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**GLOW DISCHARGE REACTORS FOR HYDRAZINE SYNTHESIS**

by

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SUMMARY

The synthesis of hydrazine from ammonia at a pressure of 10 torr has been studied in two types of glow discharge reactors, viz., a crossed discharge reactor and a beam scanning reactor. These reactors were developed in an attempt to eliminate the problems associated with beam constriction phenomena. A limited amount of work was carried out with the first reactor and when it became apparent that it had no real advantages, it was abandoned in favour of the beam scanning reactor. The latter has now been studied in depth using both continuous and pulsed DC power supplies. It has been found that both hydrazine formation and ammonia conversion are improved by beam scanning. Under certain conditions, the effects of operating variables may be described through two parameters; the product of the discharge current and mean residence time in the continuous discharge and the pulse number in the pulsed discharge. Decreasing values of these parameters are associated with an increasing efficiency of hydrazine production.

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## 1.0. INTRODUCTION.

### 1.1. General.

For more than a hundred years the phenomenon of electric discharges has been the subject of extensive study and as a consequence voluminous literature has accumulated. Most of this work, however, has been dedicated to the atomic and subatomic phenomena but nevertheless some of it was directed towards the development of a commercial method of chemical synthesis using non-disruptive electrical discharges. Ozone production on a commercial scale was the only breakthrough provided by this new technique of chemical synthesis. The failure to utilize this technique in other processes was mainly due to the complexity of the discharge reactions and the insufficient data available to assess the effect of operational variables on the yield of the desired products. Another and more serious problem was that, the manufacture of the appropriate electrical generating equipment was in its infancy. Despite this declining attitude, resurgence of interest emerged especially after the Second World War, when there was an increasing demand for the commercial production of a large range of specialized chemicals that could not be made readily by conventional methods. This sophistication of chemical technology has led to the necessity of synthesis and product fabrication by some means other than the conventional methods. The gas discharge appeared to have more attractive commercial potentiality than most of the other novel synthesis techniques. This is because the energy required for chemical activation could readily and quite efficiently be supplied by electric power of varying natures in contrast to other

radiation methods such as ultra-violet radiation or radioisotopes which are by comparison, very much more expensive as far as energy charges are concerned, even though, they may be more selective.<sup>(1)</sup>

At present the cost of thermal energy is cheaper than that of electrical energy and one can argue that it is more beneficial to use the conventional methods of chemical synthesis than the sophisticated and slightly more expensive technique of gas discharges. But, it is worthwhile noticing that the development of the breeder atomic reactor is going to cut the cost of electrical generation quite considerably.<sup>(2)</sup> It therefore follows that over the years ahead processes based on electrical energy utilization are going to be in a more competitive position.

Gas-phase discharge synthesis has another feature of interest over conventional techniques, and this is the possibility of producing compounds which are more reactive than their starting materials e.g. hydrazine from ammonia, ozone from oxygen and hydrogen peroxide from water. These are relatively difficult processes for conventional methods and are indeed not easy in the gas discharge, the reason being that most gas discharge reactions proceed to completion in one stage in the discharge in contrast to the multistage process used in many conventional chemical synthesis, and as such the products formed are liable to destruction by the action of the discharge. Fortunately, it now appears possible to minimize this effect by the correct manipulation of operating variables. Another drawback of the gas discharge is the incapability of reaction selectivity which will result in a spectrum of products and hence making downstream purification a problem. Again current developments have shown that reaction

selectivity can be obtained by the correct choice of operating variables<sup>(3)</sup>.

It follows from the foregoing argument that the impetus for the current gas-phase electrochemical research was inevitable. This interest has also been triggered by the commercial success of liquid phase techniques such as the industrial application of the liquid-phase electrolytic process for the production of adiponitrile from acrylonitrile in the nylon process<sup>(4)</sup>.

### 1.2. The Gas Discharge.

A gas in its normal form is almost a perfect insulator and in every day life is widely used as such. However, when an electric field of sufficient intensity is established between two electrodes, the gas can become a conductor and the transition from an insulating to an almost completely conducting state is called the electric breakdown or gas discharge. The reason for this sudden disruption is due to the build up of charged species in the region which will eventually make the conduction of electricity possible. The detailed physics of the processes involved in the initiation and maintenance of this discharge is very much complicated and for this reason has been abandoned. For further study some excellent texts such as VON ENGEL'S<sup>(6)</sup> and others<sup>(7,8)</sup> will be recommended.

In any gas discharge the prime agent responsible for most of these processes is the electron. It transfers the energy from an electrical power supply to the gas, produces ions which engage in the ion chemistry, and it excites molecules which will dissociate to form the free radicals from whence originate the chemical chain processes.

The transfer of energy takes place through collisions between the electrons and the gas molecules. There are two types of collisions which an electron can undergo, elastic and inelastic. An elastic collision is one in which there are no changes of energy in the colliding particles, only electron scattering will result. An inelastic collision on the other hand, involves in addition to electron scattering changes in the energy of the gas molecule and usually leaves the latter in some form of excitation. The mode of excitation resulting as a consequence of this collision will be dictated by the energy of the impacting electron.

In a discharge the electron energy usually follows a distribution similar to a Maxwell-Boltzmann distribution but the exact nature of this is still the subject of some controversy<sup>(7,9)</sup>. It usually concentrates around a mean value which depends on the field strength, gas pressure and collisional cross-section. The value of this mean energy is usually less than the ionization threshold. It therefore follows that there are relatively few electrons in the diminishing tail of the distribution function that are able to ionize the gas molecules. These ionization processes play an important role in the initiation of the discharge but their contribution to the chemistry of the discharge leading to product formation is negligible. The electron energy distribution can, for convenience, be broken down broadly into three different energy classes depending on the origin of the electron. There are high energy primary electrons emitted from the electrodes as the result of positive ion impact, field emission at sharp points on electrodes, and thermionic emission in the case of arc-type discharges where electrodes become strongly heated. There

are secondary electrons of lower energy emitted by the gas molecules as they are ionised by primary collisions of the form,



where, A is a ground state neutral molecule or atom. These secondary electrons do not possess enough energy to ionise the gas, but play a predominant role in other activation phenomena leading to chemical reaction. Finally, there are very low energy electrons which originate from other secondary processes.

For each gas there is a certain threshold value of electron energy below which only inelastic collision occurs. It therefore follows that, since the thresholds for excitation are lower than for ionization and also the cross-section for excitation rise more rapidly with energies above the thresholds than do those for ionization,<sup>(11,95)</sup> electrons at the diminishing tail of the distribution function can be more effective in producing excitation than in producing ionization. Several modes of excitation are possible. A molecule can be excited either rotationally, vibrationally or electronically. The most important of these is the vibrational excitation. A vibrationally excited molecule or atom could be ionised on future impact with electrons or (itself) could ionise particles whose ionization potential is lower than the excitation energy (Penning ionization). However, the most important consequent event of molecular excitation is the dissociative decay of the molecule with a subsequent formation of free radicals, i.e.



For this process to be feasible, the colliding electron must have energy in excess of the dissociation energy. The above process will be

followed by free radical reactions leading to product formation. Free radical reactions have comparatively low rate constants of approximately  $10^7 - 10^9$  lit./mole.sec., and therefore the rate of neutral production is the rate of free radical reactions.

In a gas discharge electrons produced by the foregoing processes must be balanced by loss mechanisms in order to keep a steady state condition. The most common of these electron loss processes is through the external circuit, in discharges with electrodes, though a certain amount is lost by ambipolar diffusion to the walls and to a lesser extent by recombination. The foremost among the latter processes is the loss of electrons by ion recombination reaction, viz.



Electron-ion reactions can be strongly exothermic and coulombic attraction between the ions and electrons means the rate constants are as high as  $10^{-6} - 10^{-7} \text{ cm}^3 \cdot \text{sec}^{-1}$  (12,13,14). The process is strictly two-body, and the rate of electron loss can be described as,

$$\frac{dn_e}{dt} = -\alpha_d n_e n_+ \quad \dots\dots\dots(1.4)$$

where,  $\alpha_d$  is the rate constant. Since the plasma is very nearly electrically neutral,  $n_e = n_+$ , and the rate of loss can be re-written as,

$$\frac{dn_e}{dt} = -\alpha_d n_e^2 \quad \dots\dots\dots(1.5)$$

At electron densities of around  $10^{10} \text{ cm}^{-3}$  (typical of a glow discharge), the life time of an electron against recombination is around a millisecond.

At higher electron densities say  $10^{12} \text{ cm}^{-3}$ , a second recombination process will be of interest and this is the third-body recombination with an electron as the third body



For most laboratory gas discharges in which  $n_e \approx 10^{10} \text{ cm}^{-3}$  this process is not significant.

Another recombination process which occurs so slowly as to be negligible is radiative recombination, i.e.,



Electrons can also be lost through attachment to form negative ions in gases for which negative ions exist. Three-body attachment,

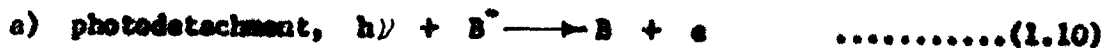


can exist at all energies and have a rate constant of the order  $10^{-30} \text{ cm}^6 \cdot \text{sec}^{-1(15)}$ . A second attachment process is the dissociative attachment of molecules,



This process usually requires the electrons to have an energy of a few e.v. in order to proceed. In general the rate coefficients for this process can range as high as  $10^{-10} \text{ cm}^3 \cdot \text{sec}^{-1}$  for ground state molecules or could be higher if the molecules are vibrationally or electronically excited. Even with rates of up to  $10^{-10} \text{ cm}^3 \cdot \text{sec}^{-1}$  and gas pressures of a fraction of a mm Hg the electron lifetime against this kind of attachment is of the order of a microsecond and therefore this process completely overwhelms dissociative recombination as an electron loss mechanism. However, it is incorrect to assume that such a rapid process will describe the removal of electrons. The reason being that when an electron recombines with an ion, it is bound

tightly in an atom, while in forming a negative ion the electron binding energy is an order of magnitude less. Numerous processes will operate to dislodge the electron from the negative ion, such as,



The most probable of these in a gas discharge is the associative detachment. For these reasons the concentration of negative ions in a discharge is low. MELTON<sup>(16)</sup> has shown that in ammonia with 100 e.v. electrons, only 0.4% of the species produced were negative ions.

