

THE POSSIBILITIES OF PRODUCING ELECTRIC POWER
BY THE OXIDATION OF CARBON IN AN ELECTROCHEMICAL CELL.

by

Francis Neeld Green

A THESIS SUBMITTED FOR THE DEGREE OF
BACHELOR OF SCIENCE
ELECTRICAL ENGINEERING COURSE

The University of Tennessee

1927

CONTENTS

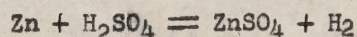
	Page
INTRODUCTION,.....	1
CHAPTER I - GENERAL THEORY OF THE CELL,.....	2
CHAPTER II - SOME CELLS WHICH FURNISH ELECTRICITY BY THE OXIDATION OF CARBON,.....	7
CHAPTER III— A THEORETICAL CELL THAT WILL PRODUCE CURRENTS FROM CARBON AND ATMOSPHERIC OXYGEN,.....	10
BIBLIOGRAPHY,.....	21

INTRODUCTION

Since the transformation of the chemical energy stored in coal to electrical energy in a steam power plant is extremely wasteful, other methods of accomplishing this transformation have been proposed. Among the proposals which do not use a heat engine are the thermopile and the electric cell. Since the thermopile is even more wasteful of energy than the steam engine, it is evident that the electric cell is the better proposal. In this thesis I have made a study of the possibilities of such a cell both theoretically and experimentally.

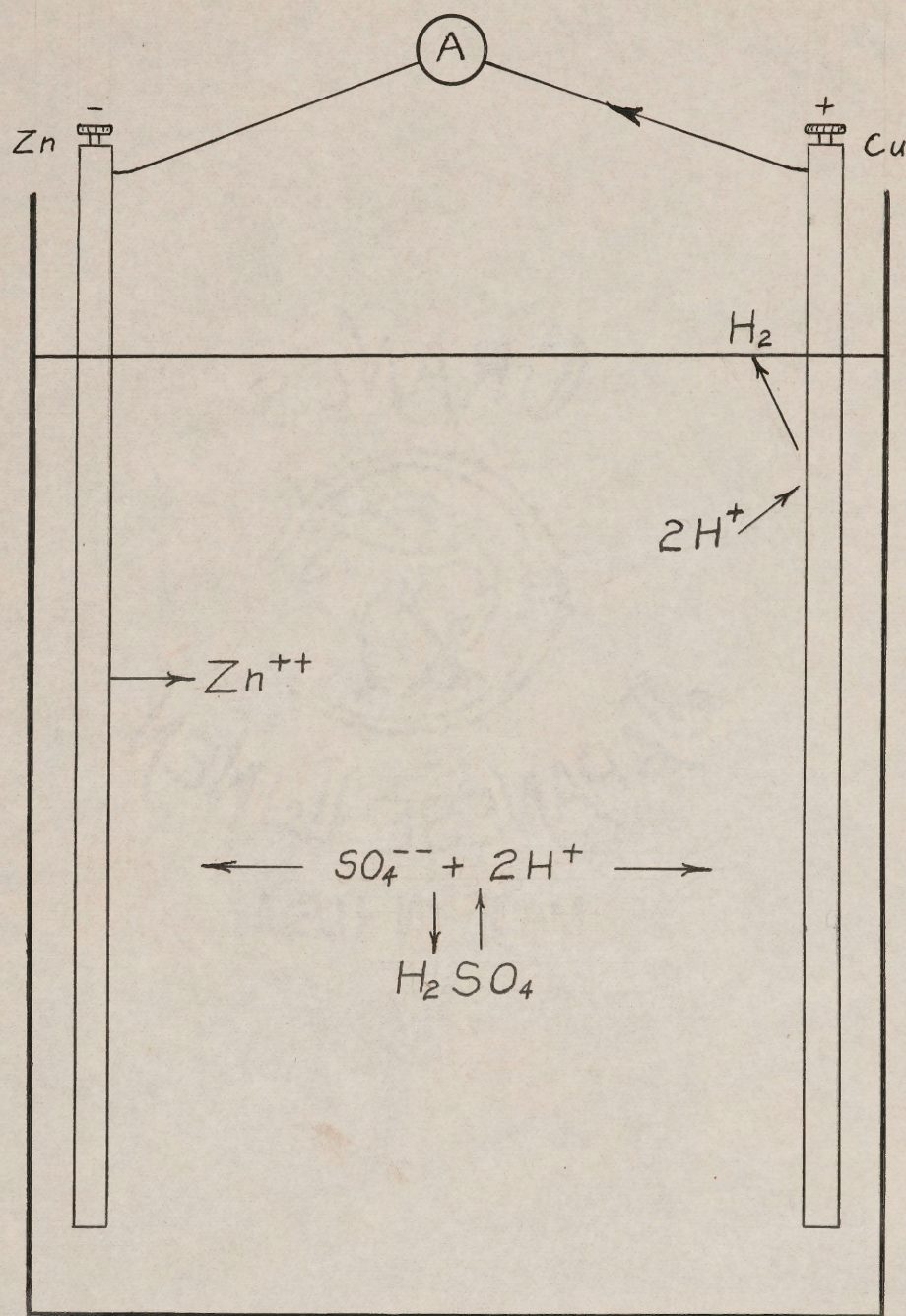
CHAPTER 1 — GENERAL THEORY OF THE CELL.

