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A Study of

THE LOW TENSION ARC DISCHARGE

IN LIQUIDS.

by

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A T H E S I S

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I N T R O D U C T I O N .

The physical and chemical effects produced when electric discharges are operated in liquids have been studied by a number of investigators from the time of Sir Humphrey Davy to the present day. Discharges in gases however, have received much more attention, and apart from some qualitative work done in the early part of this century very little exact information is to be found regarding either the products or the mechanism of under-liquid discharges. Several workers have made careful studies of the emission spectra of spark and arc discharges in water, but without reference to chemical effects.

I have found that an arc can be struck in pure water by bringing together the ends of carbon or metallic electrodes with applied potentials as low as 10 volts, the current being either alternating or direct. The reactions taking place in such very low voltage arcs are of interest since few chemical studies have been made with discharges employing less than 400 volts; furthermore, the electrodes are found, in the case of under water discharges, to be intimately involved in the resulting chemical changes, giving rise to unusual products.

In the work outlined below carbon electrodes have been employed almost always, with water as the liquid medium,



for such a combination was considered to be the simplest from a chemical standpoint. The potentials have been in the neighborhood of 20 volts, since values much below this do not give sufficiently stable arcs.

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The study was made with the following main objects in view:

- (1) To determine qualitatively and quantitatively all of the products of the discharges.

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  - (2) To obtain evidence indicating the probable mechanisms of the reactions taking place.
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HISTORICAL.

Davy<sup>1</sup> was the first to observe that the electric arc would continue to "burn" when immersed in water. Fifty years later Grove<sup>2</sup> made electrical measurements on similar arcs and Masson<sup>3</sup> observed certain peculiarities in their spectra. The products of the decomposition of water vapour by electric sparks were first briefly studied by Perrot<sup>4</sup>, whose work was extended by Buff and Hoffman<sup>5</sup>. About the same time the spectra of quite similar discharges were studied in detail by Liveling and Dewar<sup>6</sup>, Konen<sup>7</sup> and others.

Lepsius<sup>8</sup> employed carbon electrodes in an arc burning in water and analysed the gaseous products; his work was extended by L<sup>ö</sup>b<sup>9</sup>, with considerably different results, the conclusion reached being that the reactions were of a purely "pyrogenetic" nature, exactly the same as those induced by electrically heated wires. Organic liquids as well as water were employed, but solids, other than particles of the electrodes, were apparently not observed in the residual liquids.

About this time Bredig<sup>10</sup> commenced his well known work on the production of colloids by arcing metals in liquids, and Svedberg<sup>11</sup> noted a difference in the products of direct and alternating current arcs, and modified the Poulsen

rectifier by burning the arc in organic liquids<sup>12</sup>. Chapman and Lidbury<sup>13</sup>, Holt and Hopkinson<sup>14</sup> and J. J. Thomson<sup>15</sup>, working mostly with spark discharges in water vapour observed the wide divergence from Faraday's electrolysis law, but failed to provide a suitable hypothesis for the reaction. The work of Kernbaum<sup>16</sup> with brush discharges and Makowetzky<sup>17</sup> with glow discharge tubes has shown that the products are more complex than at first believed, and that they vary greatly with the type of discharge and electrodes employed. These workers advanced theories of the reactions, but were hampered by the lack of stoichiometrical relationships in the products obtained by them.

Müller<sup>18</sup> studied the spark discharge in liquid air, showing how completely the reactions taking place differed from those in the ordinary air spark, and observing a solid product not colloidal in nature but of unknown constitution. Recently Shipley and Goodeve<sup>19</sup> investigated high voltage arcs in alkaline electrolytes with various electrode materials, the electrical characteristics being studied in detail; high frequency alternating current was employed, and all of the products were not analysed.

Many papers, notably those by Tarczyński<sup>20</sup> and Fowler and Mardles<sup>21</sup> have been published dealing with various discharges in organic liquids, but the existing knowledge of these reactions is very incomplete.

In making a general review of the past work on electrical discharges it is at once observed that there is a serious lack of experimental evidence. Attempts have been made to relate data obtained with discharges of widely differing character, and in a great many cases certain products of the reactions have been disregarded entirely. For example the extent of formation of hydrogen peroxide in the glow discharge in water vapour has been neglected by several, and has been shown by some to be appreciable and by others to be negligible.

The glow discharge is receiving most attention at present, since it supplies easily controlled conditions. The pressures employed in it are however, very low, and the potentials rarely under 500 volts. Discharges in gases at atmospheric pressure represent quite different conditions, as pointed out by Lind<sup>22</sup>; and if the electrodes be involved in the reactions, this being the case with low voltage arcs, the problem assumes a different nature.

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THEORETICAL.

In this section a review of the existing knowledge of the electrical and chemical characteristics of the various discharges together with modern theory of the various reactions which have been widely studied is given; such a summary is necessary in order to satisfactorily consider the data obtained with liquid discharges, in which the effects found in several types of discharges may be superimposed.

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I. THE TYPES OF ELECTRIC DISCHARGES:

Many types of discharges are recognized by the physicist but these may be grouped in a few divisions for chemical purposes.

(A) The Silent Discharge:

This term is applied to all discharges of positive characteristic, i.e. those in which an increase in applied potential results in an increase in current, and vice versa; among these are the non-luminous, the glow, brush and certain spark discharges. Many of these are not silent and may merge into one another; in some cases more than one discharge may take place simultaneously from the same electrodes.

While the characteristic is positive this does not indicate that Ohm's law is followed, since the resistance of

all discharges is a function of many variables, e.g. discharge length, electrode material and temperature, potential and current. Also, certain silent discharges including the non-luminous may reach a "saturation" current which cannot be increased by applying a higher potential.

The glow discharge has received most attention, its distinctive feature being the visible light emitted and the fact that considerable currents may be passed through it with medium potentials. It must however, be operated at pressures much below atmospheric and chemical reactions occurring in it are to a great extent limited by this factor.  
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(B) The Spark Discharge:

Spark discharges are readily obtained at high pressures in any gas, but require very high potentials applied to the electrodes. Their characteristic is negative since an increase in current is followed always by a decrease in voltage; they are intermittent, disruptive types, so unstable that they cannot be maintained continuous, and the current is very low. Their nature and "length" is a complex function of the shape of the electrodes, temperature and pressure of the gas medium, moisture conditions and other variables. Ions must be present in the gases to be sparked, these being supplied usually by the photoelectric effect of daylight on the electrodes; the "retardation of the spark" in a dark room



is a familiar phenomenon. Some consider that the temperature of spark may be very high, others that the discharge is a cool one except within very small regions.

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(C) The High Tension Arc:

This is an indefinite term applied to discharges of high voltage and considerable currents; the only satisfactory method of defining the arc is to consider all the discharges resulting from increasing the current passing between two electrodes. At a certain current the spark discharge will become steadier and intensely hot and the characteristic "flame" of the arc will appear. The high tension arc has a negative characteristic and is therefore very unstable; it cannot be operated without series resistances with D.C. or series inductances with A.C.

The high tension arc has been much studied from the standpoint of the synthesis of nitric oxide, but very little is known regarding its action. Recent work has shown that the chemical reactions occurring in it vary greatly with the electrodes, current, length of arc, potential and temperature, many of these being interdependent. With D.C. the potential drop practically all takes place near each electrode, the gradient in the glowing region being very small; the effects with A.C. are very complex.

(D) The Low Tension Arc:

When the current in a high tension flame arc is increased beyond a certain indefinite limit the discharge changes its potential abruptly and the low tension arc occurs. It is most distinctive in that very low voltages may be employed even to start it: the electrodes are merely touched together and then separated. The high tension arc may be extended to several meters length but the low tension type is really unstable when the electrodes are more than a few centimeters apart at atmospheric pressure. The characteristic is negative, but a small series resistance or inductance makes the arc quite stable.

The electrical properties of the low tension arc have been studied by large numbers of workers but very little is known concerning its mechanism. The vaporisation of the electrode material is probably a necessary preliminary to arcing and certainly a very high temperature is maintained over a considerable region. The chemical effects of true low tension arcs at atmospheric pressure are almost unknown.

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## II. DISCHARGE TEMPERATURES:

The temperatures of the various electric discharges have been shown to vary from very low values with dark discharges in surroundings of liquefied gases, to indefinitely high temperatures with certain vacuum arcs. In some the highest temperatures are close to the electrodes while in others the column of glowing material is the hottest portion; in nearly every discharge there exists a very great temperature gradient.

The total radiation, optical, spectroscopic and kinetic theory methods of estimating temperatures have been used in connection with electric discharges, ordinary temperature measuring devices being of little use. Wilson<sup>23</sup> found the temperature of an under water spark with 20,000 volts to be 5115°C, employing the spectroscopic method; this value refers to the general discharge region which appears to be uniform. Sparks in gases may represent temperatures much higher than the above.

Mason<sup>24</sup> illustrates the great variation in experimental results obtained by various workers in this field. Thus the temperature of the so-called cathode "cold region" of the low pressure mercury arc has been variously estimated as being from 600°K to 2300°K. Tanberg and Berkey<sup>25</sup> measured the temperature of the cathode of vacuum copper arcs from consid-

erations of the velocity of the vapour emitted by the cathode and of the force on small rotating vanes suspended near the electrode surface; on the basis of the kinetic theory the temperature thus indicated was in excess of 500,000°K! The optical pyrometer however, gave 3250°K, which was considered to be nearer the correct value, the discrepancy being explained by assumptions concerning the field near the electrode.

It may be said that while the optical pyrometer gives a fairly accurate value for the temperature of large regions, there is no suitable method of estimating the highest temperatures obtaining in portions of the various electric discharges. And the temperature undoubtedly affects the chemical reactions taking place in most discharges, as will be shown later.

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### III. PRODUCTION OF IONS IN DISCHARGES:

Only in recent years has the fundamental nature of ion production been realised insofar as it affects chemical reactions in discharges; it is probable that ionisation plays the most important part in most, but not all electric discharges in which chemical change is an important consideration. It is of value therefore to consider the various means by which "ions" may be produced, and the factors controlling production in each case. The term "ion" is derived from the ion of electrolysis, but not nearly all ions in discharges are connected with the carrying of current.

They are charged particles of two general types, positive and negative. The simplest negative ion is the electron or ultimate particle of negative electricity, while the simplest positive ion is an atom which has lost a single electron. Doubly positively charged ions, both of the atomic and molecular variety are possible, and an atom or molecule may attach one or more (rarely more than one) electron to form negative ions. Other types are considered below.

(A) Electrons:

These are considered separately since they play such a fundamental part in all ion production. All electrons belong to one of two groups, the "atomic electrons" and the "atmosphere" electrons. Atomic electrons, with positive protons form the base material of all matter and a great deal is known about their emission from substances. The electrons of the "atmosphere" have a definite existence, but are not usually considered to be much involved in ionisation phenomena, at least in cold discharges.

Thermionic emission of electrons is of importance whenever high temperatures exist in regions containing solid substances, especially the metals. Gases and vapours can exhibit thermionic emission, and on the basis of the kinetic treatment of the ideal "ion gas" the percentage ionisation of various substances has been calculated, with considerable certainty. At atmospheric pressure calcium would be 2% ionised when a temperature of  $5000^{\circ}\text{K}$  was reached, whereas

hydrogen would show no ions until about  $9000^{\circ}$  was obtained. The thermal ionisation would be greater at lower pressures. The theory has been extended to consider double ionisation, i.e. loss of two electrons; complete ionisation of this type could be obtained at  $10,000^{\circ}\text{K}$  for most elements, if under sufficiently low pressure.

Since the electrons thermally removed from the substance are not atomic, the energy required to remove them has no relation to the familiar "ionisation" energy of atoms; it is usually of a much lower order but the difficulties attending experimental verification are so great that little confirmation of the theory has been obtained.

Because of the very high temperatures obtainable in high and low tension arcs, particularly on the electrode surfaces, thermionic emission must play an important part in gas ionisation, or at least in the production of the electrons. In addition to this effect, thermal energy may "excite" the atomic electrons, i.e. move them to orbits farther removed from the nucleus than the stable orbits or energy levels, without actually ionizing the atom. Some authorities consider that such excitation may be capable of producing chemical effects, but the idea is much disputed at present.

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Electrons may be removed from solids simply by the application of electric fields, such electrons being the

familiar "cathode rays". The mechanism by which atomic electrons are emitted from a substance by the application of potentials is entirely unknown and the quantum theory has not thrown much light on this subject.

Some confusion exists in regard to the electrical emission of electrons due to the fact that cathode rays are usually studied in relation to discharge tube phenomena. In these cases the stream of particles proceeding in the general direction "cathode to anode" do not by any means all come from the cathode itself, the majority being electrons produced in other ways. J. J. Thomson<sup>26</sup> recently considered this problem and concluded that most of the cathode ray particles were electrons emitted from the cathode by the action of the radiant energy (photoelectric effect) produced when the positive ions reaching this electrode were neutralised there.

While electrical emission of electrons plays an important part in ionisation in silent discharges, it is probable that thermionic emission is of much more significance when arcs are considered. In all cases the secondary and tertiary ionisation resulting from the original electrons is of equal importance from the point of view of chemical change. Electrons emitted by action of electric fields are of necessity acted upon by those fields, with resultant increase in their velocity and kinetic energy; their study is thus complicated, in contrast to thermal electrons which possess "emission energy" only.

Electrons are emitted spontaneously by substances undergoing radioactive disintegration, and these "beta" rays have been employed by many workers in studying the effects of electron impact ionisation; as with thermal electrons there is no electric field to complicate the energy calculation.

The photoelectric effect is the phenomenon of the release of electrons from substances by the action of radiant energy. This effect was earlier considered to be confined solely to certain solid substances, but it is now definitely known that gases and vapours may exhibit it. For this reason photoelectrons are attracting considerable attention in the field of the chemistry of electric discharge reactions; there is no evidence of any value available at the present time.

Electrons are always "produced" or emitted when positive ions are formed, and the latter are considered in the next section.

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(B) Positive Ions:

These ions are now believed to be the most important, if not the sole instigators of chemical action in electric discharges; their production and properties are therefore considered in detail below.

Positive ions were originally observed as the "kanalstrahlen" of vacuum discharge tubes, but they do not come from the anode; there is no evidence whatever indicating that positive ions may be produced by mere application of an



electric field. Positive ions may however, be emitted thermally just as electrons are, this being a phenomenon rarely found discussed in texts. Only "fresh" surfaces exhibit the effect, the emitted ion being the charged atom of the substance heated. The facts indicate that these positive thermions are similar in production to the thermionic electrons, and this leads to great difficulty in the theory since the existence of an "atmosphere" of atoms can hardly be credited. It is not known to what effect the emission is due, nor to what extent it takes place in discharges.

A positive ion may be formed when any particle collides with an atom or molecule inelastically, providing that the available energy resulting from the collision is sufficient to remove one or more electrons from the neutral particle. High velocity electrons are the most important ionizing agencies of this type, and the velocity required to cause excitation or removal of atomic electrons is very exactly known. The energies of electrons are expressed in "volts", meaning the potential required to give a velocity corresponding to a definite electronic energy; and atoms are said to possess ionisation and resonance potentials, in that electrons with corresponding potentials (energy) can ionize or excite the atoms.

The mechanism and quantitative relationships of ionisation and positive ion formation, so important in chemical reactions, are best studied from a spectroscopic standpoint.

It is well known that the return of a "displaced" electron to its normal position results in the emission of radiant energy, regardless of the nature of the energy which disturbed the electron. The "arc" spectrum is emitted when the electrons of a group of atoms return to their stable orbits by all possible paths, from all possible orbits in those atoms, including the orbit infinitely distant from the nucleus. If this change takes place with a second electron completely removed from the atom, then the enhanced or "spark" spectrum is observed, all of the lines being present only when large numbers of atoms are available.

Spark spectra were at first thought to be produced only by application of very high potentials; but according to the Bohr theory the potentials for the production of the complete spark spectra of all elements lie between 10 and 50 volts. In practice it is found necessary to take into consideration the "mean free electronic path", when calculating the kinetic energy of electrons. The important factor is therefore the potential gradient per mean free path of the electron, and this involves many factors besides the potential. For example the mean free path of Hg vapour at 400°C. and atmospheric pressure is about  $10^{-4}$  cm., so that a potential of 100 volts corresponds to only 0.001 volt potential per mean free path of the electrons. This is far below 4.9 volts, the potential required to excite the simplest Hg spectrum.

These ideas have been thoroughly verified in careful studies of low voltage arcs (such as used in the experimental work described in this thesis) and other discharges. It is found that the complete enhanced spectra of nearly all elements can be obtained easily in the low voltage arc, indicating a high degree of ionisation. The explanation lies in the fact that the partial pressure of the metal or other substance in the arc stream or plasma may be extremely low, and this is conducive to the phenomena of ionisation by successive collision; the electrons gain their energy in multiple collisions, finally attaining sufficient to ionize any atom in their path. But there are other reasons of equal importance: the high temperatures of arcs promotes thermo-emission of electrons on a large scale, some of these being ejected from the electrodes with great velocities. Finally, the space potential gradient must be considered; as stated previously in certain arcs the potential drop may take place practically entirely near the electrodes giving an enormous space potential, in some cases millions of volts per centimeter as claimed by Mason<sup>24</sup>.

Recently the theory of cumulative ionisation of the photo-impact type has received much attention; this considers that arcs may operate below the lower ionisation potential due to the fact that there may be absorption of radiant energy produced in the arc itself, a sort of photo-electric effect self induced. With high vapour pressure and electronic emission by thermal action, as in arcs, this factor may be

of fundamental importance. It is easily seen however, that the experimental facts of arc operation at low voltages are satisfactorily explained in several ways, none of which are in any way conflicting; all indicate a high degree of ionisation, which is of importance where chemical reactions are concerned.

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The positively charged helium atoms emitted by certain radioactive substances have been much employed in the study of the chemical effects of positive ions in general, since in the case of these "alpha rays" there is no complicating electric field; positive ions particularly accentuate chain reactions.

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(C) Negative Ions:

Negative ions are formed only by electron addition, and this usually occurs when a low energy electron collides with an atom. The energy of both particles being insufficient to ionize the atom, the latter is brought into an "excited" condition, the exact nature of which is at present vaguely known. Negatively charged atoms exert a strong attractive force on positive ions and collisions between the two usually involve higher orders of energy transfers, such as are suitable for endothermal chemical reactions. Therefore negative ion formation may play a part in discharge reactions, although there is little evidence to support the theory.

Many dissociation processes involve negative ion formation, for example the dissociation of water vapour is believed to take place almost entirely through the preliminary step:  $H_2O = H^+ / OH^-$ . Here an electron is transferred from one hydrogen atom to the OH particle. But such processes are usually secondary or even tertiary phenomena in electric discharges because of the large amounts of energy necessary to bring them about; some sort of preliminary ion formation is usually found.

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While the various physical theories of electric discharges have proven useful in the study of ion formation, the wide disagreement in the present theories of electric discharges as a whole have made it impossible to take them into consideration when studying chemical effects. In fact studies of the glow discharge reactions have assisted in formulating physical theories more in accordance with experimental facts than the earlier mathematical hypotheses. S. C. Lind<sup>27</sup> has given a review of the present knowledge in this connection.

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I. THEORIES NOT INVOLVING IONISATION:

Cavendish

and Priestly early studied the formation and decomposition of nitrogen oxides by the action of the spark discharge; after the acceptance of Faraday's electrolysis law there were attempts made to apply it to discharge reactions, with immediate failure. Following this the "thermal" theory involving the Mass Action law was widely accepted, but finally discarded in favor of various electrical theories. Present opinion recognizes the futility of establishing any single theory to apply to all the discharges; the most important are outlined below.

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(A) The Thermal Theory:

According to this reactions proceed in the electric discharge because of the high temperatures available, and the "abnormal" equilibrium values obtained are held to be due to the very great temperature gradient, i.e. the sudden cooling effects. The Mass Action law provided an explanation for the fact that nitric oxide may be formed and decomposed in spark discharges, depending upon the concentration; the theory enabled the approximate temperatures of arc discharges to be calculated, but this involved questionable extrapolation from known data for low temperatures.

Nernst<sup>28</sup> calculated equilibrium constants for the nitrogen-oxygen reaction by the analysis of rapidly cooled discharge products; his values were in accordance with the thermal theory. But it was soon found that the very great velocity of the reaction at high temperatures indicated that no cooling method could be sufficiently rapid to "freeze" the equilibrium existing in the discharge. However, the facts that the reactions were independent of pressure as required by the Mass law, and that the equilibrium was fairly constant regardless of the composition of the reacting substances, lent great support to the thermal theory.

Most of the earlier equilibrium calculations were based on the thermal theory to begin with; for instance the temperature of the discharges was estimated by extrapolation from known thermal data for low temperature conditions free from electrical influences. The celebrated work of Haber and Koenig<sup>29</sup> showed that while temperature undoubtedly affects chemical reactions in arcs, these effects are not the result of any simple thermal equilibrium.

In general, the high<sup>er</sup> the temperature existing in any discharge the more likely are purely thermal effects; but modern theory is inclined to consider primarily the extent of thermionic electron emission at high temperatures, rather than the equilibria to be expected from the simple Mass action law.

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(B) Critical Activation Theory:

This was first definitely advanced by Elliott, Joshi and Lunt<sup>30</sup> and is really a broad generalisation of the "activation by collision" idea. It holds that chemical action in discharges is a result of collisions with particles possessing sufficient kinetic energy to supply the necessary "heat of reaction", whatever this may be. It is immaterial whether the particles be ions moving under the influence of an electrical field, or simply atoms and molecules with high velocities due to thermal agitation. It suffices that the sum of the available energies of the colliding particles exceed the critical activation energy.

While this theory predicts a definite temperature coefficient (positive) for discharge reactions, such a prediction is found to follow from most theories, and should it be experimentally verified it can hardly point to any definite conclusion. Furthermore this theory is vague in application to reactions involving a combination of chemical entities, e.g. the NO synthesis, since there is no picture of the transfer of kinetic energy from a single particle to another with resulting union of the two. Lind (loc. cit.) claims that this theory is entirely unsupported by fact.

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(C) Photochemical Theories:

In 1910 Lind, Warburg and others believed that certain discharge decompositions were the result of photochemical processes; for example, hydrogen peroxide was observed by some to be a product of water decomposition in the glow discharge and in ultra violet light. With the advance of the ionisation theories this hypothesis was abandoned.

