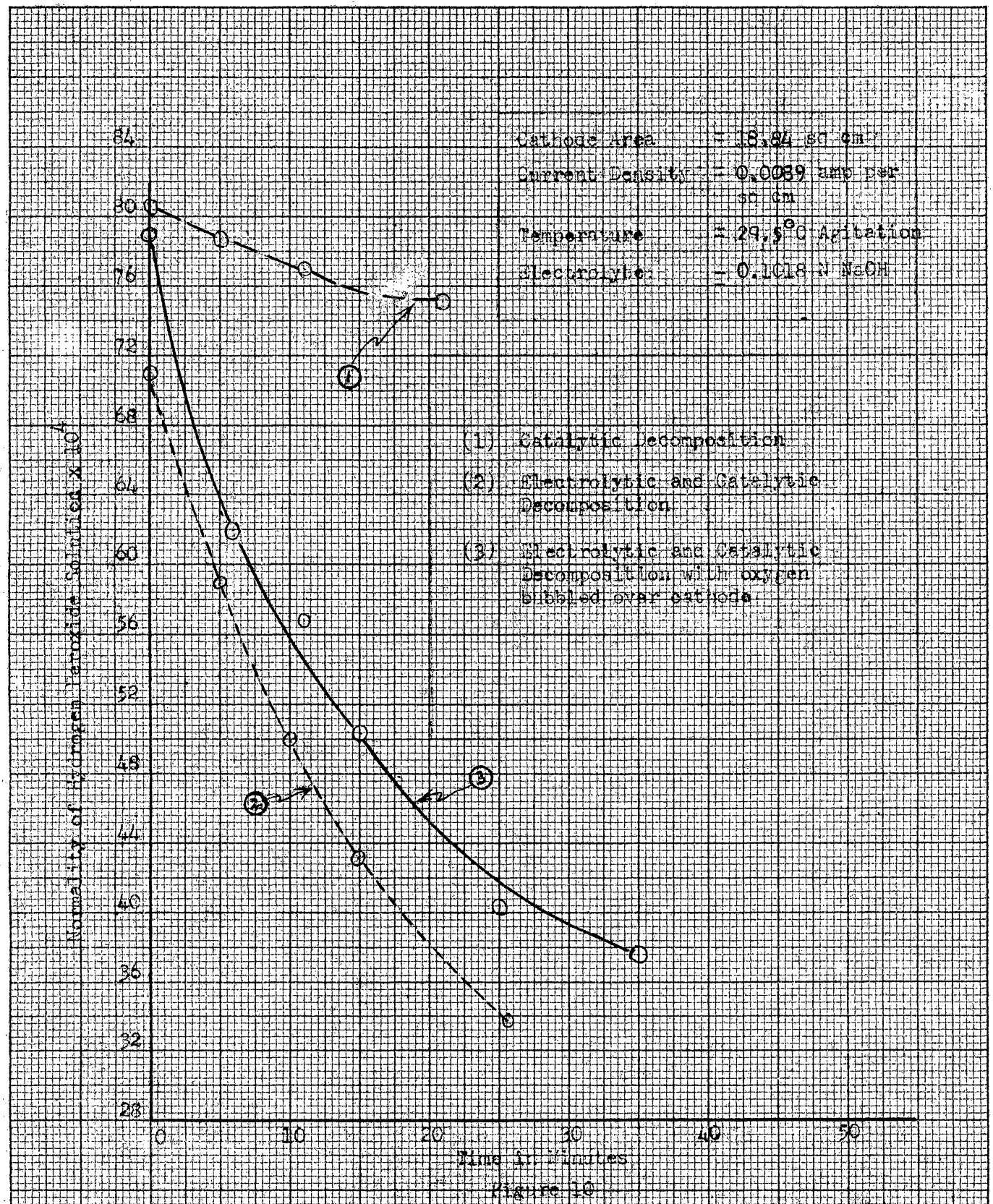


Figure 10

Behavior of Hydrogen Peroxide in 0.1 Normal Sodium Hydroxide Solution at Zinc Cathode.