One of the simplest illustrations of reactions which can easily be carried out in cells, to furnish electricity instead of heat is the voltaic cell. If a strip of zinc be immersed in sulphuric acid, bubbles of hydrogen will appear at its surface and the reaction



occurs with the evolution of heat. If a strip of copper be also immersed in the solution, nothing further will happen unless an electrical connection is made between the strips; in which case a current will flow from the copper to the zinc and bubbles of hydrogen will appear at the copper pole. The zinc pole will be eaten away, but the copper pole will not be attacked. If a strip of chemically pure zinc be used, the hydrogen will be evolved at the copper pole only. The hydrogen evolved at the zinc pole when an impure metal is used is due to the local currents between the metal and its impurities.

It is evident that there are really two chemical reactions in the cell; namely, the zinc goes into solution at the anode, and the hydrogen comes out of solution at the cathode. Now these reactions can be considered separately. If zinc be placed in a solution of zinc chloride, there is at once a difference of potential between the metal and the solution. The atoms of the metal have an individual tendency to assume the ionic state, or, in other words, to give up electrons. On the other hand, the ions in the solution have a tendency to take up electrons and become neutral. If the tendency to give up electrons is the stronger, as it is with the more active metals, then a difference of potential is produced, with the solution positive with respect to the metal. If the tendency to take up electrons is



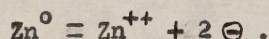
Pos. ions $\longrightarrow$

Neg. ions $\longleftarrow$

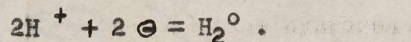
Fig. 1 - Voltaic Cell

the stronger, the solution will be negative with respect to the metal.

In the voltaic cell, the zinc atoms go into solution and form zinc ions, leaving two electrons on the anode:



The solution now contains zinc ions and hydrogen ions. Since copper is less active than any ion in the solution, there will be a tendency for the ions to come out of solution at the cathode, taking up electrons and leaving it positive. When the external circuit is closed, the electrons given up at the anode will be received at the cathode. Since hydrogen is the less active of the anions, it comes out of the solution:



Current flows from the cathode to the anode in the external circuit. It is evident that positive ions move from the anode to the cathode, and that negative ions move from the cathode to the anode in the solution. This completes the circuit.

If the zinc can be prevented from coming into direct contact with the acid, all of the zinc which goes into solution will produce electrical energy. In order to accomplish this, the zinc may be surrounded by a solution with which it will not react chemically, but which contains ions. Zinc sulphate, zinc chloride, or even sodium chloride solution will do. This solution is separated from the acid by a porous partition through which the ions can migrate but the solutions will not readily diffuse. The zinc pole will at once acquire a negative potential relative to the solution on account of the tendency of the zinc to form ions. The copper will acquire a positive potential because the tendency for the hydrogen ions to come out of the solution is greater than the tendency of the copper to go into solu-

