GENERAL INTRODUCTION
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While the vast majority of chemical reactions are brought about thermally, a large number of them are known which can be brought about by absorption of visible-ultra violet light (photochemical reactions) or by interaction with high energy radiations (radiation chemistry). In addition, however, a novel method of causing chemical changes is by means of electric discharge in gases and vapours. The first observed chemical reaction of this type was the formation of ozone and oxides of nitrogen during lightning discharge. The physical and electrical phenomena occurring in electrical discharge have been studied by numerous investigators, but still it must be said that no complete understanding of them has been attained yet.

Several types of electrical discharges are known such as the glow discharge, corona discharge, silent electric discharge and plasma. Although they differ in details, yet they are all based on the principle of electrical breakdown of gases and dielectrics.
Mechanism of Electric Discharge in Gases

Ordinarily gases are very poor conductors of electricity and hence are classified among the best insulators. Therefore when an electric field is applied between two plane parallel metal electrodes surrounded by a gas in a suitable envelope, hardly any current is observed to pass through the gas. Highly sensitive current detectors would, however, be able to detect a minute current and this is due to the incipient ionization brought about by cosmic radiations and any other ionizing radiations in the vicinity. Under the influence of the electric field, the ions and the electrons migrate to the respective oppositely charged electrodes. In addition to this, some of the ions recombine with the electrons, particularly in three body collisions with gas molecules or with the walls of the container. The ions and electrons would be making numerous elastic collisions with the gas molecules in addition to migrating towards the respective electrodes, so long as the applied electric field is low. As the field is increased the electrons and the ions are accelerated more due to which a less number of them is lost by recombination and hence the current reaches a limiting value $i_o$. At sufficiently high fields the electrons are accelerated so
much within their mean free paths that they acquire sufficient energy to cause ionisation of molecules by collision. The electrons produced by this ionisation, in their turn, are accelerated towards the anode due to the electric field and bring about further ionisation. Thus, starting with a few electrons it ends up in an avalanche of them reaching the anode. The positive ions produced being relatively much heavier, are less mobile than the electrons and hence build up a space charge in the vicinity of the cathode and this takes a relatively long time to clear up.

The average energy $E$ acquired by an electron of charge $e$ in the electric field $X$ before colliding with a gas molecules is given by,

$$E = Xe\lambda \quad \ldots (1)$$

where $\lambda$ is the mean free path of the electrons in the gas. If $E > V_1$ where $V_1$ is the ionisation potential of the gas, the electrons can ionise the gas molecules by inelastic collisions.

Townsend$^1$ has shown that the discharge current $i$ when the field $X$ is sufficient to cause ionisation by collision is given by

$$i = i_0\exp(\alpha d); \quad X/p = \text{constant} \quad \ldots (2)$$
where \( I_0 \) is the initial current mentioned earlier, \( d \) is the inter electrode distance and \( p \) is the gas pressure. \( \lambda \) is called the first Townsend coefficient and is defined as the number of electrons (and ions) produced by an electron per cm length of the path in the field direction. For plane parallel electrodes \( X = V/d \) where \( V \) is the potential difference between the electrodes. For non uniform fields the current is given by

\[
i = I_0 \exp \left( \frac{b}{\lambda} \right)
\]

This is because \( \frac{\lambda}{p} \) is a function of \( X/p \) and \( X \) depends upon the position co-ordinate \( x \). So, the integration is carried out between the limits \( x = a \) and \( x = b \) for the two electrodes where \( a \) and \( b \) are the \( x \) co-ordinates of the electrodes.

At low pressures and high \( X/p \) values the discharge current increases more rapidly than given by the equation (2). This is due to the emission of secondary electrons. Townsend assumed that the positive ion, when accelerated sufficiently towards the cathode due to the electric field, would bring about ionisation of molecules by collision. Accordingly he introduced the second Townsend coefficient \( \beta \) to account for the emission of secondary electrons by this mechanism. However, this assumption turned out later to be incorrect. Hence Holst and Oosterhuis concluded
that the secondary electrons were being liberated from the cathode surface by the impact of positive ions. Indeed a few other mechanisms also contribute to the emission of secondary electrons, such as photoelectric emission from the cathode surface and also photoionisation of the gas. All these mechanisms can be represented by a single coefficient \( \gamma \) denoting the number of secondary electrons released per positive ion\(^2,4\). The discharge current would then be given by the expression

\[
i = \frac{i_0 \exp(\gamma d)}{[1-\gamma (\exp(\gamma d)-1)]}
\]

From the above equation it is seen that when \( i_0 \rightarrow 0 \), the discharge current also approaches zero. The discharge current thus owes its existence to \( i_0 \) which is due to the presence of an external ionising agency. Such a discharge is called the Townsend discharge or the non-self sustained electric discharge. However, at high enough applied fields \( (\exp(\gamma d)-1) \) can assume such a value that \( \gamma (\exp(\gamma d)-1) = 1 \) and the denominator of the equation (4) becomes zero. Under these circumstances, the discharge current becomes very large and is controlled only by an external resistance. Significantly, at this and higher fields, the discharge when once started, maintains itself and no longer depends on external agencies for its existence. The electric discharge is now called a self sustained electric discharge.
(B) **Mechanism of d.c. discharge in a gas with dielectric electrodes:** The overall mechanism of electric discharge in a gas with dielectric electrode differs from the mechanism with metal electrodes in two significant ways. Firstly, the distribution of charge over the dielectric surface is not uniform. Secondly, following a discharge pulse, a certain time interval elapses for the charge to leak across the dielectric and restore the potential of the surface to its original value.

With dielectric electrodes the surfaces are often not equipotential. Hence such a surface can be considered to be divided into small elementary areas called 'sites', at different potentials. The discharge takes place between pairs of such sites on the opposite walls due to the wall charge field produced by the applied field. The electrical field in the gas, $E_g$, due to the wall charge is given by the equation

$$E_g \varepsilon_g = E_w \varepsilon_w$$

where $E_w$ is the field across the dielectric walls (Fig. 0.1A) and $\varepsilon_g$ and $\varepsilon_w$ are the permittivities of the gas and the wall material respectively. In a system where the discharging walls are made of glass such as in Siemen's type ozonizer, $\varepsilon_w (4.83)$ is greater than $\varepsilon_g$ (approx. 1). So the electrical field $E_g$ in the gas medium is greater than in the surrounding wall insulation, i.e. $E_g \gg E_w$. The charges on
A - MECHANISM OF D.C. DISCHARGE BETWEEN GLASS ELECTRODES

B - EQUIVALENT CIRCUIT OF THE DISCHARGE SYSTEM

FIG. 01
the inner glass surfaces in contact with gas are held under two opposite forces (a) the electrical field in the gaseous medium and (b) the electrical field across the glass walls. On account of these forces the charges on the walls are not held firmly and can be released easily when the potential across the gas phase is greater than its breakdown potential. In the discharge process, the electrons released from the negative wall produce electron avalanche in the gas, which, after reaching the opposite wall reduce the positive charge on its surface. Thus when the potential difference becomes smaller than the breakdown potential the discharge is terminated. The subsequent discharge takes place when the potential is restored as a result of leakage of the charges through the glass wall and also, in part, by surface conduction. The finite time interval between consecutive pulses occurring between a pair of sites on the opposite walls is the leakage constant \(^{9,10}\).

El-Bakkal and Loeb\(^{11}\), studying the electrical breakdown of argon between plane parallel glass plates with externally applied voltages, have given the following expression for the change in charge on the wall surface \(\Delta Q_d\).

\[
\Delta Q_d = (V_A - 2V_g)(C_g/2) - V_A C_g \\
\text{.. (6)}
\]

where \(V_A\) is the externally applied voltage, \(V_g\) is the potential drop across each of the two glass electrodes, each
having the same capacity $C_g$ and $C_G$ is the gas capacity. This is illustrated in Fig. 0.1B by the equivalent circuit of the discharge system. When the discharge passes through the gas, the electrons and positive ions move towards the respective oppositely charged electrode and an opposite charge is thereby sprayed on the glass electrodes. This results in the establishment of a back potential at the walls. The resultant potential difference acting on the gas thus diminishes and the discharge is choked off.