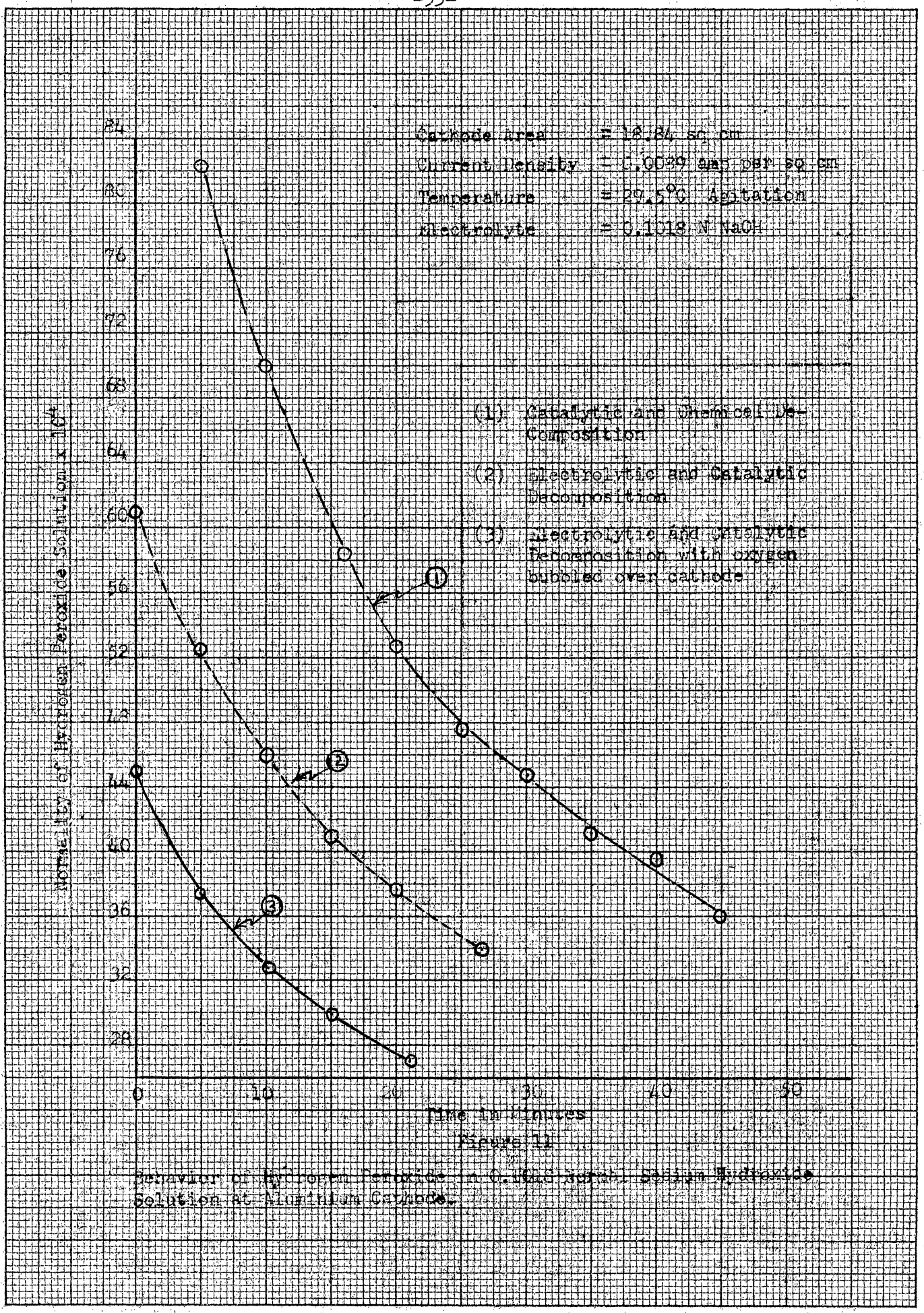


Figure 11

Behavior of Hydrogen Peroxide in 0.1018 Normal Sodium Hydroxide Solution at Aluminum Cathode.

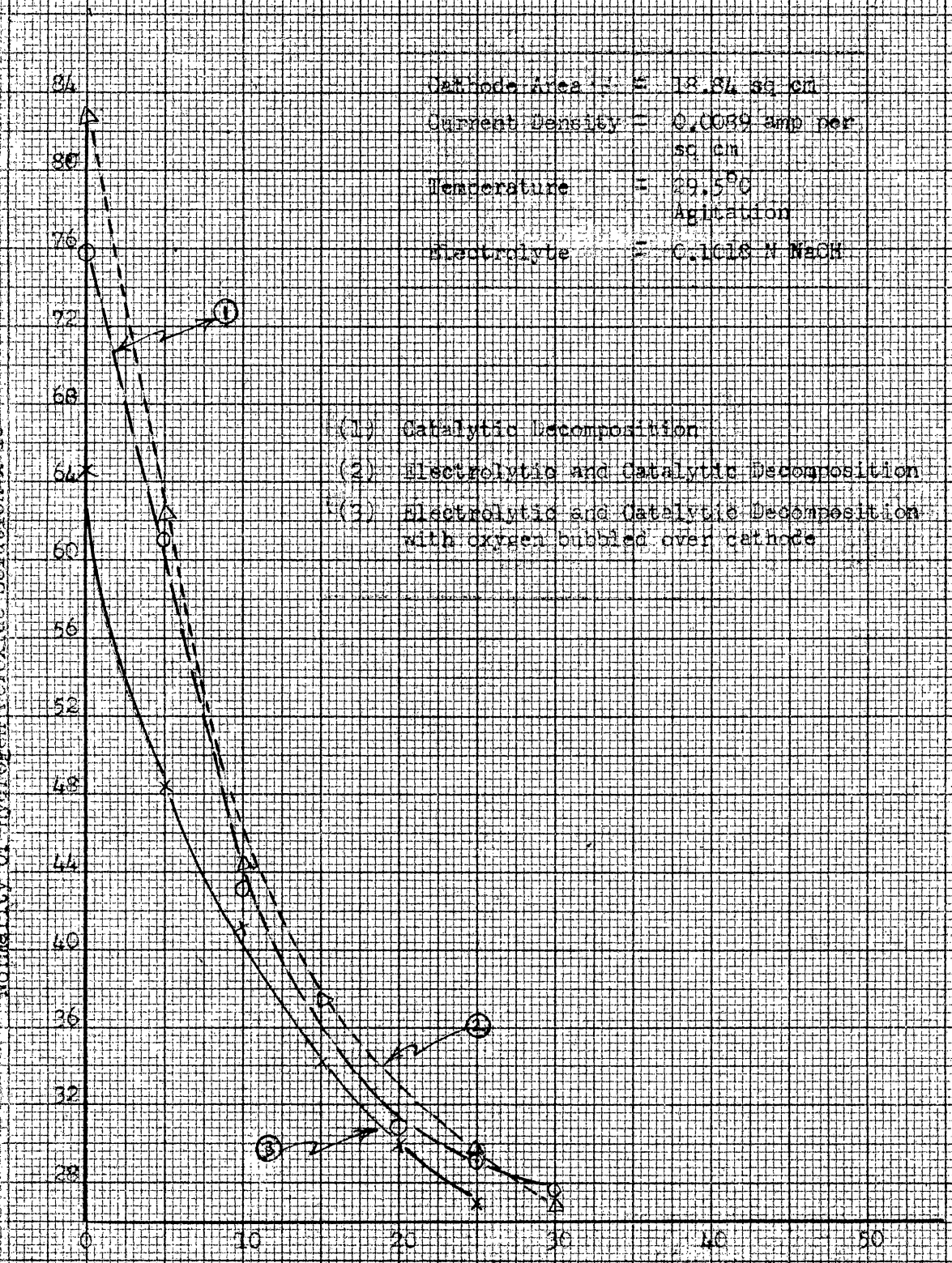


Figure 12

Behavior of hydrogen peroxide in 0.1 normal sodium hydroxide solution at lead cathode.

G. Sample Calculations

Sample calculations for the data obtained for Tables IV, V and VI are given below:

Titration Data. The following table represents the milliliters of 0.0106 N potassium permanganate solution required to titrate 10 ml of hydrogen peroxide solution from the experimental cell at various time interval.

Volume of catholyte = 100 ml (kept constant)

	Time in Minutes			
	0	5	10	15
Ml of 0.0106 N $KMNO_4$ required for titration with 10 ml of catholyte	6.55	5.85	5.15	4.6

(1) Equivalents of H_2O_2 present in catholyte at start $= \frac{6.55 \times 100 \times 0.0106}{10 \times 100}$

$= 69.43 \times 10^{-4}$ equivalents/l

Now 10 ml of fresh electrolyte containing no hydrogen peroxide were added to the experimental cell.