### 1.3. Electric Discharge Devices.

#### 1.3.1. General.

The nomenclature of most electric discharge reactors employed in gas discharge research ~~is~~ somewhat descriptive of the physical nature of the given device and the plasma environment formed in it, and ~~is~~ sometimes influenced by the individual who was closely associated with the study of the particular device. For example, a glow discharge reactor is one in which the plasma glows and the pressure of the gas is below 20 mm Hg whereas an ozonizer is a device for producing ozone.

An examination of the numerous types of electric discharge devices would reveal that each almost without exception has three

elements illustrated below,

| (1)                                                            | (2)                                  | (3)                                                                                                                            |
|----------------------------------------------------------------|--------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|
| POWER<br>SUPPLY                                                | COUPLING<br>MECHANISM                | PLASMA<br>ENVIRONMENT                                                                                                          |
| D.C.<br>Pulsed D.C.<br>A.C. }<br>R.F. } or pulsed<br>Microwave | Resistive<br>Capacitive<br>Inductive | Current level<br>Pressure<br>Gas flow, temp.etc.<br>boundaries: solid<br>liquid phases<br>Electrical fields<br>Magnetic fields |

Every device is sustained by an electrical source (1) through a given coupling mechanism (2), to a plasma with a particular environment (3). It is clear that this simplified picture becomes much more complicated if one considers the number of ways with which these three elements can be combined. Therefore, it is not the intention to discuss the classification of these devices as this has been dealt with elsewhere<sup>(3,17,18)</sup>. Only those which I have experimented with are going to receive any attention.

### 1.3.2. The D.C. Glow Discharge.

This is the simplest form of all gas discharges. It was first studied by FARADAY between 1831 and 1835<sup>(19)</sup>. At low pressure (1 mm Hg) he found that the discharge consisted of glowing areas separated by dark spaces of the form shown in Fig. 1.1. The sequence of these regions has been recognised as Aston dark space, cathode layer, cathode dark space, negative glow, Faraday dark space, positive column, anode glow and finally the anode dark space. The reason for the nature of these dark and glowing regions lies in the fact that in the former

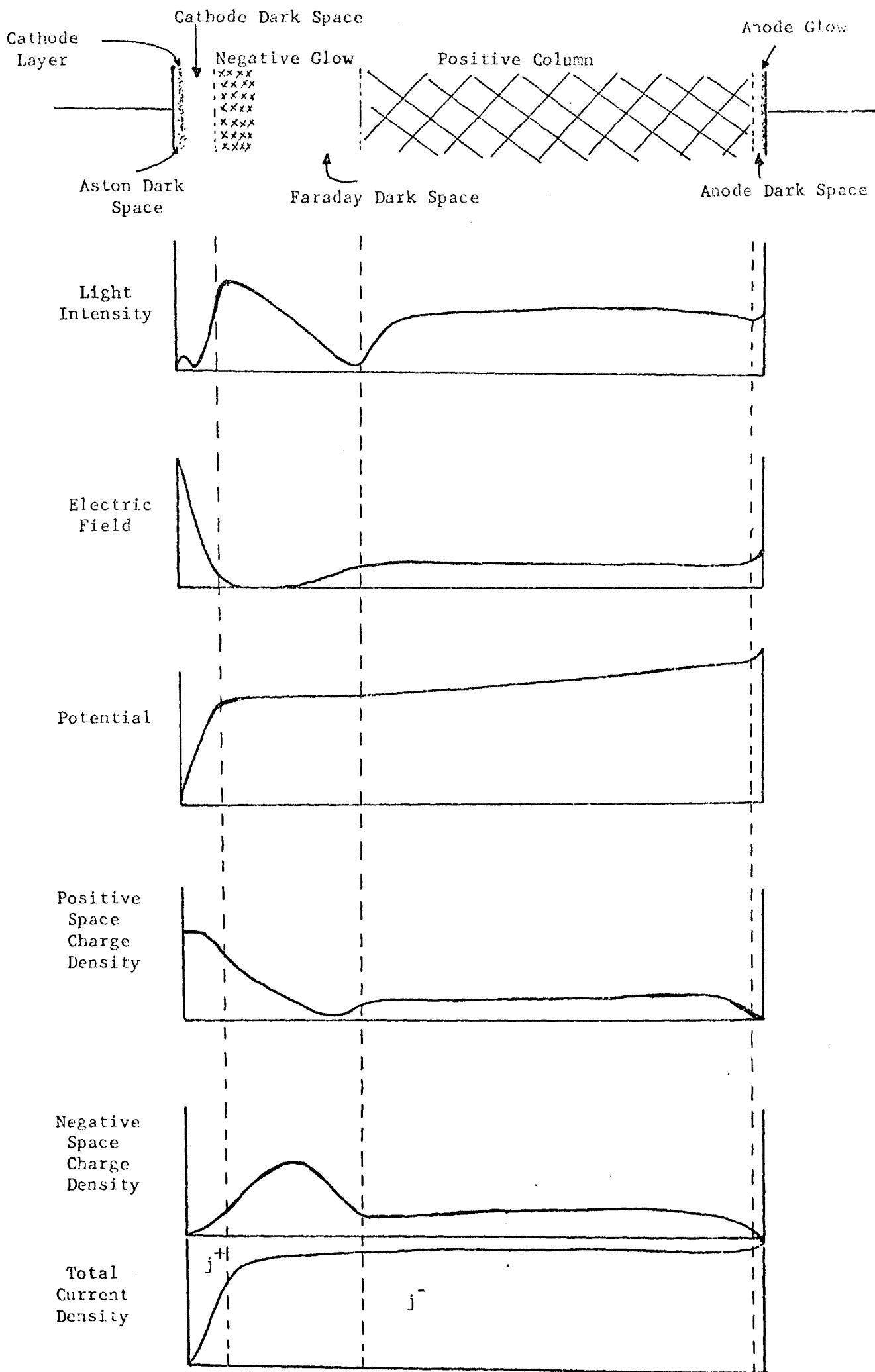


Figure 1.1. Characteristics of a Glow Discharge.

electrons are being accelerated while in the latter electron impact causes ionization and excitation of the gas molecules with the subsequent emission of light. It therefore follows that due to the different characteristics of these regions it is reasonable to expect that certain different reactions will proceed preferentially in one region or other in the discharge. This has been shown to be the case in the nitrogen-hydrogen discharge where ammonia and hydrazine are found to form preferentially in the negative glow and positive column respectively<sup>(20)</sup>.

The physical sizes of these different regions depend on the pressure of the gas and the electrode separation. In the case of ammonia at low pressures (fraction of a mm Hg) the whole of the discharge tube is filled with the negative glow while at higher pressures ( $>10$  mm Hg) the positive column expands to practically fill the whole cell. The size of the positive column is also magnified at the expense of the negative glow and other dark spaces when the electrode separation is increased. For example, for ammonia at 10 mm Hg and electrode spacing of 6.3 cm, SAVAGE<sup>(21)</sup> has found that the positive column was 5.0 cm. It therefore follows that from a hydrazine synthesis viewpoint, it will be more beneficial to operate at both high pressures (maximum for glow discharge is 20 mm Hg) and large discharge gap, but it must be realized that these conditions will entail high voltage requirements which will in turn pose a safety problem besides the expensive cost of the generating equipment.

A summary of the electrical properties of a glow discharge is shown in Fig.1.1. The most significant of these is the variation in the potential drops across these different regions. It is clear

that most of the applied potential is dissipated in the cathode dark space while the potential difference across the positive column is rather small giving it a constant field strength of the order of a few volts/cm. This field is not sufficient to cause considerable ionization, indicating that ionization is not obtained from the electron motion in the direction of the field but rather from the large random velocity which the electrons acquire by elastic collisions. The potential drop across the cathode dark space is known as the cathode drop or fall, and it is found to be proportional to the current density<sup>(22)</sup>.

The glow discharge could be operated in three different regions depending on the value of current. There is the subnormal region characterised by a fall in the operating voltage as the current is increased, the normal glow region where the voltage is independent of the current, and finally the abnormal glow where further increase in current is usually accompanied by an increase in the operating voltage. These transitions from one region to another are attributed to electrode effects by some<sup>(6)</sup>, or electron-ion recombinations in the positive column by others<sup>(23,24)</sup>.

In order to sustain the non-disruptive nature of the D.C. glow discharge a ballast resistor is to be connected in series with the discharge cell. The value of the resistor will depend on the operational requirements such as pressure, discharge gap and current levels and may range from  $2K\Omega$  to as much as  $100K\Omega$ . It is the power dissipated in this load which puts the D.C. glow discharge at an economical disadvantage.

### 1.3.3. The Pulsed D.C. Discharge.

In this type of discharge the gas is first broken down, a glow discharge then generates which will last for a certain time interval, followed by a voltage cut off. The discharge then decays electrically and chemically until the next pulse is applied. It follows that both the voltage and current will be of a rising and falling nature whose exact characteristics will depend on the type of gas used and the vast number of operating variables such as pressure, pulse duration, pulse repetition rate, peak current. Some typical waveforms are depicted in Fig. 1.2.