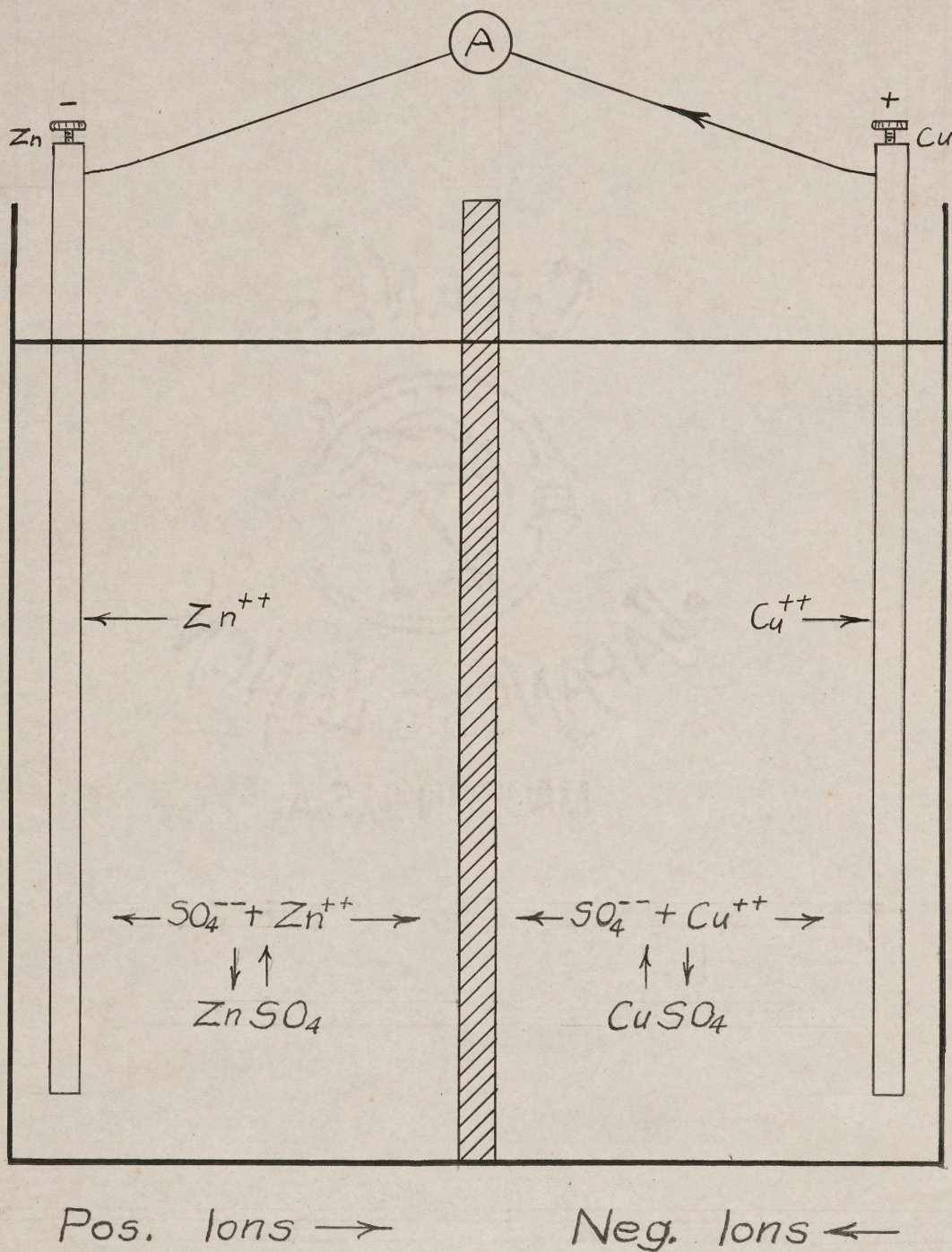


Fig. 2 — Daniell Cell

tion. When the circuit is closed zinc ions will migrate through the partition towards the cathode and SO_4 ions towards the anode, hydrogen will be evolved at the cathode, zinc will go into solution at the anode, and zinc sulphate will be formed in the electrolyte. The results of the chemical action are the same as before.

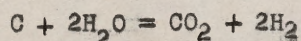
In both the above cells, the internal resistance is greatly increased by the hydrogen liberated at the cathode. To eliminate this trouble, copper sulphate may be used instead of sulphuric acid. The copper liberated at the cathode is deposited. The Daniell cell, shown in fig. 2, is of this type.

CHAPTER II —

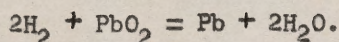
SOME CELLS WHICH FURNISH ELECTRICITY BY THE OXIDATION OF CARBON.

J. W. Mellor, in his Comprehensive Treatise on Theoretical and Inorganic Chemistry, describes several such cells:

"D. Tommasi described a cell using a carbon rod surrounded by lead dioxide in one compartment, and a carbon rod with a solution of calcium chloride in the other. The reactions are said to be



and

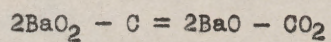


G. J. Reed said that 42 Calories of energy are consumed and not generated by such a cell.

"According to F. Haber and L. Bruner, there is a potential difference of about 1 volt between iron and carbon rods immersed in fused NaOH. The iron rapidly dissolves, but it may become passive. If the iron is immersed in fused sodium nitrate, it is covered with a dark skin of oxide which is difficult to remove; such iron is passive. The addition of an alkali manganate to the sodium hydroxide also produces the passive condition, and the more rapidly the less water the hydroxide contains. This is explained by the fact that dry NaOH does not yield any hydrogen when electrolyzed, and therefore, since no hydrogen can be evolved at the surface of the iron, the skin of oxide is formed more completely. Since all NaOH, especially when fused in contact with iron and air, contains more or less manganate, it appears that iron protected by a skin of oxide and immersed in fused NaOH is really an oxygen electrode; the part played by the manganate being that of an intermediary by means of which the atmosphere of oxygen can pass into the ionic condition. The E.M.F. of passive iron in fused NaOH (calomel electrode) was found to be - 0.265 volt at 312°, increasing