(2) Amount of 0.0106 N hydrogen peroxide solution after removal of 10 ml of testing solution at start = 65.5 - 6.55
= 58.95 ml per 100 ml of catholyte

(3) Amount of 0.0106 N hydrogen peroxide in solution after second electrolysis period, at the beginning of second titration = 5.85 x 10
= 58.5 ml/100 ml of catholyte

(4) Amount of 0.0106 N hydrogen peroxide solution decomposed during the interval zero to five minutes = 58.95 - 58.5
= 0.45 ml

(5) Amount of 0.0106 N hydrogen peroxide solution that would have remained in the cell if no samples had been removed, just before the second titration

$$= 65.5 - 0.45$$
$$= 65.05 \text{ ml}$$
$$= \frac{65.05 \times 0.0106}{100}$$
$$= 6.893 - 10^{-4} \text{ equivalents/l}$$

(6) Amount of 0.0106 N hydrogen peroxide remaining after removal of 10 ml of testing solution after the second titration

$$= 58.5 - 5.85$$
$$= 52.65 \text{ ml}$$

(7) Amount of 0.0106 N hydrogen peroxide solution decomposed during the interval five to ten minutes

$$= 52.65 - (10 \times 5.15)$$
$$= 1.15 \text{ ml}$$

(8) Amount of 0.0106 N hydrogen peroxide solution that would have remained in the cell if no samples had been removed, just before the third titration

$$= 65.05 - 1.15$$
$$= 63.9 \text{ ml}$$
$$= \frac{63.9 \times 0.0106}{100}$$
$$= 67.7 \times 10^{-4} \text{ equivalents/l}$$

<u>Calculations of Current Efficiency</u>. Consider the curves (Figure 6) for the formation and decomposition of hydrogen peroxide solution in 5 normal sodium hydroxide when the current passing is 1000 x 18.84 x 0.0089 = 168 ma. (0.0089 = amps per sq cm) (18.84 = cathode area, sq cm)

According to the equations:

$$H_2O_2 + H_2 = 2H_2O$$
$$H_2 + O_2 = H_2O_2$$

the formation or the decomposition of hydrogen peroxide in ten minutes calculated from Faraday's laws would be $\frac{168}{1000} \times \frac{10 \times 60}{965.00} = 1.045 \times 10^{-3}$ equivalents.

From Figure 6:

(a) Total electrolytic and catalytic decomposition of hydrogen peroxide during 10 minutes starting at 60.0×10^{-4} equivalents per liter

$$= (60.0 - 44.8)\ 10^{-4}$$
$$= 15.2 \times 10^{-4} \ \frac{\text{equivalents}}{\text{liter}}$$

(b) Catalytic decomposition of hydrogen peroxide during 10 minutes starting at 60.0×10^{-4} equivalents per liter

$= (60.0 - 56.2)\ 10^{-4}$

$= 3.8 \times 10^{-4}\ \frac{\text{equivalents}}{\text{liter}}$

(c) Electrolytic reduction of hydrogen peroxide during 10 minutes starting at 60.0×10^{-4} equivalents per liter

$= (1) - (2)$

$= (15.2 - 3 - 8)\ 10^{-4}$

$= 11.4 \times 10^{-4}$ equivalents per l

$= 11.4 \times 10^{-5}$ equivalents per 100 ml of starting solution

∴ % current efficiency of electrolytic reduction

$= \frac{11.4 \times 10^{-5}}{1.045 \times 10^{-3}} \times 100$

$= 10.9\%$

(d) Electrolytic and catalytic decomposition of hydrogen peroxide with oxygen bubbled over at the cathode from figure 4 starting at 60×10^{-4} equivalents per l

$= 60 - 50.4$

$= 9.6$ equivalents per l

(e) Hydrogen peroxide formed and decomposed

$= (1) - (4)$

$= (15.2 - 9.6) \times 10^{-4}$

$= 5.6 \times 10^{-4}$ equivalents per l

$= 5.6 \times 10^{-5}$ equivalents per 100 ml of starting solution

% current efficiency of formation of hydrogen peroxide

$= \frac{5.6 \times 10^{-5}}{1.045 \times 10^{-3}} \times 100$

$= 5.35\%$

IV. DISCUSSION

Accuracy of Measurements. Before going into a discussion of the results, it would be better to consider the accuracy of the measurements with which the data was obtained. A milliammeter with range 0-200 milliampere was used. The graduation on the scale was 4 milliamperes. The millimeter had a 2½" scale with forty graduations marks evenly distributed on it. It was possible to read half way between each graduation mark or ± 1 milliampere. Another milliammeter used, a multi-scale, had the ranges: 0-1, 0-5, 0-10, 0-25, 0-50, 0-100, 0-250, 0-500 and 0-1000 milliamperes. The graduation on each scale was 0.02, 0.1, 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 milliamperes respectively. The milliammeter had a two-inch scale with fifty graduation marks evenly distributed over it.

The vacuum tube voltmeter would give a full-scale deflection for five volts on a 2¼" scale. The scale had fifteen graduation marks evenly distributed over it. It was possible to estimate half-way between the graduation marks.

When the full scale reading was adjusted to five volts, the scale could be read to ± 0.08 volts. The voltmeter of the circuit tester used to measure the cell-voltage had a 3½" scale with ninety graduation marks evenly distributed over it. Its full scale deflection was 9.0 volts. It was possible to read each graduation mark, or ± .10 volts.

Accuracy of Titrations. About 0.010 N potassium permanganate was used for all the titrations of the hydrogen peroxide solution. Oxalic acid, 99.8% pure, was used to standardize potassium permanganate. The endpoint of the titration could be determined with one drop of 0.01 N potassium permanganate. Each sample required about 6 ml of potassium permanganate, so the accuracy was about 1% of the result.

Development of New Procedure. In preliminary work, oxygen was bubbled at the cathode of the experimental cell and analysis of the catholyte was made by titration with 0.01 N potassium permanganate at definite time intervals. Cathode materials used were zinc, copper, tin, nickel and platinum in 0.1 N potassium chloride, 0.15 N phosphoric acid and 1.5 N potassium hydroxide. The current density was varied from 0.002 to 0.020 amperes per sq cm. Insufficient hydrogen peroxide was formed at any of the above electrodes to permit quantitative determinations. However, faint qualitative tests for the presence of hydrogen peroxide were obtained with potassium iodide and starch solution at a current density of 0.002 amps per sq cm at zinc, lead and copper electrodes at 24°C in 0.15 N phosphoric acid. Phosphoric acid was used as the electrolyte since it eliminates the possibility of the formation of a per-acid at the anode which might diffuse into the catholyte.

Berl[3], Weisz and Jaffe[27] report quantitative formation of hydrogen peroxide at activated carbon electrodes by the cathodic reduction of oxygen. Hence it seemed well to study the formation of hydrogen peroxide at activated carbon cathode.

For this purpose, a graphite rod was used and activated carbon was applied to it. Ethyl cellulose was used[29] as the binding agent for the activated carbon. 1.5 N potassium hydroxide was used as suggested by Berl[3]. Hydrogen peroxide was formed by the cathodic reduction of oxygen. Unfortunately, the activated carbon particles did not adhere to the graphite rod long enough to permit quantitative study. Berl points out that the use of activated carbon electrode is similar to using very high pressures since oxygen is adsorbed at the surface and acts as if compressed under a high pressure. However, it would be well to determine if hydrogen peroxide is formed and then decomposed at metal cathodes, at atmospheric pressure, or if it is never formed at all. To solve this, it was a problem to isolate the three possible reactions affecting the hydrogen peroxide, namely, (a) catalytic decomposition at the metal electrode surface, (b) electrolytic reduction at the cathode, and (c) cathodic formation by reduction of oxygen with nascent hydrogen.