When the pulse width is varied two effects come into play. Firstly, if the pulse width,  $t_p$ , is greater than the formative time lag,  $t_f$ , then it is possible to extend the shoulder,  $t_s$ , without a consequent distortion of the waveforms. Secondly, if the cut off time,  $t_d$ , is shorter than the formative time lag,  $t_f$ , then the peak voltage,  $V_p$ , increases slightly and also the slope of the leading edge of the voltage pulse increases so as to decrease the rise time,  $t_r$ , without a change in the current waveforms.

The power dissipated in the pulse discharge is not constant throughout the pulse but varies with time. So, in order to compute the overall energy in a pulse, it is necessary to calculate the power at every instant and then integrating over the whole pulse time taking into account the pulse decay time  $t_d$ . This could be done efficiently by oscilloscopic display of the current and voltage waveforms followed by graphical integration of the expression,

$$\text{Energy/pulse} = \int_0^T I_t V_t dt$$

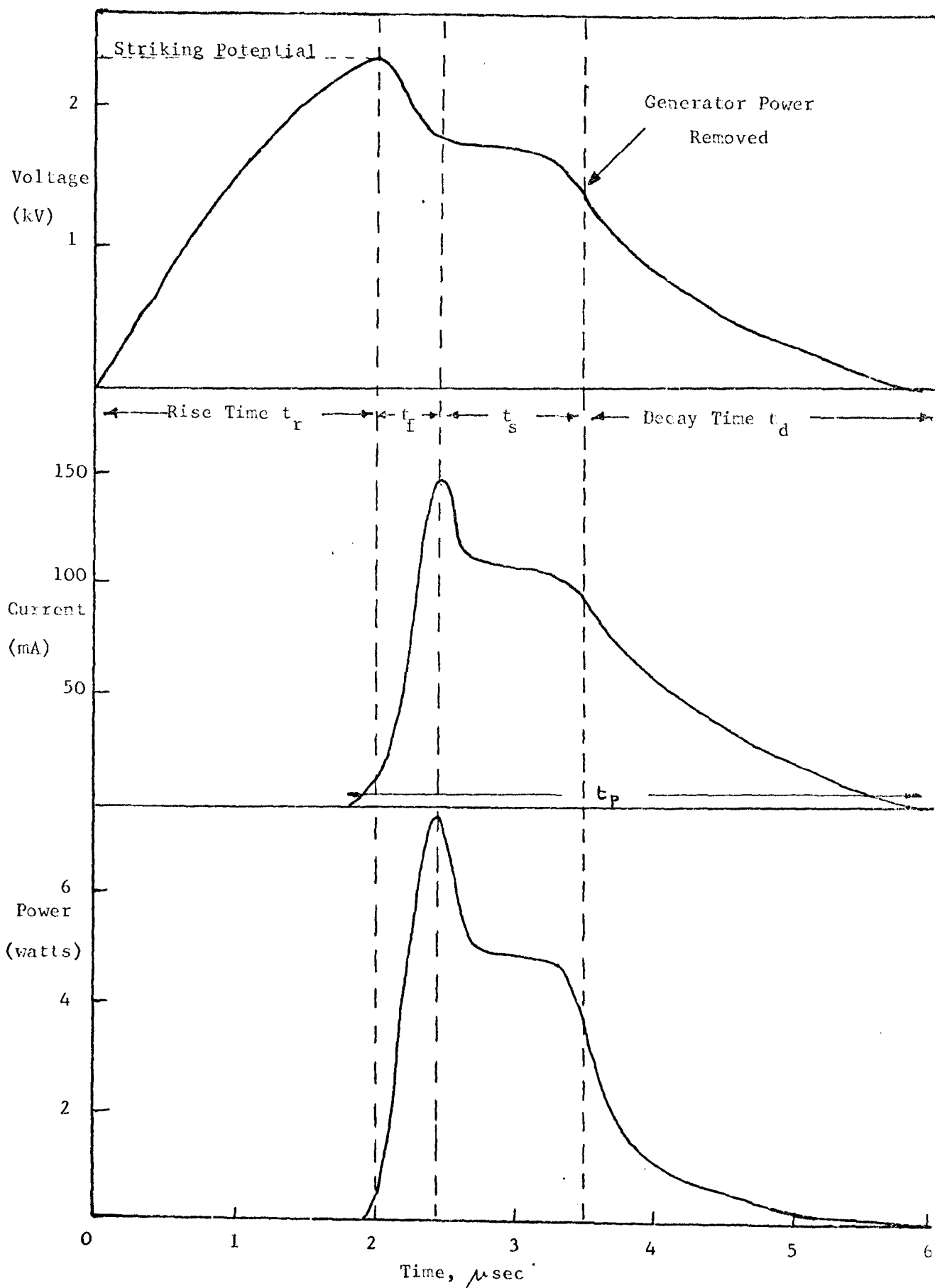


Figure 1.2. Typical Voltage, Current, and Power Waveforms for a Pulsed Discharge.

using Simpson's Rule of integration.

Due to the intermittent nature of the pulsed discharge, the running voltage is usually higher than that for a correspondingly similar direct current discharge. This is due to the fact that at the beginning of each pulse the number of electrons available for ionisation is much lower compared with that in a D.C. discharge, hence necessitating the requirements of a higher potential in order to produce the extra electrons needed for discharge initiation. It follows that by applying the power in the form of discreet pulses of short duration at low repetition rates, it is possible to operate at a voltage in the vicinity of the striking potential. In principle, therefore, by applying the pulsed techniques it would be possible to enhance the axial field and thus increase the electron energy. This is by comparison far superior to the direct current discharge where variation in the parameter,  $E/p$ , is only brought about by either varying the gas pressure, or the reactor and electrode geometry, or the current density. Another characteristic of the pulsed discharge is the ease with which the maximum value of the axial electric field could be controlled by simply varying the pulse off-time. BROWN, HOWARTH and THORNTON<sup>(25)</sup> have shown that the peak pulse voltage increased with increasing pulse-off times until a plateau was reached.

The pulsed discharge technique was first employed as a device for reducing the gas activation time, especially with systems where product selectivity was important, e.g. synthesis of hydrazine from ammonia<sup>(22,26)</sup>. It was not until later that other aspects of the pulsed technique were realised<sup>(21,25)</sup>. One of the major drawbacks

of the pulsed technique, however, is the constriction of the visible zone, hence primary reaction zone, under conditions of low pulse duration<sup>(27)</sup>. The latter was preferred to long duration from the chemical synthesis standpoint, especially when the products are liable to destruction by the action of the discharge. This constriction will pose a severe problem when scaling up of these laboratory units is to be considered for industrial utilization.

#### 1.3.4. The Barrier Discharge.

In this type of discharge the electric power is delivered through electrodes which are physically separated from the plasma by a dielectric barrier such as quartz. The discharge is of a more uniform nature and with desirable current limiting properties. Hence, the complications arising from spark and arc build-up, which are encountered in conventional double electrode discharges such as the D.C. discharge, are eliminated. Also, due to the absence of contact between the gas and metal electrodes, higher product purity could be expected.

Breakdown in this type of field is usually due to randomisation of electron motion caused by collisions with the gas molecules. If we consider an electron moving in an A.C. field which is of the form  $E(t) = E_0 \cos \omega t$ , then Newton's law for the electron becomes in the absence of collisions,

$$\ddot{x} = \frac{q}{m} E_0 \cos \omega t$$

where  $\ddot{x}$  is the acceleration due to the field and  $\frac{q}{m}$  is the charge to mass ratio for the electron. The above equation will then solve to give

the velocity of the electron as

$$v = \frac{e}{m\omega} E_0 \sin \omega t$$

the rate of energy pick-up from the field i.e. the power,  $W$  is then given by

$$W = e E v = \frac{e^2 E_0^2}{m\omega} \cos \omega t \sin \omega t$$

which, if evaluated over a full cycle will give zero, thus indicating that there is no net transferral of energy from the field to the electron. This is of course a result of the fact that the applied field and the electron velocity are  $90^\circ$  out of phase. To explain why breakdown takes place one has to take into account the role of collisions in building up the energy of electrons to the point where ionisation can occur. An electron will be accelerated by the field during a portion of its cycle and then deflected in a collision. The energy parallel to the electric field is thus converted to energy perpendicular to the field. The field then proceeds to give the electrons additional energy in the direction of the field. Energy is therefore being pumped from kinetic energy of motion parallel to the field to kinetic energy in all directions.

The power supply associated with this type of discharge is of oscillatory nature typically ranging from 1 MHz to 10 MHz. The striking voltage,  $V_g$ , for this discharge usually depends on the thickness and type of barrier, electrode separation, frequency of the power source,  $f$ , as well as the nature of the gas and its pressure,  $P$ . It is usually found that  $V_g$  increases with increasing barrier thickness and discharge gap but its dependence on  $f$  and  $P$  is more irregular.

At frequencies when the transit times of charged particles are very short compared with the period of the field, the breakdown potential,  $V_g$ , is almost the same as in the case of steady fields. As the frequency is increased, however,  $V_g$  remains substantially constant and then starts to lower when the half period of the field becomes comparable with the positive ions transit time. The lowering of  $V_g$  is due to the incomplete removal of these ions during the half cycle and thus resulting in an accumulation of positive ion space charge. Further increase in  $f$  will not result in a decrease in the value of  $V_g$  as the space charge will be limited by the rate of loss of ions due to diffusion etc.

At yet higher frequencies a further reduction in  $V_g$  is noted when the period of the field approaches the transit time of electrons. Here, not all the electrons will be swept to the external circuit during half a cycle and the result will be to produce more electrons and positive ions by further ionization. At very much higher frequencies, when the period of the field will approach the electron mean free time, ionization efficiency of the field is reduced and an increase in  $V_g$  will be expected.

The  $V_g$  -  $P$  characteristics of this type of discharge have the same familiar form as the Paschen Curves for a D.C. glow discharge, i.e. a decrease in the operating pressure will result in a lower  $V_g$  until a minimum point is reached after which any further reduction in  $P$  will result in higher values for  $V_g$ . At high pressures electrons will suffer continual collisions with the gas molecules and hence not acquire enough energy to start ionization, while at very low pressures, restriction in ionization is due to a very much reduced collision rate

and also because of the ease at which electrons will be lost by diffusion to the walls.