In most discharges the percentage of input energy converted into light is very small, consequently photochemical effects cannot be prominent; with certain arcs however, this is not the case. The under water spark and arc have been found to be extremely intense sources of low wavelength ultra violet radiations. J. J. Thomson<sup>26</sup> considers that the high frequency radiations in discharges play a large part in ionisation phenomena, but at present there are no attempts made to include photochemical reactions in general discharge theories.

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## II. THEORIES INVOLVING IONISATION:

At the present time only electrical theories involving ionisation are applied to discharge reactions studied in the laboratory; in the glow discharge and general silent low pressure discharges there is little thermal or radiant energy to consider and these are disregarded. The question of the extent of electrical influences in any complex discharge such as the arc can best be settled by consideration of the agreement between the experimental facts and the various electrical theories.

### (A) The Static Ion Theory:

This was first advanced to explain the lack of any connection between the discharge current and the amount of chemical change taking place (Faraday's law). It assumes that the chemical actions are the direct result of the recombination of positive and negative ions which never reach the electrodes, and therefore such actions have no relation to the current flowing between the electrodes. In electrolysis it is known that only the ions which reach the electrodes are chemically active. It is admitted that discharge ions conducting the current and reaching the electrodes may undergo changes on becoming discharged, but "the proportion is negligibly small relative to the total ionisation under usual conditions" (Lind<sup>27</sup>).

This theory is very indefinite in regard to decomposition reactions and has received little attention; the difficulty of estimating the extent of ionisation in discharges renders verification difficult.

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(B) The "Clustering" Hypothesis:

Ionisation is a necessary preliminary change in this theory, which considers that the kinetic energy available in collisions is transferred almost entirely to the positive ion; this results in a high concentration of potential energy (200 to 500 Cals. per mol.) in the discharge gases. The positive field attracts neutral particles and positively charged "ion clusters" are formed.

The formation of the cluster does not expend much of the potential energy of ionisation, hence when an electron collides with the cluster there is available the combined energy of the two bodies; the result is the formation of highly endothermal compounds, but the mechanism of the energy exchange is as usual entirely unknown.

The clusters may be in dynamic equilibrium in which the number making up the group is constantly fluctuating, but this does not affect the principle. In the field of synthetic reactions there has been obtained much experimental verification, but the obvious limitation is that decompositions are not included. The theory is regarded by many as definitely

established insofar as polymerisation reactions are concerned.

(C) Two-Stage Synthesis Theory:

This was advanced by Lind to overcome difficulties in H. A. Wilson's thermodynamic theory of polymerisation from a thermal viewpoint, since the latter does not explain the formation of triple and higher orders of molecular weights commonly found in electric discharges. The molecule is believed to split up into its component parts and subsequently the parts group together to form a higher order condensation product. Little verification has been obtained.

(D) Intermediate Complex Theory:

This chain mechanism idea was advanced by Bodenstein<sup>31</sup> and fully discussed by Linder<sup>32</sup>. The author claims that "there is formed an unstable intermediate product, rich in energy, which on further reaction gives rise not only to the final product but also to another intermediate product which regenerates the same process again and again". This idea is a familiar one in the field of photochemistry and is gaining much support; it is too early to draw any conclusions from existing data.

(E) Excitation Theory:

In has been advanced in photochemistry that atoms which have had an orbital electron displaced to an outer orbit may be in an excited condition, chemically speaking; that is, on contact with another atom they would tend to transfer their potential energy into a reaction heat of some sort. At present there is no evidence to show that atoms become chemically active until an electron is completely removed.

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S U M M A R Y :

Many theories have been advanced to explain the chemical reactions in discharges, but there is no widely proven nor accepted hypothesis available. Only recently has it been realised that no single theory can be applied to all reactions, and that many discharges are very complex in their thermal and electrical nature. There is a noticeable lack of experimental evidence, but much valuable information has been published in the last five years.

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EXPERIMENTAL.

A. Characteristics of the Discharges Studied.

1. The essential feature of the arc discharge in gases is the production of heat, light and chemical change, and in this respect the arc burning in liquids differs but little. To the eye however, the two types of discharges are quite dissimilar. The characteristics of low voltage arcs in water have been incompletely described by Konen<sup>7</sup> in papers dealing with the spectroscopic problem; this worker does not distinguish between an arc with both electrodes deeply submerged in water, and an arc with one electrode in air and the other just at the surface of the liquid. Shipley and Goodeve<sup>19</sup> did much work with high tension A.C. arcs in electrolytes, the discharges taking place between widely separated electrodes, and the conductivity of the liquid medium being increased until the arc passed from one electrode to the solution.

The arcs I have employed in the work described here have several very characteristic features. They are produced by STRIKING, a method to which no reference has been found in the literature; of course low tension air arcs are always formed by striking. When carbon electrodes are brought together in distilled water a more or less violent action starts as soon as a potential in excess of 10 volts is applied.



An audible vibration is produced, of variable pitch and intensity, and distinct from the sound of the escaping gas bubbles; with A.C. the noise is more pronounced and with high currents may become very loud. A brilliant blue white light is emitted from the arc "crater", which appears to be a very small region; the light is rich in ultra violet and heavy goggles must be worn by the operator, otherwise conjunctivitis symptoms (coagulation of albumins in the eye) appear in a few minutes. Considerable heat is produced and the water must be cooled to prevent boiling.

While the electrodes must be touched to start arcing, it is not necessary to separate them at all as is the case with the arc in air. Indeed, vigorous arcing may be maintained while pressure is applied to the points, and with low currents the action is most stable when such pressure is maintained. The arcs appear therefore to be "contact arcs" and their appearance explains why L<sup>öb</sup> believed them to be simply sources of high temperature produced by the high resistance contact, and not true arcs at all. Careful examination reveals that this is not the case, since the electrodes can be separated as much as 4 mms. with heavy currents, and neither the arc appearance nor the gaseous products are appreciably altered by this change. It is probable that a layer of gas at very high pressure is always separating the electrodes, even when pressure is applied.

2. Under water arcs can only be started and maintained in water of very low conductivity. The addition of small amounts of sulphuric, hydrochloric or nitric acid results in complete cessation of arcing and commencement of electrolysis. Any of the electrolytes tested, e.g. simple salts, organic acids etc., had similar effects; in the case of substances only slightly dissociated in water considerable amounts must be added.

During arcing with either A.C. or D.C. a strong field which may be detected by the fingers, exists in the surrounding liquids, similar to that observed by Pfanhauser<sup>33</sup> during electroplating under special conditions.

3. The steadiness or stability of the arcing increases with the current, but even with 30 amperes it is impossible to secure steady action for more than a few seconds. Many types of attachments were experimented with in attempts to make the arcs fully or semi-automatic, but none were found suitable. With even a simple screw feed mechanism the arcing cannot be carefully controlled, so that a hand feed was finally adopted. The ends of the electrodes are continually wearing away, and only by having one electrode quite free to move in all directions can the discharge be kept operating; this is especially true for very low currents.

If a mechanical vibrator be employed the discharge appears to resemble the arc, but actually the arc is broken frequently and when in this "open" condition electrolysis takes place, giving products not associated with the true arc reactions.

4. Metal electrodes give very inferior under water arcs because of their tendency to weld together on touching. With 50 volts and currents up to 30 amperes intermittent arcing can be secured; experiments conducted with such metal arcs will be outlined later. Carbon electrodes were employed in nearly all of the quantitative work.

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B. The Products of the Discharges.

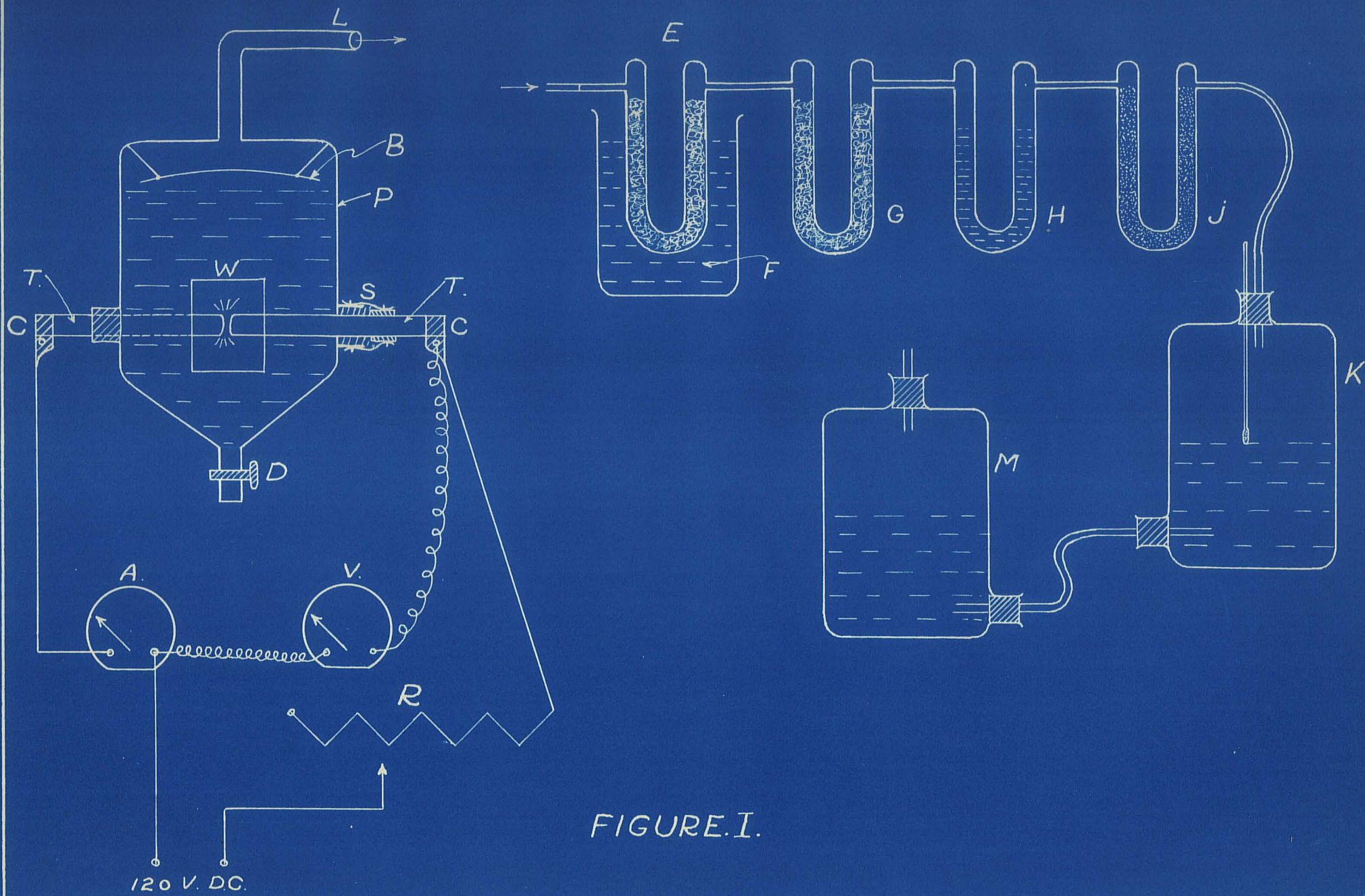


FIGURE I.

1. Gaseous Products from Carbon Electrodes:

(a) Apparatus:

The apparatus employed in determining the nature of the gaseous products from the arc with carbon electrodes is illustrated diagrammatically in Figure 1, in which the arcing chamber is drawn on an enlarged scale. The current was obtained from a line supplied by a storage battery of 120 volts, and was passed through the heavy resistance R; a series resistance must always be employed since under water arcs are similar to air arcs in that their characteristic is negative. Also, the resistance of the arc on striking is very small, hence a protective series resistance is essential. The ammeter A and the voltmeter V measured the current through and potential across the arc electrodes T-T, connection being made by the heavy clips C-C.

The arc was contained in the copper chamber P of approximately 500 ccs. capacity; this chamber was always kept immersed in a large vessel of water not shown in the figure, in order to keep the arc liquid below the boiling point or at a constant temperature. The chamber was equipped with a small mica window W and an internal baffle plate B, the latter preventing expulsion of large amounts of water through the exit tube L. The left electrode passed into the chamber through

a gas tight stopper, while the right or feed electrode slipped through a flexible sealing device S, of lubricated rubber tubing. The liquid and solids remaining after arcing were drained off by means of the pipe D.

The gas train is shown to consist of a tube of glass wool immersed in a freezing mixture F, a pumice-sulphuric acid tube G, one or more KOH bulbs H and a soda-lime tube J. The action of this train was to successively remove water droplets, water vapour, carbon dioxide and residual water vapour from the gas, before passing it to the gas holder K. The gas remaining from carbon dioxide absorption was collected in K by displacement of water into M, at atmospheric pressure. Carbon dioxide was removed by bulb absorption so that the gas could be collected over baryta water, and subsequently transferred to the gas analysis apparatus.

A different method of dealing with small amounts of the gas is described in Section "G", including analysis following collection over mercury.

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(b) Electrodes:

Several types of hard and soft carbons were tested, but after analysis a hard uncured "projector" type was selected for the gas tests. This sample contained 96% carbon, the impurities being silica (2%), iron (1.4%), alumina (0.6%) and traces of lime. It will be shown later that these

impurities, because they are present in fully oxidised form, can have little effect upon the gaseous products; catalytic effects are highly improbable, since results with carbons differing widely in composition showed little variation. The compositions of the carbon samples were determined by the combustion method, followed by analysis of the residues; a special combustion tube was developed, consisting of a steel-sheathed pyrex tube to withstand the high temperature necessary to effect complete combustion. Graphite rods were ignited with great difficulty, even in finely powdered form, and the source of heat (blast lamp) had to be removed instantly the combustion started, otherwise the results were useless due to rapid burning and carbon monoxide formation. Oxygen was used in all tests.

-----

(c) Gas Analysis:

When collection was made over water the carbon dioxide was absorbed in weighed KOH bulbs, included in the train shown in Figure 1; this method was found to absorb all but minute traces of carbon dioxide. There was usually 200 ccs. of water in the discharge chamber, however, and the carbon dioxide dissolved in this was determined by the excess baryta-succinic acid method; the correction was found to be very small. The air in the apparatus was either estimated and a correction applied, or the train was filled with the gas before weighing.



The gas analyses were done in a Burrell apparatus, fully described in a U. S. A. Bureau of Mines Bulletin<sup>34</sup>; carbon monoxide and hydrogen were estimated by the copper oxide method with electrical heating. It was found that the closest control of the temperature of the copper oxide tube was necessary, since below 300°C. considerable amounts of hydrogen remained unburned; this may have been due to the fact that the gas was rich in carbon monoxide. In the Bulletin referred to fuming sulphuric acid or saturated bromine water is recommended for the absorption of unsaturated hydrocarbons, the residual gas being washed with KOH before measurement. I found that the addition of KBr, as recommended by Reilly, Rae and Wheeler<sup>35</sup>, was apparently necessary in order to obtain consistent results with the bromine method. The cuprous chloride method for carbon monoxide was found to be quite unreliable, in accordance with the results of many workers.

While the analyses of any one gas sample gave results checking to 0.2%, successive gas samples showed a wide variation, as will be seen in Tables 1 and 2 (P 36). Table 1 contains results obtained with no KBr in the bromine water (i.e. no unsaturated hydrocarbons indicated) and with the temperature of the CuO tube not above 300°C. The "residue" is to a great extent unburned hydrogen and nitrogen from the contained air, and is fully discussed later.

T A B L E "1".

CO <sub>2</sub>	CO	O <sub>2</sub>	H <sub>2</sub>	Saturated Hydrocarbons.	Gaseous Residue.
9.9%	16.6%	1.7%	53.4%	6.1%	12.5%
9.8%	17.0%	3.1%	47.0%	Traces.	16.3%
11.5%	18.1%	3.8%	44.4%	5.3%	16.9%
8.1%	20.9%	4.6%	52.3%	1.4%	12.7%

T A B L E "2".

CO <sub>2</sub>	CO	O <sub>2</sub>	H <sub>2</sub>	Hydrocarbons		Gaseous Residue.
				Sat.	Unsat.	
8.6%	19.2%	1.4%	60.6%	0.3%	1.7%	8.2%
10.3%	16.4%	1.7%	61.5%	----	1.1%	9.0%
9.2%	17.8%	2.3%	57.4%	0.7%	0.8%	11.8%

The higher percentages of hydrogen and lower residue values shown in Table 2 are no doubt the result of employing temperatures in the neighborhood of 325°C. in the CuO tube; traces of unsaturated hydrocarbons were obtained with the KBr bromine solution.

Lepsius<sup>8</sup> claimed the formation of equal volumes of carbon monoxide and hydrogen in his under water carbon arcs, but L**ö**b could not confirm this; in one paper<sup>9</sup> this last worker gave the following analysis: hydrogen 50%, carbon monoxide 40% and carbon dioxide 7%; traces of saturated and unsaturated hydrocarbons were noted. Both these researches involved the use of cuprous chloride solutions in carbon monoxide determination and must therefore be critically examined. I have never obtained carbon monoxide in excess of 25% regardless of the type of electrode employed. L**ö**b gives percentages which add up to 99.8% exclusive of any nitrogenous residue, which indicates that he may have expressed his results in round figures. With water and carbon electrodes, nitrogen and oxygen are certain to be in the collected gas, unless great precautions are taken, with resultant non-combustible residue. Konen<sup>7</sup> has discussed the matter of "occluded" air very fully.

-----

(d) Free Oxygen:

The question as to whether or not free oxygen is produced in the discharge is of importance theoretically, and special tests were made to clear this up. Estimation of the air content of the apparatus shown in Figure 1 is subject to error, and therefore runs were made in which the gas was collected by displacement of water from a cylinder held directly over the arc.

During the runs the water, previously distilled and boiled to expel all air, was kept boiling vigorously in a pyrex vessel to prevent any dissolving of air. The electrodes were electrically preheated to white heat in air, and then boiled in distilled water, this treatment having been found by Konen (loc.cit.) to be sufficient to remove air from such carbon rods.

The gas produced was led directly through water-filled tubing into the burette of the gas analysis apparatus. Absorption with fresh alkaline pyrogallol solution showed only traces of oxygen, less than the limit of accuracy of the apparatus (0.2%), when care was taken to keep the arc in operation during the entire period of gas collection. Since it is virtually impossible to prevent the arc breaking for a second or so during such a test, the electrolysis which takes place during such periods probably explains the presence of oxygen in the gas mixture, and it may be said that no free oxygen is produced by the discharge itself. The oxygen percentages in Tables 1 and 2 are corrected for a large part of the air present in the apparatus, and are no doubt the result of electrolysis.

-----

(e) Gaseous Residue:

In most cases there remained in the analysis burette a 5 to 10% non-combustible gas residue, not accounted for by the nitrogen in the contained air. When a run was made for free oxygen, as above, and the CO and H<sub>2</sub>

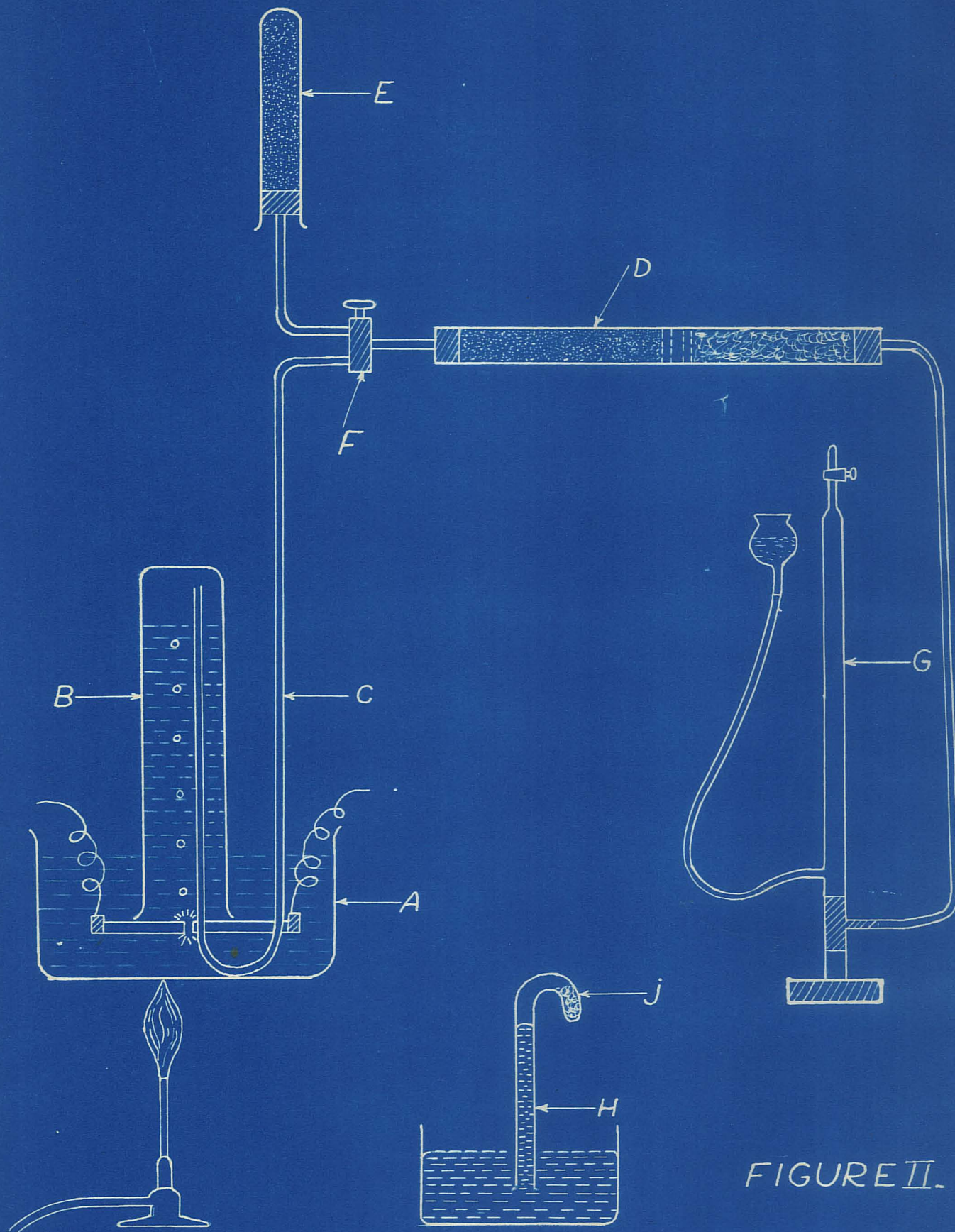


FIGURE II.

and hydrocarbons removed, this residue was reduced to 4%; since there was apparently no air in the gas it was not thought justifiable to dismiss it as nitrogen. A special apparatus was employed to remove all gases except nitrogen, the gas sample being produced in the air-free conditions outlined in the preceding section; the apparatus is illustrated diagrammatically in Figure 2. The arc was operated in the vessel A, in boiling water, and the gas collected in the tower B previously filled with water by suction through the delivery tube C. The three-way stopcock F admitted either the gas or carbon dioxide from the generator E to the combustion tube D. The latter contained 15 cms. of copper oxide and 10 cms. copper turnings, the whole being kept at red heat by gas burners. Any residual gas was collected over concentrated KOH, which absorbed the carbon dioxide, in the nitrometer G. With the exception of rubber joints at the ends of the combustion tube the train was entirely glass and was well tested for leaks; before each run the system was swept out and filled with carbon dioxide.