(C) **Mechanism of a.c. discharge in a gas with dielectric electrodes** : Harries$^{12}$ has studied the breakdown mechanism in a gas between glass electrodes but under a.c. potentials. The current occurs in pulses. The size and the shape of these pulses were studied by using a cathode ray oscillograph. These observations revealed that just at the breakdown potential applied to be electrodes, only one pulse is observed at each half cycle of the applied potential, occurring near the peak. As the potential is increased a group of pulses appears, the first pulse of the group being at a phase earlier than the peak of the half cycle. When a single pulse occurs, the electrons multiply rapidly and on being deposited on the end wall, set up reversed field in the gas. This stops further development of the electron avalanche which constitutes the current in the pulse. If the external field is still increasing, the field in the gas will again reach a sufficiently high
value for another pulse of current to pass in the same half cycle. This goes on till the peak of the applied voltage passes over. In the next half-cycle, the applied field and the wall charge field assist each other and pulses start at an earlier phase. This causes the initial wall charges to decrease and the walls to get charged oppositely. Indeed the discharge mechanism is basically the same as in the d.c. mode of excitation, the primary ionisation in the gas being sustained by a secondary wall process. According to Von Engel a single pulse represents a discharge along a narrow channel causing the wall charges to collect over a small area of the glass surface. Different areas will not breakdown simultaneously because the breakdown potential and the subsequent size of the pulse depends upon the secondary emission from the walls and this varies from point to point. Once a pulse starts, the voltage drop in the external circuit will prevent any other discharge until the pulse is complete.

(2) **Types of Electric Discharge in Gases**

The most common type of electric discharge is the one obtained in a gas at low pressure. When high enough electric fields are applied, a luminous discharge can maintain itself by process of ionization and electron emission at the cathode. The various glowing and dark regions can readily be distinguished at low enough gas
pressure. For purposes of bringing about chemical reactions, electric discharges which operate at higher pressure (about one atmosphere) have been frequently used. These are of different types such as the glow discharge, the corona discharge, the arc discharge and the silent electric discharge. These forms of discharges are closely related to the glow discharge in the sense that the electrical phenomena taking place in them are essentially the same. The differences are due to the higher pressure employed in these devices.

(A) The glow discharge: The glow discharge is conveniently described as a discharge in which the cathode emits electrons under the bombardment of particles and light quanta from the gas. Thermal effects are either absent or at least not a necessary condition for maintaining the discharge.

The glow discharge derives its name from a luminous zone which develops near the cathode and is separated from it by a dark space. When a direct current glow discharge is established in a long cylindrical tube which is filled with a rare gas at a pressure of between 0.1 and 1 mm Hg, the visible light emitted from the discharge is distributed over the length of the tube as shown in Fig. 0.2.

Starting at the cathode there exists sometimes a very narrow dark space called the Aston's dark space close to it followed by a thin relatively feeble sheath of luminous layer
FIG. 0.2 - SCHEMATIC DIAGRAM OF THE GLOW DISCHARGE
called the cathode glow which in turn is followed by the cathode dark space. Aston's dark space and the cathode glow are not always clearly visible. A sharp boundary separates the cathode dark space from the negative glow, which becomes progressively dimmer towards the Faraday dark space. At the positive end of this is the positive column. At the positive end of the positive column there is sometimes visible an anode dark space followed by the anode glow close to the anode itself.

It is known that there are a variety of glow discharges and their appearance varies with the nature of the gas, the pressure, the dimension of the vessel, the type, size, separation and material of the electrodes.

When the distance between anode and cathode of a glow discharge is varied it is found that the axial length of the negative zones, i.e. those near the cathode, remain unchanged while the length of the positive column varies. In fact the positive column can be extended to any length provided the voltage for maintaining and starting the discharge is sufficiently large. Further, if a plane cathode is mounted in a large spherical bulb and rotated with respect to a fixed anode, the negative zones swing round as if they were fixed to the cathode dark surface while the positive column simply fills the remaining space between the Faraday
dark space and the anode. From these observations one can conclude that the motion of the charged particles in the negative zones must be of a beam like nature whereas the motion in the positive zones appear to be essentially of the random type. Consequently there should be little influence from the walls in the cathode region, i.e. the light emitted and the potential distribution should not depend on the diameter of the glass cylinder, whereas the positive column should depend on the diameter of the tube.

When the gas pressure is increased above, say \( .1 \text{ mm Hg} \) it is seen that the negative zones of a glow discharge contract towards the cathode. Above \( 100 \text{ mm Hg} \) only the Faraday dark space is clearly visible. The positive column always fills the remainder of the gap, but it contracts radially at higher pressures.

The transport of current through a glow discharge occurs by the axial motion of electrons and positive ions. The flow of current through the cathode zones can be understood by referring to the distribution of the electric field, that is its axial component. The field has been found to be large at the cathode, decreasing in intensity towards the negative glow, and after passing a minimum in the Faraday dark space, it stays constant throughout the positive column and only rises again at the anode.

Consider an electron emitted from the cathode, for
example by a positive ion which impinges on it. This electron is first accelerated in a strong field, but initially it executes few ionising collisions because energy is not sufficiently far above ionization potential. However, further from the cathode, though the field has become weaker, the electron ionizes more efficiently and electron multiplication will take place. Near the boundary between the cathode space and the negative glow the field has become very weak, and thus only the fast electrons which have not lost energy by inelastic collisions will be able to ionize in that region. However, a large number of electrons will cross the boundary and enter the negative glow. Due to multiplication the number of electrons able to ionize has increased between the cathode and the glow boundary, and a large number of positive ions has been formed representing a dense positive space charge. These positive ions will move through the cathode dark space and impinge on the cathode. Also metastable atoms, fast unexcited atoms and radiation will fall on the cathode with the result that secondary electrons are emitted from it.

In a glow discharge an electron usually starts at the cathode with a very small initial energy of the order of 1 eV. It is not able to excite gas molecules unless its energy has reached at least the excitation potential, which will not occur within the short distance from the cathode corresponding to Aston's dark space. The cathode layer is
the region within which the electron acquires an energy corresponding to the maxima of the excitation functions. Since the maxima for different spectral lines lie at different energies it follows that the lines should be observed in such order that the lowest energy should lie nearest to the cathode. This is actually the case. At higher cathode fall, the Aston's dark space and cathode layer are replaced by the cathode glow. At larger distances from the cathode most electrons have speeds which lie far beyond the maximum of the excitation functions and thus little visible light is emitted from the cathode dark space. At the negative glow boundary the number of slow electrons has become very large and their speed decreases with increasing distance from the cathode, thus in general these spectral lines appear in the reverse order as one approaches the negative glow.

The electrons entering the negative glow consist of at least two groups. The first group is of fast electrons which have been produced at or near the cathode and which have not suffered energy losses by collisions in the dark space. The other larger group is of electrons which have made many inelastic collisions or those which have been created in the dark space and are therefore slow. Since the slow electrons have energies below the ionization maximum but above or at excitation maximum, they experience many
exciting collisions and produce the negative glow. Afterwards their energy becomes so small that recombination with positive ions can take place. This process is likely to occur in and beyond the negative glow since the concentration of ions and electrons in that region is large and the field is low. The emission of light due to recombination is, however, in general small. With increasing distance from the boundary fewer fast electrons are found and less visible light is emitted. Beyond this the field rises gradually, the probability of recombination decreases and the Faraday dark space develops. This is the anteroom to the positive column and its properties are probably intermediate between those of the positive column and those of the negative zones.