to -0.472 volt at 532° . This E.M.F. is independent of the amount of manganate in the electrolyte so long as this is not very small or very large. The E.M.F. of combination (carbon in fused NaOH), calomel electrode, varies greatly with the nature of the carbon employed, -0.66 volt being found with artificial graphite and -1.4 volts with a partially disintegrated arc lamp carbon. The carbon is attacked by the fused NaOH, hydrogen being evolved. The more rapid the evolution of hydrogen, the greater the E.M.F. When a very rapid evolution of hydrogen is produced by the heating of the NaOH to 500° , the E.M.F. rises to -1.5 volts. When a platinum tube, through which a stream of hydrogen is passed, is substituted for the carbon electrode, the same E.M.F. is produced, namely, -1.48 to -1.50 volts. It happens therefore that the carbon electrode is really a hydrogen electrode. That an E.M.F. of less than -1.5 volts is often observed is explained by the partial depolarization of the electrode by the manganate present in the electrolyte. It is only when the temperature is sufficient to produce a rapid evolution of hydrogen that the full value is observed. When the carbon is once charged with hydrogen, however, it retains its E.M.F. for some time at a lower temperature. The carbon electrode is really a hydrogen electrode, the hydrogen being formed by the action of carbon on NaOH; the reaction to which the E.M.F. of the cell is due is the formation of water from this hydrogen and the atmospheric oxygen at the iron electrode. The E.M.F. of the cell agrees with the E.M.F. necessary to decompose into hydrogen and oxygen the small amount of water dissolved in fused NaOH."

"A mixture of barium dioxide and carbon was found by J. L. Gay Lussac and L. J. Thénard to be decomposed by heat with the evolution of oxygen. D. Korda found that if a piece of barium dioxide and a carbon rod be dipped in molten potassium carbonate while the free ends are in contact, a current of about one volt is produced and the reaction



occurs".

None of these cells is by any means practical, since the cell either becomes inactive after slight use or expensive chemicals are used which enter into the reaction and must be replaced when consumed.

CHAPTER III— A THEORETICAL CELL

THAT WILL PRODUCE CURRENTS FROM CARBON AND ATMOSPHERIC OXYGEN.

In order to produce power from coke electrochemically that will compete with steam power, atmospheric oxygen must be used as the oxidizing agent, either directly or indirectly. As the production of currents by the direct oxidation of carbon by oxygen is practically impossible because of the non-conductivity of atmospheric oxygen, some indirect method must be sought; where a substance is oxidized by oxygen, and is then reduced by carbon with practically the same heat of reaction as that of the union of carbon and oxygen.

The E.M.F. of a cell may be found by the following equations:

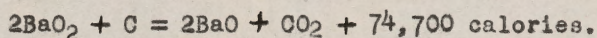
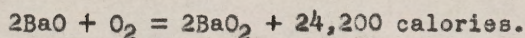
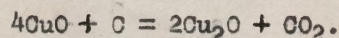
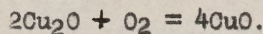
$$\text{Volts} = \text{heat of reaction in calories per gram molecular weight times } 0.000,043,4 \text{ divided by the valence change,}$$

or

$$\text{Volts} = \text{heat of reaction (B.T.U. per pound)} \text{ times the molecular weight times } 0.000,024,1 \text{ divided by the valence change.}$$

If carbon be oxidized to produce electrical energy with the same heat of reaction as when uniting with oxygen to form CO_2 , the E.M.F. generated would be 1.050 volts according to the above equations. If carbon be oxidized to CO with the same heat of reaction as when burning in air to CO, 0.64 volt would be produced. The ampere hour capacity of a cell of this type would be very high. Since 96,540 coulombs times the valence change are produced by the reaction of one gram molecular weight of a substance, the capacity of a cell oxidizing carbon to CO_2 would be 2.175 ampere hours per gram of carbon or 986 ampere hours per pound of carbon, if its action were perfect. The capacity of a cell oxidizing carbon to CO would be 493 ampere hours per pound of carbon. There are several indirect methods by which car-

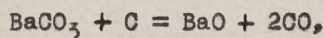
bon can be oxidized by atmospheric oxygen:



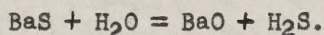
The latter reaction was studied carefully. BaO is a molten liquid at $2,000^\circ$ and is not decomposed at $2,500^\circ$ C. BaO₂ is formed from BaO when the latter is heated in the presence of oxygen to $400^\circ - 650^\circ$ C. A slight amount of moisture is necessary in the oxygen. Vapor pressure of evolved oxygen from BaO₂ is one atmosphere at 750° C. At ordinary temperature BaO₂ can be kept for many years without deterioration. J. B. D. Boussingault tried to apply BaO₂ — BaO process for obtaining oxygen industrially, but it was found that after the baryta had oxidized about a dozen times, it lost its power. M. Gondolo claimed to have used the baryta over 100 times without deterioration by mixing the BaO with a little lime or magnesia, and potassium permanganate. The cause of the trouble was recognized by M. M. Brin in 1879. The BaO can be reoxidized over and over again provided the air be freed from CO₂, organic matter, dust, and any substance which forms a compound which does not decompose under the given conditions.