Catalytic Decomposition of Hydrogen Peroxide. This was studied in aqueous solutions and the results were recorded in Table IV. The results indicate that the metals studied, and having a catalytic effect can be arranged in the following sequence in order of their decreasing catalytic action on aqueous solutions of hydrogen peroxide: lead, platinum, copper, zinc and nickel. This agrees with the data given by Machu[19]. Aqueous solutions of hydrogen peroxide were found to decompose spontaneously but the decomposition was smaller compared to the catalytic effect of the metals (Table IV). It is reported in the literature[5] that the catalytic

activity of various metal surfaces on 90% hydrogen peroxide is much smaller than the results obtained in these experiments.

Electrochemical Reduction of Hydrogen Peroxide. Next important step in the study of the decomposition of hydrogen peroxide was to determine whether hydrogen peroxide is reduced electrochemically. It was found that hydrogen peroxide solutions are reduced electrolytically by the action of nascent hydrogen at zinc, lead, aluminium, magnesium alloy F-S-1 and mercury, but not at graphite.

The above data indicated that hydrogen peroxide solutions decompose spontaneously, catalytically and electrolytically. Hence it is probable that in preliminary experiments, the absence of formation of hydrogen peroxide was due to the fact that the hydrogen peroxide was decomposed faster than it was formed. In order to test the validity of the above statement, the decomposition of hydrogen peroxide was studied in the electrolytic cell (a) catalytically, (b) catalytically and electrolytically together, and (c) catalytically and electrolytically with oxygen bubbled at the cathode. Now if hydrogen peroxide is formed but decomposed at a faster rate, then the decrease in concentration of hydrogen peroxide in the electrolyte would be slower in case (c) than in case (b). This proved to be true. Hydrogen peroxide was formed at mercury, magnesium alloy F-S-1, zinc, and lead cathodes at atmospheric pressure and at 29.5°C, but was decomposed faster than it was formed. In the case of magnesium, the rate of reduction of concentration of hydrogen peroxide while oxygen was bubbled over the cathode was even less than when it was destroyed by catalytic means only. In no case, except for activated carbon was there any net formation of hydrogen peroxide.

It is well known in the field of electrochemistry that the cathode materials of high hydrogen overvoltages are most suitable for electrolytic reduction. Newbury[30] has published the hydrogen overvoltages of various metals and non-metals. For the range of current densities employed in the present investigation, Table VIII (Page 63) was prepared from Newbury's data.

Since the present investigation is concerned with the electrolytic reduction of oxygen to hydrogen peroxide, better results would be expected in case of magnesium, zinc, and mercury than with other metals. In order to test this, cathode materials of different overvoltages were tried.

Effect of Electrode Material Used as Cathode. The effect of electrode materials on the formation and decomposition of hydrogen peroxide was studied at 29.5°C with electrode area of 18.84 sq cm and a current density of 0.0089 amp per sq cm.

The cathode materials can be arranged as follows in order of their decreasing catalytic activity to hydrogen peroxide solutions in 0.1018 N sodium hydroxide (Table V): lead, aluminium, mercury, magnesium alloy F-S-1 and this order is practically the same as for aqueous solution.

While studying aluminium for its catalytic action on hydrogen peroxide solution in the experimental cell, gas was evolved. The high decomposition rate of aluminium on hydrogen peroxide solution can thus be attributed to the chemical formation of nascent hydrogen, a chemical decomposition, and not a catalytic one. If the chemical action could be avoided, hydrogen peroxide would probably be more stable to aluminium than most other metals. In fact, aluminium vessels are used in industry for the storage[24] of hydrogen peroxide in faintly acid or neutral solutions. This behavior of aluminium is evidence that hydrogen peroxide can be reduced with metals with electrode potential more reducing than

TABLE VIII [30]

HYDROGEN OVERVOLTAGES

Material	Hydrogen Overvoltage
Magnesium	0.7
Mercury	0.7
Zinc	0.7
Aluminium	0.45
Lead	0.4
Carbon	0.4

(30) Newbury, E. "Overvoltage" J. Chem. Soc. 105, 2420 (1914).

hydrogen.

Study of the effect of the above metals on the electrolytic and catalytic reduction of hydrogen peroxide in 0.1018 N sodium hydroxide (Table VI) enables one to arrange the cathode materials in the following sequence, in order of their decreasing effect on electrolytic reduction only: zinc, magnesium, mercury, aluminium, lead and graphite. This order checks that of Table VIII, in which the above materials are arranged in their decreasing hydrogen overvoltage. It would be well to note that the metals like lead that show great catalytic activity towards the decomposition of hydrogen peroxide reduce hydrogen peroxide electrolytically (correcting for catalytic action with less efficiency).

It is found that lead, which has the lowest effect of electrolytic reduction on hydrogen peroxide solution, has lowest cathode potential compared to rest of the metals studied. It is reasonable to believe that metals with low cathode potentials are less efficient in reducing hydrogen peroxide solutions.

In a set of experiments, the data of which are plotted in Figures 5 and 7, the decomposition of hydrogen peroxide at mercury and graphite were compared under the following conditions:

Electrolyte - 5 N sodium hydroxide

Temperature - 29.5°C ± 1.5°C

Current density at mercury cathode - 0.0089 amps per sq cm

Area of mercury used - 18.84 sq cm

Current density at graphite - 0.01 amps per sq cm

Area of graphite used - 15.07 sq cm

In case of mercury, hydrogen peroxide was formed at a current efficiency of 5.35% (Table VII) while no hydrogen peroxide was formed at graphite cathode. Electrolytic reduction of hydrogen peroxide took place at mercury while no hydrogen peroxide can be reduced at graphite cathode (Table VI). This agrees with the observation of Weisz and Jaffe[27]. The reason for this behavior of graphite is due to the low reduction potential of graphite compared to mercury (Table VI). As expected, the catalytic effect of graphite towards the decomposition of hydrogen peroxide in 5 N sodium hydroxide is much more pronounced (Figures 5 and 7).

Comparing the data on current efficiency of electrolytic reduction of oxygen (Table VII) and hydrogen peroxide (Table VI) with the hydrogen overvoltage as given in Table VIII, it can be concluded that the metals with high hydrogen overvoltages are most suitable for electrolytic reduction of either oxygen or hydrogen peroxide.

<u>Formation and Decomposition of Hydrogen Peroxide in Various Electrolytes</u>. The effect of using different electrolytes on the formation and decomposition of hydrogen peroxide at mercury cathode is shown in Figures 6 and 8. The conditions used in the experimental cell were:

Current density: 0.0089 amp per sq cm

Temperature: 29.5° ± 1.5°C

Cathode area: 18.84 sq cm

5 N sodium hydroxide and 0.1018 N sodium hydroxide were used as typical basic solutions. Saturated ammonium chloride and 0.042 N phosphoric acid were used as neutral and acidic solutions.