In the uniform positive column the axial component of the electric field is found to be constant at any point. It follows that the net space charge is zero or that the concentration of electrons at any point is equal to that of positive ions. Because of the small mobility of positive ions the electrons carry practically the whole discharge current while the positive ions compensate the electron space charge. The field in the positive column is several orders of magnitude smaller than that found in the dark space. This fact as well as the uniform appearance of the positive column indicates that ionization is not obtained
from the drift velocity of the electrons in the field direction but rather from their large random velocity acquired by numerous elastic collisions in the electric field.

At the anode side of the positive column the electrons are attracted by the anode and the positive ions are repelled. Consequently a negative space charge is set up in front of the anode. This gives rise to an increase of the electric field as well as a rise in potential - the anode fall in potential. An electron emerging from the positive column enters the anode fall region with a small initial energy. It is now accelerated towards the anode and after having crossed the anode dark space it has acquired a speed which is sufficient to excite and ionize the gas in front of the anode. The anode is therefore covered with a luminous sheath of the anode glow which is sometimes divided into several luminous spots.

Certain characteristic structural features of the glow discharge: Under many conditions, but usually in mixed or impure gases and perhaps in some pure ones, between 0.01 and 1.0 mm pressure, the discharge in the positive column has a beaded appearance. This is known as the striated discharge and the beads are known as striations. The moving striations, however, are different
in mechanism and character from the fixed ones. They may occur in pure gases and are presumably due to electrical plasma oscillations.

The cathode glow at lower currents will not cover the whole cathode, but as the current increases it will cover the cathode. As long as the cathode is not covered by glow, one finds, the potential across the tube is constant as current increases. Once the glow covers the cathode, further current increase requires increase in potential across the tube. This is an important feature of the glow discharge.

The positive column is not a vital feature of the glow discharge. It really consists of a conducting and luminous path for the discharge from the end of the Faraday dark space to the anode. As the anode is brought nearer the cathode, the positive column merely shortens in length and the potential to maintain the discharge falls by the amount of potential fall in this section.

(B) The corona discharge : This type of gas discharge has received its name from the crown like shape of a glow which was first observed on points or along wires in air raised to high potentials with respect to their surroundings. The corona occurs at any pressure and in any gas but is quite pronounced when the pressure is relatively high. It appears
on lightning conductors and masts of ships when densely charged clouds are overhead or discharging. It appears on high voltage transmission lines and is probably closely related to discharges in point and wire counters. It is used extensively to produce electric charges in gases, particularly in electro filters, where the charges becoming attached to dust, smoke and other particles are gathered by an electric field, and in ozonizers for sterilizing water. Physically it is very much the same as a glow discharge in a highly non uniform electric field. One can regard the corona as a glow discharge without positive or negative zones, according to whether the point or wire is negative or positive.

A corona discharge is readily established between a fine wire or a point and a cylinder. As the potential difference is gradually increased no current passes until a certain potential is reached when a visible discharge takes in the form of a glow if the wire is fine and the surrounding cylinder is large, but is a spark if the reverse is the case, or if the pressure is low. In the case of negative wire the discharge is rather irregular and often concentrates at certain points forming beads. Increasing the voltage or current tends to break up the sheath into isolated brushes which increase in number with the voltage. At low pressures increasing the voltage may turn the discharge into one of
the ordinary vacuum tube type over a part of the wire.\textsuperscript{14}

Corona discharge in helium and neon have been studied by Huxley\textsuperscript{15} and in hydrogen by Bruce\textsuperscript{16}. Both worked at relatively low pressures. The mobilities of the positive ions, as calculated by Townsend's method, were in all cases larger than the values found by the usual methods; and showed a tendency, in most cases, to increase with increasing field strength.

The alternating current corona is complicated by the fact that the space charge is driven by the field of the wire when the wire is negative. When the field changes its direction this space charge is attracted by the wire, but at the same time ions of opposite polarity are repelled. Thus in the steady state there is a considerable phase difference between the field on the surface of the inner wire and the velocity of the ions which results in a corresponding phase difference between the peak value of the applied field and the discharge current. The alternating current corona is of considerable practical concern since the losses of power on transmission lines caused by such discharges can be very large.

Corona discharges have been used to initiate chemical reactions for well over 150 years with much of the early work being confined to inorganic gases.\textsuperscript{17} 

electrons are accelerated by the applied voltage to an energy level of 10-20 eV, which is sufficient to break the covalent bond. This represents a very efficient approach when compared with high energy radiolysis (MeV range) where the actual chemical change is effected by secondary electrons with an energy of 10-25 eV, formed after a series of energy dissipating steps. Potentially, corona energy can deliver electrons to the reaction site at the desired energy level to give products which are not readily obtainable by more conventional means. The energy available in corona discharge is somewhat above that commonly encountered in photochemistry (upto 6 eV). Since corona discharge is obtained at a small electrode opposed by a much larger one, there is a very large change in field through the corona, but very little change over the remaining distance to opposing electrode.

(C) The arc discharge: It was discovered by Davy\(^{18}\) and Petroff\(^{19}\) in the year 1800, who found that if two horizontal cylinders of hard carbon were pressed together and placed in series with a galvanic battery giving a potential difference of 100 volts, on separating the carbons an exceedingly bright discharge, shaped like an arc with its concavity downwards passed from one carbon to the other. The ends of the carbons became incandescent and produced most of the light. From its shape the discharge was called the 'arc discharge'. In such an electric discharge a current of several amperes flows.
Though this type of discharge appears commonly in atmospheric air, it is also observed at lower or higher pressures and in various gases and vapours. The short arc in air is by no means a form suitable for the study of its essential features. This is because violent chemical and thermal processes take place in the gas as well as at the electrode surfaces. The arc exists in a turbulent mixture of gases or vapours which come partly from the electrodes and partly from the surrounding atmosphere and from the reaction products. In addition, the discharge column anchored between the spots at the electrodes varies in diameter and composition over its length. Thus short arcs which have been studied most extensively in the past do not lend themselves readily to simple deductions.

A convenient definition of an arc is given by comparing its cathode region with that of a glow discharge: the cathode of the glow has a fall of potential of about 100 to 400 V and a low current density. Except at high pressures and currents, the positive column always fills the tube. Thermal effects do not contribute to the working of the cathode of a glow discharge and the light emitted from the region near the cathode has the spectrum of the gas. The arc cathode, however, has a fall of potential of the order of 10 V and a very high current density. Thermal effects are essential for its working and the light emitted
has the spectrum of the vapour of the cathode material. Further, the positive column is constricted near the two electrodes. Thus with a copper cathode in nitrogen at one atmosphere (with interelectrode distance < 1 cm) on applying a potential difference of 350 V if the current density at the cathode is of the order of 1 A/cm², and if the light emitted from the cathode region is due to nitrogen bands, then a glow discharge is present. But if with a potential difference of the order 30 V, the current density at the cathode spot is $10^4$ to $10^6$ A/cm² and the light emitted from the cathode region shows mainly the green copper lines, then an arc discharge is present.

A common feature of all types of arc discharges is that they are not self starting. To begin a discharge the arc must be struck by separating the electrodes which had previously been in contact with a large current flowing across the junction. This warms the electrodes and enables the discharge to begin. Another characteristic of arcs is that the cathode must be hot while it is not necessary for the anode to be so. Thus if we have two electrodes, one of which is hot and the other is cold, placed in series with an alternating current, the current will get through when flowing in the direction which makes the hot electrode the cathode but not in the opposite direction.

Another feature of the arc discharge is that both
the cathode fall of potential and the cathode dark space are much smaller than those in the glow discharge. Thus the minimum value of the cathode fall in the glow discharge is, for most gases, of the order of 200-300 volts, while that for the arc may be as low as the ionising potential of the gas ($\approx 15$ eV).

The dark space in the arc discharge is so thin that it has never been observed. Because of the enormously greater current density in the arc discharge, the space charge effects are predominant. Thus if the current density is 100 amp/cm$^2$ it will require a potential difference of about 1000 volts to drive the current across 1 mm if in this space it is to be carried entirely by the electrons and not by positive ions to diminish the effect of the space charge. This shows that in the arc there must be ionisation or emission of positive ions right up to the anode.