It is evident that hydrogen and carbon monoxide were removed by the hot copper oxide, oxygen by the glowing copper (reduced before each run) and carbon dioxide absorbed by the KOH; a very slow rate of flow was used, never exceeding 10 ccs. per minute input. Regardless of the rate a gas residue collected in the nitrometer, amounting to from 1.0% to 1.3% of the original volume. 500 to 1000 ccs. were passed into the

train each time, so that the residue always amounted to over 5 ccs.

Tubes containing first magnesium and then freshly polished calcium metal were included in the train, and heated to a dull red heat, but a 1.2% residue still passed through. The gas in the nitrometer was then transferred to the pyrex tube H shown in Figure 2, at the upper end of which was blown a small thick-walled bulb J. This bulb was filled with calcium chips, and the residual gas passed into it by means of mercury filled tubing. On heating the calcium to a yellow heat the gas was finally "absorbed", the level of the mercury rising and falling violently for several minutes. The ammonia test for calcium nitride could not be applied because of the small amount of gas present.

A 1.2% residue was obtained by treating the gases evolved from an arc with soft "graphite" electrodes produced under exactly similar conditions as the gas from hard carbon rods discussed above. Evidently the physical nature of the electrode has little effect upon the production of this non-combustible gas.

A sample of the gas in the nitrometer was well dried over phosphorous pentoxide and passed into a Geissler tube. Examination in the spectrometer revealed an intense

hydrogen spectrum, several lines of the secondary spectrum being present. When the discharge tube was swept out with dry air no such spectrum reappeared, which showed the tube to be free of hydrogen and water vapour.

Kernbaum found only hydrogen produced when water was decomposed by the action of light, radium and electric discharges; in a paper on the brush discharge<sup>16</sup> he claims that the oxygen was all in combination with hydrogen in hydrogen peroxide, which substance he detected qualitatively in the discharge products. In several papers dealing with the decomposition of water by different methods there has been mentioned an absence of stoichiometrical relations in the quantity of hydrogen and oxygen produced. Linder<sup>26</sup> observed this with the glow discharge in water vapour, and could not trace the oxygen to hydrogen peroxide or ozone. Urey and Lavin<sup>37</sup> and Senftleben and Rehren<sup>36</sup> failed to find any error in similar results with a discharge tube; Bates and Taylor<sup>38</sup> reported the same thing in the photochemical decomposition of water. In some of this work a gas remaining after analysis was assumed to be nitrogen.

The residual gas obtained in the above work was no doubt almost entirely nitrogen although its source is by no means clear. Konen<sup>7</sup> found his treatment, which I employed, sufficient to remove even spectroscopic traces of nitrogen from carbon rods; but in this case it was the "cyanogen" band



spectrum as obtained in under-water arcs to which reference was made. Considering the adsorbing power of carbon it is not unlikely that the nitrogen was obtained from this source.

A test was made to determine whether or not the gases from the discharge were ionised; a large ionisation chamber such as used in radioactive gas experiments was connected to a charge electroscope, but no loss in charge was observed over a long period of time.

It may be concluded therefore that there is no unusual gaseous product evolved, and that the "residue" is nitrogen mixed with sufficient hydrogen to give an intense spectrum.

Attempts to find a "mass balance" in the amounts of hydrogen and oxygen produced in the arc gave no conclusive results, the discrepancies being far beyond the limit of error of the methods employed. In most cases there was about 10% (by weight) excess of hydrogen over the theoretical amount corresponding to the total oxygen, free and in combination; this pointed to the existence of products other than the gases already discussed.

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2. Solid Products from Carbon Electrodes:

(a) Insoluble Substance:

Practically every paper on arcs under liquids mentions the formation of "cloudy dispersions" or "muddy" liquids during the operation of the discharge with carbon or metal electrodes. Before the work of Bredig<sup>10</sup> such effects were not further studied, but in later papers the dispersions were dismissed as being purely colloidal suspensions of the electrode material.

When carbon electrode arcs with about 15 amperes at 30 volts D.C. have been operated in pure water for a considerable time (15 minutes in 300 ccs. of water, externally cooled) the water becomes dense black, and if allowed to stand for half an hour a very characteristic substance settles out. With soft carbon electrodes the substance is very flocculent and light, closely resembling metallic hydroxides in character except that it usually has only the faintest tinge of green or yellow color. Under the microscope this substance is quite distinctive, although granules of solid carbon may be seen mixed with it; it takes the form of almost transparent yellow plates, joined together in long chain-like strings. In some cases the plates are faintly green by transmitted light.

By carefully shaking a freshly produced dispersion of this sort the flocculent substance was obtained almost free of carbon particles, the latter sinking to the bottom relatively easily. The light substance could then be filtered off and dried. It was found to lose considerable water when dessicated over sulphuric acid at room temperature and pressure; after four hours drying the loss was much smaller.

Combustions of this substance were made in the same tube used for analysing the electrodes, in which the sample could be heated to a white heat while visually observed. The full heat of the blast lamp was required to completely burn the substance in oxygen, the combustion being even slower than that of the powdered electrodes. The samples were first air dried and then dessicated as above for 48 hours. On heating to a bright red heat a partial combustion took place, the loss in weight being 24% to 25%; very little carbon dioxide and some water was produced. When carried to completion the "dried" combustion gave the following results:

Hydrogen: 2% to 3% .

Oxygen: 25% to 30% .

Carbon: 65% to 70%.

Variations in the results were probably due to the varying amounts of solid carbon contained in the substance, it being impossible to eliminate this impurity entirely.

The composition was practically the same whether the hard or soft carbon electrodes were used in the preparation of the sample, and extended drying had no effect.

It is evident that the hydrogen and oxygen in this substance is not all present in the form of water, the oxygen percentages being about twice the theoretical. The percentage composition agrees well with that of the so-called "graphitic oxide" or graphitic acid which was first studied by Brodie. Hulett and Nelson<sup>39</sup> have given a complete historical review of graphitic oxide followed by a critical study of its probable nature. They have shown that the combustion method of analysis of this substance gives only approximate results due to the large amount of adsorbed water always present. As typical percentage compositions obtained from combustion they give the following figures:

	Carbon.	Hydrogen.	Oxygen.	Ash.
Sample "A":	50.7%	2.7%	44.9%	1.6%
Sample "B":	51.3%	2.6%	43.6%	2.5%

These workers attempted to find the formula of graphitic oxide by determining<sup>74</sup> its vapour pressure under diminishing pressures; water corresponding to 90% of the hydrogen in the substance was removed with no indication of a "break" in the vapour pressure curve. They conclude that

all of the hydrogen present is in adsorbed water, and that the excess oxygen is in chemical combination with the carbon as a higher oxide; the probable formula of this oxide is stated to be  $C_{11}O_4$ . Graphitic oxide is, according to this viewpoint, simply a highly "hydrated" solid oxide of carbon; there is much supporting evidence.

It is probable that such a higher oxide of carbon is produced in the discharge; Mellor<sup>40</sup> states that carbon suboxides have been frequently observed in electric discharges with carbon electrodes. With the under water discharge the conditions are favorable for extensive hydration or adsorption, resulting in the production of the highly flocculent substance. It is known that graphitic oxide changes at red heat to a soft black substance, "pyrographitic" acid, of approximate formula  $C_{22}H_2O_4$ ; this change in weight is approximately a 23% loss, which agrees with the loss observed when the flocculent substance was heated to red heat in the combustion tube.

Graphitic acid is usually explosive, but the material produced in the arc burns quietly in the bunsen flame. Dilute acids immediately flocculate the suspended substance, but it is peptised by repeated washing with water; this property is said to be possessed by graphitic acid.

A determination of the heat of combustion of the dried material was made in a bomb calorimeter, giving a result

of 8.4 Cals. per gram. It is found that the "heat of formation" of the substance, assuming it to be pure and of the approximate formula  $C_{11}H_4O_5$ , is about 1800 Cals. per gram mol (positive). This calculation has little significance however, considering recent conclusions regarding graphitic oxide. No data could be found on the heat of formation of carbon suboxides, although it is improbable that the values can be in excess of the heats of formation of the gaseous carbon oxides.

-----

(b) Soluble Substance:

Fresh solutions

from arcing carbon electrodes in boiled distilled water gave no positive tests for hydrogen peroxide, ozone, aldehyde or ketone, and no definite iodoform reaction.

After several minutes arcing in pure distilled water vigorous electrolysis always occurred when the electrodes were separated, i.e. the conductivity of the water was greatly increased. The hydrogen ion concentration of solutions in which various electrodes had been arcing was therefore taken; The colorimetric method was used and all solutions were originally neutral with pH 7.0. In the following Table the "core" relates to the metals present in a series of soft carbon electrodes employed in ultra-violet therapy work.

The values given below were reached after three minutes arcing in 200 ccs. of water, the voltage being about 30 V. and the current 15 amperes; the water was kept boiling to prevent dissolving of carbon dioxide.

Core Substance	pH Value (Saturated)
Uncored hard carbon--	6.0
Uncored soft carbon--	5.8
Cerium--	3.0
Fe, Al, Ni, Si--	6.0

The results indicated that the solutions were very slightly acid; the pH value did not change after 6 weeks standing in a corked quartz flask. On evaporation of a fresh filtered arc liquid a white substance was obtained, obviously not the same as the flocculent compound. This material was insoluble in ether, somewhat soluble in water and dissolved readily in ethyl alcohol. It melted above 350°C. but below red heat. The very dilute water solution gave a pH value of 3.0. The substance is probably an acid such as mellitic or pyromellitic produced by the solution of higher oxides of carbon, some of which are anhydrides of these acids. Such oxides are produced in electric discharges, as mentioned by Mellor<sup>40</sup>.

Distillation of the clear filtered liquid from the carbon electrode discharge failed to show the presence of any volatile substances; similar results were obtained by Fowler and Mardles<sup>21</sup>, with sparks in organic liquids, and these workers also obtained a solid substance of high melting point but undetermined formula.

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### 3. Solid Products from Metal Electrodes:

#### Electrodes

of aluminium, copper, zinc and iron yield solid substances colloidal in character but not sols, and closely resembling that from the carbon electrodes, except in color.

The copper compound is a blue-green substance, completely soluble in ammonium hydroxide and hydrochloric acid, thus resembling "cupric hydroxide". Prolonged boiling however, has little effect, and this treatment is said to turn cupric hydroxide black. The solution is distinctly alkaline with pH 8.5 when saturated, and gives tests for dissolved copper. Colorimetric determination gave 16 milligrams of copper per litre as the solubility, but no data could be found on the solubility of cupric hydroxide. The compound from the discharge is probably a hydrated hydroxide, mixed with hydrated oxides.



The compound from zinc electrodes is partially soluble in ammonium hydroxide and acids, but is flocculated by these reagents; it is soluble in ammonium chloride and is probably a hydrated hydroxide or oxide similar to "zinc hydroxide" which Mellor<sup>40</sup> shows is not definitely a compound. A saturated solution of the substance is alkaline with pH 7.6 approximately; furthermore, arcing with zinc electrodes in a boric acid solution of pH 5.0 renders the solution basic (pH 7.5) in five minutes.

-----

S U M M A R Y:

The following conclusions may be drawn regarding the products of the low tension arc discharge in water.

1. With carbon electrodes the gaseous products are mainly hydrogen, carbon monoxide and carbon dioxide, with small amounts of saturated and unsaturated hydrocarbons. The proportions of these gases are not those found by earlier workers.

2. There is no appreciable amount of free oxygen evolved from the discharge.

3. With carbon electrodes there is always at least 1% nitrogen in the gaseous products, and traces of the hydrogen resist oxidation by red hot copper oxide.

4. The proportions of hydrogen and oxygen in the gaseous products are not stoichiometric, there being considerable "excess" of hydrogen.

5. With carbon electrodes an insoluble flocculent substance is formed, very probably graphitic oxide, which recent work shows is really a hydrated carbon oxide.

6. With carbon electrodes a soluble substance (or substances) is formed, definitely acidic and of high melting

point. This material is probably one or more of the organic acids of which the carbon suboxides are anhydrides.

7. With metal electrodes hydroxide-like substances are formed the nature of which is indefinite; authorities disagree as to the existence of hydroxides of the metals employed.

8. There is no hydrogen peroxide or ozone formed as a final product of the discharge, no traces of these substances being observed in the liquids and gases.

9. The oxygen found to be "missing" in the gases is probably accounted for by the soluble and insoluble substances formed in the discharge; due to the indefinite nature of these substances a "mass balance" can hardly be obtained, but they definitely contain oxygen.

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In 1911 Makowetzky<sup>17</sup> conducted what he termed a complete study of the effects of the glow discharge on water vapour, including the "relations between current and energy consumed". This paper reveals little regarding the energy supplied to the discharge in relation to the heat and chemical energies evolved. Shipley and Goodeve<sup>19</sup> conducted detailed investigations of the energy consumed by high voltage A.C. arcs in electrolytes. There has however, been no attempt to relate the energy input in discharges to the chemical and heat energies evolved, and it was considered most important to measure these factors in under water arcs in which large amounts of heat energy are evolved. This work led to a search for a suitable input electrical energy measuring device, and the methods developed, including those not found satisfactory for the special purpose considered, are given in the first section below.

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#### 1. A Note on Power Measurement:

Electrical power is generally measured by two separate factors: the current (C) or capacity factor, and the voltage (E) or intensity factor; the product of the two, when they are in amperes and volts respectively, is "wattage". Wattage, being power, is by definition a rate and by multiplying by time gives the energy.

In 1933, an attempt was made to determine the energy efficiency of the electrolysis of water. This was done by measuring the heat evolved in the electrolysis cell and the electrical energy consumed. The heat evolved was measured by the method of the calorimeter, and the electrical energy consumed was measured by the method of the wattmeter. The results showed that the energy efficiency of the electrolysis of water is about 70%.

C. Energy Relationships .

The energy efficiency of the electrolysis of water is a function of the current density and the temperature of the electrolyte. The energy efficiency is generally higher at lower current densities and higher temperatures.

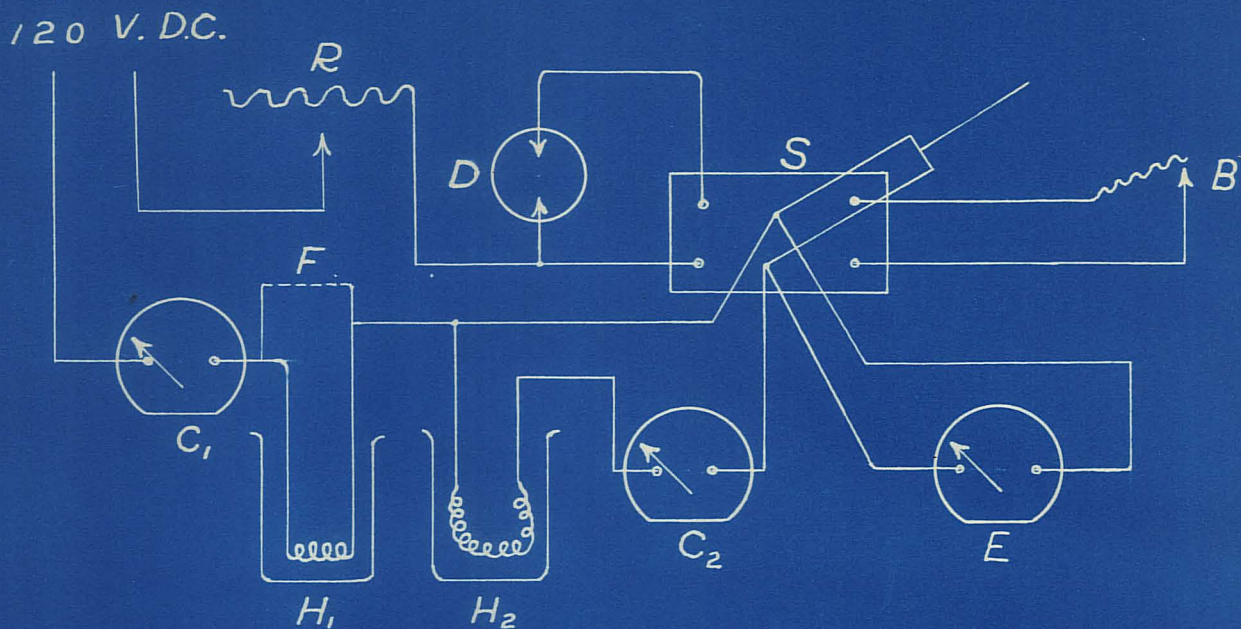
Energy Efficiency of the Electrolysis of Water

The energy efficiency of the electrolysis of water is a function of the current density and the temperature of the electrolyte. The energy efficiency is generally higher at lower current densities and higher temperatures. The energy efficiency of the electrolysis of water is about 70% at a current density of 100 A/m<sup>2</sup> and a temperature of 60°C.

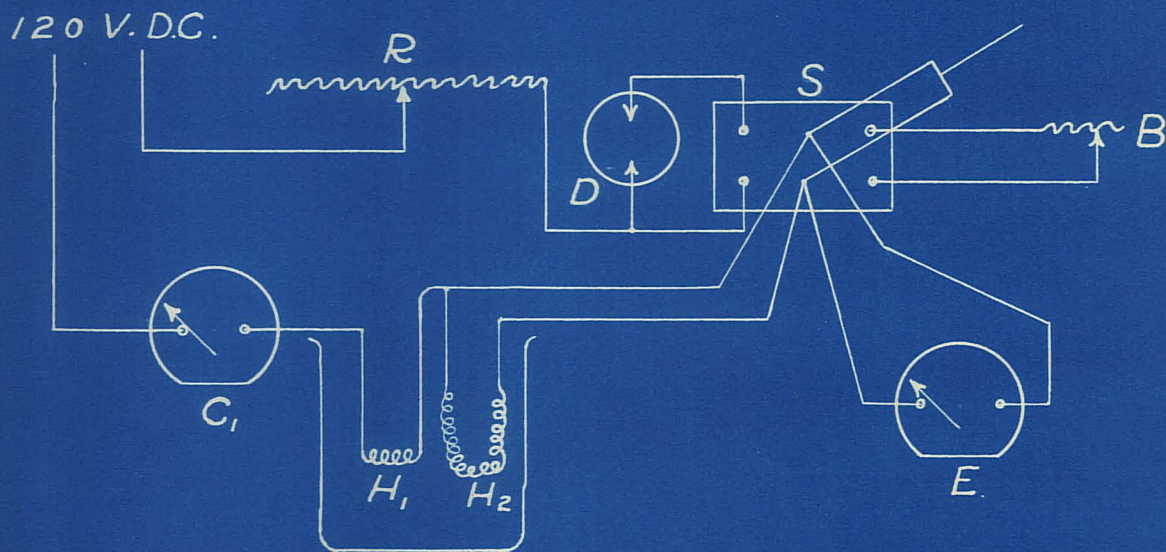
Current is usually measured directly by calibrated ammeters, and voltage by the voltmeter; instruments are available reading directly in watts, some of them being recording.

It was soon found that the ammeter and voltmeter could not be used to measure the power supplied to the discharge for any length of time due to the extreme rapidity with which the current and arc potential changes. These changes can be divided into two types: the rise in voltage and drop in current following on an increase in the arc length, such increases usually being very minute, and the extreme conditions of "open" and "shorted" arc, when the current is very low and very high respectively. Even with 30 amperes and 50 volts the under water discharge is so fluctuating that the meters cannot be kept steady for periods longer than 10 seconds; with lower currents the stability is even poorer.

Instruments can be obtained which record voltage and current fluctuations on recording paper passed under the pen by some mechanical means; investigation showed however, that the construction of such devices, suitable for measuring the excessive fluctuations discussed above, would be prohibitively expensive. The same applied to recording wattmeters, which possess a further disadvantage discussed later. Furthermore, after each run, it would be necessary to laboriously "average up" (by means of a Fourier machine, for instance) the values recorded by the instruments.



CIRCUIT. A.



CIRCUIT. B.

FIGURE III

The heating effect of the electric current provides a very convenient method for measuring electrical energy when the rate is fluctuating rapidly, since the total heat developed in a given time is equal to the total energy consumed in the heating circuit. The application of this principle to measure the heat developed, or the energy supplied, in a second circuit, was the basis of the devices described below.

(a) The heat developed in an electrical conductor can be conveniently measured by immersing the conductor in water in a calorimeter, this being the well known electrical calorimeter. In Figure 3 two simple circuits are given, of which "A" will be discussed here.

The line is passed through the heavy resistance R to the arc discharge represented by the gap D or to the variable resistance B, the change being made by the switch S. The current flows from the switch through  $H_1$  (a low resistance heating coil contained in a special calorimeter) and the ammeter  $C_1$  and thus back to the line. The coil  $H_2$  is shunted across the arc D and the current through this shunt is measured by the ammeter  $C_2$ . The voltmeter E indicates the voltage across the arc terminals.

The characteristics of the circuit are as follows:  
 $H_1$  and  $H_2$  are constant resistances, and R is constant during any run; the arc D however has an "apparent" resistance which



varies from an infinitely great value to practically zero. Therefore R cannot be made large enough to prevent the line voltage from changing with the load through D; in practice the normal 120 volts was sometimes reduced to less than 100 when heavy currents were drawn. Hence not only does the changing resistance of D affect the potential differences across all the resistances in the circuit, but it also alters the line voltage, with resultant change in potentials all through the circuit. This multiplicity of variables makes power measurement rather complicated.

Since the resistance of  $H_1$  is constant, the heat developed in the calorimeter depends upon the square of the current flowing; if T is the rise in temperature exhibited in the calorimeter in time t then we have:

$$T \propto C^2 t. \text{ or } C \propto \sqrt{T/t}.$$

A calibration curve may be drawn relating the current to the factor  $\sqrt{T/t}$ ; in practice T was measured by having the heating coil, of approximately .2 ohms resistance, immersed in water in a well-lagged calorimeter, efficiently stirred. The current was measured with  $C_1$  and was kept steady during calibration by substituting the resistance B for the arc D. In this way the current flowing through the circuit could be determined directly from the curve, by observing the total rise in temperature during a given measured time interval.