The electrolytes used can be arranged in the following order in order of their decreasing catalytic effect on hydrogen peroxide solutions: 0.1018 N sodium hydroxide, 5 N sodium hydroxide, saturated ammonium chloride, 0.042 N phosphoric acid. This conforms with the view expressed[18] that the stability of hydrogen peroxide increases from basic to neutral to acidic solutions. The OH^- ion concentration decreases in the same order as the decrease in catalytic effect. Hence, it can be concluded that the increase in OH^- ion concentration decreases the stability of hydrogen peroxide solution or an increase in H^+ ion concentration increases the stability of hydrogen peroxide.

The above electrolytes can be arranged in the following sequence in order of their decreasing efficiency of electrolytic reduction of hydrogen peroxide with mercury cathode: 0.042 N phosphoric acid, saturated ammonium chloride, 5 N sodium hydroxide, 0.1018 N sodium hydroxide. Thus the effect of various electrolytes on the efficiency of the reduction of hydrogen peroxide decreases from acidic to neutral to alkaline solutions. This is exactly in opposite order to the effect of the same electrolytes on the catalytic decomposition of hydrogen peroxide. From this observation it can be inferred that the efficiency of electrolytic reduction of hydrogen peroxide is a direct function of the hydrogen ion concentration of the solution. This can mean that either the hydrogen peroxide is a stronger oxidizing agent in acid solution or the nascent hydrogen is a stronger reducing agent in acid solution. Bancroft and Murphy[2][20] have shown that the oxidation reduction potential of hydrogen peroxide referred to the normal hydrogen electrode, is 1.16 in

normal acid solution and falls to 0.30 volts in normal alkali solutions.

Effect of Current Density. In order to study the effect of current density, the area of mercury used as cathode was 18.84 sq cm and the current was varied. The electrolyte used was 5 N sodium hydroxide at 29.5°C (Figure 7).

The formation of hydrogen peroxide at mercury cathode took place with a current efficiency of 5.35 per cent at a current density of 0.0089 amp per sq cm. No hydrogen peroxide could be produced at a current density of 0.0143 or at 0.00403 amp per sq cm. The electrolytic reduction of hydrogen peroxide took place with a current efficiency of 10.9% at a current density of 0.0089 amp per sq cm. When the current density was increased, the efficiency of reduction of hydrogen peroxide decreased to 5.35%. When the current density was decreased, the current efficiency also decreased. Thus, it seems that in 5 N sodium hydroxide solution, hydrogen peroxide can be decomposed at a maximum current efficiency of about 10.9%. The optimum current density is about 0.0089 and definitely lying between 0.00403 and 0.0143 amp per sq cm.

Effect of the Presence of Sodium and Potassium Ions in Alkaline Electrolyte. The catalytic and electrolytic decomposition of hydrogen peroxide in sodium and potassium hydroxide, using magnesium alloy F-S-1 as cathode, is shown in Figure 9. The current efficiency of electrolytic reduction of hydrogen peroxide in solution hydroxide was 7.27% but no hydrogen peroxide was electrochemically reduced in potassium hydroxide. However, more hydrogen peroxide could be catalytically decomposed in potassium hydroxide. The current efficiency of formation of hydrogen

peroxide in sodium and potassium hydroxide was 8.05% and 6.12% respectively.

There is confirmation that the statement that was made with regard to the electrode material, "a poor catalytic material is a good electrolytic reduction material," also applies to the electrolyte. For here the potassium ion was a good catalyst but a poor electrochemical reducing medium.

There appears to be very little difference in the behavior of sodium and potassium ions in the efficiency of reduction of oxygen in hydrogen peroxide. This does not parallel the action of the cathodes.

Effect of Agitating the Electrolyte. The effect of agitation on the decomposition of hydrogen peroxide at a mercury cathode was studied only in ammonium chloride electrolyte. The cathode area was 18.84 sq cm. The temperature was 27°C and the c.d. was 0.0049 amp per sq cm. The results are illustrated in Figure 8.

Hydrogen peroxide was formed with a current efficiency of 2.4% when the electrolyte was stirred. When unstirred, no hydrogen peroxide was formed. The curve of electrolytic and catalytic decomposition of hydrogen peroxide actually fell above the curve for the catalytic and electrolytic reduction when oxygen was bubbled over at the cathode. In other words, the electrolytic and catalytic reduction of hydrogen peroxide when the electrolyte is stirred is much more than when the electrolyte is unstirred which was as expected.

It was impossible to bubble oxygen over at the cathode without stirring the electrolyte. However, the comparison of two curves numbered(3) on Figure 8 indicate that bubbling oxygen provided sufficient stirring and mechanical stirring had no effect during the reduction of oxygen.

Effect of Gas Bubbles on the Cathode. Nitrogen gas, instead of oxygen, was bubbled over the magnesium alloy F-S-1 cathode in order to determine whether the gas bubbles had any blocking effect on the cathode surface. This means that the gas bubbles might prevent access of the peroxide to the cathode surface, resulting in less decomposition than when no gas was bubbled. The curves (Figure 9) for the catalytic and electrolytic decomposition of hydrogen peroxide when (a) nitrogen was not bubbled, and (b) nitrogen was bubbled, run parallel to each other. This proves that the gas bubbles did not have any blocking effect upon the cathode material, and that the decreased decomposition of hydrogen peroxide when oxygen was bubbled compared to that when no gas was bubbled can be ascribed to the formation of hydrogen peroxide by cathodic reduction of oxygen.

Hydrogen Peroxide Theory of Corrosion. During the brief life span of Dunstan's[10] hydrogen peroxide theory of corrosion, a great deal of importance was attached to the formation of hydrogen peroxide during the corrosion of metals. The presence of hydrogen peroxide has been demonstrated by various workers[8,10,11] at aluminium, zinc, cadmium, copper and magnesium surfaces during corrosion. In the present investigation it was found that hydrogen peroxide is formed at magnesium, zinc and mercury surfaces in presence of oxygen. All this data points to the fact that hydrogen peroxide is definitely a product of the reaction taking place during atmospheric corrosion. Churchill[8] has found that the amount of hydrogen peroxide produced at aluminium surface during submerged corrosion is directly proportional to the amount the metal cor-

roded and the rate at which oxygen is supplied to the surface.

In atmospheric corrosion, conditions are in general highly favorable for the production of hydrogen peroxide. The large excess of oxygen and high diffusion rate of oxygen promotes the conversion of hydrogen (formed at the metal surfaces) to hydrogen peroxide.

Application of Hydrogen Peroxide Formation to Theory of Corrosion. The accepted theory of metallic corrosion postulates an anodic and cathodic reaction. At the anode surface, metal ions are formed as follows:

$$Fe = Fe^{++} + 2e$$

at the cathodic area, the cell is completed by the following primary reaction:

$$H^{+} + e = H$$

The velocity of corrosion depends upon how fast the monatomic hydrogen can be removed by secondary reactions, which may be one of the following:

(a) Formation of diatomic hydrogen from monatomic hydrogen and evolution as a gas.