The transition from the glow to the arc discharge can be traced conveniently by using as cathode a lime-covered platinum wire heated to redness by an electric current and having a thermojunction fused on to the platinum to measure the temperature. The anode is a cold metal plate and the gas in the discharge tube is at a low pressure. The electrodes are connected with a battery of cells, and the number of cells in the battery is gradually increased. When the number of cells is small, the temperature of the cathode
is low. If the number of cells in the battery is increased steadily a stage is reached when the temperature of the cathode and the current through the tube very rapidly increase while the potential difference between the anode and cathode, inspite of the increase in the voltage in the rest of the circuit, decreases. The increase in the temperature of the cathode and in the current through the tube occurs with great rapidity; the cathode soon gets white hot and the current rises from a few milliamperes to several amperes, the potential difference between the cathode and anode falling to about 30 volts. The high temperature of the cathode is due to its bombardment by positive ions; at this stage we may switch off the current used to heat the cathode, and the cathode will remain hot and the arc continues to pass.

If we raise the temperature of the cathode to white heat before applying the field the arc will begin almost immediately.

In considering the connection between the arc and the glow discharge, it is interesting to find what would be the current density and the thickness of the dark space in a glow discharge at the pressure of the arc discharge in air. In a glow discharge at a pressure of 1 mm the current density with flat iron electrodes in nitrogen is, according to Guntherschulze\(^20\), \(40 \times 10^{-5}\) amp/cm\(^2\) and the dark space
is 0.375 cm. The current density is proportional to the square of the density of the gas. If we take the temperature of the gas in the arc discharge to be 3000°K; the density of the gas will be 76 times that at normal temperature and 1 mm pressure. The current density is therefore \((76)^2 \times 42 \times 10^{-5}\) or 2.4 amp/cm\(^2\) and the thickness of the dark space is 0.005 cm.

The arc may take several different forms, (1) the anode and cathode may both be hot and give off metallic vapours, (2) the cathode may be hot, while the discharge at the anode concentrates in a bright spot, (3) the cathode may be hot while the anode is cold and the discharge in the gas between the electrodes shows the characteristic spark lines of the glow discharge.

(D) The silent electric discharge: The electric discharge occurring in ozonizer type discharge tubes is commonly known as silent electric discharge. The ozonizer consists of two co-axial glass tubes and the gas is introduced into the annular space. Electric discharge is excited by applying high a.c. voltage between outer surface of the outer tube and the inner surface of the inner tube. For making the electrical contacts the surface of the glass may be in contact with either an aqueous electrolyte solution or a metal foil. Fig. 0.3 represents ozonizers which have been extensively used by many investigators for
INNER GLASS AND OUTER METAL ELECTRODE

TWO METAL ELECTRODES

METAL OUTER AND WATER INNER ELECTRODE

TWO WATER ELECTRODES

FIG. 0.3 - GLASS OZONIZERS (CYLINDRICAL TYPE)
the purpose of studying chemical reactions. The very name, of course, suggests that they have served for the preparation of ozone from oxygen. Warburg\textsuperscript{21} and Berthelot\textsuperscript{22} have carried out a great number of reactions by means of the silent electric discharge. The original form of this type of discharge tube was first used by Siemens\textsuperscript{23}. Since then most investigators have made some minor changes in design without, however, affecting the type of discharge obtained. Perhaps the most important improvement was made by Frolich\textsuperscript{24}, who built the inner electrode of metal as shown in the above figure.

The electric discharge in an ozonizer occurs in the form of a positive and negative point discharge as explained earlier in the mechanism of a.c. discharge in gases with dielectric electrodes. The discharge as a whole consists really of a series of brush discharges which increase in number as the current density increases, when the whole annular space appears to be filled with luminosity. Alternating current is employed, since in this case the necessary charging of electrodes occurs which make the production of a current in the gas space possible.

Since the current in ozonizers is produced and carried by positive and negative point discharges, one may expect the chemical action to be the same as in the point-plate discharge. As the name implies in a point-plate
discharge the electric discharge occurs between a point electrode and a plate electrode. In such a discharge if the point electrodes are negatively charged and hence serve as cathodes, then there are developed about them the usual cathode dark space and negative glow. These regions can be distinguished only under the microscope, but they become visible to the naked eye as the pressure is lowered. Depending on the point-plate distance, a positive column may or may not be developed. When the point serves as anode and is then positively charged, one sees again at high pressure a glowing region near it which easily goes over into a brush discharge formed by the positive column. The negative point discharge with its well-developed negative glow would show greater chemical activity than the positive point discharge, since it is recalled that the greatest chemical action in luminous discharge is found in the cathode glow.

In a silent electric discharge the discharge is completely contained within the envelope of the glass or the other non porous insulating material without direct contact between the gas and metal electrodes. The elimination of metal electrodes often brings about an increase in the yield of discharge products since the metals are generally good catalysts and may promote either decomposition or undesired recombination of free radicals.

Ozone formation in point to plate discharge : Oxygen
gas is allowed to pass through the annular space and the exit gas is analyzed for ozone. Since ozone is also decomposed by the electrical discharge the results are extrapolated to zero concentration of ozone \( (A_0) \). If \( m \) grams of ozone are formed in \( t \) hours with a current of \( J \) amperes then the yield is \( A = \frac{m}{Jt} \). It has been found that the processes of formation of ozone in the point discharge are not of the type of an electrolysis where Faraday's laws hold. For the negative point discharge it is shown that the chemical reaction takes place in the luminous portion around the negatively charged wire. Here the yield is constant as long as the current remains at a given value, even though the distance of point to plate and the potential be increased.

Warburg\(^{21}\) has made the most extensive studies of the behaviour of ozonizers from two points of view. Firstly he investigated the chemical reactions occurring in such devices, and secondly he considered the electrical circuit involved. Since the production of ozone in such an apparatus is of some technical importance, it is of interest to know the efficiency of the units employed and to determine the chemical yield per unit of energy consumed. It is necessary to measure the energy input and hence to determine the voltage, current and power factor. A convenient method of applying the voltage to the system is by the use of a high tension transformer. Voltages ranging usually from about 2000 to 25,000 volts are employed. They
can be measured by a high tension voltmeter. The current can be determined by a thermojunction and galvanometer or by observing the voltage drop over a high resistance by means of a quadrant electrometer as shown in Fig. 0.4. In this figure T(I) is an autotransformer connected to the alternating current supply which feeds varying voltage to the high tension transformer T(II) as desired. In the particular arrangement shown, the current is measured by determining the drop in voltage over a resistance $R_Q$ by means of an electrometer $Q$. The resistance $R_Q$ is part of a high resistance $R_{(ab)}$ which should be of the order of 300,000 ohms. The condenser $C$ placed in parallel with the resistance $R_Q$ serves as a by-path for high frequency harmonics.

Considered as an electrical circuit the ozonizer is seen to be a system of three condensers placed in series. The arrangement of a cylindrical ozonizer is shown in Fig. 0.5A and the potential variation during the process of charge and discharge is shown (after Warburg) in Fig. 0.5B. If we consider the electrode $j$ at zero potential and bring $a$ to the potential $E$ then a charge $C.E$ will accumulate on the electrode $a$ if the glass tubes are perfect insulators and $C$ is the total electrical capacity of the condenser system. It is assumed that the removal of the potential from $a$ takes place after any displacement currents in the
FIG. O-4- ELECTRICAL CONNECTIONS FOR THE OZONIZER
A - POTENTIAL DISTRIBUTION IN AN OZONIZER DURING THE ALTERATION OF CHARGE AND DISCHARGE

B - CROSS SECTION OF OZONIZER

\[ V_a = \text{Applied potential between a and d} \]
\[ V_{bc} = V_b - V_c \]
\[ Q = \text{Charge on a} \]
\[ +q = \text{Charge on b or c} \]
\[ C = \text{Capacity of condenser} \]
\[ C_2 = \text{Capacity of bc} \]

FIG. 0.5
dielectrics and any ion currents in the gas have vanished. The potential situation brought about by the charging of electrode $a$ is shown by curve I. However, when the potential difference between $b$ and $c$ becomes large enough an ion current will set up in the gas space $bc$ whereby $c$ becomes positively and $b$ becomes equally negatively charged. At the same time more charge will accumulate on $a$ and the potential in the gas space $bc$ will be reduced to a certain minimum value $M(d_2)$ when the ion current in the gas phase will stop and the whole charging process will have come to an end. The potential situation is now shown in curve II. If the cylinder $a$ is now brought to zero potential, the charge $C_E$ would leave it if the gas were non-conducting. The potential assumed by the various surfaces is shown in curve III. The potential difference $V_b-V_c$ is now of opposite sign and larger in absolute value. Hence an ion current will be produced in the gas region until the difference in potential between $b$ and $c$ has reached the minimum value $M(d_2)$, where further conduction will cease, even though some charges remain on electrodes $b$ and $c$ and also on plate $a$.