Finally, knowing the arc resistance and mean voltage across it, the current is known.

Similar reasoning applies to the shunt calorimeter coil  $H_2$ . In this case however we desire the voltage across the arc, not the current through the shunt, so that a different equation is employed. The rise in temperature will be proportional to  $E.C.t.$  where  $E$  is the voltage,  $C$  the current through the shunt as measured by the ammeter  $C_2$ , and  $t$  is the time. Since  $C$  is equal to  $E/r$ , where  $r$  is the constant resistance of the calorimeter coil, we may write:

$$T \propto E^2 t. \quad \text{or} \quad E \propto \sqrt{T/t}.$$

As in the previous case a calibration curve is drawn, relating the voltage across the shunt coil to the heat developed as in the above equation.

Hence by measuring the heat developed in a given time in the calorimeters  $H_1$  and  $H_2$  the voltage across the arc and the current through the complete circuit may be obtained. It is necessary however, to obtain the current flowing through the arc alone which is less than the total current; since the shunt calorimeter coil represents a constant and measurable resistance the calculation is simple. The arc voltage  $E$  determined from the curve for  $H_2$ , divided by the total current  $C$  from the curve for  $H_1$  gives the mean resistance of the double circuit arc-plus-shunt calorimeter. The inverse of this value is the sum of the inversed resistances of the arc and the shunt calorimeter; the latter being known the mean arc resistance follows at once. Finally, knowing the arc resistance and mean voltage across it, the current is known.

There are several variations of the calculating method possible. With a steady load and line voltage the series calorimeter may be dispensed with, since when the arc resistance is constant the heat developed in the shunt calorimeter is a function of the current through the shunt and also through the main circuit. Calibration curves may be drawn, and by the use of a single calorimeter the mean power flowing through the constant load may be easily obtained.

If the calorimeters are well constructed and have very low radiation and conduction losses the heat developed may be measured directly in calories, knowing the heat equivalent. From the relationships E.C.t. and  $C^2.r.t.$  the current and voltage may be measured directly without the use of any calibration curves, since the resistances may be determined accurately. This method was found to be satisfactory, subject to the discussion below.

-----

(b) In Circuit "B", Figure 3, is shown a variation of the calorimeter principle in which the two coils, series and shunt, are immersed in a single calorimeter liquid and the total heat measured. This is somewhat the same as the well known Siemen's Dynamometer for measuring watts directly. As with the above circuits the heat may be measured directly in calories or the instrument may be calibrated and the mean watts during a run determined from a calibration curve.

(c) All of these devices were found to give very satisfactory results when measuring the power consumed by various constant loads; when applied to the arc discharge however, wide discrepancies were found. The thermal energy evolved by the discharge was measured by methods discussed in the next section, and in every case this evolved energy was found to be much smaller than the input energy even after correcting for the chemical energies involved. For example several runs gave the following results:

	Energy Input Converted to Calories.	Energy Output (heat).
Run "A"---	35,400 cal.	17,600 cal.
Run "B"---	9,850 "	6,525 "
Run "C"---	11,440 "	7,630 "

The energy unaccounted for usually amounted to from 25% to 50% of the total input energy as measured by the various calorimeter methods. By a process of elimination the error was found to lie in the power measurement.

Simple calculation shows that when the power or wattage supplied to any device varies considerably, the true mean power obtained by averaging the individual rates with regard to the time of flow of each, is vastly different from the value obtained by multiplying together the mean current and the mean

voltage registered on any recording instruments. The following calculation makes this clear:

Consider the power divided into four rates, each rate flowing for 100 seconds, the total run being 400 seconds. The load, as in the case of the arc, is not a constant resistance, so that there is no relationship between the current flowing and the applied voltage; this is the key to the whole difficulty. Let the rates be:

Volts:	3	5	80	60	Mean volts:	37.
Amperes:	20	18	2	4	Mean current:	11.
Watts:	60	90	160	240.	Mean wattage:	137.5

Here the mean wattage is obtained by averaging the individual values of the power given above; but, the product of the mean current by the mean voltage gives 407 watts, a 300% error!

This was the source of error in all determinations made with the "ampere-volt" calorimeters. It must be noted however that the error is independent of the method used, and would be evident with the best recording meters. The only solution would be to multiply each individual value of the current and voltage, measure the time for which each value flowed, and average the results; perfect accuracy is of course far from possible and the method would be extremely laborious.

It is therefore desirable to employ an instrument reading directly the average watts during a run, and such a device was outlined above. The errors found with this calorimeter wattmeter were of a much smaller order than those previously discussed, being generally about 10%. This was beyond the limit of error of the methods, insofar as the actual measurements were concerned.

In alternating current practice it is well known that even with a power factor of unity the current registered upon a meter is not the true current. The ammeter registers the square root of the mean square value of the current, and this is considerably different from the mean current. This error is inherent in the calorimeter method as well, since voltage and amperage are both determined from either of the two equations E.C.T. or  $C^2$ .r.T.; actually both contain the term  $C^2$ , so that the calorimeter measures the square of the current. Over any length of time the heat is a measure of the square of the current, so that finally the square root of the mean square value is determined. Obviously, this is not the mean current.

The error was found to be approximately equal to the "excess" current indicated in the power measurement. Correction cannot be made, since it is impossible to employ a "distribution" formula, nothing being known regarding the probabilities connecting the mean current and the time during which that mean value actually flows.

It appears that there is no instrument available that would conveniently measure the wattage under the conditions of these experiments; construction is by no means impossible, but considering the flexibility and rapidity of response required, would present difficulty.

-----

## 2. Measurement of the Heat Energy Evolved:

Since the arc discharge operates in liquid water it was necessary to employ this liquid in all heat measurements, directly or indirectly. In this section the method used, together with the final and accurate device developed, is given briefly.

-----

(a) The simplest calorimeter employs the discharge liquid as the calorimetric liquid, the rise in temperature being read on a thermometer. This is impractical however, because the collection of the gaseous products is essential in calculation of the chemical energies involved; the stirrers, thermometer etc. would have to be introduced into the discharge liquid through gas tight joints. The large bulk of water makes long electrodes necessary, and there are other minor difficulties.

(b) A suitable device employs two chambers, one forming the discharge chamber and the other the calorimeter. The former is as small as possible and is immersed in the larger vessel. Only the discharge vessel need be gas tight and the

calorimeter can be of conveniently open construction.

(c) As will be shown later, many characteristics of the discharge depend upon the temperature of the water, so that it is desirable to keep the liquid at a constant temperature during an energy run. Circulation of the calorimeter water is a rough method, and it was found that operating the arc at the boiling point of water was the most satisfactory. The heat developed can easily be measured by the heat evolved on condensing the steam.

This last method was employed in all accurate runs. The arc was operated in a small metal or glass chamber, heat insulated as perfectly as possible with asbestos and cotton wool, and the steam led to some form of calorimeter where it was condensed by cool water. Several precautions were observed. The method depends upon the assumption that all the heat evolved is spent in vaporising water, so that the discharge must be started in water just at the boiling point. This was assured by the use of an electrical heating coil in the discharge chamber, by means of which the water was brought to boiling; the coil was shut off a second or two before the arc started, and before connection was made to the condensing calorimeter. Also, it was necessary to correct for the heat given up in the calorimeter by the condensed water, in cooling from 100°C. down to the temperature of the calorimeter water.



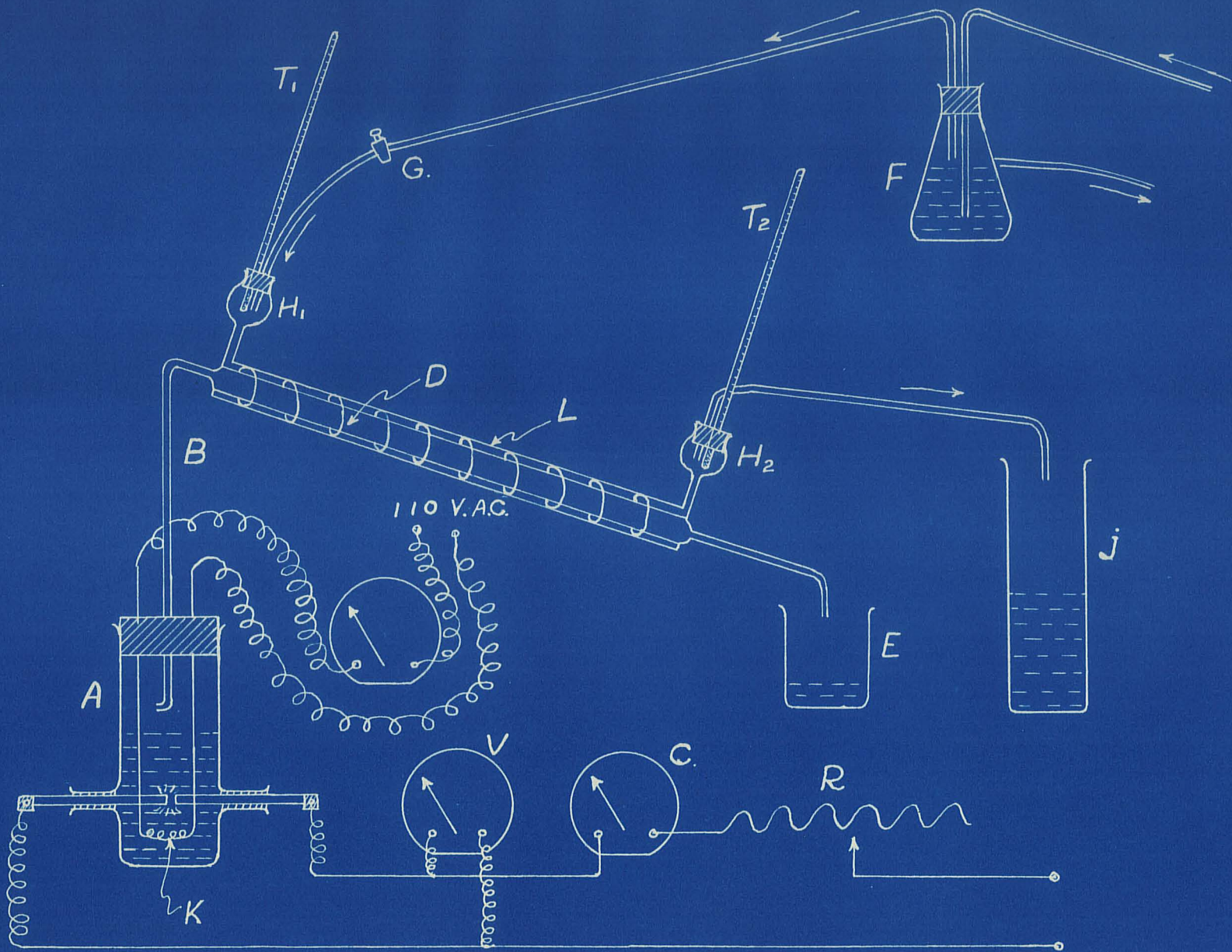


FIGURE IV

Some of the "lost heat" was traced to resistance heating in the electrode terminal connections, carbon-metal contacts being of high resistance. The rods were therefore copper plated, so that all current was conducted right to the arc region, within a centimeter or so of the discharge. The heat equivalents of the calorimeters were determined with more accuracy than the other measurements, so that all errors were finally traced to the power measuring devices.

-----

(d) The instability of the arc as regards the power input has been repeatedly mentioned. The fact that with currents over 10 amperes the current and voltage may be kept practically constant for 10 to 15 seconds led to the development of a calorimetric method which could give accurate results in this very short time interval. The basis of the method was the novel Constant Flow Calorimeter of Callendar and Barnes<sup>41</sup> originally employed in determining the dynamical equivalent of heat by the electrical heating method. The modified apparatus, as used with the discharge, is shown in Figure 4.

The arc operated in water in the chamber A, the whole being raised to the boiling point before the run by means of the A.C. electrical heating coil K. The steam passed through B to the heat exchanger and condenser D; the inner tube was of thin metal for rapid heat conduction, while the outer was of glass.

A spiral of heavy copper wire fitting loosely between the two tubes served to guide the water in a spiral motion. The cooling water was obtained from the "constant head" device F, which maintained an absolutely constant flow of water as long as an excess was supplied to it; the special clip G was of fine construction, enabling close control to be kept on the water flow rate. The intake cooling water circulated around the Beckmann thermometer bulb  $T_1$ , passed between D and L, and through  $H_2$  to J, a measuring cylinder. The two chambers  $H_1$  and  $H_2$  were designed so that the water circulation was efficient, and the two Beckmann thermometers  $T_1$  and  $T_2$  were very sensitive to temperature change. The volume of water in the tube L did not exceed 20 ccs. so that with a flow rate of 600 ccs. per minute the tube was completely emptied every 2 seconds. There was a slight lag in the response of the output thermometer  $T_2$ , but this registered any change in heat input in about 3 seconds, reaching a steady state in 5 to 10 seconds depending on the amount of heat. The water flow rate was measured by means of J and a stop watch, while the expelled or condensed water from A was collected and measured in E.

The advantages of this method are numerous; all the conditions are perfectly steady so that the observations can be made with almost no corrections. Of course the entire apparatus was very well insulated (not shown in the diagram)

and since the rise in temperature in the "calorimeter" tube was only 4 or 5 degrees, the radiation loss was practically zero. The water entered at a temperature slightly below that of the surroundings, and left a little above; the calculations do not involve the measurement of the water equivalent. A full discussion of the high accuracy of the principle is given by Callendar and Barnes (loc. cit.), but the variation introduced here, namely the "steam calorimeter" principle, of necessity lowered the accuracy. The one correction introduced was the constant radiation loss of the chamber "A"; this was entirely invariable since the chamber was always at 100°C, regardless of the rate of energy input, and was determined by blank experiments using the heater K. This correction was found to be approximately 50.0 calories per minute, providing that the water flow exceeded 300 ccs. per minute; below this flow rate the calorimeter system did not function properly, since the circulation of water between D and L was irregular.

The greatest advantage of the method however is its convenience, and the rapidity with which measurements may be made. The thermometer  $T_1$  soon reaches a steady state, and  $T_2$  becomes steady in about 5 seconds after a change in steam input occurs. The water flow rate being constant, it is only necessary to keep the arc operating steadily for 10 to 15 seconds, reading the current and voltage on the conveniently placed meters C and V; the thermometer  $T_2$  is then read and

the experiment is complete. For highest accuracy the rate of flow of the condensed water is measured in E, since the cooling of this water from boiling point to calorimeter temperature represents heat not supplied to the water by the arc. Since only the difference in temperature of the intake and exhaust cooling water is required, the two Beckmanns are not compared to a Centigrade thermometer, but only their differences taken when both are immersed in a constant temperature bath. By adjustment of this "zero difference" any range of temperature difference is obtainable. In practice however, it is more convenient to vary the range of the device by altering the flow rate by means of G; thus by doubling the flow rate the calorimeter will measure twice the input energy with the thermometers in the same position.

An actual calculation will serve to illustrate the method clearly. In a run the arc was held steady for 15 seconds with 16 amperes at 26 volts; this was more than sufficient time to enable the output thermometer  $T_2$  to reach a steady condition because just before the run the heater K had been operated at a wattage about equal to the pre-determined arc wattage. The intake thermometer  $T_1$  read  $1.25^\circ$ , the output reading  $5.25^\circ$ , the difference being  $4.00^\circ$ ; to this was added  $3.40^\circ$ , i.e. the "zero difference" between the two thermometers, making a total temperature difference of  $7.40^\circ$ . The rate of flow of water through the calorimeter was found to be 780 ccs.

per minute, constant over a period of two hours. Hence the heat developed in the calorimeter by condensation of the steam from A was 5770 calories per minute. From this must be subtracted the heat from the cooling condensed water, amounting to approximately 250 calories; 50 calories per minute are lost by radiation, so that the net heat developed in the calorimeter may be taken as 5270 calories per minute. The input energy was ~~495~~<sup>416</sup> watts, or ~~7100~~<sup>5970</sup> calories per minute, so that an amount of energy equivalent to ~~1630~~<sup>700</sup> calories per minute was "used up" by the discharge.

-----

(3) Chemical Energies Involved in the Discharge:

In this section an attempt will be made to account for the energy used up by the discharge, on the basis of the chemical changes taking place in it. A considerable amount of data is at hand regarding the specific heats, reaction heats, etc. of hydrogen, oxygen, steam, water, carbon dioxide and carbon monoxide. These are the principal substances involved, but the solid substance discussed previously ~~must~~ necessarily enter any energy calculation; beyond a very questionable determination of its heat of formation there is no thermodynamic data available regarding it. Therefore the calculations can at best be only an approximation.

-----

(a) The heat of formation of water from its elements has been investigated by many; the variation of this factor with temperature may be calculated thermodynamically, but the available data is meagre. Lowenstein<sup>42</sup>, Langmuir<sup>43</sup> and Bjerrum<sup>44</sup> employing different methods have determined the degree of thermal dissociation of water vapour at high temperatures, and the specific heats of water, hydrogen and oxygen. At 1000°C. water is less than .01% dissociated, but at 3000°C. the degree of dissociation is 11% approximately; the specific heat at constant volume changes from 8.0 at 2100°C. to about 11.0 at 3350° C. There is however, a notable discrepancy observed in the literature. Thus Taylor<sup>45</sup> shows that the heat of formation of water rises with rise in the temperature at which the reaction takes place; but Haber<sup>39</sup> shows that data from other sources results in opposite conclusions being drawn.

(Note: at the time of writing work is proceeding which it is hoped will make possible an accurate calculation of the various heats of reactions involved in the discharge; the figures given below must be considered as approximations only).

Since the water, carbon and gaseous products all enter and leave the reaction region at a temperature of 100°C. this figure may be taken as the basis of the calculations.

Taylor (loc. cit.) gives the heat of formation (or decomposition) of water vapour as 58,057 calories per gram mol at 100°C. The water decomposed by the arc is however vaporised before decomposition so that the heat of vaporisation must be added; the value of this is approximately 9710 calories per gram mol at this temperature. Hence the heat of formation of liquid water from gaseous hydrogen and oxygen is 67,768 calories per mol.

(b) Similar heats of formation of carbon dioxide and carbon monoxide are respectively 96200 and 28890 calories per gram mol. These heats are more accurately known than in the above case, but authorities at present disagree.

(c) In the energy test outlined on Page 68 the figures given were the mean of a series of closely agreeing runs, also the figures for one of these runs. The gaseous products were evolved at the rate of approximately 700 ccs. per minute, the analysis being 60% hydrogen, 15% carbon dioxide and 22% carbon monoxide for these particular electrodes; it is seen that there is an appreciable amount of oxygen "missing" here, the amount in the solid oxide compound discussed earlier. These percentages represent 360 ccs. hydrogen, 105 ccs. carbon dioxide, and 137 ccs. carbon monoxide (all measured at S.T.P.) evolved per minute.

To decompose liquid water at 100°C. to produce 360 ccs. of hydrogen would require 1088 calories, considering the above



heat of formation to be exact. Similarly the production of 105 ccs. of dioxide and 137 ccs. of monoxide would result in the release of 451 calories and 177 calories respectively. The net heat used up in the resultant reaction is therefore 460 calories; this is the energy required to maintain the reactions for a period of one minute, with the input power rate as given above.

On page 68 it was found that some 700 calories were apparently lost each minute the discharge operated; of this amount of heat 460 calories have been located in the chemical reactions discussed above, leaving 240 calories unexplained.

At the present time it would be of no advantage to discuss these results from the standpoint of experimental errors; more approximations have been made in the calculations than in the actual measurements described here. However, it is not at all improbable that the "missing" energy is involved in the formation of the solid products; this energy is about 4% of the total input. This subject will be further discussed in this thesis.

-----

S U M M A R Y:

The following conclusions may be drawn regarding the energy relationships in the low tension arc discharge in water:

1. The attempt made here to relate the energy input and output, considering the chemical reactions as well, is apparently the first work of this nature done with under liquid discharges.

2. Power measuring instruments available are liable to serious errors when employed with the discharge studied; the errors inherent to several novel devices have been studied.

3. The heat energy evolved by the discharge may be measured in several ways, of which the "steam calorimeter" method is probably the most convenient and accurate.

4. A modified form of the Callendar and Barnes constant flow calorimeter has been found very satisfactory in measuring evolved heat energy; by means of this device this latter quantity can be related to the input energy very easily, and with considerable accuracy. A complete energy measurement can be made in 15 seconds.

5. Calculations indicate that the discharge reactions are in their net effect slightly endothermal, but comment is withheld until the reactions have been more fully studied.

-----

D. The Temperature of the Discharges.

It was stated on pages 10 and 11 that few measurements have been made of the temperature of under liquid discharges; there has been no work of this nature done on low tension arcs in water. Löb<sup>9</sup> and other early workers believed that the arc merely represented a source of very high temperature and that the current played no part in the chemical reactions. Strange to say no attempt was made to verify this by determining this high temperature, and correlating it with the products of the reaction.

It is also interesting to compare the temperature of the under water arc with carbon electrodes, to the temperature of a similar arc in air, the latter being one of the highest known. At first it might be thought that operation in a cold liquid medium would greatly lower the temperature; but it must be remembered that the actual discharge probably takes place in a steam mantle, and that certain highly exothermal chemical reactions are taking place.

Experimental results only are outlined in this section; theoretical conclusions will be taken up later.