(b) Solution and diffusion of monatomic hydrogen or the diatomic hydrogen without visible evolution.

(c) Reaction of the monatomic hydrogen with a depolarizer which may be oxygen, organic compounds or chemical solutes.

It is usual to postulate that the depolarizing action of oxygen is to form water according to the equation:

$$4H + O_2 = 2H_2O$$

The evidence presented above indicates that this is an incorrect assumption and the equation is more likely to be:

$$2H + O_2 = H_2O_2$$

with subsequent decomposition of the hydrogen peroxide before it has an opportunity to build up to appreciable concentrations.

The drawback of hydrogen peroxide theory of corrosion is that the addition of hydrogen peroxide to the corroding medium accelerates the rate of corrosion instead of retarding it. This can be explained with the present theory by noting that H_2O_2 can be reduced at most metal cathodes. Then addition of hydrogen peroxide to a corroding medium would accelerate the rate of corrosion by depolarizing the cathodic surface and removing the monatomic hydrogen more rapidly than it would be removed by reaction with atmospheric oxygen. Since hydrogen peroxide was not reduced at lead cathodes in alkaline media, one would not expect to get an increase rate of corrosion of lead in this medium by addition of H_2O_2.

Another argument used against the hydrogen peroxide theory of corrosion is that no hydrogen peroxide was detected during the corrosion of iron. Dunstan[10] explained the peculiar behavior of iron by saying that iron decomposed hydrogen peroxide as soon as it was formed. Few people, however, accepted that explanation. Recently, Chaudron and Herzog[31] have detected the presence of hydrogen peroxide during the corrosion of iron at slightly elevated pressure. The effect of pressure is that more hydrogen peroxide is formed than is decomposed catalytically. This observation breaks down one of the popular arguments against the hydrogen peroxide theory.

<u>Reaction Taking Place in Hydrogen-Oxygen Cell</u>. A hydrogen-oxygen cell consists of two inert electrodes (e.g. platinum) dipping into an aqueous electrolyte. Hydrogen and oxygen gases are bubbled over the two

electrodes so that the system forms a gas-cell in which hydrogen and oxygen gases serve as electrodes to hydrogen and hydroxyl ions in solution. The reaction taking place in the cell has been a matter of controversy. There are two possibilities, first is the formation of water and the other is the formation of hydrogen peroxide.

(a)
$$2H_2 \quad 4H^+ + 4e$$
$$4e + 2H_2O + O_2 = 4OH^-$$
$$2H_2O + 2H_2 + O_2 = 4H^+ + 4OH^- \quad 4H_2O$$

or

(b)
$$H_2 = 2H^+ + 2e$$
$$2e + O_2 = O_2^{2}$$
$$H_2 + O_2 = 2H^+ + O_2^{-2} = H_2O_2$$

The voltage of the oxygen-hydrogen cell measured experimentally by various workers[4,12,15] does not agree with the value expected if the reaction (a) is assumed to be correct.

On the other hand, the formation of hydrogen peroxide from hydrogen and oxygen has been demonstrated by various workers[11,22,25]. In the present investigation hydrogen peroxide was formed at atmospheric pressure from cathodic reduction of oxygen. Hence the formation of hydrogen peroxide is the reaction taking place in the hydrogen-oxygen cell. The measurement of the cell-voltage also leads to the same conclusion.

<u>Mechanism of the Reaction $H_2 + O_2$</u>. Lewis and Randall[32] give the value of free energy change involved in the formation of water and hydrogen peroxide.

(a) $H_2 + \frac{1}{2}O_2 = H_2O$; $\Delta F^{o}_{298^{o}} = -56560$ calories

(b) $H_2 + O_2 = H_2O_2$ (ag); $\Delta F^{o}_{298^{o}} = -31470$ calories

Thus, both the above reactions would take place spontaneously. But since the value of ΔF^{o} is more negative in case (a) than in (b), the reaction between hydrogen and oxygen would tend to take place in two stages with the intermediate formation of hydrogen peroxide. Thus,

$$H_2 + O_2 \rightarrow H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

The present investigation indicates that the formation of hydrogen peroxide is the result of the reduction of oxygen by nascent hydrogen. Thus:

$$2H + O_2 \rightarrow H_2O_2.$$

There may be considerable doubt that oxygen can be reduced by ordinary diatomic hydrogen to hydrogen peroxide. It would be interesting to study the oxidation of hydrogen at an anode. The mechanism of formation of hydrogen peroxide, if any is formed, may be either:

(a) $2OH^- \rightarrow H_2O_2 + 2e$

in which case no hydrogen need be bubbled over the anode, or:

(b) $OH^- \rightarrow OH + e$

$2\ OH \rightarrow O + H_2O$

$2O \rightarrow O_2$ (nascent)

$H_2 + O_2$ (nascent) $\rightarrow H_2O_2$.

In case (b), the reaction:

$$H_2 + O \rightarrow H_2O$$

appears to be more probable.

Recommendations

The following recommendations are offered for future investigations:

Anodic Oxidation of Hydrogen. The mechanism of anodic formation of hydrogen peroxide (if any is formed) may be either:

(a) $2OH^- = H_2O_2 + 2e$

In which case no hydrogen need be bubbled over at the anode, or:

(b) $2OH^- \rightarrow 2OH + 2e$

$2OH \rightarrow O + H_2O$

$2O \rightarrow O_2$ (nascent)

$H_2 + O_2$ (nascent) $\rightarrow H_2O_2$

In which case, hydrogen must be bubbled over the anode. The oxidation of hydrogen at the anode would be an interesting problem to study.

Effect of pH on Overvoltage. It was found that in case of mercury the decrease in pH of the electrolyte increased the efficiency of electrochemical reduction. Once again, using cathode materials of increasing hydrogen overvoltage, the efficiency of electrochemical reduction also increased. Hence, it would be interesting to study the effect of pH on the hydrogen overvoltage of different materials.

Effect of Temperature on the Formation and Decomposition of Hydrogen Peroxide. Fischer[11] has found that decreasing the temperature of the electrolyte increased the efficiency of the reduction of oxygen to hydrogen peroxide. It would be interesting to find out how the temperature affects the efficiency of the reduction of oxygen.

Effect of Pressure. Fischer's[11] original observation that "increasing the pressure increases the efficiency of reduction of oxygen" has made possible the electrolytic oxidation of methyl glucoside (with hydrogen peroxide) to methyl gluconamide[31]. Thus using high pressures in the oxidation reactions opens a new field.

Effect of Cathode Materials and Different Electrolytes on the Formation of Hydrogen Peroxide. A change in the formation and electrolytic and catalytic decomposition was noticed in each case when using different electrolytes at the same cathode material or using different cathode materials at the same electrolyte. It would be interesting to continue work in this field to explain the behavior of different electrolytes and cathode materials.