One of the advantages of the barrier discharge as a tool for chemical synthesis is the possibility of operating at much higher pressures than that admitted with say a D.C. discharge. This is a valuable proposition from an economic viewpoint since it is better to operate at these elevated pressures where pumping costs will be more desirable. There are several disadvantages associated with this type of discharge and the most serious is the excessive dielectric heating which apart from being an expensive process in terms of power wastage, will necessitate some form of efficient cooling. The other disadvantage is that the operating voltage will be greater than normal because of the voltage drop across the barrier. This will only be so at the lower end of the frequency band and it becomes less troublesome at higher frequencies, but, unfortunately at these frequencies power losses from transmission lines to the surroundings could account for a substantial fraction of the overall power input to the system. In practice, however, there is much scope for ingenuity on the part of electrical engineers to overcome this problem.

#### 1.3.5. The Crossed Discharge.

The crossed discharge arrangement comprises a low frequency discharge at right angles to one of high frequency. The reactor assembly can take one of many forms as depicted in Fig. 1.3.

This type of discharge was first claimed by COTTON<sup>(28)</sup> who did an extensive study on the effect of this new technique on the

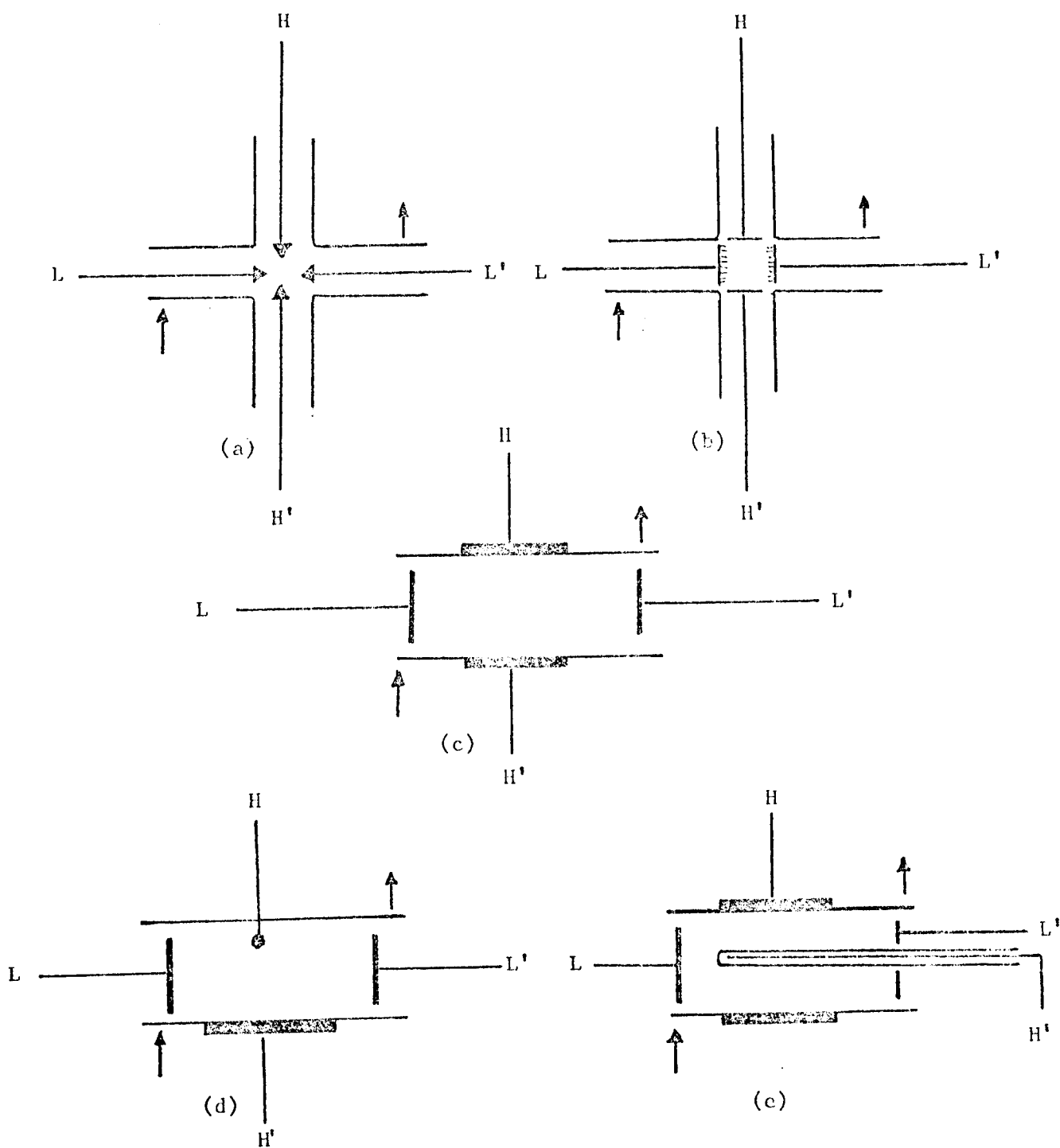


Figure 1.3. Schematic Diagram of Crossed Discharge Reactors.

L, L' = Low Frequency Terminals; H, H' = High Frequency Terminals

→ = Direction of Gas Flow.

production of nitric oxide from air and was later granted six patents<sup>(29)</sup> for his up to date discovery. The crossed discharge, he claimed, was as distinct from the previously known types of discharges such as the silent discharge, spark discharge or the glow discharge as each of these were distinct from one another. The characteristics and distinguishing features of the new device were as follows:

- a) It was possible to extend the limit of the glow discharge characteristics up to about 350 mm Hg as compared with a maximum pressure of less than 20 mm Hg for the usual D.C. discharge.
- b) It was a relatively cold discharge.
- c) This type of discharge showed a low power density due to the diffusion of the discharge zone.
- d) It resulted in unexpectedly high activation of gases and relatively high yields of reaction products.

The mechanism that resulted in these characteristics were not well understood and <sup>ure</sup>as yet not clear. Further it was observed that as the difference in frequency of the two exciting components discharges increased, the benefits and characteristics, as a rule, became more pronounced.

Most of COTTON'S work concentrated on the nitric oxide/air system and some of his studies showed that when a low frequency discharge (60 Hz) was simultaneously crossed with a high frequency discharge (1 MHz) in an assembly similar to that of Fig. 1.3(a) the yield of nitric oxide expressed as gas of nitric acid/K.V.A.hr was as much as 300% more than that when using either low or high frequency

discharge alone. He found that the energy yield of nitric oxide passed through a maximum with increasing percentage of high frequency power when plotted at a constant overall power input. The value and position of this maximum depended on the frequency of the high frequency power as well as other factors such as the electrode material and their geometries. He showed that for every reacting system there existed a band of critical frequencies known as the reaction and electrode critical frequencies. When the values of these two critical frequencies for a given system coincided, <sup>a</sup> substantial increase in the energy yields resulted.

COTTON'S remarkable achievements led to another investigation by THORNTON<sup>(3)</sup>. This research was directed towards the application of COTTON'S crossed discharge idea to the decomposition of methane at a pressure of 31 mm Hg, using a reactor similar to that employed by COTTON and within the same range of power frequencies. The results of this study showed the amount of methane decomposed steadily increased with increasing fraction of high frequency power but no maximum point on the curve was observed. The conclusion that followed suggested that there were no apparent advantages in using the crossed discharge and the characteristics claimed by COTTON were still to be confirmed.

#### 1.4. Scale-up of a Gas Discharge Reactor.

##### 1.4.1. Similarity Principle.

A laboratory scale reactor must have some desirable features from chemical synthesis standpoint in order to give the process commercial viability. An economically acceptable unit should fulfill three basic requirements,

- (a) High energy yield of product.
- (b) High percentage conversion per pass.
- (c) High degree of selectivity for the desired product, i.e. side reactions with their consequent wastage of material and energy should be reduced to a minimum.

Once these satisfactory design features have been established, the next step would be to consider the probability of scaling up such a unit to handle the larger gas throughput required in industrial scale operation.

A large scale reactor may be considered similar to a laboratory unit if the net rate of product formation per unit volume is the same in each case. This situation will only arise if physical and chemical similarity exist in both reactors. By physical similarity, it is meant the similarity in the physics of the discharge which determines the activation phenomena leading to primary reactions. Under conditions of low pressure, small voltage gradient and low frequency, these primary reactions, which include single-electron collision phenomena such as ionization and excitation, are direct functions of the reduced electric field,  $E/p$ . It therefore follows that excluding influences of secondary processes, it would be possible to find the factors governing the similarity of discharges of dissimilar dimensions by maintaining the same  $E/p$  ratios. The latter condition can be achieved by varying either the operating pressure or the voltage.

Consider two similar discharges contained in two geometrically similar reactors each provided with two parallel plate electrodes  $A_1, B_1$  in system one and  $A_2, B_2$  in system two. If the linear

dimensions of the first can be characterised by  $a$ , and the second by  $Ka$ , then the potentials at corresponding points  $\bar{p}_1$  and  $\bar{p}_2$  in the electrode gap of the two reactors are,

$$V_1 = \int_{A_1 B_1} \delta_1 \frac{dS_1}{r_1}$$

$$V_2 = \int_{A_2 B_2} \delta_2 \frac{dS_2}{r_2}$$

where  $dS$  is an elementary surface area on an electrode distance  $r$  from  $p$ , and  $\delta$  is the surface charge density. Now, since  $dS_2 = K^2 dS_1$  and  $r_2 = Kr_1$

then

$$V_2 = \int_{A_2 B_2} \delta_2 \cdot K \cdot dS_1 / r_1$$

It follows that when the voltages on the two reactors are the same, i.e. when  $V_2 = V_1$ , then  $\delta_2 = \delta_1/K$  and when  $\delta_1 = \delta_2$  then the voltages must follow the relation,  $K V_1 = V_2$ .