In order to oxidize carbon by BaO₂ to produce electrical energy, it is preferable that the baryta be dissolved in a fused salt at a temperature suitable for the formation of BaO₂, for several reasons. If an electrode of undissolved BaO₂ be used, it will have to be removed from the cell and freed from the fused electrolyte which clings to it, and reduced to a powder for reoxidation; and then molded again before it is ready for use. When dissolved in a fused salt, the carbon may be immersed directly into the

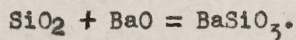
active solution, as the zinc in a voltaic cell, or a porous partition may be used. Since CO_2 will be liberated, carbon may be thrown in to reduce the BaCO_3 which forms:



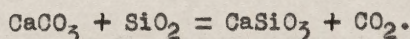
or the solution may be allowed to circulate past the carbon electrode. If coke is used as the source of carbon, sulphur, silica, silicates, oxides of iron, aluminum, etc. will be present. The sulphur will give no trouble with the baryta; and if any BaS is formed, it will be decomposed by the traces of moisture present:



Silica will react with barium carbonate or oxide:



If there is any silica present in the ash of the coke, the coke should be mixed with a small amount of powdered limestone while hot:



The salt in which the baryta is dissolved must fuse at about 400°C , must not react with any of the common metals, such as iron copper, or zinc, must not decompose or volatilize at 700° or 800°C , must not react chemically with baryta or the ash of coke, and must dissolve baryta and barium carbonate. Since BaO and BaO_2 are mutually soluble in each other, anything that will dissolve one will dissolve the other.

Zinc chloride was tried and found entirely unsatisfactory. When

barely fused, there was a marked volatilization, and when barium carbonate was added there was a slow reaction with the evolution of a gas. The barium carbonate was dissolved when added to the fused zinc chloride. The reaction was probably due to the fact that zinc chloride is an acid and barium carbonate is an alkali by hydrolysis, and the small amount of water present. When carbon and copper electrodes were immersed in the solution, a voltage varying from 0.2 to 0.5 volt with the temperature, was obtained. The carbon was the positive pole. Both the carbon and the copper were attacked by the solution.

Mellor describes several double salts of anhydrous aluminum chloride and chlorides of the alkali or alkaline earth metals, with low melting points. These double salts do not volatilize or decompose at high temperatures, but when dissolved in water, the original salts crystallize out on evaporation; the aluminum chloride, of course, being in the hydrated form. Hydrated aluminum chloride cannot be dehydrated by heating; it decomposes into HCl and $\text{Al}(\text{OH})_3$. Magnesium chloride (anhydrous) also forms double salts of low melting points with sodium chloride and with cuprous chloride, although it behaves like aluminum chloride towards water. The following salts were described:

Sodium tetrachloroaluminate; $\text{NaCl}, \text{AlCl}_3$ — m. p. 185°C .

Sodium enneachloroaluminate - $3\text{NaCl}, 2\text{AlCl}_3$ —
melting point below 500°C .

Lithium tetrachloroaluminate - $\text{LiCl}, \text{AlCl}_3$ —
melting point not given.

Potassium tetrachloroaluminate — $\text{KCl}, \text{AlCl}_3$ —
melting point not given.

Potassium enneachloroaluminate — $3\text{KCl}, 2\text{AlCl}_3$ —

melting point not given.

Potassium hexachloroaluminate — $3\text{KCl}, \text{AlCl}_3$ —

melting point not given.

Caesium tetrachloroaluminate — $\text{CsCl}, \text{AlCl}_3$ —

melting point not given.

Cuprous tetrachloroaluminate — $\text{CuCl}, \text{AlCl}_3$ —

melting point 233°C .

Calcium octodecachlorotetraluminate — $4\text{AlCl}_3, 3\text{CaCl}_2$ —

melting point 300°C .

Strontium octodecachlorotetraluminate — $4\text{AlCl}_3, 3\text{SrCl}_2$ —

melting point below 300°C .

Barium tetrachloroaluminate — $\text{BaCl}_2, \text{AlCl}_3$ —

melting point 290°C .

Barium octodecachlorotetraluminate — $4\text{AlCl}_3, 3\text{BaCl}_2$ —

melting point 500°C .

Sodium Magnesium Trichloride — $\text{NaCl}, \text{MgCl}_2$ — m. p. 430°C .