Warburg$^{25}$ has developed the mathematical theory of ozonizers and has shown that the ion current in such a system is given by the motion of charge $q$ which is given by
Where $C_s$ is the apparent capacity of the ozonizer as a condenser, $C$ is the capacity of the whole system, $V_a$ is the applied potential between $a$ and $d$ and $C_2$ is the capacity of $bd$. Further he showed that the energy expended in the production of discharge current is given by

$$W = (C/C_2) \int V_a d\phi$$

It was also shown that the minimum potential in the gas phase for sustaining the discharge is

$$M(d_2) = \frac{1}{2} V_a (1 - C/C_2) (C_s/C)$$

A quantity of some significance in an ozonizer circuit is its power factor. Warburg and Leithauser investigated the power relation and Warburg has summarized their findings. As has been mentioned earlier an ozonizer is to be considered as a system of three condensers placed in series. If all the dielectrics involved are perfectly insulators then the power factor is zero and no energy is consumed in the electrical system. This would also be true if the gas phase were replaced by a metal conductor. On the other hand, for some conductivity of the gas phase between zero and infinity the power factor will have a maximum value. Warburg showed that the power factor is
1 when the ozonizer is replaced by ohmic resistance and is less than 1 when some form of discharge device is replacing the ohmic resistance.

Warburg\textsuperscript{21,27} has summarized several reactions which have been studied in an ozonizer, where electrical measurements were made which permit the calculation of the yields. The number of molecules reacting per equivalent of electricity is of the same order of magnitude for the various reactions. It must be said that theoretical considerations pertaining to these reactions, attempting to elucidate a mechanism and to connect kinetic theory impacts with these yields, involve many assumptions and most likely give little insight as yet into the complex phenomena existing in an ozonizer. Warburg and Rump\textsuperscript{23} have shown that the ozone yield per coulomb is proportional to the pressure when the oxygen pressure is less than 200 mm Hg. This situation would indicate that the processes occurring in the ozonizer under these conditions are sufficiently simple to attempt some sort of theoretical treatment.

(3) Chemical Reactions under Electric Discharge:

A large number of chemical reactions have been studied in a variety of types of electrical discharges. These reactions include both decomposition and synthesis of
a large number of gaseous compounds and vapours.

**Water vapour**:

The dissociation of water vapour in glow discharge was studied by Linder in a discharge tube with two aluminium electrodes. The discharge current was varied from 1 to 28 mA and the electrode spacing from 1 to 9.75 cm. The pressure was 0.75 mm. The gaseous reaction products were hydrogen and oxygen with a small deficiency of the latter from the expected mole ratio 2:1. Perhaps ozone was formed which would not be found by the analytical methods employed.

Formation of water vapour in glow discharge was studied by Guntherschulze. He found that increased hydrogen concentration is favourable toward a larger reaction rate, and hence the hydrogen molecules are the species being ionized in glow discharge, rather than oxygen molecules, leading to the observed chemical reaction.

Mann et al. in studying the decomposition of water vapour, observed an ion of mass 19, and by various studies they concluded that it was $\text{H}_3\text{O}^+$; probably formed by the reaction: $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$.

**Hydrocarbons**:

The decomposition of hydrocarbons in various types of electrical discharges has been widely studied. The
decomposition of a series of hydrocarbons including methane in a microwave discharge has been studied\(^{41}\) and from the results the following postulates have been advanced. If the parent hydrocarbons has a hydrogen atoms to carbon atoms ratio (H/C) greater than about 1.6, a hydrogen saturated solid film will be produced in addition to hydrogen on passage of the hydrocarbon through the electric discharge. Conversely, if the parent hydrocarbon has this ratio less than 1.6 a hydrogen deficient film will be produced and no hydrogen will be observed.

Field et al.\(^{42}\) found the disappearance of CH\(_4^+\) ion in methane to obey first order kinetics over a pressure range of about 0.1 to 400 microns.

The decomposition of methane at liquid air temperature in glow discharge was studied by Brewer and Kueck\(^{43}\) and they found that the gas yielded ethylene and hydrogen.

\[
2 \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2 \text{H}_2
\]

The rate of decomposition was found to be constant for a given current and increased proportionally with larger currents.

Bonhoeffer and Hartack\(^{44}\) studied the decompositions of methane, ethane, pentane, petroleum ether, ethylene,
acetylene and benzene. The main reactions were hydrogenation, dehydrogenation and ring rupture. The dehydrogenations followed the reaction scheme.

\[ C_nH_m + H \rightarrow C_nH_{m-1} + H_2 \]

Methane, however, did not react at room temperature by exchange of the type

\[ CH_4 + H \rightarrow CH_3 + H_2; \quad CH_3 + H \rightarrow CH_4 \]

as could be deduced from the fact that the glass walls of the reaction tube never became warm.

The hydrogenations seemed to take place on the wall, since the most likely gas phase mechanism

\[ C_2H_4 + H \rightarrow C_2H_5; \quad C_2H_5 + H \rightarrow C_2H_6 \]

would involve association reactions which are not supposed to occur in bimolecular collisions. The cracking action of hydrogen atoms may be

\[ C_2H_6 + H \rightarrow CH_3 + CH_4 \]

All these changes were observed in a stream of gas coming from the discharge tube where atomic hydrogen was produced.

Bertholot\textsuperscript{45} reduced benzene to \( C_6H_8 \) in what appears to be the first exposure of an aromatic compound to the corona discharge.
Linder, Davis and et al. exposed benzene vapour to 37,000 volts and found biphenyl, gaseous products and evidence of polymerization.

Ozone:

Warburg studied the formation of ozone in a point to plate discharge. It seemed that various amounts of electricity were necessary for the formation of the same amount of ozone depending on the conditions. These results indicated that the processes of formation of ozone in the point discharge were not of the type of an electrolysis where Faraday's laws hold.

Ozone formation with high frequency discharge was studied by Starke using A.C. from 50 to 10,000 Hz. He found that the yield and the concentration of ozone in the efflux gas did not vary with frequency.

Water gas:

The interaction of carbon dioxide and hydrogen was studied by Lunt in a quartz ozonizer energized by alternating currents of $1.5 \times 10^7$ Hz. The pressures were noted on mercury manometer. The discharge consisted of a series of sparks and was not smooth and uniform. The carbon dioxide decomposed to the extent of about 76% at 50 mm pressure in five minutes. In some of the experiments the
carbon monoxide was reduced mostly to methane, indicating that other reactions can take place besides the water gas reaction.

**Carbon monoxide**:

It has been known that carbon monoxide alone decomposes in the electric discharge to form carbon, CO₂ and C₃O₂. Caress and Rideal⁴⁷ found the same reaction in the case of electron activation. They studied the rate as a function of the electron speed and noted that 14 eV were needed before the decomposition commenced. Increased reaction occurred at 19 eV.