Limitations

The limitations under which this investigation was made are as follows:

The only materials studied as cathodes were mercury, zinc, aluminium, magnesium alloy F-S-1, lead and graphite. The exact composition of lead was unknown.

Five and 0.1018 normal sodium hydroxide 0.1010 normal potassium hydroxide, saturated ammonium chloride at 29.5°C and 0.034 normal phosphoric acid were the only electrolytes studied.

Not all the cathode materials were studied in all the electrolytes. Mercury was studied in all the electrolytes. Graphite was studied in 5 normal sodium hydroxide only. Magnesium alloy F-S-1 was studied only in 0.1018 N sodium and potassium hydroxide. Aluminium, zinc and lead were studied only in 0.1018 N sodium hydroxide.

The investigation was conducted under atmospheric pressure and at 29.5°C.

The catholyte was kept saturated with electrolytic oxygen by bubbling it through a fine capillary tube.

No corrections were made for the solution diffusing from and to the porous cup.

The cathode area was measured by means of a millimeter scale.

All cathode potentials were measured by means of a vacuum tube voltmeter against a saturated calomel electrode.

V. CONCLUSIONS

On the basis of the results obtained in the present investigation, the following conclusions were drawn:

Hydrogen peroxide can be produced by cathodic reduction of oxygen at activated carbon, mercury, magnesium alloy F-S-1 and zinc electrodes at a current density of 0.009 amp per sq cm in 1.5 normal potassium hydroxide, 5 normal sodium hydroxide and 0.10 normal sodium and potassium hydroxide at 29.5°C.

In all cases the rate of formation was smaller than the rate of electrolytic and catalytic decomposition except in the case of activated carbon cathode.

The efficiency of cathodic reduction of oxygen and hydrogen peroxide was in the same order as the hydrogen overvoltage and reduction potential of the cathode material.

Increase of hydroxyl ion concentration decreased the stability of hydrogen peroxide.

The efficiency of electrochemical reduction of hydrogen peroxide decreased with increase in hydroxyl ion concentration. A poor catalytic material for hydrogen peroxide decomposition was a good material for electrochemical reduction of hydrogen peroxide.

Agitation increased the efficiency of reduction of hydrogen peroxide.

The catalytic decomposition of hydrogen peroxide solution was greater in presence of sodium than potassium ions. However, hydrogen peroxide solution could be reduced electrochemically in presence of sodium, but not potassium ions.

The presence of gas bubbles on the cathode surface did not change its activity towards catalytic and electrolytic decomposition of hydrogen peroxide solutions.

The accepted theory for metallic corrosion postulates the formation of monatomic hydrogen at the cathode. Oxygen acts as a depolarining agent for form water according to the equation

$$4H + O_2 = 2H_2O$$

However, the present investigation is an evidence that the reaction is more likely to be

$$2H + O_2 = H_2O_2$$

with subsequent decomposition of hydrogen peroxide.

The voltage of hydrogen-oxygen cell[4,15] and the formation of quantitative amounts of hydrogen peroxide[11,22] by the cathodic reduction of oxygen point to the fact that the cell reaction is more likely to be

$$H_2 + O_2 = H_2O_2 \qquad (a)$$

and not

$$2H_2 + O_2 = 2H_2O \qquad (b)$$

VI. SUMMARY

The purpose of this investigation was to study the factors affecting the electrolytic production of hydrogen peroxide from hydrogen and oxygen. The mechanism of this reaction throws light on the production and chemistry of hydrogen peroxide, electrochemistry of hydrogen, oxygen and water and the mechanism of corrosion.

This investigation involved the study of the formation and decomposition of hydrogen peroxide at the cathode of an electrolytic cell. Zinc, mercury, magnesium alloy F-S-1, aluminium, lead and activated carbon electrodes in 5 N sodium hydroxide, 0.1018 N sodium hydroxide, and .01018 N potassium hydroxide, saturated ammonium chloride and 0.043 N phosphoric acid were studied.

The apparatus consisted of a U-shaped gas generator producing electrolytic oxygen, which was bubbled over the cathode of the electrolytic cell after purification in a glass-wool trap. The experimental cell was a 600 ml glass beaker with a platinum anode outside, and different cathodes inside a porous cup.

Three possible reactions affecting hydrogen peroxide were studied, namely, (a) catalytic decomposition at the electrode surface; (b) electrolytic reduction at the cathode and (c) cathodic formation by reduction of oxygen with nascent hydrogen.

From the data obtained during the investigation, it was found that hydrogen peroxide was produced at mercury cathode, in 5 N sodium

hydroxide, at 29.5°C. But the rate of production was less than the rate of decomposition. The optimum current density for the greatest efficiency of production and electrochemical reduction of hydrogen peroxide was 0.0089 amp per sq cm.

Graphite, lead, and magnesium alloy F-S-1 decompose hydrogen peroxide rapidly in 5 N, 0.1018 N sodium hydroxide and 0.101 N potassium hydroxide solutions respectively. The same materials when used as cathodes in an electrolytic cell, have little or no effect on the electrochemical reduction of hydrogen peroxide. This is probably due to their low hydrogen overvoltages and low reduction potentials in the electrolytes specified above.

Oxygen was reduced to hydrogen peroxide at magnesium alloy F-S-1 and zinc cathodes in 0.1018 N sodium hydroxide and at mercury cathode in 5 N sodium hydroxide at a current density of 0.0089 amp per sq cm. This is probably due to their high hydrogen overvoltages and reduction potentials in the above electrolytes.

The stability of hydrogen peroxide solutions decreased in different electrolytes in the following order: 0.042 N phosphoric acid, saturated ammonium chloride, 5 N and 0.1 N sodium hydroxide. However, the efficiency of electrochemical reduction of hydrogen peroxide increased in the same order. Thus it seems that increasing the hydroxyl ions in the electrolyte increases the catalytic activity and decreases the efficiency of electrochemical reduction of hydrogen peroxide.

The catalytic decomposition of hydrogen peroxide was more efficient in presence of potassium ions but less in presence of sodium ions.

Hydrogen peroxide solutions could be electrochemically reduced in the presence of sodium ions but not in presence of potassium ions.

Stirring improved the efficiency of electrochemical reduction but did not make any appreciable change on the catalytic decomposition of hydrogen peroxide.

The mechanism of corrosion can be explained by postulating the formation of hydrogen peroxide on the surface of the corroding material by the reduction of oxygen with nascent hydrogen. It has been found that the extent of corrosion is proportional to the amount of hydrogen peroxide formed.