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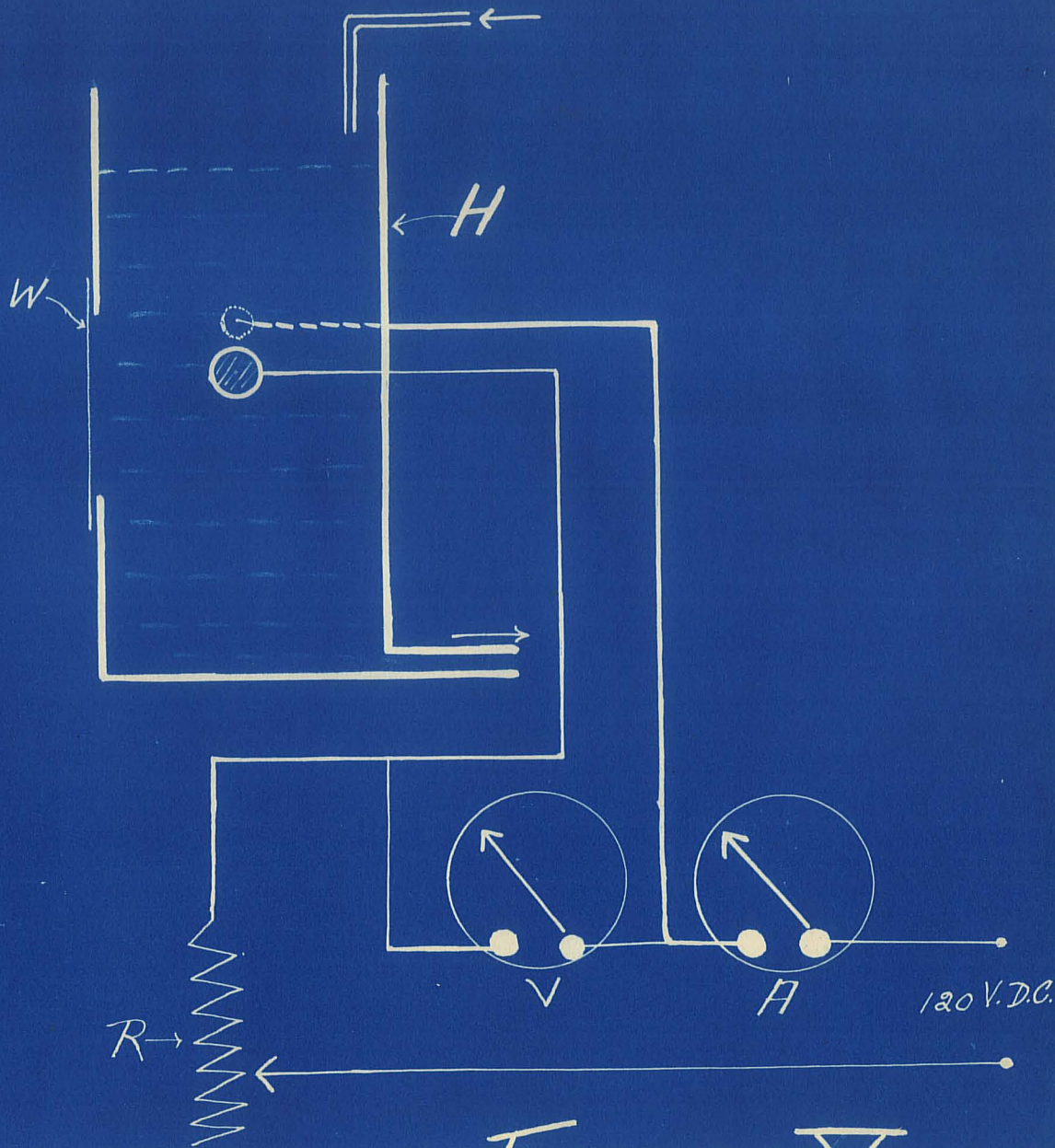
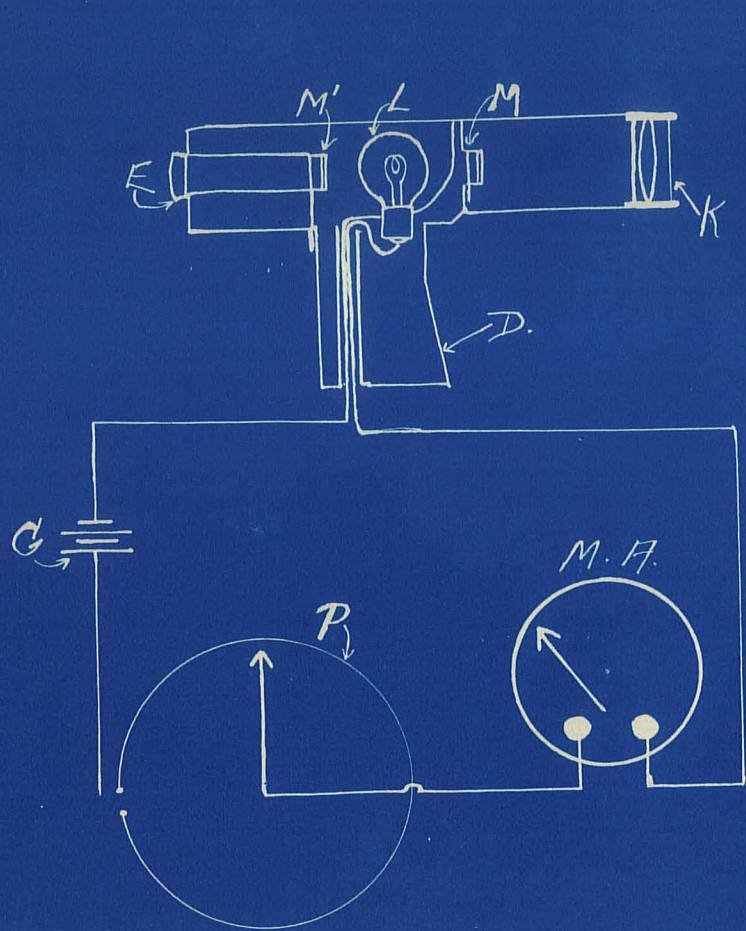


FIGURE V.

1. Method of Measurement:

In recent researches the Optical Pyrometer has been shown to give very satisfactory results when employed to measure high temperatures. In this work a "Holborn and Kurlbaum" type was used, illustrated diagrammatically in Figure 5. The instrument was housed in the case D in which the lamp L was rigidly mounted; by means of a lens system the light coming through K passes through M past the lamp L, through  $M^1$  to the eyepiece telescope E. M and  $M^1$  are monochromatic filters and limit the light received on the eye to a very narrow range of wavelengths. The hot source will appear as a bright disc of red light to the eye, and for the instrument to function properly the source should be large enough to fill the "objective". By means of the fine resistance P the current flowing to the lamp from the dry cells G can be adjusted, being observed by means of the milliammeter M.A. In this way the temperature of the lamp filament may be increased until it glows; it appears in the eyepiece as a red spiral. The instrument is factory calibrated so that when the color or intensity of the filament is the same as the uniform background due to the source the temperature of the latter may be read directly. Measurements may be made rapidly and accurately.

Since the calibration supplied did not extend into the temperature regions measured, it was necessary to increase the range. With this type of instrument a neutral absorption "filter" may be employed and extrapolation from the known calibration curve carried out employing Wien's law in modified form. Calibration of such a neutral white glass filter was carried up to 2000°C., a smooth curve being obtained; the plate was rigidly clamped in front of the instrument and is shown in the diagram as "F". The carbon arc in air was then measured, and its temperature taken as 3500°C., this being the accepted value for the crater. The curve could then be continued to this point, and to verify the soundness of this method the formula of Pirani and Meyer, as cited by Burgess and LeChatellier<sup>47</sup> was applied. It was found to agree to within 100° (maximum error) and this accuracy was sufficient since comparative temperatures rather than absolute values were desired.

The discharges were operated in the vessel H, and in the diagram the electrodes are perpendicular to the plane of the paper. The vessel was fitted with a very thin mica window W through which the discharge was observed. About one liter of water was employed and in certain cases circulation was used, as shown in the Figure; in other tests a burner was used to keep the water at a high temperature. The power supply was adjusted by the resistance R and current and voltage observed on the meters A and V.

The arc was hand operated with horizontally opposed electrodes held close to the window, and all measurements were made with the pyrometer the same distance from the arc as from the calibration sources. Because of the small size of the arc region it was not possible to discriminate between cathode and anode temperatures. The arc was viewed at right angles to the electrodes and no difference in the temperature throughout the brilliant source spot could be detected by the instrument. It is therefore evident that whatever temperature gradient may exist in these arcs, the mean temperature was the value measured.

-----

2. Experimental Results:

Three groups of tests were carried out, separately discussed below.

(a) It was very soon observed that the temperature of the discharge was dependent upon the temperature of the water medium; the relationship was then studied, with various electrode materials. In the following tables and curves the capital letters indicate the type of carbon employed, as below:

- |          |                                     |
|----------|-------------------------------------|
| "A"----- | Soft, cerium core.                  |
| "B"----- | Hard, no core.                      |
| "C"----- | Soft, Al, Ni, Fe, Si core (oxides). |
| "D"----- | Soft, no core.                      |
| "E"----- | Soft, strontium core.               |



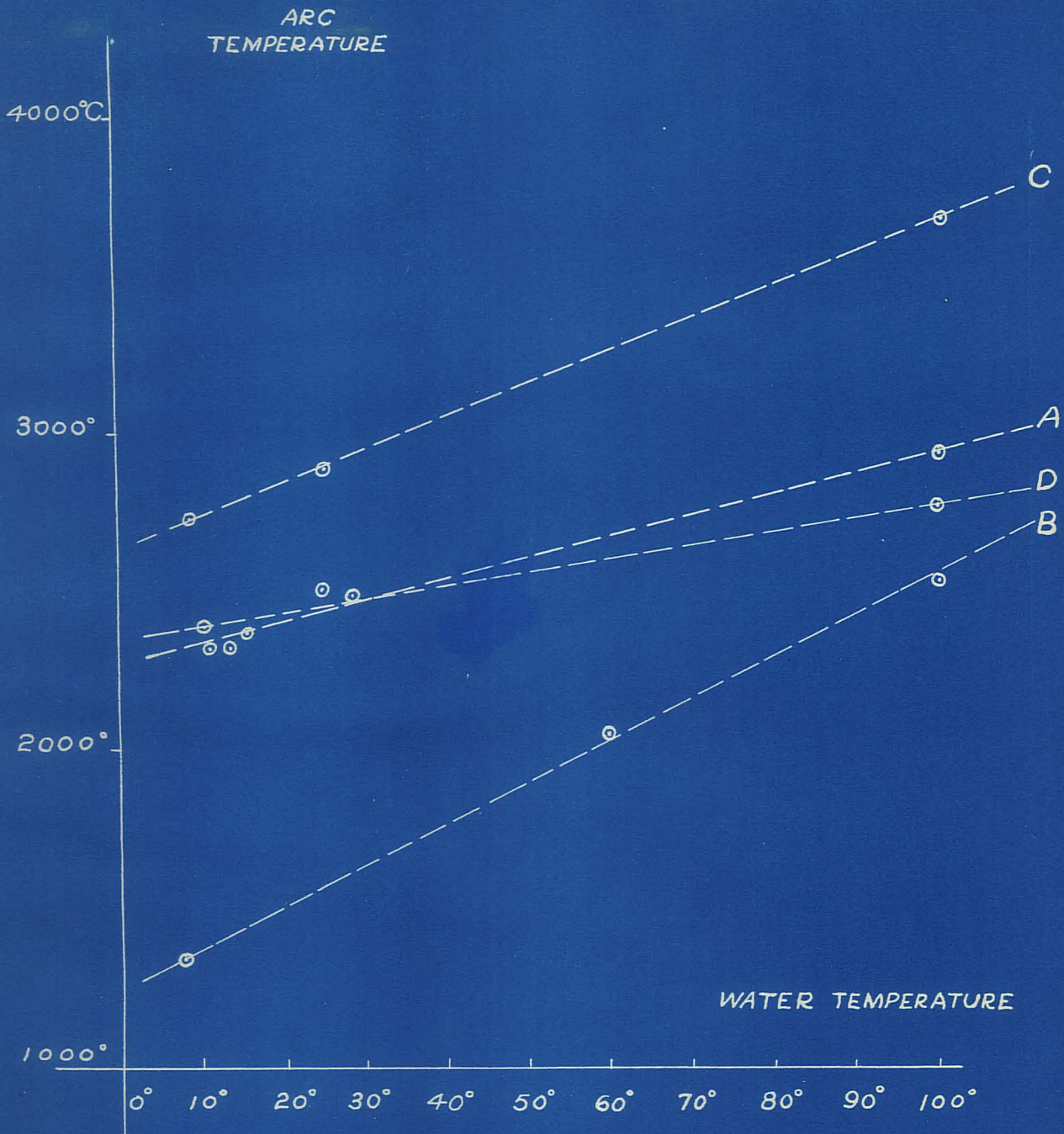


FIGURE VI

T A B L E (6).

	Water Temperature.	Arc Temperature.
	8°C.	1325°C.
"B"	60°	2025°
	100°	2500°
	11°	2300°
"A"	25°	2525°
	100°	2725°
	14°	2300°
"D"	25°	2500°
	100°	2925°
	8°	2700°
"C"	25°	2750°
	100°	3625°

In Figure (6) the above data are expressed graphically; these curves are not intended to represent exact mathematical relationships, but merely to serve as convenient representations of the effect of water temperature upon the discharge temperature. It is seen that a 1500° rise is the general effect when the temperature of the water is raised from 5° to 100°C. The hard type of electrode gave considerably lower temperatures than the soft variety.

(b) In the above tests the power, current and voltage supplied to the arcs was approximately constant. It was found that the voltage affected the arc temperature, so that care had to <sup>be</sup> taken to keep this steady for comparative results. Later work has shown that the current, and not the voltage may be the significant factor; however, the results obtained by varying the voltage with constant water temperature are given below. The interesting question as to whether the arc temperature (governed by current, voltage or wattage) affects the chemical reactions, or whether the reverse is true, will be discussed later.

The voltages given in the following Table (7) and plotted against temperature in Figure (7) were not accurately measured, due to arc fluctuation; they are however, relatively significant taken as a group. In each case the series resistance was altered to correspond to the voltage read on the meters with a constant resistance in place of the arc, the back E.M.F. being allowed for, and in this way the voltages used in the Table and curves were obtained.

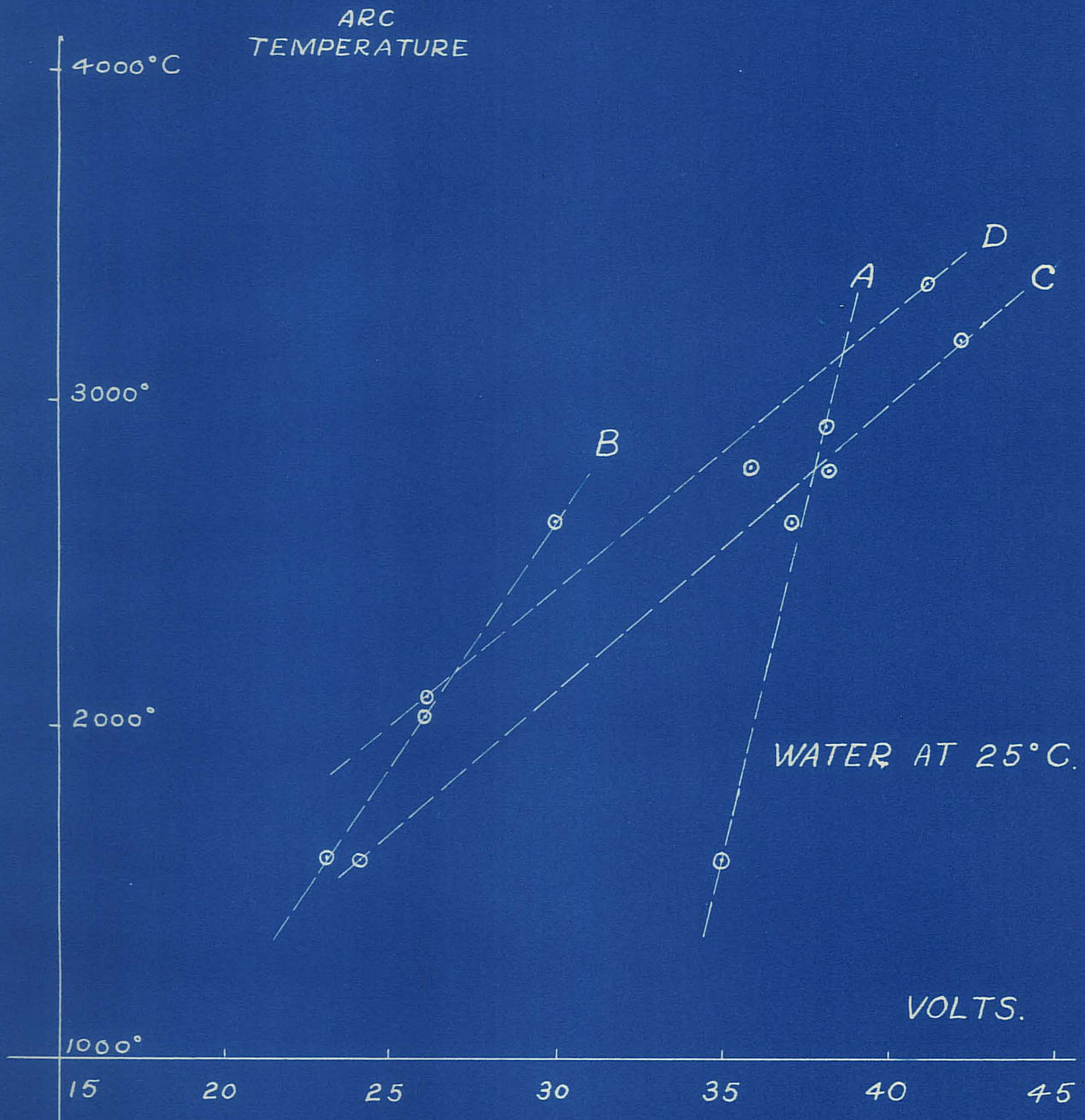


FIGURE VII

T A B L E (7).

	Arc Voltage.	Arc Temperature.
	23 volts.	1600° C.
"B"	26 "	2025°
	30 "	2625°
	35 "	1600°
"A"	37 "	2625°
	38 "	2925°
	26 "	2025°
"D"	37 "	2775°
	41 "	3350°
	24 "	1600°
"C"	38 "	2725°
	42 "	3225°

(Water Temperature constant at about 25°C.)

Figure (8), from the data in the following Table (8) is similar to the last curve discussed, but in this case the water temperature was kept at 100°C. by constant boiling; the heat was supplied by the arc itself and in certain cases by an outside burner. For corresponding electrodes the rise in arc temperature is about the same as that exhibited in Figure (7) where the water was about 75° cooler, although the actual arc temperatures are in general much higher.

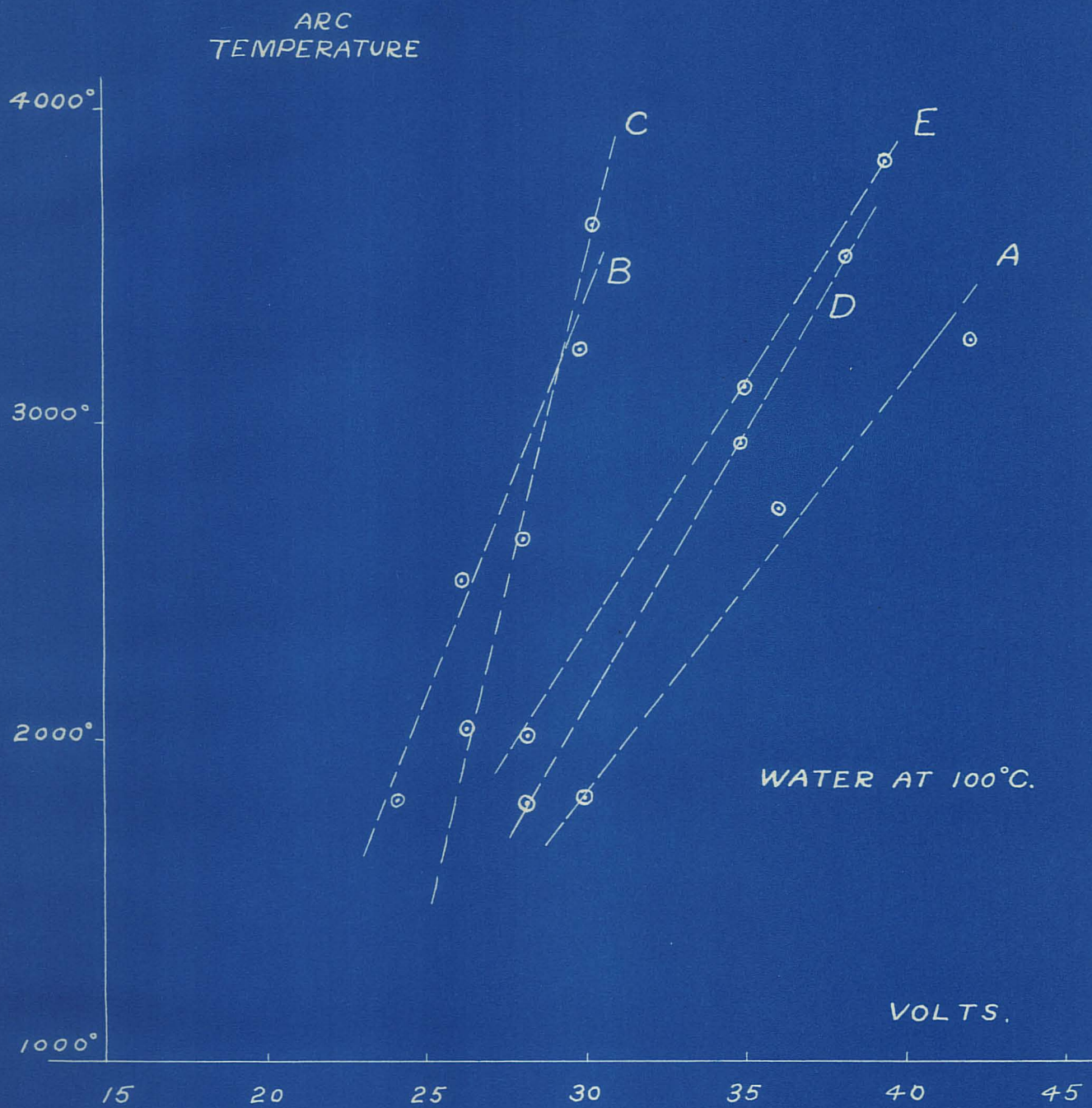


FIGURE VIII

TABLE (8).

	Arc Voltage.	Arc Temperature.
	24 volts.	1800°C.
"B"	26 "	2500°
	30 "	3225°
	30 "	1800°
"A"	36 "	2725°
	42 "	3225°
	28 "	1800°
"D"	35 "	2925°
	38 "	3500°
	26 "	2025°
"C"	28 "	2625°
	30 "	3625°
	28 "	2000°
"E"	35 "	3100°
	40 "	3650°

(Water Temperature constant at 100°C.)

-----

The lowest temperature measured was 1300°C. with a hard uncored carbon arc at 25 volts, the water temperature being 8°C. Soft "graphite" electrodes with a strontium core gave the highest temperature, viz. 3600°C. arcing at

40 volts with the water boiling. Some thirty measurements were made between these two extremes, in steps of  $75^{\circ}$ . The core substances have some effect upon the arc temperature, but the latter is greatly affected by the quality of the carbon. Under the same conditions of voltage and water temperature the hard or "projector" carbons gave the lowest, and the soft carbons the highest temperature readings.