It follows that in similar discharges, parameters depending on single electron collisions will follow in a direct relationship to the physical size parameter  $K$ . Those processes which are a consequence of these direct transformations are termed the permitted processes such as the previously mentioned single collision ionization and also Penning effect, electron attachment and detachment, drift etc. Those which deviate from similarity principle are called the forbidden processes and these include phenomena such as stepwise ionization photoionization, charge transfer etc. A full summary of these processes are outlined by FRANCIS<sup>(30)</sup>.

The main similarity transformations for the important discharge parameters when either the pressure or the voltage is varied at a constant  $E/p$  have been computed and are listed below:

| Parameter              | Reactor 1<br>Lab-Scale | Reactor 2<br>Pressure Varied | Reactor 3<br>Voltage Varied |
|------------------------|------------------------|------------------------------|-----------------------------|
| Linear Dimension       | $a$                    | $aK$                         | $aK$                        |
| Gas Pressure           | $P$                    | $P/K$                        | $P$                         |
| Operating Voltage      | $V$                    | $V$                          | $KV$                        |
| Field strength         | $E$                    | $E/K$                        | $E$                         |
| Surface charge density | $\delta$               | $\delta/K$                   | $\delta$                    |
| Space charge density   | $\rho$                 | $\rho/K^2$                   | $\rho$                      |
| Mass of gas            | $M$                    | $MK^2$                       | $MK^3$                      |
| Flight time            | $t$                    | $Kt$                         | $Kt$                        |
| Current                | $I$                    | $I$                          | $IK^2$                      |
| Current density        | $J$                    | $J/K^2$                      | $J$                         |

It is apparent from the above table that similarity laws necessitate two basic requirements, which put this procedure at some disadvantage and that is either the voltage is raised to inordinately high values or the operating pressure is very low. In both cases the cost of the process will be increased substantially; in the first case because of the capital charges of electrical gear, and in the second case due to pumping charges.

#### 1.4.2. Problems in Applying the Similarity Principle.

Although the similarity principle seems to be a useful tool in reactor scale-up procedures, its application in the gas discharge is hindered by the following:

- a) Since the synthesis of most chemicals in the gas discharge depends primarily on secondary processes, having two similar discharges will not necessarily mean that the chemistry of the discharge will follow suit. It is still not clear what parameters will control these secondary processes and hence should be preserved in scaling-up. Also, the role of the solid surfaces adjacent to the discharge zone is still undetermined. This is important in that the surface area per unit volume varies in geometrically similar reactors and matching up this difference by simply packing the reactor with solid material will only result in field distortion with its consequent effect on the value of  $E/p$ .
- b) Even if it was possible to have two reactors which were physically and chemically similar, there is still a problem which will further handicap the application of similarity principles in reactor scale-up procedures and this is, whether it is feasible in practice to maintain uniform discharges over large electrode areas under conditions of any practical interest. This has been found not to be easy<sup>(31,32,33)</sup>. An increase in the electrode cross-section is usually accompanied by constriction of the discharge zone. The latter will allow a sizeable fraction of the reactant to by-pass the reaction zone with its adverse effects on fraction of gas converted. Also, high power densities in the

discharge will result in product degradation.

Constriction phenomena are complex and as yet very poorly understood. In practice most discharges tend to constrict at higher pressures and current densities and as it has been mentioned earlier in the pulsed discharge, other operational variables such as the pulse width have some effect on the constriction. The effect of higher pressures will be to hinder the diffusion of electrons and ions that tend to spread the discharge radially hence one expects that constriction effects will set in at higher pressures for gases which have larger ambipolar diffusion coefficients as is observed for helium relative to other rare gases<sup>(34,35)</sup>. The effect of short pulse widths on constriction could also be explained in terms of electron and ions radial diffusion. Here, due to the short pulse width (order of microsecond) little time is available for such diffusion processes to take place before the power is cut off. High current densities, on the other hand, contribute to the narrowing of the conducting channel in a much more complicated fashion. A summary of some possible reasons given by PHILIPS<sup>(36)</sup> is as follows:

- i) Thermal gradients which result from the flow of heat from the centre of the arc to the wall result in a reduced gas density and higher  $E/p$  at the centre of the arc. If the rate coefficient for ionization increases sufficiently rapidly with  $E/p$  then the higher ionization rate more than compensates for the faster diffusion loss of a narrow conducting column.
- ii) Cumulative ionization. Cumulative ionization refers to the ionization of excited atoms or molecules which have been produced by electron impact. Because this process is proportional to the square of current density, this will lead to higher rates of ionization in the regions of higher current density and tend to

contract the discharge.

- iii) Electron-ion recombination. Some authors<sup>(37)</sup> propose that the recombination of electrons and ions at large radii leads to constriction of the discharge.
- iv) Electron - electron interaction. Since collisions among electrons tend to make electron energy distribution functions more Maxwellian and to increase the excitation and ionization rate coefficients, the ionization rate near the centre of a discharge will be higher and will tend to constrict the discharge<sup>(38)</sup>.

Another factor which influences the channelling of the discharge zone is the field distortion brought about by the action of the gas flow<sup>(39)</sup>. This effect becomes significant when the gas velocity is comparable to the drift velocity of the ions, i.e. in the range 40-100 m/sec. It is usually found that under these conditions the gradient in the positive column becomes non-uniform along its length and less than the normal value in still gases, and also shortening of the positive column results. Similar effects have also been observed in the case of radio frequency discharge<sup>(40)</sup>.

#### 1.4.3. Alternative Ways of Scaling up a discharge reactor.

It follows from what has been said that most laboratory size discharge reactors are not amenable to treatment by conventional scale up criteria and the need for other novel reactors remains an urgent problem. One possible way of overcoming these limitations is to have a reactor where a means for moving the discharge relative to the gas stream is provided. In this way scanning of the entire reactor cross-section will result and by-passing of reactant is cut to a minimum.

Scanning of the discharge beam could be achieved by one of three ways:

a) Scanning by Electrical Switching.

In this device a multi-electrode assembly covering the entire reactor cross-section is used. The electrodes are fired sequentially in pairs with a repetition rate depending upon the gas flow rate so that each gas molecule has the appropriate activation residence time. The electrode may be composite ones made up of mutually insulated sections separately connected to the power supply via a suitable switching device. This device was examined by CHRISTOPOULOS<sup>(41)</sup>, and later abandoned. It was clear that this system needed some considerable development because of the electronic problems associated with ultra-rapid switching of discharge currents. With current rapid advances in electronic technology this reactor should prove viable in the near future.

b) Scanning by Mechanical Means.

The problems associated with these devices are less severe and these reactors are more likely to yield an acceptable solution in the short term. Scanning is achieved by:

i) Electrode Motion.

This device will have provisions to move one or both electrodes. The area of the electrode is made small enough so that the discharge can occupy most of it and then causing this area to rotate or oscillate. This allows the discharge to scan a larger volume than would otherwise be possible with stationary electrodes. In practice it has been found that for the discharge

beam to follow the imposed rotation smoothly it is advisable to rotate the cathode rather than the anode, or still better, to make both electrodes rotate at the same time.

ii) Scanning by Means of a Perforated Insulating Barrier.

A discharge not covering the whole of an electrode surface can be made to move across that surface by the introduction of a moving insulating barrier which has a suitable aperture through which the discharge strikes. The size, shape, and dynamic path of this aperture will depend upon the nature of the discharge and the volume and geometry of the reactor which must be scanned by the discharge. This arrangement is a much better proposition than the moving electrode reactor since electrical connections to moving parts are eliminated. Also if cooling of electrodes is required, it is easier with this device than with the moving electrode reactor.

c) Electromagnetic Scanning.

A discharge struck between two electrodes may be deflected by either a magnetic or electric field suitably positioned with respect to the primary field direction. Using this principle it is possible to effect enlargement of the discharge volume if the secondary field has relative motion to the electrodes causing the primary field. Secondary fields may also be made to cause a spreading of the discharge volume without any external rotation. However, in this device assessment of the effect of beam scanning on the relative yield of product will be difficult since the magnetic field itself will have a marked influence on the discharge characteristics. Work done by

SCHMIDT and LUNK<sup>(42)</sup> shows that when a low pressure glow discharge in  $H_2$ , He, Ne, and Ar was investigated in the presence of a transverse magnetic field, a decrease in the gas impedance and ionization voltage was observed due to a decrease in the electron mean free path caused by the magnetic field.

To utilize the concept of beam scanning for industrial application one can have a combination of scanning devices in order to develop a large scale reactor. For instance, it will be possible to have a reactor in which the discharge beam length is stretched to its limit in compliance with voltage availability. This could then be coupled with horizontal scanning provided by a rotating insulator together with vertical scanning provided by a sequential switching device. An example of this type of reactor is shown in Fig.1.4. The gas will be flowing through the annulus between the rotating insulator and the stationary outer cylinder. If it is required to minimize product degradation in this unit, introduction of a suitable absorbent in the form of a fine spray could be provided by the action of the rotating insulating tube.