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APPENDIX I

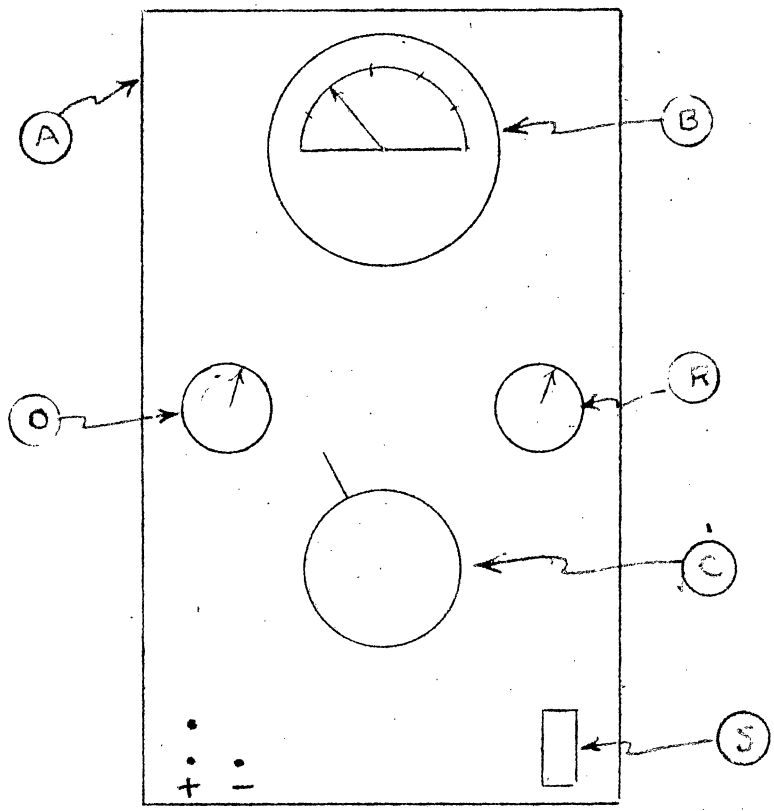
VACUUM TUBE VOLTMETER

Construction. The vacuum tube voltmeter was constructed according to the circuit diagram given in Radio-Craft Magazine[33].

Purpose. This meter measures voltage, while drawing only a small current from the circuit. It will only read d-c voltages.

Calibration. Plug the meter into a 110 volt a-c line. Wait at least five minutes for the tubes to get hot. Turn the left hand control (O) till the meter needle reads zero. Apply a known voltage at the + and - terminals. This can be done with a rheostat, dry cell and voltmeter. Switch the control "C" to proper range (0 to 5 or 0-15 volts). Turn the control "R" till the meter needle reads the applied voltage. Now the meter is calibrated.

Operation. Remove the known voltage from + and - terminals and connect the two terminals of the source of the unknown potential. From the position of the needle, read the voltage from the attached curve.



A- VACUUM TUBE VOLTMETER

B. METER

C. RANGE CONTROL

O. ZERO CONTROL

R. CALLIBRATION CONTROL

S. SWITCH

VIRGINIA POLYTECHNIC INSTITUTE
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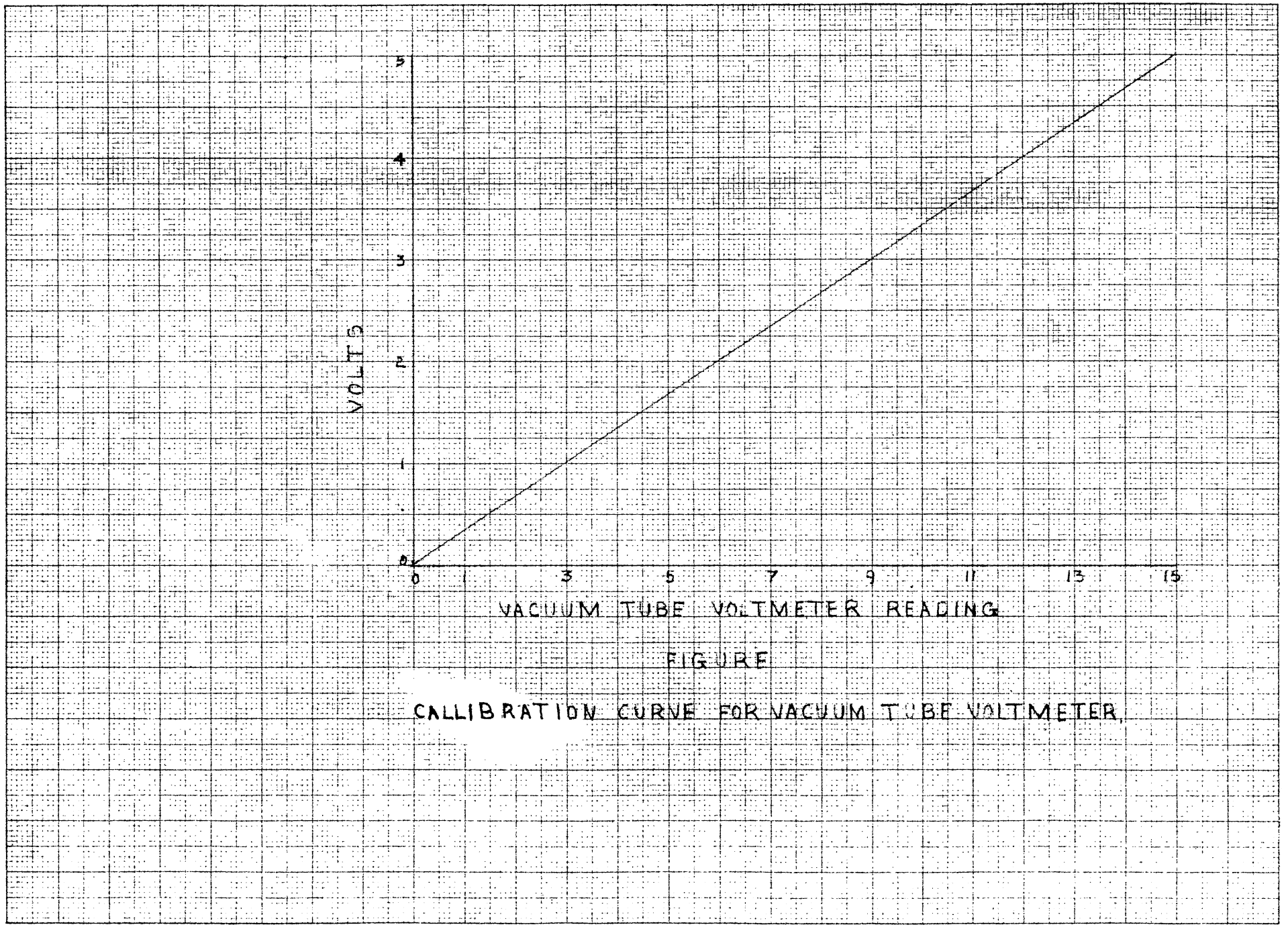
Vacuum Tube Voltmeter

Drawn by: H.J.J.
Checked by: Figure
Approved by: N.F.M. Date: 8-20-48



FIGURE

CALLIBRATION CURVE FOR VACUUM TUBE VOLTMETER.