-----

(c) Since the sensitivity of the instrument used was lessened by the addition of the neutral filter, the temperatures read have probably a maximum error of  $100^{\circ}\text{C}$ . It is not unlikely that the high temperatures measured were actually somewhat lower than the true arc temperatures, since the water diffused the light somewhat, and no correction was made for this. The temperature of  $3500^{\circ}\text{C}$ . used in calibrating the instrument was obtained with pure uncored carbon arc and a low D.C. voltage. The fact that a temperature of  $3600^{\circ}\text{C}$ . was observed with cored graphite rods under water, with a high<sup>er</sup> voltage than in the above, does not show that the under water measurements are in error, for cored rods of this sort are known to give a hotter arc than uncored types. At present it seems not unlikely that much higher temperatures are obtainable with the under water arc than with the air arc, for reasons which will be subsequently given.

---



S U M M A R Y:

(1) An Optical Pyrometer was calibrated for measurement of high temperatures by a method which was apparently accurate.

(2) The under water arc discharge temperature was found to vary greatly with the water temperature; the approximate relationship was determined for several types of carbon electrodes.

(3) Voltage also affects the temperature; two sets of determinations were made, one with the water at room temperature and the other with boiling water. The results are expressed graphically solely for convenience and the curves are not held to be significant.

(4) The maximum experimental error involved was probably less than  $100^{\circ}\text{C}.$ , but this does not take into account the method of calibration which might represent a constant plus or minus error.

-----

E. Effect of Water Temperature.

Perhaps the most striking characteristic of the discharge outlined here is the series of changes which take place when the temperature of the water is raised from room temperature to boiling point. These changes are not abrupt but gradual, and are particularly noticeable past 60°C. At first it appears as though the reactions become much more extensive at higher temperatures, that is to say much more gas is evolved; the arc stability does definitely increase with rising temperature.

In consideration of any comprehensive theory of the arc mechanism the purely physical aspects of the effect of the surrounding water must be taken into account; this effect must be practically independent of the chemical reactions, if not entirely so. On the other hand it is of greatest importance to determine whether or not the various physical factors affect the reactions; the experiments outlined in this section were done with the object of settling this question.

-----

1. Apparatus:

The apparatus first used was extremely simple and is not illustrated. The electrodes were clamped in a large vessel of water, the temperature of which was regulated to within 1°C. by means of a large electric heating coil. One of the electrodes was flexibly mounted so that hand manipulation was possible. The gases evolved were collected by displacement of water in a measuring cylinder held directly above the arc; this cylinder could be refilled with water after each run by means of a small hand pump. The measuring error was less than 2% and to average the errors due to irregularities in the arc operation (the largest source of error) ten or more tests were run at each temperature.

-----

2. Experimental Results:

As the temperature of the water approaches the boiling point the vapour pressure rises rapidly and the evolved gas mixture becomes richer in water vapour; since the power supplied to the arc was constant the rate of evolution of water vapour would be dependent solely upon the vapour pressure. Therefore, if there was no change in the rate of the chemical reactions with water temperature rise, the volumes of "gas-water-vapour" mixture evolved should have been directly proportional to the vapour pressure.

TABLE (9).

Water Temperature.	Rate of Flow: Gas-Vapour Mixture.	
4°C.	225 ccs./minute.	
7	225	"
13	215	"
16	250	"
20	300	"
26	260	"
29	325	"
34	275	"
41	375	"
43	300	"
52	375	"
55	400	"
61	410	"
63	390	"
70	400	"
75	410	"
82	450	"
83	600	"
85	650	"
90	1100	"
91	1250	"
97	2900	"

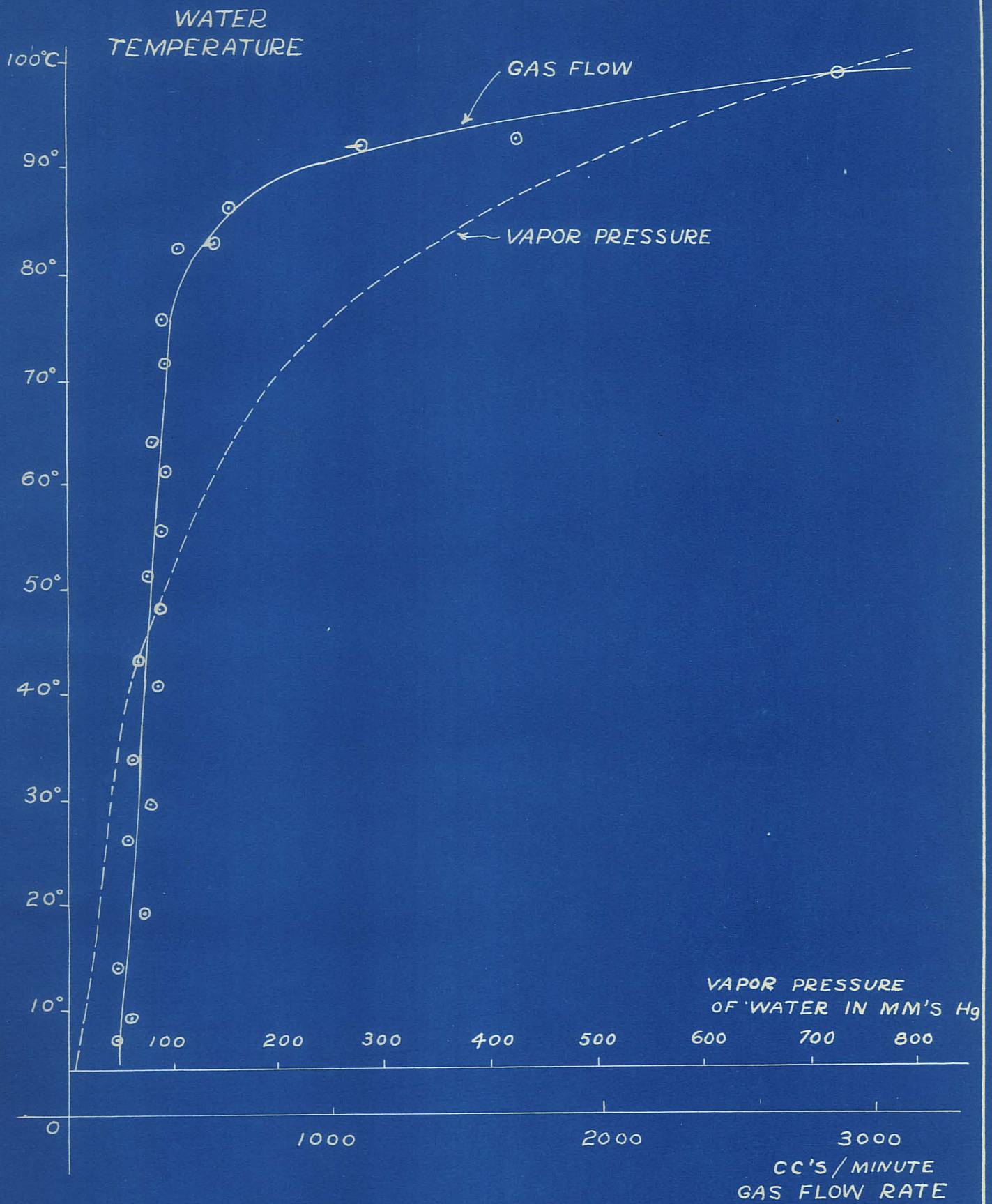


FIGURE IX.

Figure (9) gives the data in graphical form. It is seen that the curve is not perfectly regular, but exhibits a marked increased gas-vapour flow near the boiling point. In the same Figure is drawn the vapour pressure curve for water, the two curves having a common abscissae. The increase in the gas flow is not entirely accounted for by the increase in the partial pressure of the water in the mixtures collected.

-----

### 3. Collection at Constant Temperature:

In this series of tests the discharge was operated in a closed vessel, at a controlled temperature, and the gaseous products led to a separate collection vessel the temperature of which was kept constant during a group of tests. Temperatures up to 120° C. were obtained by application of pressure in an apparatus which will be described later. The results are given in Table (10) and are plotted in Figure (10). There is a considerable increase in the rate of the reaction as the water temperature approaches the boiling point, as evidenced by the increasing gas flow rate, but the curve indicates that past 100° C. there is little further rise.

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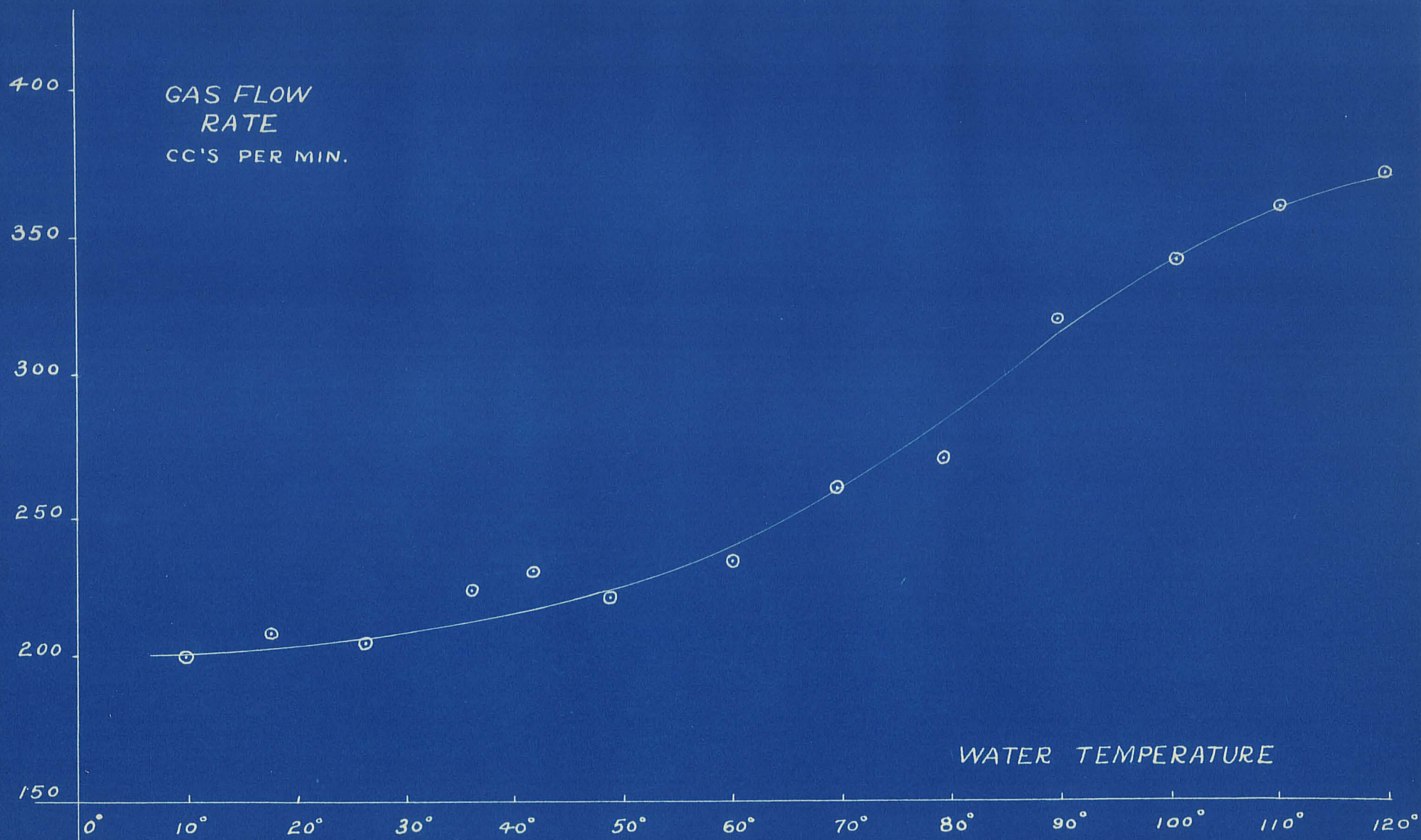


FIGURE X.



TABLE (10).

Water Temperature.	Rate of Flow of Gases.
10° C.	200 ccs./minute.
18°	210 "
27°	200 "
36°	225 "
42°	230 "
49°	220 "
60°	235 "
70°	260 "
80°	270 "
90°	320 "
100°	340 "
110°	360 "
120°	370 "

A discussion of these results is reserved for  
a later Section.

-----

S U M M A R Y:

Study of the effect of the temperature of the surrounding water upon the discharge action has yielded the following results:

(1) The considerable change in the appearance of the discharge with the approach of the boiling point of the water is largely due to the evolution of large quantities of water vapour mixed with the gaseous products.

(2) The increase in vapour pressure with rise in temperature of the water was found to be insufficient to explain the increase in rate of evolution of the gas-vapour mixture.

(3) By removing the water vapour the gaseous products were measured free from water vapour effects; there was found a considerable increase in the rate of production of the gases up to  $100^{\circ}\text{C.}$ , but the flow rates past this point, obtained by addition of pressure, showed little increase.

-----

F. Effect of Pressure.

In the tests outlined above a pressure of about one atmosphere was applied in order that the water temperature could be raised above the boiling point. The effect of the pressure was apparently nil. It seemed advisable to continue at higher pressures, since this factor is of great theoretical interest in all gas reactions. From a practical standpoint it was more feasible to increase the pressure, rather than decrease it below atmospheric; furthermore, an infinite pressure increase is theoretically possible, giving a greater range for the observation of any changes, whereas the lower limit of pressure with this discharge is the vapour pressure of water.

Pressure effect is intimately connected with the physical cooling effect of the water, since pressure raises the boiling point greatly. The importance of this will be discussed later.

-----

1. Apparatus:

All experiments so far described were done with hand manipulated arcs, this type having proven most stable and easily controlled. Operation at high pressure naturally precluded any such arrangement so that a self adjusting, or externally adjusted arc was necessary. It has been noted previously that the discharge employed was very sensitive and careful manipulation was essential if the current and voltage were to be kept steady; hence the substitution of mechanical control for "hand and eye" operation presented a problem.

Two general types of control were developed; in the first the two electrodes were fixed to small carriages sliding on rails, and held separated by small springs. A chain and drum device brought the ends together and the adjustment was very fine, so that the length of the arc could be carefully controlled; pressure on the ends, which is sometimes required, could also be obtained easily. The drum was connected to the outside control handle by means of a specially machined drive shaft, which gave easy control and at the same time effectually sealed the pressure.

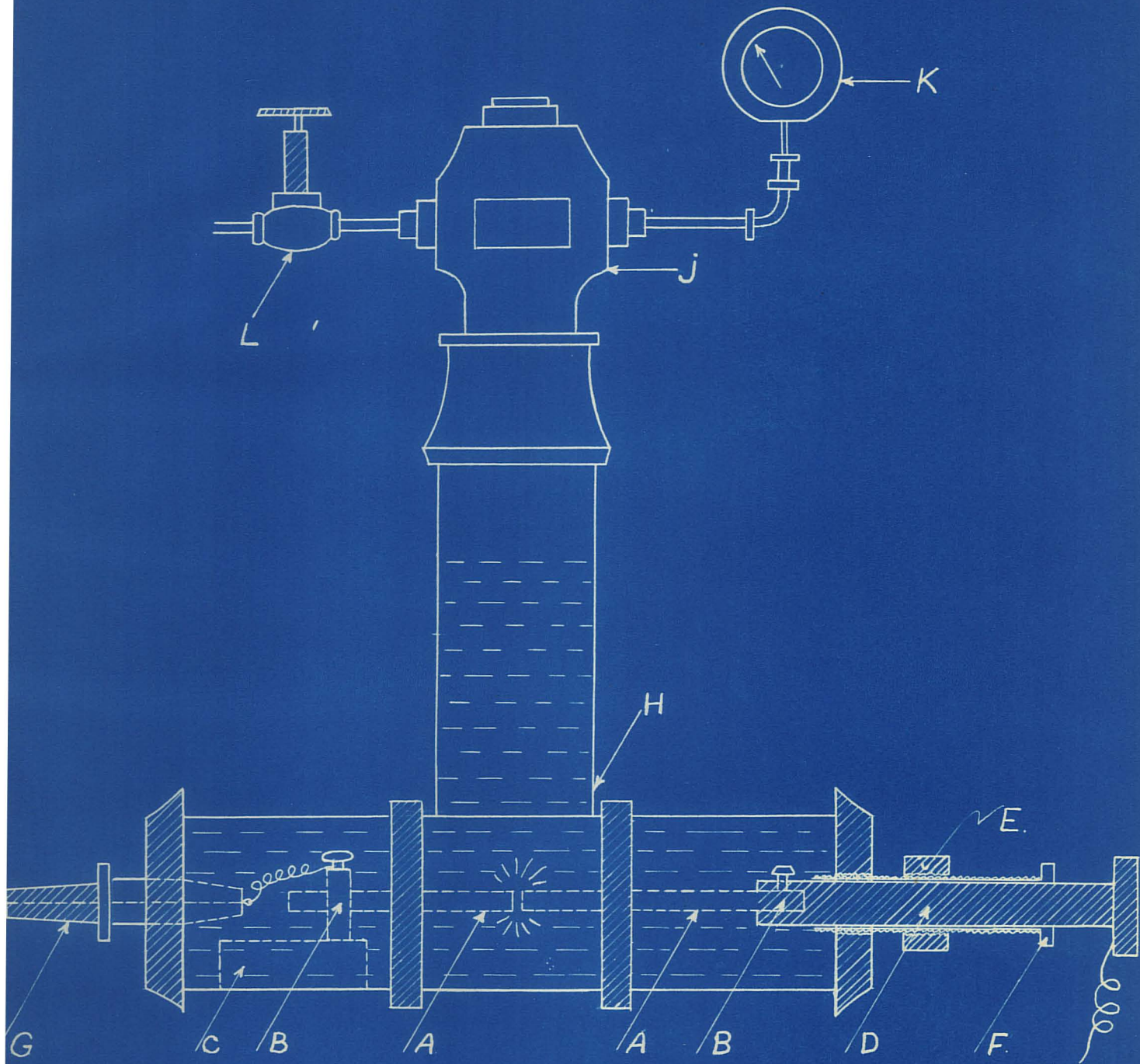


FIGURE XI

The dilute acids formed in the discharge, together with electrolytic effects, are very corrosive, so that the apparatus just described had to be frequently removed and cleaned. Apart from this, it gave satisfactory service. It was found possible however, by employing heavier currents, to maintain an arc which was less susceptible to the effects of electrode wear and consequently much more stable. In Figure 11 is shown the complete apparatus used in the pressure tests, including the arc adjusting device for use with heavier currents.

The electrodes A-A were clamped in two holders B-B the left one being immovably set in a block of cast cement C. The right electrode holder formed the movable rod D which passed through a machined gland E; at all pressures employed the joint was kept gas tight by screwing in the pressure nut F, which forced the asbestos-graphite sealing material against D. One side of the current was connected directly to the end of D, the other being sent through the conductor G. This was made from a heavy duty aviation type "spark-plug", such a device forming a very convenient means of conducting heavy currents through a wall in any apparatus in which high pressures must be maintained without leakage. Inside the apparatus a wire carried the current from the plug to the clamp B.

The main casing of the apparatus was made of high pressure steam piping (wrought iron) with asbestos graphite

packing throughout. The joint at H was specially fitted to make frequent opening of the casing possible; ordinary pipe threads were found to break down on repeated using. The tower extending from H to J formed the gas chamber, the volume of which could be conveniently altered by adjustment of the level of the water. The pressure guage K and high pressure valve L were of ordinary construction.

With this apparatus pressures up to 400 pounds per square inch were employed, although this was slightly over the safety limit. Above 300 pounds it was necessary to employ a screw device to feed in the electrode holder D against the pressure inside; otherwise, no difficulties were encountered once this simplified form was constructed. Apparently any pressure whatever may be developed, as with electrolytic gas production, since with the tower J filled almost completely with water 400 pounds pressure could be attained in one minute or less.

The cement block G required frequent renewal, being reduced to a soft mass by the corrosive action of the liquid and stray currents. Cement proved to be a convenient means of insulating the connector B from the casing metal, the latter being in electrical contact with the rod D.

-----



## 2. Experimental Results:

At pressures over five atmospheres the characteristics of the arc underwent some changes; the sound emitted and the mechanical vibration of the heavy apparatus (weight about 75 pounds) increased greatly. This effect lessened and finally disappeared when the pressure was increased to eight atmospheres. Visual observation of the arc was attempted by means of heavy lenses set into the side of the casing, but no conclusive observations were made because of the intense illumination.

To insure perfect constancy in all operating factors it was thought advisable to run pressure tests from lower to higher limit at a single experimental period; a convenient way of doing this was to observe the rise in pressure per unit time, since a uniform rise indicates a constant mass of gas produced, assuming the Gas Laws to hold. The result obtained is shown graphically in Figure 12, where pressure rise is plotted against time of arc operation. All readings were taken in a single run without altering the input power, water temperature or other conditions. The curve is quite linear, indicating that the amount of gas produced was independent of the pressure within the limits used. The data used in this curve is given in the following Table.