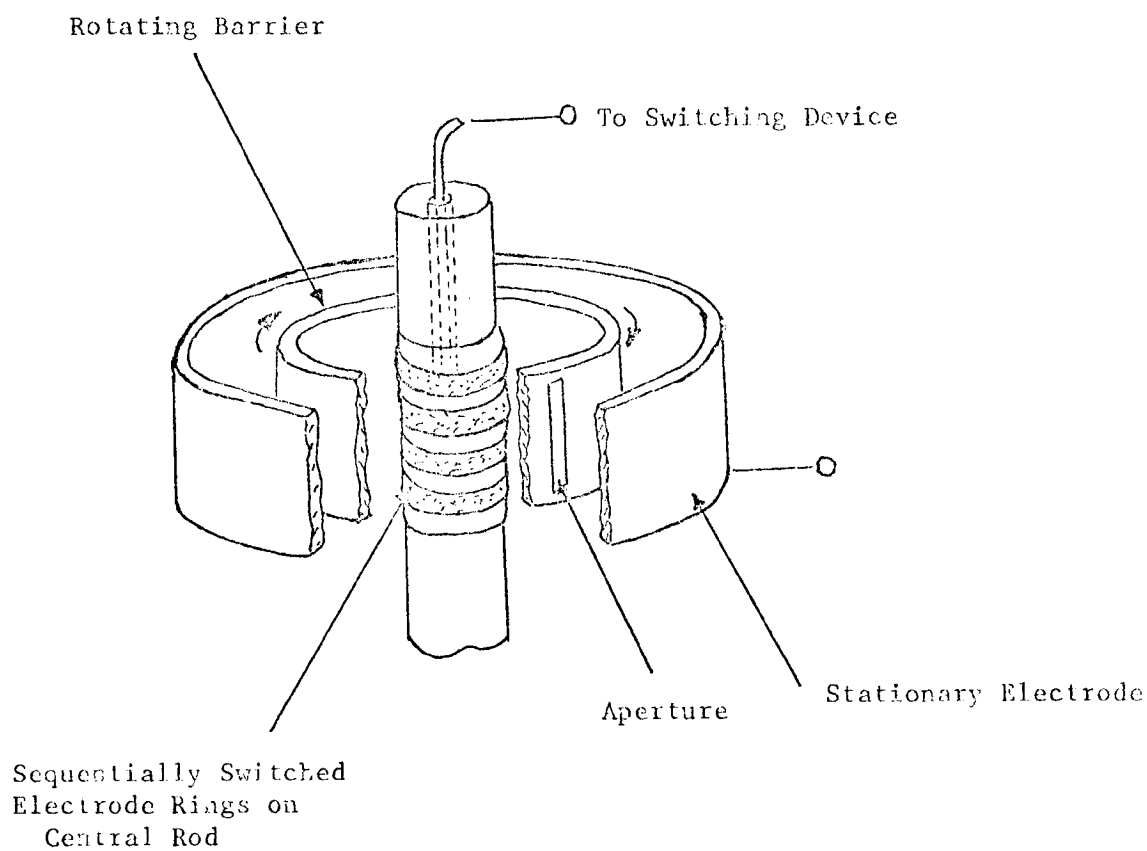


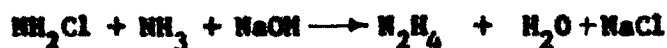
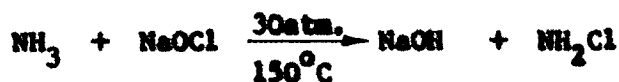
Figure 1.4. Reactor Combining Sequential Switching and  
Dielectric Barrier Movement.

## 2.0. LITERATURE RELATED TO HYDRAZINE SYNTHESIS.

### 2.1. General.

The first reported literature on hydrazine and its derivatives were in 1875<sup>(43)</sup>. Interest in these chemicals has increased through the years and today aerospace engineers have found that unsymmetrical dimethylhydrazine provides them with one of their best available rocket fuels. It has been reported<sup>(44)</sup> that the demand for hydrazine for domestic purposes only was increasing at an annual rate of 15%. Hydrazine is used widely as a starting material in the manufacture of weed killers and pharmaceuticals. It is also used as a blowing agent in the foam rubber industry and as a scavenger for dissolved oxygen in boiler water. However, the extent of its applications are severely hindered by its high cost. This is attributed to the high cost of the existing Raschig Process.

Nearly all the hydrazine is manufactured according to this classical process using chlorine and ammonia as raw materials. This process can be represented schematically as follows,



The yield of this process is about 60% based on chlorine consumption, but in order to prevent side reactions between the hydrazine and chloramine the concentration of the former is to be kept within 1-2%.

It is the cost of the final evaporation step that results in an unwanted cost increase for this process.

Since the turn of this century, the high cost of hydrazine coupled with its increasing industrial applications have stimulated many researchers to look into alternative techniques for its production. One possible and interesting proposition was its gas phase synthesis from ammonia using either electrical energy or light of an appropriate wavelength as reaction promoters. Other techniques such as electron accelerators and Cobalt 60 were also considered. Here, electrons with known energy levels could be obtained, but the relative cost<sup>(45)</sup> of supplying power to the system using these techniques as compared to direct power input of a glow, corona or microwave discharges put them at an economical disadvantage. The controllability over the level of energy input from a light source was also interesting, but the efficiency of converting electrical energy in the lamp into light was low, resulting in high costs. Due to these reasons the direct application of electrical energy to the reacting system has substituted for all the other sophisticated techniques in recent years.

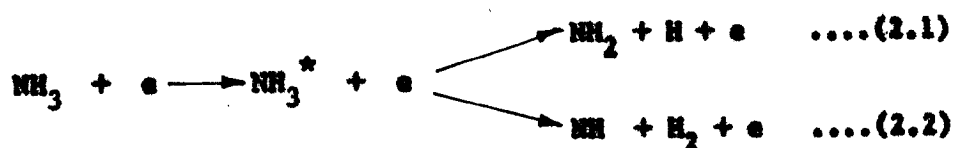
The synthesis of hydrazine from ammonia in a glow discharge was first reported by BESSON<sup>(46)</sup> who by continuously flowing ammonia through the discharge reactor for a long period was able to detect measurable amounts of hydrazine. His discovery was followed by more systematic studies carried out by other workers in this field such as BREDIG<sup>(47)</sup> and WESTHAVER<sup>(20,48)</sup>. The latter in particular contributed to the understanding of hydrazine synthesis when he found

that hydrazine could be frozen out of the positive column but not the negative glow. This sudden upsurge of interest was later followed by a declining attitude due to the complexity of the system as well as the fact that most of the hydrazine formed was degraded in the reaction vessel due to its high reactivity as compared to ammonia. It was not until the 1950's when resurgence of interest emerged especially after the pioneering works of OUCHI<sup>(22)</sup>, and DEVINS and BURTON<sup>(10)</sup> came to light. This was followed by a better understanding of the kinetic mechanisms as well as substantial improvement in yields of hydrazine.

## 2.2. Chemistry of Hydrazine Production from Ammonia.

### 2.2.1. Hydrazine Formation Reactions.

When ammonia gas is subjected to an electric discharge, the molecules are first excited by the electrons and then undergo dissociation into free radicals. There are two possible paths for this dissociation process, thus:



These free radicals are the precursors for hydrazine formation. There is a slight controversy as to which of the above reactions is the primary process and which reaction following the dissociation of ammonia will lead to hydrazine. Most of the early literature supports reaction (2.2). BREDIG, KOENIG and WAGNER<sup>(47)</sup> proposed a mechanism

whereby NH radicals are first produced which then react with more ammonia to give hydrazine. OUCHI<sup>(22)</sup> also adopted this process scheme. LUNT and MILLS<sup>(49)</sup>, however, went a little further by assuming that after the formation of NH radicals, hydrazine is produced by the combination of two of these radicals with a hydrogen molecule. Later work using both mass and absorption spectroscopy techniques revealed that reaction (2.1) was the primary process with NH radicals being produced by secondary processes.

In 1956 BAIR, LUND and CROSS<sup>(50)</sup> studied the decomposition of ammonia in a pulsed discharge followed by absorption spectroscopy of the free radicals produced. They showed that with pulse widths of 2 msec and repetition rate of 20 c/sec the primary free radical was  $\text{NH}_2$ . Their work was done at 1 mm Hg, however, they mentioned that the  $\text{NH}_2$  concentration increased with ammonia pressures up to a value depending on the limit of the power supply and trigger circuits as well as on the characteristics of the discharge used. They also pointed out that the  $\text{NH}_2$  concentration was independent of the flowrate of ammonia at high flowrate but it fell off sharply at lower flowrates. This could be explained if one realizes that at these lower flowrates the gas residence will be large enough to encourage electron induced dissociation of  $\text{NH}_2$  radicals into NH and H-atoms.

Later ROBINSON and McCARTY<sup>(51)</sup> positively identified the  $\text{NH}_2$  radicals in a high frequency discharge with the products being trapped in an argon matrix at 4.2°K.

In 1963 MANES and BAIR<sup>(52)</sup> made photolytic measurements of  $\text{NH}_2$  absorption as a function of time following a pulse discharge of

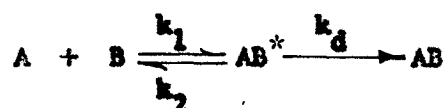
500  $\mu$ sec duration at a frequency of 15 c/sec through ammonia. They observed that  $\text{NH}_2$  appeared much earlier (after few pulses) than  $\text{NH}$  (after 50 - 100 pulses), indicating that  $\text{NH}_2$  was the primary product. They also showed that the kinetics of  $\text{NH}_2$  recombination was second order with respect to  $\text{NH}_2$  and gave a rate constant for this process as  $2.3 \times 10^9$  lit./mole.sec. This suggested that the  $\text{NH}_2$  recombination process was of the form,



rather than



HAINES and BAIR also investigated the effect of pressure on reactions (2.3) and (2.4). They assumed that free radicals associate to give an activated complex which either deactivate by a collision with a stable molecule or dissociate into its parent radicals, vis.