**Sulphur dioxide**:

According to Nekrasov and Schneerson⁴⁸ the following reaction takes place when sulphur dioxide is bombarded at low pressure (0.01 mm Hg) with slow electron from a calcium oxide covered filament.

\[
\text{SO}_2 \rightarrow \text{SO}_2^+ + e^- \quad \text{at } 12.2 \pm 0.5 \text{ eV}
\]

\[
\text{SO}_2 \rightarrow \text{SO}^+ + 0 + e^- \quad \text{at } 15.7 \pm 0.5 \text{ eV}
\]

The reaction is followed by pressure changes.

The decomposition was also studied by Joshi and Sharma⁴⁹ in ozonizer discharge. Sulphur dioxide was subjected to a.c. voltage of 4-16 kV. The pressure of the
gaseous mixture was measured as a function of time. Except at the highest voltage the reaction was rapid in the initial stage, then slowed down and finally reached an equilibrium. At this stage increasing the voltage had no further effect. The resulting mixture consisted of sulphur trioxide, oxygen and about 10% undissociated sulphur dioxide. Further unidentified solids were deposited in small amounts near the electrodes.

Formation of oxides of nitrogen:

The two gases nitrogen and oxygen are known to react in the electric arc and in silent electric discharge with the formation of oxides of nitrogen. The minimum velocities of electrons required to bring about their combination were determined by Wansbrough-Jones. He found a slight thermal reaction catalysed by the hot filament which was negligible when compared with the electron activated reaction. The rate of reaction was found to be influenced by factors like the age of the filament, the thickness of the oxide coating, and the form of the discharge. It was established that no reaction occurred unless the electrons had an energy of 17.0 eV. At this energy of the electrons, nitric oxide was the main product. At much higher energies of the electrons nitrogen dioxide was produced.
\[ e^- + N_2^+ + O_2 \rightarrow 2\text{NO} \quad \text{at 17.0 eV} \]
\[ e^- + N^+ + O_2 \rightarrow \text{NO}_2 \quad \text{at 23.0 eV} \]

This was confirmed by the deep red colour with an alcoholic solution of \(\text{\&-naphthylamine}\) and sulphanilic acid.

Henry studied the same reaction and found increased reactions at 16.8 and 23.1 eV. He identified nitrogen dioxide as the product by measuring its absorption spectrum and proposed the same reaction mechanism as done by Wansbrough-Jones.

**Nitrous oxide:**

Hinshelwood and Hutchinson found that the discharge from an induction coil in nitrous oxide at 0.7 to 2.5 mm pressure resulted in the complete decomposition of the gas. The course of the reaction was followed from pressure changes.

Joshi studied the decomposition of nitrous oxide in silent electric discharge. The velocity of the reaction, the current flowing through and the energy consumed in the ozonizer were related to the amount of nitrogen dioxide produced from the decomposition of nitrous oxide. He studied the influence of foreign gases on the decomposition, and also the effect of varying the current and the power during the reaction.
Joshi and Deshmukh\textsuperscript{54} studied the interaction of nitrous oxide and hydrogen in silent electric discharge. The effects of pressure, potential applied and ratio of $\text{N}_2\text{O}/\text{H}_2$ on the course of the reaction were studied.

Deshmukh et al.\textsuperscript{55} studied the interaction of nitrous oxide, oxygen and phosphorus under silent electric discharge due to potentials of 5 kV, 500 cps and high frequencies upto pressure of 73 cm Hg.

\textit{Metal halides}:

Lithium group compounds dissociated in both inert gases and in hydrogen to give metals. Relative reaction rates were determined for the iodides, bromides, chlorides and fluorides of lithium, sodium, potassium and caesium\textsuperscript{56,57}. It was noted that for any one metal the rate was the greatest for the iodide and least for the fluorides as might be expected from the bond energies. The rates presumably depend largely on the energy levels to which the molecules must be raised before dissociation will occur.

The glow discharge of boron trichloride has been studied by several workers\textsuperscript{58-67}. Hotzmann and Morris\textsuperscript{60} analysed the light from glows of boron trichloride at 1 mm of Hg pressure excited by $2.5 \times 10^9$ Hz field. They observed bands due to boron monochloride and lines due to atomic boron and atomic chlorine.
It has been found that the compound B$_2$Cl$_4$ can be decomposed under a variety of conditions. Rosenberg$^{61}$ used 60 Hz, 10 kV discharge and obtained BC$_3$ (g) and (BCl)$_n$, which he described as a light brown or yellow film which is hydrolysed by water to form B$_2$O$_3$, HCl and hydrogen.

**Polymerization:**

The conversion of volatile organic compounds into liquid and solid products by the action of a high voltage gas discharge has been observed by many investigators$^{68}$. Solid polymers have been made by electric discharge from vinyl monomers. Thus styrene$^{69-71}$, vinyl acetate$^{72}$, methyl methacrylate$^{69}$ and numerous alkenes have been polymerized by exposure to discharge. The products were compared with polymers made from the same monomers by conventional catalysts and the close similarity of infrared spectra indicated similar molecular structures.

Brominated and chlorinated compounds were tried in view of their known influence on the course of other polymerization reactions$^{73,74}$.

(4) **Synthesis and Decomposition of Ammonia under Electric Discharge:**

De Hemptinne$^{75}$ found that in silent electric discharge high pressures and high temperatures are unfavourable for the
decomposition of ammonia.

Pohl\textsuperscript{76} used a Siemens tube to study the decomposition of ammonia and found that Faraday's law was not applicable.

Le Blanc\textsuperscript{77} showed that the decomposition of ammonia in silent electric discharge followed the first order initially but as the reaction proceeded with the current held constant the first order constant changed. Increase of temperature from 20 to $132^\circ$C was required to double the rate of decomposition. The rate also increased with increasing voltage. When hydrogen was initially present with ammonia, the first order velocity constant decreased as the reaction proceeded while when nitrogen was initially present the rate constant increased.

Davies\textsuperscript{78} found that the first order rate of ammonia decomposition was maintained under constant current upto 80\% of decomposition, after which it dropped slightly. An increase of discharge current by 30\% caused an 80\% increase in the rate of decomposition. The rate doubled on increasing the temperature through an interval of $100^\circ$C. The velocity constant increased slightly with decrease of pressure at constant current. The increase of rate was greater for the same drop in pressure at constant voltage than at constant current. Excess of hydrogen lowered and excess of nitrogen increased the velocity constant at constant current.
McLennan and Greenwood\textsuperscript{79} studied the decomposition of ammonia under the influence of cathode rays. The progress of the decomposition was indicated by the pressure changes within the reaction vessel. A doubling in pressure indicated complete decomposition. No decomposition was observed above 4 mm of pressure while below 0.68 mm the decomposition became very rapid. The decomposition rate was independent of ammonia pressure for constant voltage and current i.e., each electron decomposed a definite number of ammonia molecules. The rate of decomposition increased with the electron speed. Excess nitrogen had no effect on the rate of the decomposition, but hydrogen lowered it.

In a series of investigations Brewer and coworkers\textsuperscript{80-83} studied the decomposition of ammonia in the glow discharge. The pressures used varied from 4 mm Hg to about 0.1 mm. The reaction vessel was immersed in liquid air, so that the reaction products were frozen out on the walls of the discharge tube. The influence of pressure, current, external magnetic fields and shape of discharge tube on the chemical reaction were studied. Pressure and temperature had no influence on the synthesis of ammonia in the glow discharge from a $3 \text{H}_2 : \text{N}_2$ mixture.

Brewer and Westhaver\textsuperscript{80} also examined the synthesis of ammonia in the presence of helium. They found that the rate of reaction was independent of the pressure as long as
the composition of the gas did not change. The partial pressure of helium could be increased upto 70% of the total without affecting the reaction rate.

De Hemptinne\textsuperscript{84} studied the rate of synthesis and decomposition of ammonia in point to plate discharge at 40 mm pressure using a Ruhmkorff coil. In decomposition it made no difference whether the point was positive or negative. In synthesis, however, the rate was slightly faster when the point was negative. No difference could be observed in rate with a static machine on reversing the poles.