Several of these salts were tried with the hope that moisture would not react with the aluminum chloride at the temperature of the cell, but this was not the case. HCl was driven off. The moisture of the flame was probably the cause of this decomposition. HCl was also given off when double salts of magnesium chloride were heated. The following salts were tried:

Sodium tetrachloroaluminate

Sodium enneachloroaluminate

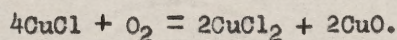
Barium octodecachlorotetraluminate

Barium tetrachloroaluminate

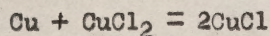
Cuprous tetrachloroaluminate

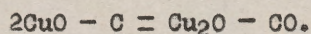
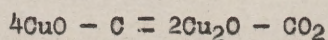
Sodium magnesium trichloride

Cuprous chloride, which melts at 418° C, was fused. Black cupric oxide, either dissolved or in a finely divided state, appeared.



The solution volatilized badly. When NaCl was added, a double salt melting at a higher temperature was formed that did not fume nearly so badly as the cuprous chloride alone. When carbon and copper electrodes were dipped into the solution, a potential difference of 0.66 volt was obtained when the salts were barely fused; the carbon being the positive pole. When the temperature of the cell was raised, the voltage was lowered. The E.M.F. of the cell seemed to depend on the temperature of the carbon alone. When the copper electrode was heated to redness and plunged into the solution, it had no effect on the voltage. When the carbon was heated to a bright red and plunged into the solution, a negative reading of - 0.2 volt was obtained. The voltage rose to zero and then to the former E.M.F. as the carbon assumed the temperature of the solution. Both the carbon and the copper electrodes were attacked. The reactions were probably as follows:

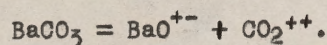




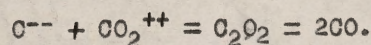
The explanation of the above voltage variation is probably that both the copper and the carbon were negative with respect to the solution. At a low temperature, the reaction of the carbon was very slow, so that the copper assumed the higher negative potential relative to the solution. When the temperature was raised, the carbon reacted more vigorously and assumed the higher negative potential. This shows that when carbon goes into solution to react with oxygen ions, it forms positive ions. This is often the case with non-metals; even phosphorous exists in the positive ionic state in a few solutions.

When sodium sulphide, sodium sulphate, and sodium chloride were heated together, they fused just before coming to a red heat; forming a clear solution which did not volatilize at a high temperature. When BaCO_3 was added, it dissolved and did not react chemically with the solution. When carbon and copper electrodes were immersed in the solution, an E.M.F. of about 0.4 volt, which decreased when the temperature was raised, was obtained. The carbon electrode was attacked with the evolution of a gas. Since the bubbles of gas flashed when they reached the surface, the gas being evolved was CO (combustible). The copper electrode was not attacked. The chemical reaction taking place in the cell was endothermal. The energy which operated the cell, and supplied the energy absorbed by the chemical reaction, came from the flame. As the copper electrode did not form ions, it assumed a positive potential relative to the solution. When connected to the voltmeter, the carbon was positive and the copper was negative. This shows that the carbon was positive relative to the solution, and was forming

negative ions. This is what was expected, since the voltage becomes less as the heat of reaction decreases, and would be negative when the heat of reaction is negative. Since the carbon forms negative ions, it unites with positive ions in the solution. The ionization that occurs in the solution is probably as follows:



The reaction with the carbon ions would be:



Although barium carbonate dissolved readily enough in this fused mixture of sodium sulphide, sulphate, and chloride, BaO_2 would not dissolve in it; and the BaO formed by the reaction with carbon was precipitated. The action of a theoretical cell of the type proposed is shown in fig. 3. The BaO_2 will form BaO^{++} and O^{--} ions. The carbon will go into solution to form C^{--} ions. These react with the O^{++} ions to form CO_2 . This gas will form throughout the solution, but mostly towards the center, where the carbon is located. It will have no polarizing effect, as when a gas is liberated by ions discharging at the surface of an electrode. The BaO^{++} ions will migrate to the cathode, which is the walls of the cell, and discharge, forming free BaO . As the CO_2 rises towards the top of the cell, it will come into contact with some of the BaO present in the solution and form BaCO_3 . This ionizes into BaO^{--} and CO_2^{++} ions. The latter react with C^{--} ions to form CO , which rises to the top as bubbles. The BaO^{--} ions migrate to the cathode, which really serves as an anode for this reaction, and are discharged, forming free BaO . The reduction of BaCO_3 causes a current to flow in a direction opposite to that caused by the reduction of CO_2 . The effect is the same as short-circuiting a cell which oxidizes carbon by BaCO_3 alone