The observed rate constant for this process was given as,

$$K_{\text{ob}} = k_1 k_d P / k_2 + k_d P$$

where  $P$  is the total pressure. To justify their assumption that reaction (2.3) was responsible for  $\text{NH}_2$  removal rather than (2.4), they calculated the observed rate constant at different pressures. Their results are shown in Fig.2.1. It is clear that at their operating pressures, reaction (2.3) was predominant with (2.4) becoming much more important at higher pressures. Their findings

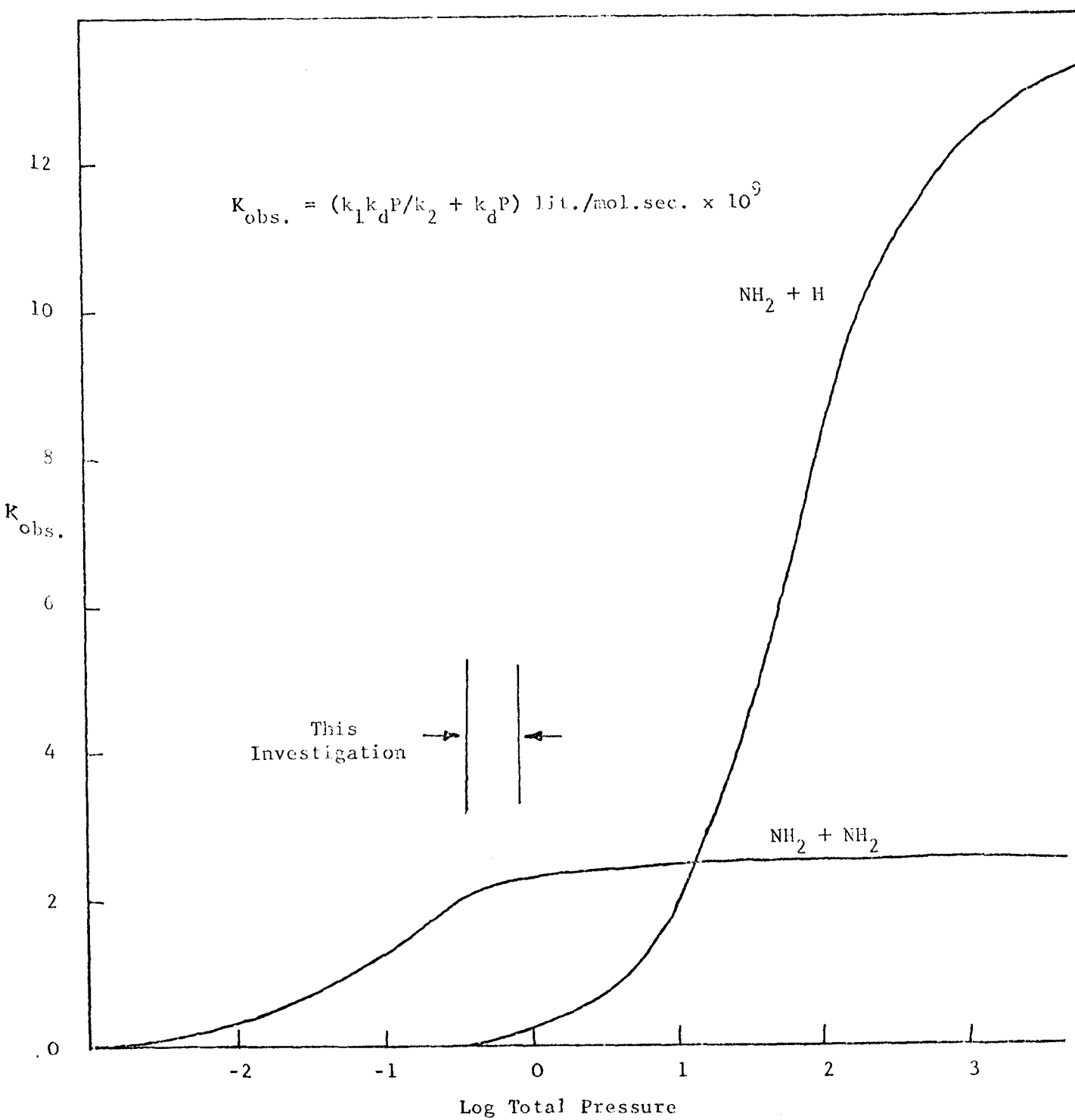


Figure 2.1. Calculated Relative Rates of Competitive  $\text{NH}_2$  Reactions.  
(After Haines and Bair)

are consistent with the photolysis work of McDONALD<sup>(53)</sup> and the gas discharge work of RUBSTOVA<sup>(54)</sup>. The former found that the quantum yield in ammonia decreased with increasing pressure while the latter observed a 30% reduction in ammonia decomposition when the pressure was raised from 84 to 636 mm Hg.

CARBOUGH, MARCHELLO, and MINNO<sup>(55)</sup> studied the decomposition of  $\text{NH}_3$  in a glow discharge at pressures of 1.7 - 3.4 mm Hg. In addition to pure ammonia, mixtures of ammonia and Krypton were also treated. In both cases using emission spectroscopy they were able to identify the presence of  $\text{NH}_2$  radicals and atomic hydrogen. They concluded that  $\text{NH}_2$  was the product of the primary decomposition reaction with  $\text{NH}$  radicals being produced by secondary processes such as,



The feasibility of reaction (2.5) was later confirmed by SALZMAN and BAIR<sup>(56)</sup> who, using flash photolysis method at 5 - 10 mm Hg gave a rate constant of  $0.5 \times 10^9$  lit./mole.sec. for reaction (2.5).

When talking about the kinetics of this complex system, one cannot underestimate the effort of photochemists who added considerable contributions to the understanding of these processes. Although photolysis and gas discharges are two different techniques, the basic steps leading to hydrazine formation are regarded by many workers in this field to be almost identical. The only difference is that in the former the agents for gas molecule dissociation are photons with known energy while in the latter case electrons of

varying energy levels act as the agents for the primary processes of decomposition.

Most of the photochemical work on ammonia decomposition supports the view that  $\text{NH}_2$  is the primary product of decomposition. HERSBERG and RAMSAY<sup>(57)</sup> decomposed ammonia at 10 mm Hg using flash photolysis followed by absorption spectroscopy of the products within 1 msec of the photolysis. About 50 absorption lines were observed between 5700 - 6900 $^{\circ}\text{A}$ . These absorption bands (normally called  $\alpha$ -bands) were due to  $\text{NH}_2$  radicals. The complicated structure of the  $\alpha$ -bands was attributed to the asymmetry of the  $\text{NH}_2$  radical.

McNEESBY, TANAKA and OKABE<sup>(58)</sup> found that when ammonia was photolysed at 1849 $^{\circ}\text{A}$ , it almost entirely decomposed to  $\text{NH}_2$  and H-atoms, but at 1236 $^{\circ}\text{A}$  using  $\text{C}_2\text{D}_4$  as scavenger for hydrogen atoms, about 17% of the hydrogen resulted from molecular processes of the form,  $\text{NH}_3 \longrightarrow \text{NH} + \text{H}_2$ . BECKER and WELDE<sup>(59)</sup> observed an emission band from NH in the photolytic decomposition of ammonia at 1165 $^{\circ}\text{A}$  and 1236 $^{\circ}\text{A}$  and also at 1295 $^{\circ}\text{A}$ . They did not find NH emission with 1470 $^{\circ}\text{A}$  radiation. CROTH and RUSSEL<sup>(60)</sup> studied ammonia photolysis at 1849 $^{\circ}\text{A}$ , 1470 $^{\circ}\text{A}$ , 1236 $^{\circ}\text{A}$  and 1165 $^{\circ}\text{A}$  both in stationary and flowing systems. At 1849 they found the primary process to be due to reaction (2.1), while at 1470 $^{\circ}\text{A}$ , 12 - 13% of the ammonia decomposed according to (2.2) with the rest according to (2.1). At 1236 $^{\circ}\text{A}$  and 1165 $^{\circ}\text{A}$ , 14% decomposed according to (2.2) while the rest decomposed according to (2.1) or,



The study showed that the stationary concentration of H-atoms was

about 3.5 times higher at 1236<sup>o</sup>A and 1165<sup>o</sup>A than at 1470<sup>o</sup>A due to the significance of (2.6) at these lower wavelengths.

One of the most recent studies on NH<sub>2</sub> and NH radicals in ammonia decomposition was done by MANTEI and BAIR<sup>(61)</sup>. They used kinetic spectroscopy following flash photolysis in the 1500 - 2000<sup>o</sup>A region at a pressure of 1 mm Hg. They showed that NH radicals produced by secondary reactions of the primary photolysis products, thus



The NH radicals will then decay according to,



The rate constant for reaction (2.9) was found to be pressure dependent in the range 0 - 1.0 mm Hg. At the high pressure limit, the rate constant was given as  $1.0 \pm 0.3 \times 10^{10}$  lit./mole.sec. at 300<sup>o</sup>K. Later MEABURN and GORDON<sup>(62)</sup>, who studied the pulse radiolysis of ammonia, showed that the more likely process for NH disappearance was the recombination reaction



with a rate constant of  $7 \times 10^{11}$  lit./mole.sec. Although the rate constant for this reaction is far greater than that for (2.9), the rate of reaction (2.9) will probably be as important if one realises that the concentration of NH<sub>3</sub> in a gas discharge is far in excess of NH concentration. It would therefore be concluded that both of these reactions will compete for NH disappearance.

In the glow discharge the mean electron energy in the positive column is taken not to be in excess of 2.2 e.v, and since most of the photolysis work on ammonia have indicated that for wavelengths of 1849<sup>0</sup>Å and over (< 7 e.v) the product of the primary reaction is NH<sub>2</sub>, it will not be unreasonable to suppose that this radical will also be the product of the primary decomposition process in the glow discharge case. Some NH will inevitably be produced by secondary processes of the kind,

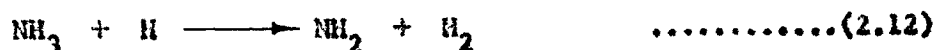


with (2.11) becoming rather important at high electron densities<sup>(63)</sup>. Most of the NH<sub>2</sub> radicals will recombine to give hydrazine according to (2.3). The rate of this reaction is about 5 times greater than that of (2.5). The NH radicals will then decay according to (2.9) and (2.10) with the latter becoming more important at higher current densities. Some ammonia will also be regenerated by (2.4) and (2.5). The latter becomes particularly important at higher pressures (> 10 mm Hg).