200  
150  
100  
50  
0

PRESSURE IN POUNDS  
PER SQUARE INCH

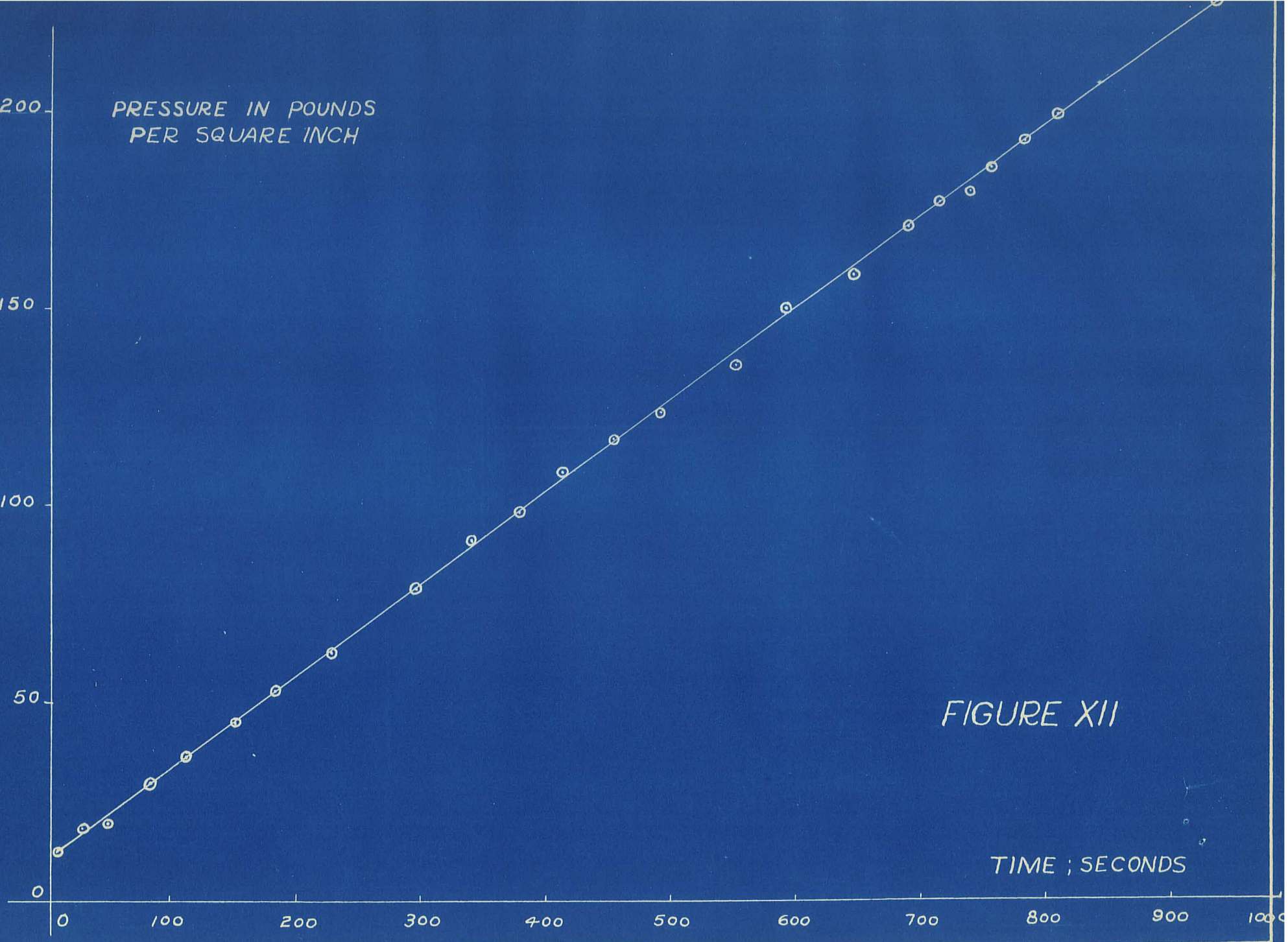


FIGURE XII

TIME ; SECONDS

1000

T A B L E (12).

Elapsed Time.		Pressure.
(Start)	0 seconds.	10 pounds/square inch.
	50	15
	60	17
	75	20
	110	30
	145	35
	195	42
	230	50
	275	57
	340	58
	360	72
	375	77
	395	85
	450	92
	495	98
	525	106
	575	118
	650	125
	720	135
	730	141
	770	152
	810	158
	835	165
	880	175
	940	180
	1040	205

As a check on these results tests were run at pressures throughout the range of Table (12), in which the gas evolved was expanded to atmospheric pressure and the volume measured at constant temperature. From atmospheric pressure to 23 atmospheres the volume of gas evolved per unit time did not vary more than 5% from the mean, and there was no regularity in the fluctuation.

It is evident that pressure has little if any effect upon the production of gaseous products; this is significant both in regard to the chemical reactions and the physical factors affecting the arc operation in liquid medium.

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Discussion of these results is reserved for a later Section.

-----

S U M M A R Y:

Determination of the effect of pressure upon the discharge has been discussed as follows:

(1) An apparatus capable of standing pressures up to 30 atmospheres, providing for discharge operation at all pressures with a minimum of interruption, was developed.

(2) The rise in pressure per unit time with the discharge operating in a sealed system was determined, the relationship being perfectly linear up to 20 atmospheres.

(3) Direct collection experiments showed that the above tests indicated a constant mass of gas evolved per unit time, regardless of pressure, within the limit of error of the measurements.

-----

G. Discharge Spectra.

An attempt was made to obtain spectroscopic evidence which might give some information as to the mechanism of the reactions taking place in the discharge; this was unsuccessful. The results, which at present do not appear to be of particular significance, are briefly outlined below.

-----

A standard glass prism Hilger spectrometer was employed, using extra fast Kodak plates. The discharges were operated in a metal vessel with a thin mica window and exposures of from 10 seconds to 20 minutes were made; standard helium, hydrogen and mercury tubes were used for comparison purposes, and the lines were measured by means of a travelling microscope.

Liveing and Dewar<sup>6</sup> found the hydrogen and so-called "water" spectrum prominent in spark discharges in water and water vapour; they always obtained brilliant hydrogen lines when water was "dropped into the electric arc". The discharge operated in water however, yields no such spectra when carbon electrodes are employed; no indication of hydrogen lines was ever observed on the plate, so that the discharge must be of different nature to the air arc as employed by the above workers.

In agreement with Konen<sup>7</sup> two calcium lines 3934 and 3969 Å were observed in all under water carbon arcs; except those with pure mercury electrodes, metal arcs gave faint lines

at these positions.

Copper electrodes in pure water gave brilliant hydrogen red and blue lines (wavelengths 4861 and 6563 Å), but this was the only direct indication of the effect of the water.

Carbon electrodes gave a much weaker continuous spectrum when operated in water than when in air, for a given intensity of the prominent lines; reversals were frequent, as has been observed by numerous investigators.

No definite conclusions have been obtained from this work.

-----



H. Current, Potential and Energy Relationships.

In the last three years there has been a widespread effort to relate the current factor in some way to the extent of the chemical reactions taking place in various discharges. Numerous workers claim very definite relationships have been established in this connection; among these may be mentioned Linder<sup>32</sup>, Bodenstein<sup>31</sup> and Brewer and Westhaver<sup>50</sup>, working with very different reactions. The results of these investigators appear the more interesting when it is recalled that workers at the beginning of this century were unanimous in their decision that the current played little if any part in discharge reactions.

With the development of the theory of ionisation potentials there grew up the opinion that voltage was the controlling factor in discharge reactions; Wansbrough-Jones<sup>48</sup> and Lozier<sup>49</sup> conducted researches along this line. While the importance of voltage is now fully realised, it must be remembered that most discharges operate with space potentials far above the voltage required to produce the ions of almost any substance which may be present. Recent work has been directed, therefore, towards obtaining some explanation for the pronounced effects occurring with potentials higher than the ionising value, without in any way discrediting the established theory that the production of ions is the primary essential.

As mentioned previously Lob claimed that the action of the carbon arc in water was of a purely thermal nature, without advancing any experimental proof. Preliminary work showed that a "water gas equilibrium", which might be suspected from the presence of carbon dioxide, monoxide and hydrogen in the gaseous products, was hardly probable, so that a search for possible electrical effects seemed indicated.

A study of the three factors current, voltage and wattage, insofar as they affect the rate of the chemical reactions taking place in the under water discharge, was made and the evidence obtained is outlined below.

-----

1. Apparatus:

It was decided to employ the method of investigation outlined in Section "C", Part (2), that is to say the principle of measuring all the factors simultaneously during a period of steady arc action. A convenient method of measuring the reaction rate rapidly involves the use of a sensitive flowmeter; this procedure was found to be satisfactory.

The type of flowmeter employed was essentially the same as that discussed very fully by Benton<sup>51</sup>; it was of very simple construction, being made up of a capillary tube and long manometer tubes. By the use of flexible connections

several capillaries were interchangeable, greatly extending the sensitivity range of the device. Water was used in the manometer for the smallest flow rates; Nujol or similar oil is recommended by some, but oils have a high viscosity and give sluggish response in the monometer. For the highest flow range a short capillary (and mercury manometer) was found best. Calibration was carried out with an air stream, volumes being measured by water displacement and time with a stop watch; perfectly linear curves were obtained and in no case was the "turbulence" condition reached.

The current and voltage factors were observed on ordinary meters so placed that almost simultaneous observation of meters and flowmeters was possible; no time or other measurements were required.

-----

## 2. Experimental Results:

(a) The effect of current upon the reactions was accurately determined when it was found that the voltage across the under water carbon arc could be kept constant to within 1 volt, by proper manipulation and control of the length of the discharge; to insure uniformity of conditions all tests were made with the water brought to vigorous boiling by an auxiliary heating coil.

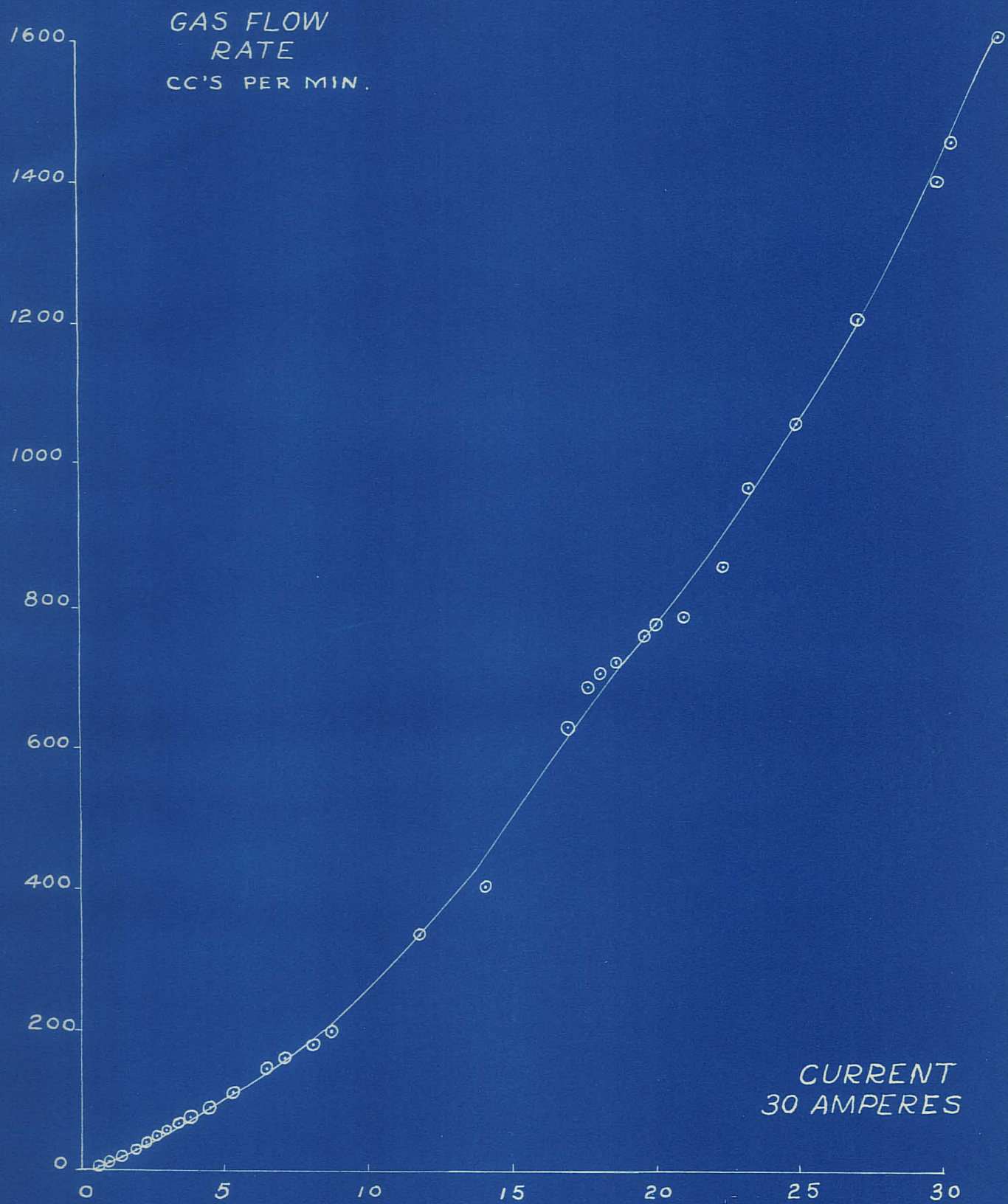


FIGURE XIII

The line resistance was altered to give currents from about 1 ampere to 32 amperes, the voltage being constant at 26 volts approximately; it appeared that this potential was peculiarly suitable for constant measurements. The electrodes employed were soft carbon copper-plated to within one centimeter of the arc; in this manner the electrical energy was conducted with negligible loss right up to the region of discharge, so that potential falls along the electrodes were eliminated.

In Figure (13) the results are represented graphically, the current being plotted against the rate of flow of the gaseous products. This curve noticeably slopes towards the vertical axis, but appears to be quite smooth, and a marked relationship between the gas flow and current is apparent. Since the voltage was constant in these tests any potential effects may be assumed to be constant.

The data used in this curve will be found in the table on the following page.

-----

T A B L E (13).

Discharge Current.	Rate of Gas Flow.
1.8 Amperes.	30 ccs./minute.
2.2	37
2.4	38
2.8	45
3.4	50
3.6	64
4.4	85
5.0	115
6.4	145
7.0	157
8.0	172
8.6	237
11.5	350
14.0	400
15.0	500
17.0	625
17.5	675
18.0	700

(continued--next page)

T A B L E (13)-(continued).

Discharge Current.	Rate of Gas Flow.
18.5 Amperes.	715 ccs./minute.
19.5	750
20.0	760
21.0	775
22.0	850
23.0	975
25.0	1050
27.0	1200
30.0	1400
30.5	1450
32.0	1500

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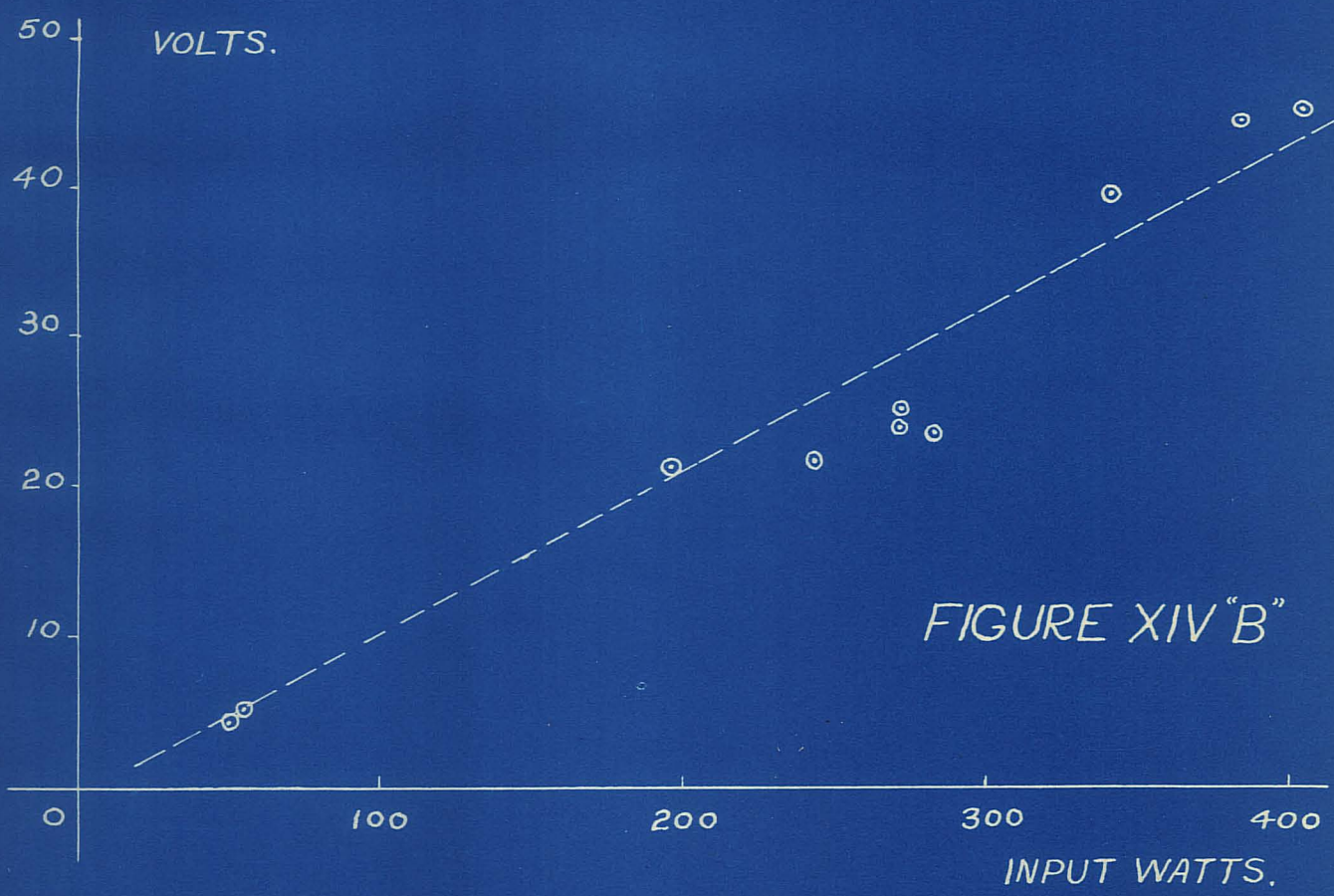
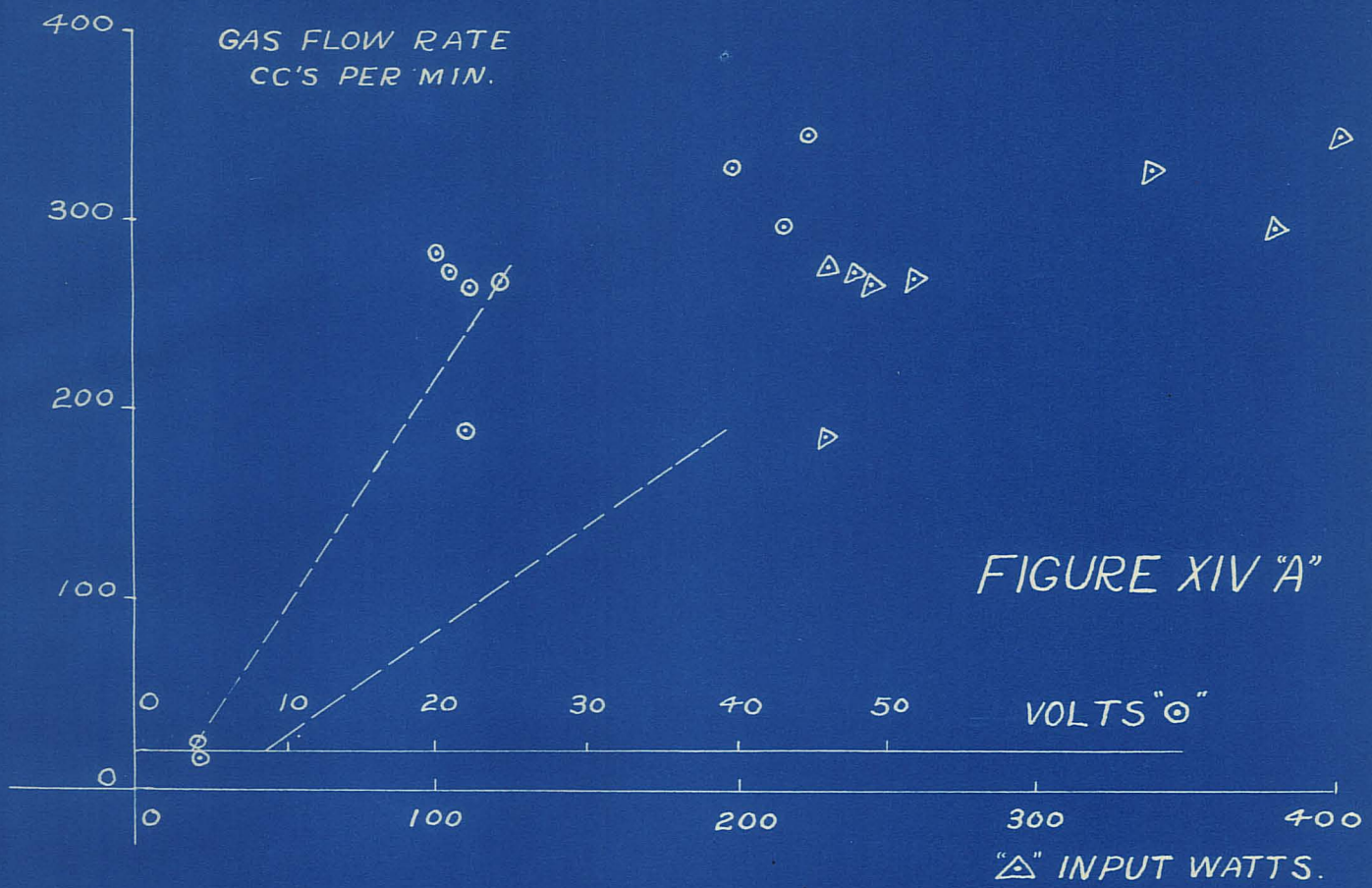
By keeping the line resistance constant and varying the length of the discharge it was found possible to vary the potential across the arc over a considerable range; the current however, also changed with the voltage, and could not be kept constant. It was believed that a series of readings of this sort would give definite indication of the effect, if any, of voltage upon the discharge, provided that the previously determined effect of current were kept in mind. In discriminating between the "thermal" and "electrical" discharge theories it is of importance also to consider the power or wattage factor, since this represents energy developed in the discharge.

Experiments of this sort were carried out with the same apparatus described in the current tests section; the gas flow was measured by means of the flowmeter and the current and voltage direction meters. It is important to record that no voltages intermediate between 4 volts (approx.) and 20 volts (approx.) could be obtained with the carbon arc; it is believed that the lower potential is obtained only with a "shorted" arc which is entirely different in physical and chemical nature to the "contact" arc, although both are secured with the electrodes in apparent contact. A discussion of this point will be given later.

In the following Table are given the data used in drawing Figures 14A and 14B. They are typical of several different runs with various line resistances; all readings were obtained by variation of the arc length only, and the temperature, pressure, electrodes, etc. were the same in each case.

T A B L E (14) .