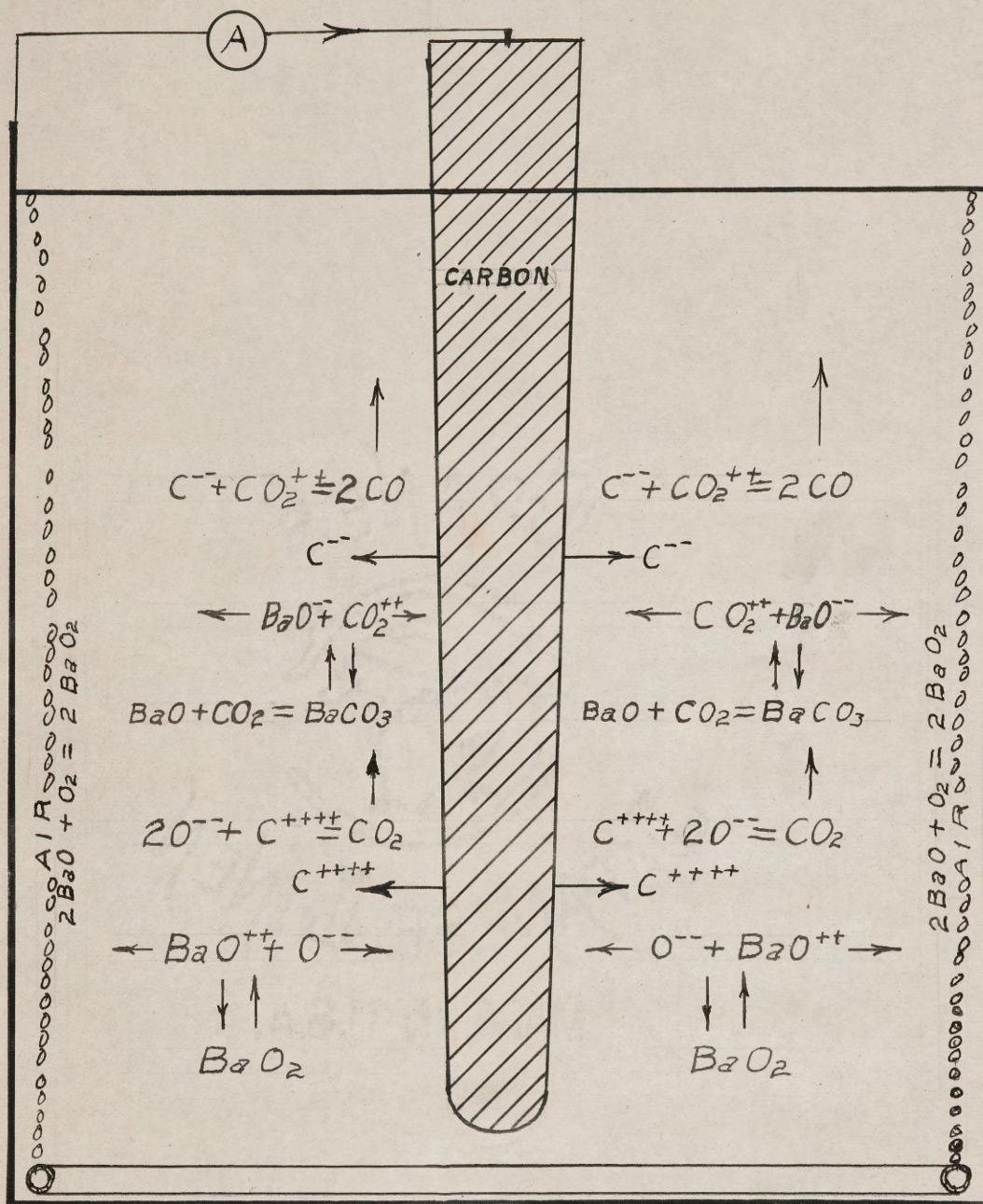


Fig. 3

in series with a cell described above which oxidizes carbon by BaCO_3 alone. In fig. 3, the cycle of operation is shown by the equations from the bottom to the top of the cell. If all the CO_2 reacted with BaO to form BaCO_3 , the reverse current caused by the reduction of BaCO_3 will be only half that caused by the reduction of BaO_2 . This is true because the carbon goes ~~thru~~ through a valence change of 2 in one case and 4 in the other. This is not a total loss, since CO is an excellent fuel gas.

Any BaO_2 or BaCO_3 which comes into direct contact with the carbon will be reduced, forming a gas at the surface of the electrode which will greatly increase the internal resistance of the cell. This can be practically eliminated by passing the air through the cell close to the walls, and preventing the circulation of the solution by baffles. Practically all of the BaO_2 will be consumed by carbon ions before it reaches the carbon. The air will then reach most of the BaO , which will be near the walls of the cell, where it is liberated. If circulation of the solution be prevented, the concentration of BaO in the center of the cell, where most of the CO_2 will be liberated, will be very low. This will almost eliminate the BaCO_3 losses. The air could be guided by baffles towards the outside of the cell, and the CO_2 and CO collected and used industrially.