Lsanitsch\textsuperscript{85} studied some addition reactions of ammonia with unsaturated hydrocarbons in silent electric discharge. Ethylene and ammonia gave an oily yellow liquid with strong odour and basic properties which was soluble in ether, benzene and acids but insoluble in water.

Comanducci\textsuperscript{86} found that a mixture of ammonia and oxygen while yielding traces of hydroxylamine, gave no hydrazine or nitrous acid.

Makowetzky\textsuperscript{87} synthesized ammonia in glow discharge between an electrode in the gas phase and the other in liquid water.

Besson\textsuperscript{88}, while studying the decomposition of a mixture of ammonia and hydrogen in a silent electric discharge
obtained traces of hydrazine. He further showed that a mixture of ammonia and water vapour gave a test for hydroxylamine which could not be obtained with oxygen and ammonia, while excess of ammonia in oxygen gave both ammonium nitrite and nitrate.

Lob\textsuperscript{89} observed that a solution of ammonia in alcohol under silent electric discharge yielded a mixture of hexamethylene tetramine and ammonium formate.

Briner\textsuperscript{90} studied ammonia synthesis in the arc and arrived at the conclusion that the reaction was mainly thermal. Briner and Baerfuss\textsuperscript{91} made further investigations regarding the best conditions for producing ammonia in the electric arc. The best yields with respect to energy or current were obtained with a 1:3 mixture of nitrogen and hydrogen at atmospheric pressure, but at 100 mm the most favourable mixture was 5 N\textsubscript{2} : 1 H\textsubscript{2}. Platinum electrodes were found superior to iron or nickel with respect to yields. At low pressures the electrode separation made no difference regarding the yields.

Warburg\textsuperscript{92} compared the decomposition of ammonia by light and in electrical discharge. Later with Rump\textsuperscript{125} he noted that ammonia synthesis occurred principally on the outer edge of the discharge region and suggested that it might be associated with a catalytic wall effect.
Burk studied the Stark effect in ammonia decomposition by examining its thermal rate at the heated surface of a molybdenum or platinum wire inside a copper cylinder.

Moens and Juliard measured the rate of synthesis of ammonia in silent electric discharge and reported that it was faster in the presence of sulphuric acid.

The formation of ammonia in the presence of mercury vapour at 10 kV and 50 Hz was studied by Van der Wijk at 45°C and 100 mm pressure. The reaction occurred at the mercury surface and was proportional to its area. The following mechanism was proposed.

\[ \text{H}_2 \rightarrow \text{H} + \text{H}^+; \quad \text{H}^+ + \text{H}_2 \rightarrow \text{H}_3^+; \quad \text{H}_3^+ + \text{Hg} \rightarrow \text{H}_3\text{Hg}; \]

\[ \frac{1}{2} \text{N}_2 \rightarrow \text{N}^+; \quad \text{HgH}_3 + \text{N} \rightarrow \text{NH}_3 + \text{Hg} \]

In silent electric discharge, in the presence of mercury vapour, Van der Wijk found that the rate of synthesis was given by \( kp_{\text{H}_2} p_{\text{N}_2}^{\frac{1}{2}} \) with a maximum rate at 67% hydrogen and 33% nitrogen.

Lavin and Bates decomposed ammonia in a discharge tube and obtained the products as \( \text{NH}_2 \) and \( \text{NH} \) radicals.

Rinkel, Alsfeld and Wilhelmy studied the decomposition of ammonia in high frequency glow discharge regarding the dependence of the rate upon the presence of the
decomposition products or excess of either. At initial pressures of 1.6-4 mm the rate of decomposition remained proportional to the partial pressure of ammonia upto 80% of the reaction. With excess of nitrogen the rate was greater than with excess of hydrogen. The reaction followed first order kinetics. Rinkel et al. found the maximum rate of synthesis in a 1:1 mixture, whereas Wilhelmy and Alsfeld found it at 60% nitrogen. They found equilibrium at about 2% ammonia. For synthesis the effectiveness of the electrode materials increased as follows

$$\text{Al} < \text{Ta} < \text{Cu} < \text{Fe}$$

Bredig, Koenig and Wagner\textsuperscript{100} sought the best conditions for the formation of hydrazine from ammonia in the Siemens tube with either alternating or direct current discharge. They assumed a stepwise dissociation of the ammonia.

$$\text{NH}_3 \rightarrow \text{NH}_2 \rightarrow \text{NH} \rightarrow \text{N}$$

They decomposed the gas both at low and high pressures and at the cooled high voltage arc. Low voltage and high rate of flow of ammonia were found to be the most favourable conditions.

Schumb and Hunt\textsuperscript{101} synthesized ammonia from a 3 $\text{H}_2 : 1$ $\text{N}_2$ mixture in electrodeless discharge.
Westhaver studied the decomposition of ammonia in glow discharge. He discovered that some hydrazine was formed in the positive column but none in the negative glow. The rate was proportional to the current but was independent of the pressure. The ions \( \text{N}_2^+ \), \( \text{A}^+ \), \( \text{He}^+ \), \( \text{O}_2^+ \) and \( \text{Hg}^+ \) could initiate the decomposition but \( \text{H}_2^+ \) could not.

Schumb and Goldman carried out investigation of ammonia synthesis in electrodeless discharge at pressures of 0.5 to 1.5 mm of stoichiometric mixture with currents of 5.8 amperes. He showed that the synthesis under these conditions was a wall reaction.

Koenig and Brings measured the production of hydrazine by glow discharge in ammonia and considered that the \( \text{NH} \) or \( \text{NH}_2 \) radical might be the intermediate product.

\[
\text{NH} + \text{NH}_3 \rightarrow \text{N}_2\text{H}_4 \quad \text{or} \quad \text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_4
\]

They observed that as much as 94% of the ammonia was converted into hydrazine at 4.2 kV but only 60% at 14.5 kV.

Jolibois claimed that the synthesis of ammonia could be accomplished in glow discharge by introducing hydrogen and nitrogen into the cathode region at pressures up to 50 mm and with a current intensity sufficiently low to allow the electrodes to remain cold.
Erich Tiede and Emil Hey\textsuperscript{106} studied the influence of the electrode material and contact catalysis in the production of ammonia in the glow discharge. The ammonia yield from a mixture of 70\% nitrogen and 30\% hydrogen in the glow discharge between different electrodes was measured. The primary process of ammonia formation and role of nitrogen atom were investigated obtaining at the same time new experimental data concerning ammonia catalysis. The ability of the electrode metal to adsorb nitrogen atoms and thereby accelerate their union to molecules increased in the order W, Al, Ni, Cu, Fe, Pt. The results indicated that the various steps in the catalytic reaction were

(a) $N \text{ adsorbed} + H \text{ adsorbed} + \text{Metal} \rightleftharpoons \text{Metal NH}$

(b) $\text{Metal NH} + H_2 \rightleftharpoons \text{Metal} + \text{NH}_3$

The temperature dependence of the rate constant on the decomposition of ammonia in the electric discharge was studied by Zakhavaeva\textsuperscript{126}. A glass tube was provided with a tungsten wire along the axis and a tungsten spiral along the wall. The tube was filled with ammonia at 64 torr. When the voltage between wire and spiral was raised, corona discharge started at a voltage which decreased with increase in temperature (1500 volt at $-20^\circ$, 600 volt at $180^\circ$). The gas pressure decreased during the discharge. The rate constant $K$ had a maximum at $10-20^\circ$. The final degree of decomposition of ammonia was 1.0 at $10^\circ$ and 0.9 at $-10^\circ$ and
When the electric power was increased, K passed through a maximum at 9.5 watts.

Lebedev et al. \(^{107}\) studied the decomposition of ammonia in glow discharge in the presence of mercury and sodium vapour in connection with the theory of 'energetic catalysis' and found that mercury had a positive and sodium had a negative catalytic effect. The sensitizing effect of mercury was similar to that found in the photochemical decomposition of ammonia.