Discharge Current.	Discharge Potential.	Input Wattage.	Rate of Gas Flow.
8.5 Amperes	40 volts	340 watts	332 ccs./minute.
8.7	44	382	300
9.0	45	405	350
10.2	24	245	270
10.3	23	236	282
10.4	22	229	192
10.4	25	260	270
11.0	22	242	275
12.5	4	50	15
12.8	4	52	18



It is evident that no curve could be drawn for the points given in Figure 14A, in which the Gas Flow Rate is plotted against both voltage and wattage; a clear relationship is however, evident between the voltage and wattage. This is shown graphically in Figure 14B. Within the experimental error the equation of the curve is simply:

$$W = k.V,$$

where W is the input wattage and V the voltage across the arc.

It is obvious that within the range 20 to 40 volts the potential across the discharge has no effect upon the rate of chemical reaction taking place in it; however it is most probable that a minimum voltage is required to maintain a true under water arc. This "critical potential" is perhaps the value necessary to give a space potential sufficiently great to produce the ions which play a fundamental part in the arc.

-----

A general discussion of all the experimental work presented here follows in the next Section.

-----

S U M M A R Y:

Experiments on the effect of current, voltage and wattage upon the discharge reactions have made possible the following conclusions:

1. An almost direct relationship exists between the discharge current and the "rate" of chemical reactions taking place in the arc.
  2. A certain critical voltage is required to produce true arcing under water; above this potential the chemical reactions are entirely independent of voltage in the range studied.
  3. The chemical reactions are quite independent of the input wattage providing this be sufficient to maintain the arc.
-

THEORETICAL DISCUSSION.

Many careful studies have been made of simple reactions such as the dissociation of water vapour and the synthesis of ammonia gas, taking place in easily controlled "glow" discharges, and yet it may be said that at present there is no completely satisfactory theory to account for all of the observed facts; nor is it probable that all the important factors have been investigated. Bearing this in mind, no attempt will be made here to advance a comprehensive theory of the operation of the low tension arc discharge in water; it is fully realised that the experimental work in this connection is far from complete.

The low tension arc, even when operating in a vacuum, still presents a serious problem for the physicist; an investigation of chemical effects which may take place in such a discharge is therefore hampered by the lack of knowledge of the purely electrical aspect of its operation. Furthermore we must consider that when the electrodes are involved in the reactions we are faced with a double complication: first, the electrical characteristics may be completely changed, particularly as regards the effect of thermal electron emission; and second, any chemical changes which take place as a result of the electrical effects of the discharge may be "masked" or altered by subsequent reactions of the primary products with the electrode

materials.

But these are not the only difficulties; with the under water discharge it was soon found that the liquid medium has a very great effect upon the discharge action and upon the reactions taking place in it. The chemical energies involved are small compared to the heat given to the water. The arc temperature is very high over a considerable region, yet there is a relatively very cold region in close proximity to the electrodes.

The study of the discharge mechanism became naturally divided into two branches: the physical effect of the liquid medium, and the chemical reactions; this division is followed in the following discussion.

-----



1. Physical Effects of the Surrounding Medium:

With the arc in liquid water a high temperature is produced when the electrodes are brought together, due to the great resistance of the irregular ends, and the formation of steam follows immediately. The arcing no doubt takes place in steam and other gases, but separation of the electrodes is not necessary in order to maintain the discharge, as discussed previously. The most pronounced effect is the conversion of large amounts of electrical energy into heat, and the mechanism by which this change takes place will be considered first. The theory outlined here has been successful in explaining all the facts now available.

-----

(a) Temperature Gradients and Heat Exchange:

From the very high temperature in the arc region, which the pyrometer showed existed over a considerable space, to the surrounding water there must exist a well defined temperature gradient. For convenience assume the mean discharge temperature is  $3000^{\circ}\text{C}$ . and the water temperature  $0^{\circ}\text{C}$ . How is the transition made between these two extremes?

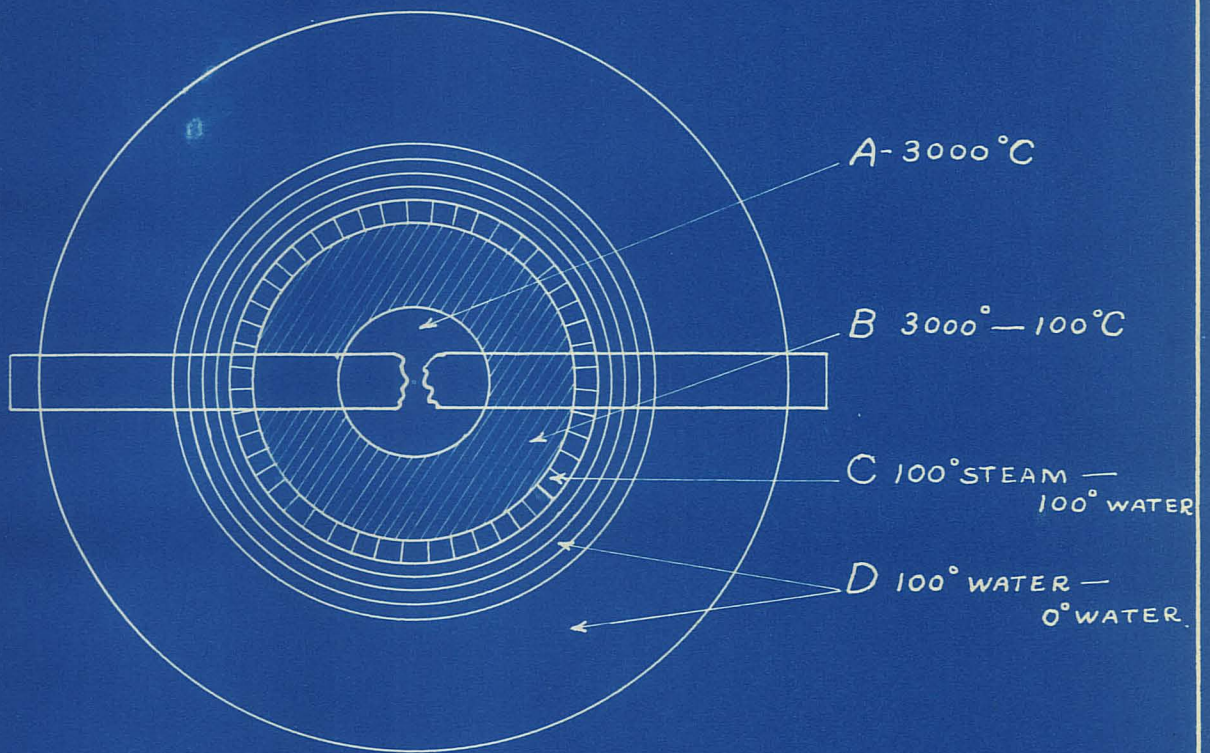


FIGURE XV.

In Figure 15 is shown a highly diagrammatic and "ideal" theoretical discharge region. Closely surrounding the electrodes is the region "A" assumed to be at  $3000^{\circ}\text{C}$ ., in which probably only gases exist, exclusive of water vapour. Adjoining this region, and represented by the area between the first and second circles is the region "B" containing water vapour and gases at temperatures ranging from that of "A" to  $100^{\circ}\text{C}$ ., the boiling point of water. It is an experimental fact that large amounts of heat are transmitted from "A" to the cold surrounding water (assumed to be at  $0^{\circ}\text{C}$ .). This transfer must take place via the region C, much enlarged in the sketch; in this heat energy is transferred from steam at  $100^{\circ}$  or a little higher, to water at  $100^{\circ}$ , that is to say the latent heat of vaporisation is supplied to an infinitely thin layer of water here. This water may or may not vaporise. It may, in theory, absorb an amount of heat insufficient to vaporise it and lose this again to the nearby cold water; but this is improbable, and the true condition is probably an alternation between vaporisation and condensation taking place at  $100^{\circ}$ .

The water at  $100^{\circ}$  considered above is in contact with a layer infinitely near this temperature, but slightly cooler; thus the change from water at  $100^{\circ}$  to water at  $0^{\circ}$  takes place in a continuous gradient, represented by the region "D".

It is known that large amounts of steam are produced near the discharge and escape from it; if the water is cold it condenses above the arc, but if the temperature is near the boiling point it escapes with the gases. Therefore the "static" heat exchange diagram of Figure 15 is not complete; we cannot consider that the region "B" is of constant size, made up always of the same vapour which merely transfers the heat to the region "C". Steam is being removed from "B" by chemical decomposition and by physical agitation and the sweeping effect of the escaping gases. This steam is supplied by the water in "D", vaporised in the region "C". Of course all these gradients may exist in a very small volume due to the violence of the gas and steam removal, and the relative sizes indicated in the Figure have no significance except for discussion.

We may now consider the rates of heat exchange in the various gradients. Conduction of heat from water at  $100^{\circ}$  to that at  $0^{\circ}$  involves a considerable time interval for the heat must "travel a distance". But conduction, or rather transference of heat from steam at  $100^{\circ}$  (kept at that temperature by a constant source of heat) to water at  $100^{\circ}$  can take place without any such time interval; the exchange can take place in an infinitely small region with large amounts of heat transferred without any rise in temperature.

It must be remembered that a very rapid heat exchange rate will be maintained in the gradient "B" because of the large difference in temperature (here assumed to be  $2900^{\circ}\text{C}.$ ); this follows directly from Newton's law of cooling. Therefore the region "C" has available heat which it may transmit to the water in contact with it, thus vaporising the latter, at a rate much greater than the water at "C" transmits heat to the neighboring layers and finally to the region "D" at  $0^{\circ}$ . This is the main assumption of the theory presented here.

It has been shown that only a small part of the energy absorbed by the discharge is used in chemical changes, the greater part being expended in heating the water or forming steam. It has also been observed that apparently the size of the very hot region "A" depends upon the energy input to the arc. A logical extension of the gradient theory is that for a given input energy there is a given area of the spherical (theoretically) exchange region "C". This area is just large enough to transfer the energy available continuously to the surrounding water; the greater part of the energy goes into vaporising liquid, and a small part is directly conducted away into the cold water. If the input energy is increased the radius, and area of "C" increases until a new "equilibrium" condition has been reached.

Several deductions follow immediately from the theory outlined above:

1. The temperature of the surrounding water has no effect upon the rate of heat exchange between the hottest part of the arc region and the cold water.

2. The most important quantity of energy involved is the latent heat of vaporisation of water, because large amounts of steam are formed in the arc region.

3. A factor of secondary importance is the specific heat of water, since all steam is formed from water which is heated from the temperature of the bulk of the liquid up to the boiling point; if the water is all at  $100^{\circ}$  this factor completely disappears.

-----

(b) Thermal and Chemical Energies:

It was shown in Section "C" that practically all of the input energy was accounted for as heat supplied to the water and as chemical energy, the former far exceeding the latter. The extent, or rate, of the chemical reactions is therefore a measure of the heat energy given to the water, the conservation of energy principle being assumed to hold true.

The rate of chemical reaction is conveniently measured by the rate of gas flow, at least in the experimental range as yet investigated. In the following discussion this relationship will be made use of, insofar as the experiments are related to the thermal energy evolved.

-----

(c) In Section "F" it was shown that pressures up to 20 atmospheres have no effect upon the rate of chemical reaction; regardless of the significance which this may have in regard to the purely chemical reactions, the facts are difficult of explanation except on the basis of the "gradient theory".

At the highest pressure employed the temperature of the water was kept constant (room temperature) but the boiling point was raised to approximately 225°C. Considering that the water was always at 0°C. (for convenience), this corresponds to a rise in the difference between the temperature of the cold water and its boiling point of some 125°C. But no difference whatever was observed in the rate of chemical reaction, which indicates no difference whatever in the rate of heat loss to the cold water, considering the input energy always constant.

This is predicted definitely by the gradient theory, which considers the temperature difference in the region "C-D" in Figure 15 to have negligible effect upon the rate of heat exchange.

This refers only to rates. What of the actual energies involved? When the boiling point is raised  $125^{\circ}$  this more than doubles the amount of heat required to raise a gram of water to the boiling point, the water being originally at  $0^{\circ}$ . An examination of reference tables will reveal however, that as the temperature of the boiling point rises, the latent heat of vaporisation decreases. On page 114 it was pointed out that both specific heat and latent heat of vaporisation must be considered. To heat one gram of water from  $0^{\circ}$  to  $100^{\circ}$  and vaporise it at this temperature requires the expenditure of  $100 \times 540 = 640$  calories. To heat the same amount from  $0^{\circ}$  to  $225^{\circ}$  and vaporise requires  $225 \times 446 = 670$  calories. These two total amounts of energy are almost identical, because of the marked drop in the latent heat of vaporisation; the figures are approximate only.

The theory is thus in excellent agreement with the experimental facts concerning the effect of pressure. Further applications are given below.

-----

(d) Water Temperature and Gas Flow:

In Section "E" it was shown that as the water temperature was raised to  $100^{\circ}$  the gas flow increased approximately 50%, but did not rise past this point as pressure was applied and the temperature raised over  $100^{\circ}$ . Reference to Figure 15 again shows that as the



boiling point is reached the gradient "D" vanishes. This gradient does not affect the rate of heat loss but it does affect the amount of energy required to vaporise a given amount of water; hence when the gradient is eliminated only the latent heat of vaporisation is required. Applying the idea expressed on page 113, if less energy is required to produce a given quantity of steam the spherical area of the gradient "C" must increase to keep the heat loss constant. At present it is believed that the "volume" of the discharge region has a direct influence upon the rate of chemical reaction, so that the increase in volume just mentioned might account for the increased gas flow observed. This point will be further discussed in the next Section.

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(e) Water Temperature and Arc Temperature:

In Section

"D" it was shown that raising the water temperature from 5° to 100° results in a rise of about 1500° in the arc temperature; the gradient theory may be applied satisfactorily to explain this fact.

Here we must consider the region "B" in Figure 15; obviously the larger the area of "B" the larger the area of "A", and the same applies to the volumes. The mean discharge temperature as measured by the pyrometer depends upon the extent of the region in which the temperature approaches that of the very hot electrodes. As "B" increases (with increase in the water

temperature) an increase in the volume of "A" will follow, so that the mean temperature of "A" will rise.

This explanation may however, be incorrect; evidence now at hand indicates that the discharge temperature, at least in the region "A", depends upon the rate of the chemical reactions only, and not vice versa as one might expect.

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It is believed that the theory expressed here gives an approximate picture of the conditions existing in the low tension arc discharge in water, and it has been successful in explaining qualitatively the experimental facts available.

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2. Nature of the Chemical Reactions:

While it is realised that the evidence is incomplete it is believed advantageous to theorize regarding the nature of the chemical changes taking place in the discharge, with particular attention to the products discussed in this thesis and to the existing discharge theories. The general "thermal" and "electrical" theories will be treated separately.

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(a) The Thermal Theory:

We must distinguish here between the thermal dissociation of water and the thermal reaction between water and the electrode materials. On page 69 the present knowledge regarding the dissociation of water at high temperatures was reviewed; it is obvious that at the temperatures obtaining in the under water discharge there would be considerable dissociation of water vapour into its elements. Recombination on cooling would be prevented by union of the oxygen with the carbon of the electrodes, the hydrogen escaping free; a test of such a theory would be the relationship between the rate of the reactions at constant conditions of electrical input energy, and the temperature of the discharge.

A critical examination of Figures (6) and (10) will show that a rise of  $1500^{\circ}$  in discharge temperature results in

an increase of about 50% in the rate of the reactions, these being approximate figures only. Bjerrum<sup>44</sup> and others have shown that in the region 2000° to 3000° a rise of 500° would increase the dissociation of water vapour more than 400%. It does not seem possible therefore that the thermal dissociation theory explains the reactions occurring in the discharge satisfactorily; nevertheless such decomposition may be a preliminary to other more important and extensive changes.

The gaseous products are of such nature that at first the action of the arc was considered to be purely thermal; that is to say the carbon electrodes were heated to a high temperature and reacted with the water directly giving rise to a "water-gas" equilibrium. This equilibrium has received much attention for many years and was found to be conveniently expressed by the following equation:

$$K = \frac{C_{CO} \times C_{H_2O}}{C_{H_2} \times C_{CO_2}}$$

in which K is the equilibrium constant and the other terms are the concentrations of the various components. The value of K has been the subject of much dispute but its variation between 100° and about 1000°C is fairly well known; at higher temperatures the uncertain values of the specific heats of the gases involved make the thermodynamical calculation of the constant of little use. Recent work indicates that the reactions

are not as simple as previously believed. Langmuir<sup>52</sup> pointed out that a surface reaction was intimately involved and Rhead and Wheeler<sup>53</sup> found that an unstable complex carbon oxide was one of the intermediate products; the latter view was held by Lowry and Hulett<sup>54</sup> and seems to be generally accepted today. Haber<sup>46</sup> advances the various arguments which tend to the belief that the value of "K" changes sign at about 2800°C. at which temperature the heat of the (net) reaction becomes actually positive, instead of negative as it is at ordinary temperatures. Thiele and Haslam<sup>55</sup> investigated the steam-carbon reaction at temperatures over 1000°C. with four different types of carbon, and found considerable difference in the equilibrium values in each case; this is of course quite contrary to conventional thermodynamic theory. Furthermore these workers found the reaction with retort carbon to be of a "negative" order, since the amount of steam decomposed increased as the pressure was decreased; also, the reaction rate doubled for a 30° rise in temperature when above 1000°.

There is definite evidence that the reactions in the arc are not related to the water-gas equilibrium; most convincing is the fact that the reaction rate is not greatly affected by the discharge temperature. Nor do the concentrations of the various gases correspond to those in the thermal

reaction. The actual calculation of the constant "K" from the analysis of the discharge products has not yet been made with any accuracy, because of the indefiniteness of the value of " $C_{H_2O}$ "; this corresponds to the concentration of the water vapour actually taking place in the reactions and this quantity is not easily determined.

Two recent papers deserve comment here. Peters and Kuester<sup>56</sup> investigated the reaction between carbon dioxide, monoxide, water and hydrogen in the electric discharge; high voltages and low temperatures were employed, the pressures being less than atmospheric. A definite current relationship was observed and the products were found to be very different from those calculated on the basis of the thermal theory. On the other hand Lefbvre and Montagne<sup>57</sup> (whose original paper has not been examined) found the equilibrium between carbon dioxide, monoxide and oxygen, in the discharge, to agree perfectly with the thermal data. It is difficult to see how they arrive at this conclusion, since the experimental methods employed have long been known to give erroneous results. Knox<sup>58</sup> reviews the experimental work done on the nitrogen-oxygen reaction in various discharges, and shows that the estimation of spark temperatures, assumption that the products are instantly "chilled" and other early mistakes, led to false conclusions.

In view of the vast amount of evidence to the contrary, it is hard to believe that any gas reaction is unaffected by the electric discharge.

Saturated and unsaturated hydrocarbons have been found in the products of the under water discharge. Pring and Hutton<sup>59</sup> obtained such products by heating carbon and hydrogen to a high temperature but some consider the hydrocarbons to come from impurities in the carbon and not from any reaction. Their formation in the discharge may possibly be due to either or both of these factors, and there is no evidence in this connection at present.

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CONCLUSION:

Beyond assuming that the thermal dissociation of water vapour in the high temperature region of the discharge is a probability, and may be the preliminary reaction, it cannot be claimed that thermal reactions are the most predominant; possibly they are inappreciable compared to the "electrical" effects.

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(b) The Electrical Theory:

Shipley and Goodeve<sup>19</sup> have reported volumes of hydrogen evolved in excess of 1000% of the amount predicted by Faraday's law for the currents employed; but with the low tension arc with carbon electrodes the excess may reach ten times this figure. It is evident therefore that the electrolysis law does not apply to discharge phenomena. Early workers abandoned the attempt to obtain a current-yield relationship but recently there is a growing belief that the current is a fundamental factor. It is known that the current is a measure of the ions reaching the electrodes, which in certain discharges are related to the total ionisation. But at best the relationship is variable and it can only be said that in some cases the chemical reaction rates, insofar as they are dependent upon the extent of ionisation, are functions of the current in the discharge.

It was shown in the preceding section (a) that thermal dissociation of water vapour probably takes place to a considerable extent in the discharge. But the intense ionisation in low tension arcs would be favorable to the electrical dissociation of water vapour, with resultant production of a variety of ions. Even if we consider the drop in potential to be uniform throughout the arc length, the gradient must be



in excess of 300 volts per centimeter, since the length of the arc rarely exceeds 1 millimeter. Such a gradient is sufficient to produce many ions from the substances available in the arc, as shown by Senftleben and Rehren<sup>36</sup> and Bleakney<sup>41</sup>. Also, the hydrogen and oxygen produced by thermal decomposition might become ionised by the electron stream, these ions subsequently attaining sufficient velocity in the arc field to bring about further decomposition by collision.

The close dependency of the rate of the reactions upon the current (Section "H") is very indicative of the electrical nature of the primary reactions; Linder<sup>32</sup> points out the fact that careful work done with nearly every type of discharge and gaseous reaction has shown such a relationship.

The reaction of the oxygen with the carbon of the electrodes may of course be a purely "thermal" reaction; but evidence which is not yet complete tends to show all the oxygen or the carbon, or both, is ionised before the reactions take place. At any rate the fact that all the oxygen is found in combination with carbon is an indication that the reactions take place at or near the electrodes (where the potential gradient is greatest); some free oxygen would almost certainly be given off if the water were simply thermally dissociated.

An interesting fact is that the electric discharge through water vapour has been known to produce the so-called "water" bands and lines, and Konen<sup>7</sup> has observed these with under water arcs. Watson<sup>61</sup> has recently shown these bands to be due to the  $\text{OH}^\wedge$  ion, and Barton and Bartlett<sup>62</sup> have demonstrated how extensive the production of these ions is. Lozier<sup>49</sup> considers that the formation of the OH particle is a necessary step in the dissociation of water vapour, and considering these facts it is possible that the ionisation in the under water arc may result in the production of H and OH particles, variously charged. Negative OH ions might reach the anode and there react with the electrode material; such reaction might explain the production of "hydroxidic" compounds discussed in Section "B", parts 2 and 3. Even graphitic oxide may be hydroxidic in nature since its oxide structure is purely hypothetical at present, and some of its hydrogen is very tenaciously held; Hulett and Nelson<sup>39</sup> did not consider this possibility, although they could not remove all the hydrogen from this compound without explosive decomposition. More evidence in this connection may be obtained later.

There is also the possibility that photochemical reactions play a part in these arcs, since under water discharges have long been known to be sources of intense, low wavelength radiations. There is no evidence for or against this theory at present; however no products (aldehydes, ketones, ozone, hydrogen peroxide, etc.) usually associated with photo action

have been detected, although repeated tests have been made.

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CONCLUSION:

The evidence at present available is all in favor of the electrical dissociation theory, although no attempt has been made to discriminate between the various ionisation theories outlined on Pages 25-27.

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