If a suitable porous partition could be found, the action of the cell could be greatly improved. The construction of such a cell is shown in fig. 4. The cathode is perforated and placed close to the partition. This arrangement entirely eliminates the loss due to the BaO_2 coming into contact with the carbon. Since the CO_2 is liberated between the electrodes, it will come into contact with almost no BaO , and the BaCO_3 loss will be almost eliminated. The gas evolved within the partition will be almost pure CO_2 , which can be purified and used commercially.

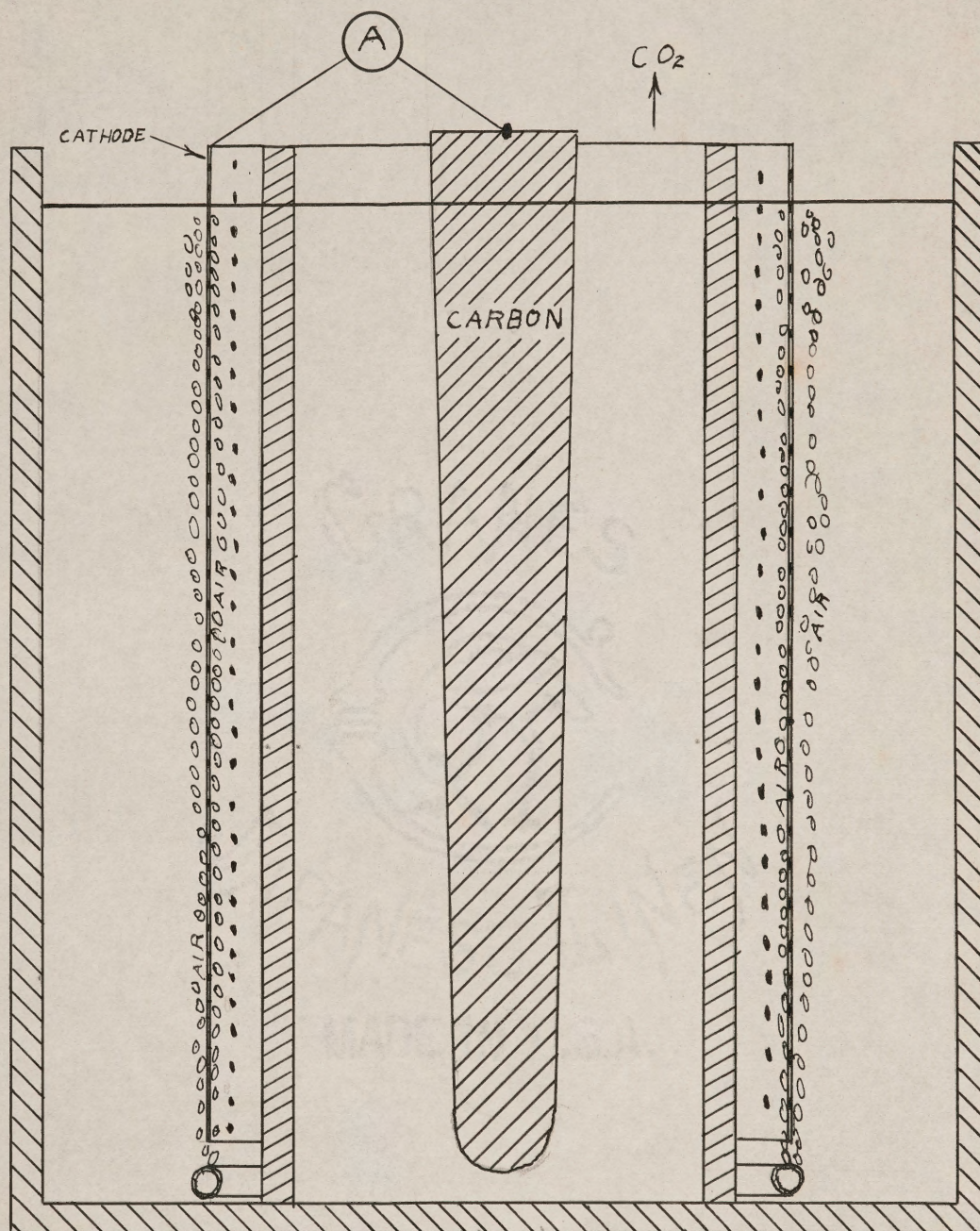


Fig. 4

BIBLIOGRAPHY.

A System of Physical Chemistry, by Lewis.

Smith's College Chemistry.

A Comprehensive Treatise on Theoretical and Inorganic Chemistry,
by J. W. Mellor.



APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

Name _____

Title _____