A method has been described by Kenichi Ouchi \(^{108}\) for measuring the rate of decomposition of ammonia in the discharge tube at the instant when the discharge begins. He found that at longer discharge currents the decomposition rate was higher. The rate was the highest at the center of the positive column in the glow discharge. Kenichi Ouchi and Toshibumi Takamatsu \(^{109}\) showed that the decomposition energy of ammonia in the negative glow in a discharge tube was 23.5 eV. They further showed that the value was lower than the ionization energy of ammonia and so the decomposition of ammonia in the negative glow could be attributed entirely to the ionization of ammonia.

It was found by Kenichi Ouchi \(^{110}\) that most of the hydrazine was found near the boundary between the Faraday dark space and positive column. The amount of ammonia
decomposed in the region of negative glow was greater than in the positive column. The decomposition of ammonia in the negative glow could be entirely attributed to ionization.

Devins and Burton\textsuperscript{111} studied the formation of hydrazine in the decomposition of ammonia in a direct current electric discharge at a pressure of 0.6 to 11 mm. They found that $\text{N}_2\text{H}_4$, N as well as H were produced by apparently unconnected processes. Hydrazine only was produced in the positive column. The nitrogen yield was unaffected by any back reaction.

Kenichi Ouchi\textsuperscript{112} calculated the ionisation efficiencies of nitrogen, hydrogen, argon, helium and ammonia in the glow discharge from the cathode potential drop and the length of the negative glow. He showed that the decomposition of ammonia in the positive column was not due to ionization.

Kenichi Ouchi and Toshibumi Takamatsu\textsuperscript{113} studied the mechanism of ammonia decomposition. They measured the electron energy in the positive column by Langmuir's probe method and further analysed the spectra of the glow. They proposed the probable mechanism as:

\[
\begin{align*}
\text{NH}_3 + e & \rightarrow \text{NH}_3^* + e \\
\text{NH}_3^* & \rightarrow \text{NH} + \text{H}_2 \\
\text{NH} + \text{NH}_3 & \rightarrow \text{N}_2 + 2\text{H}_2
\end{align*}
\]
(5) **Mechanism of Chemical Reactions in Electric Discharge**

Several mechanisms have been suggested to account for the observed chemical reactions under electric discharge.

(A) **Dynamic clusters**: This theory is originally due to Lind and it has been modified by several investigators. According to this theory the positive ions produced in the electric discharge attract the molecules around them forming clusters and chemical reaction originates in these clusters. Mund considered the interaction between the central ion and the clustered or co-ordinated molecules of the gas on the basis of the electrostatic forces acting between the charged ion and the permanent and/or induced dipoles of the neutral molecules. For an ion of charge $e$ and molecules of dipole moment $\mu$ this force, at distance $R$ is,

$$F = \frac{2e\mu}{R^3}$$

Consider a molecule of kinetic energy $W$ in the immediate neighbourhood of the ion, attempting to leave it. When $W < \int F dR$ the molecule will be held by the attraction of the ion. Hence all molecules of energy $W$ and lower will be captured when they enter the region defined by the radius $\xi$,

$$\xi = \left(\frac{e\mu}{W}\right)^{1/3}$$
if $W = 5.7 \times 10^{-14}$ erg. = mean K.E of a gas molecule at 0°C
$e = 4.77 \times 10^{-10}$ e.s.u., and $\mu = 1$ debye, $\zeta$ is found to be 9.1 Å.

Since the average distance between molecules is 33 Å (N.T.P.) one notes that the radius of certain capture is about $1/3$ of the distance between the molecules. Mund suggested that each ion is enveloped by a small region of gas density higher than the average concentration in the main body of the gas. In a mixture of gases the proportions of molecules in the cluster will depend upon their relative concentrations, their permanent dipole moments and on their polarizabilities. The cluster pictured here is a dynamic agglomerate of molecules which will be constantly leaving the vicinity of the ion, being replaced by new comers. While the molecules are in the neighbourhood of the ion, they are in a distorted or strained state and may be able to undergo reactions which they cannot enter into while in field free space. In other words they are activated in the field of the ion. The molecules attached to the ion are in motion and in their motion about the charged center, they have opportunity of making impacts and rearranging themselves into new chemical configurations. The ion thus assumes the role of a catalyst. Gunther and Cohn favor this variant of the cluster theory. The molecules which are caught at large distances from ion will not furnish any
appreciable potential energy which might be used for activation within the cluster. If however they enter the first layer of molecules attached to the ion, considerable energy will be released. In any case, the question arises regarding the process of formation of the cluster. There are attractive forces acting, but the energy must be removed if the cluster is to be stable. The energy may leave the system as radiation, be taken away in a collision or be distributed into various degrees of freedom if the system is complex enough.

Rideal\(^{120}\) and Mund\(^{115}\) have attempted to calculate the radius of the dynamic cluster in terms of the dielectric constant of the gas. The induced dipole \(\mu_i\) of a nonpolar molecule located in an electric field \(E\) is given by

\[
\mu_i = \alpha E
\]

where \(\alpha\) = polarizability of the substance. The critical radius of the dynamic cluster is given by

\[
\zeta = (\varepsilon - 1)^{1/2} \times 2.8 \times 10^{-7} \text{ cm}
\]

where \(\varepsilon\) = dielectric constant. This is valid for non-polar molecules.

Eyring Hirschfelder and Taylor\(^ {122}\) believe that the formation of cluster is a prominent feature of the
mechanism of reaction. These investigators calculated the equilibrium constant of cluster formation for the reaction,

$$A + B^+ \rightleftharpoons AB^+$$

$A =$ neutral molecule; $B^+ =$ ion; $AB^+ =$ cluster

and at equilibrium

$$K = \frac{[AB^+]}{[A][B^+]})$$

This constant can be expressed in terms of the partition functions of the interacting species and leads to the expression

$$\frac{[AB^+]}{[B^+]} = 6.46 \times 10^{-4} \left( \frac{MA + MB}{MAMB} \right)^{\frac{1}{2}} d^2 P_A \exp \frac{277 a}{d^2}$$

(B) The hot spot theory of ion clusters: Livingston\textsuperscript{121} developed the hot spot theory of cluster reaction. This type of mechanism was tested by Lind and Livingston\textsuperscript{123} in respect to HBr synthesis and decomposition. It is called the 'hot spot' theory because the central idea involves the concept of a high temperature region about the cluster where reaction takes place. An ion either positive or negative produced by any means whatever will cluster other molecules in accordance with their dipole nature, their polarizabilities and their relative amounts. No reaction occurs until neutralization sets in, when the large recombination energy becomes available, which raises the cluster to a 'high
temperature' i.e. the cluster is now having an energy content which it could attain only if it existed at some equivalent high temperature. The energy of recombination spreads over the whole cluster, activating bonds and hence initiating chemical reactions. The whole agglomerate will then separate into the reaction products.

(C) Atomic mechanism: The reactions in discharge or by alpha radiations may be considered on the basis of a non cluster mechanism in opposition to the views just described. The reactions of atomic hydrogen, oxygen, nitrogen and chlorine studied in flow systems can be explained by atomic mechanism. Byringer, Hirschfelder and Taylor\textsuperscript{122} studied the ortho and para hydrogen conversion and synthesis and decomposition of hydrogen bromide. In the latter case they considered the possibility of a variety of ions and atoms and several of these have actually been found in mass spectrographic studies. However none of these is important except hydrogen atoms in the present reaction mechanism where hydrogen atoms react with either HBr or Br\textsubscript{2}.

\[
\begin{align*}
    \text{H} + \text{Br}_2 & \xrightarrow{k_3} \text{HBr} + \text{Br} + 36 \text{ kcal} \\
    \text{H} + \text{HBr} & \xrightarrow{k_4} \text{H}_2 + \text{Br} + 16 \text{ kcal}
\end{align*}
\]

The relative rate \( (k_3/k_4) \) of these two reactions was known to be 8.4 from the work of Bodenstein and Jung\textsuperscript{124}. 
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