### 2.2.2. Degradation of Hydrazine by Secondary Processes.

Degradation of hydrazine in the glow discharge decomposition of ammonia has resulted in a relatively low energy efficiency for this process. The most common of these degradative reactions is the hydrogen atom attack and to a lesser extent, the electron-induced decomposition reaction. Hydrogen atoms are known to react efficiently

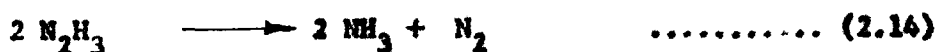
with hydrazine, and one of the first investigations on this system was conducted by DIXON<sup>(64)</sup>. He showed that with ammonia only a very slight reaction occurred accounting for ~ 2% of the ammonia being decomposed. The reaction suggested was of the form,



with an activation energy of 8.5 k cal/mole. With hydrazine, on the other hand, between 42 - 100% decomposition took place with the extent of the reaction being favoured by high hydrogen atom concentration and low gas velocities. His quantitative measurements were consistent with the proposed mechanism,



A more up to date study on this system was carried out by SCHIAVELLO and VOLPI<sup>(65)</sup>. They not only substantiated the above mechanism but also put forward rate constants for reactions (2.12), (2.13) and (2.14). A flow system, employing a mass spectrometer for the measurement of the steady-state concentrations of the gases, was used. Using deuterium instead of hydrogen, they found that about 95% of the ammonia produced was not deuteriated suggesting that the mechanism was the rupture of (N-H) bond rather than the (H-H) bond. From their experimental findings, they suggested the following reaction scheme,



The rate constants for reactions (2.13) and (2.14) were given as,

$$K_{2.13} = 3.5 \times 10^8 \exp.(-2000/RT) \text{ lit./mole.sec.}$$

$$K_{2.14} = 3 \times 10^9 \text{ lit./mole.sec. at } 150^\circ\text{C.}$$

The ratio of  $\text{NH}_3/\text{N}_2$  was always 2:1 suggesting that reactions (2.15) and (2.16) were unimportant. The reaction between hydrogen atoms and ammonia was also investigated and showed only about 0.5% of the ammonia was consumed. On this basis and with the knowledge of H-atom flowrate, they gave an estimated value for the rate constant of reaction (2.12) as  $10^4$  lit./mole.sec. with an activation energy of 10 - 15 k cal/mole. This agrees reasonably well with DIXON'S estimate of 8.5 k cal/mole.

The reaction between H-atoms and hydrazine was also investigated by GHOSH and BAIR<sup>(66)</sup> at a later date. A hydrazine concentration of somewhat 500 to 5000 times smaller than that of H-atoms were used. Emission spectroscopy for following the course of the reaction was employed. They found that the emission was mainly due to  $\text{NH}_2$  radicals which were thought to have been produced by,



However, estimate of emission quantum yield showed that this was a relatively minor process. Accepting the conclusions of SCHIAVELLO and VOLPI that the major decomposition process was reaction (2.13) with a rate constant of  $3.5 \times 10^8 \exp.(-2000/RT)$  lit./mole.sec., the temperature dependence of the emission intensity was interpreted in terms of these competing processes to give a rate constant of

$1.2 \times 10^5 \exp.(-2600/RT)$  lit./mole.sec. for reaction (2.17). The unexpectedly high concentration of  $\text{NH}_2$  radicals was thought to have been the result of the reaction,



becoming important when  $[\text{H}]/[\text{N}_2\text{H}_4]$  is large.

The rate constant reported by SCHIAVELLO and VOLPI corresponds to a value of  $1.25 \times 10^7$  lit./mole.sec. at  $300^\circ\text{K}$ . This is a factor of ten slower than the rate constant of  $1.7 \times 10^8$  lit./mole.sec., with no temperature dependence between  $251 - 315^\circ\text{K}$ , reported by GERRING et al<sup>(67)</sup> using a fast flow system. This apparent uncertainty about the value of the rate constant prompted a further investigation by FRANCIS and JONES<sup>(68)</sup>. Here, the reaction between hydrazine and H-atoms was studied in a flow system at a pressure of 5.0 mm Hg. The initial concentration of hydrazine to that of hydrogen atoms was kept at a ratio of 20 and over, thus ensuring a pseudo-first order reaction with the rate constant given as,

$$K = \ln ([\text{H}]_{\text{N}_2\text{H}_4=0}/[\text{H}])/[\text{N}_2\text{H}_4] \ t$$

where,

$K$  = pseudo-first order rate constant

$[\text{H}]_{\text{N}_2\text{H}_4=0}$  = steady-state concentration of unreacted H-atoms

$[\text{H}]$  = Initial concentration of H-atoms

$[\text{N}_2\text{H}_4]$  = concentration of hydrazine in the tube

determined from the linear flow velocity, the cross-sectional area of the flow tube and the hydrazine mass flowrate.

$t$  = reaction time

An ESR (Electron-spin Resonance) atom detection method was used to measure the concentration of H-atoms. A wide temperature range of 300 - 540°K was used. From the Arrhenius plot the rate constant of reaction (2.13) was found to be  $(1.5 \pm 0.3) \times 10^9 \exp.(-1300 \pm 200/RT)$  lit./mole.sec. corresponding to a value of  $1.27 - 1.35 \times 10^9$  lit./mole.sec. at 300°K. This is significantly higher than the previous two figures reported by GEHRING et al and VOLPI. However, the activation energy of  $1300 \pm 200$  Kcals/mole agrees reasonably well with VOLPI'S 2000 Kcals/mole. The general conclusion from what has been said is that hydrogen atoms react efficiently with hydrazine, but as far as the value of the rate constant is concerned, there exists some element of uncertainty.

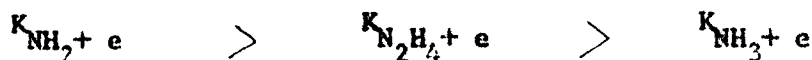
It was mentioned earlier that the other source for hydrazine decomposition by secondary processes was its attack by electrons. The importance of this process becomes more pronounced at higher electron densities. Since the energy required to rupture the (N-H) bond in hydrazine is only 3.3 e.v.<sup>(69)</sup> as compared to 4.5 e.v. required to dissociate ammonia<sup>(70)</sup> into  $\text{NH}_2$  and H-atoms, the number of electrons capable to dissociate hydrazine is greater than that for ammonia dissociation. By assuming a Maxwellian distribution of energies in the positive column of an ammonia glow discharge with mean electron energy of 1.25 e.v., SAVAGE<sup>(71)</sup> found that about 6.5% of the electrons present had enough energy to break the  $(\text{NH}_2\text{-H})$  bond while 25% had sufficient energy to break the  $(\text{H}_2\text{NNH-H})$  bond. By further assuming the area of the hydrazine molecule being approximately twice that of ammonia, he was able to give a first estimate of the relative rates of

reactions between electrons and hydrazine and electrons and ammonia as 7.7:1. Another indication of the relative rates of reactions between electrons, hydrazine and ammonia is apparent from the work of TERASHI<sup>(72)</sup> using 100 and 250 MHz discharge. From the initial slopes of her data and assuming no difference between electron energies in the 0.4 mm Hg and 11.0 mm Hg discharges, it could be seen that with a 100 Hz discharge the rate of reaction of hydrazine with electrons is 10.0 times faster than that of the reaction of electrons with ammonia. This agrees reasonably well with the previous estimate despite the inherent assumptions of both methods.

At higher electron densities another electron-induced decomposition reaction comes into play, namely the reaction between electrons and  $\text{NH}_2$  radicals.



This will not only remove the  $\text{NH}_2$  radicals necessary for hydrazine formation but also produce more hydrogen atoms which will engage in hydrazine degradation reactions. BARKER<sup>(63)</sup> found that electrons react more efficiently with  $\text{NH}_2$  radicals than they do with hydrazine and accounted for a significant loss of hydrazine. By assuming a Maxwellian distribution of electron energies and taking the bond dissociation energies as  $D(\text{NH}-\text{H}) = 3.8 \text{ e.v.}^{(70)}$ ,  $D(\text{H}_2\text{NNH}-\text{H}) = 3.3 \text{ e.v.}^{(69)}$ , and  $D(\text{NH}_2-\text{H}) = 4.5 \text{ e.v.}^{(70)}$ , he showed that the rate constants for the electron-induced decomposition reactions were in the order



### 2.3. Methods of Minimizing Hydrazine Decomposition by Secondary Processes.

The degradative reactions discussed earlier have hindered the commercial viability of the ammonia/hydrazine process and it follows that any minimisation in these reactions should be reflected as an overall improvement in the efficiency of hydrazine production. The extent to which these reactions proceed can be controlled by one or a combination of the following techniques:

(a) Using a low residence time in the discharge zone.

One way of reducing the residence time will be to increase the gas flowrate and thereby cause the rapid removal of hydrazine from the discharge zone. Fig.2.2 shows typical curves depicting the effect of gas flowrate on the energy yield and concentration of a product which is first produced and then degraded by back reactions. It is clear that before reaching the maximum, an increase in the gas flowrate will result in an increase in the energy yield (expressed as gms.product/kWh) and a corresponding fall in the concentration of the product in the issuing gas stream. It therefore follows that in order to cut down the degree of the degradative reactions one has to operate at a relatively high gas throughput and tolerate the dilution effect of the product. From practical point of view this will pose a big problem in so far as the separation of the product and the mounting pumping costs are concerned. Despite these practical drawbacks, the use of high gas flowrate as a means for reducing the residence time has been reflected in almost all electric discharge work.

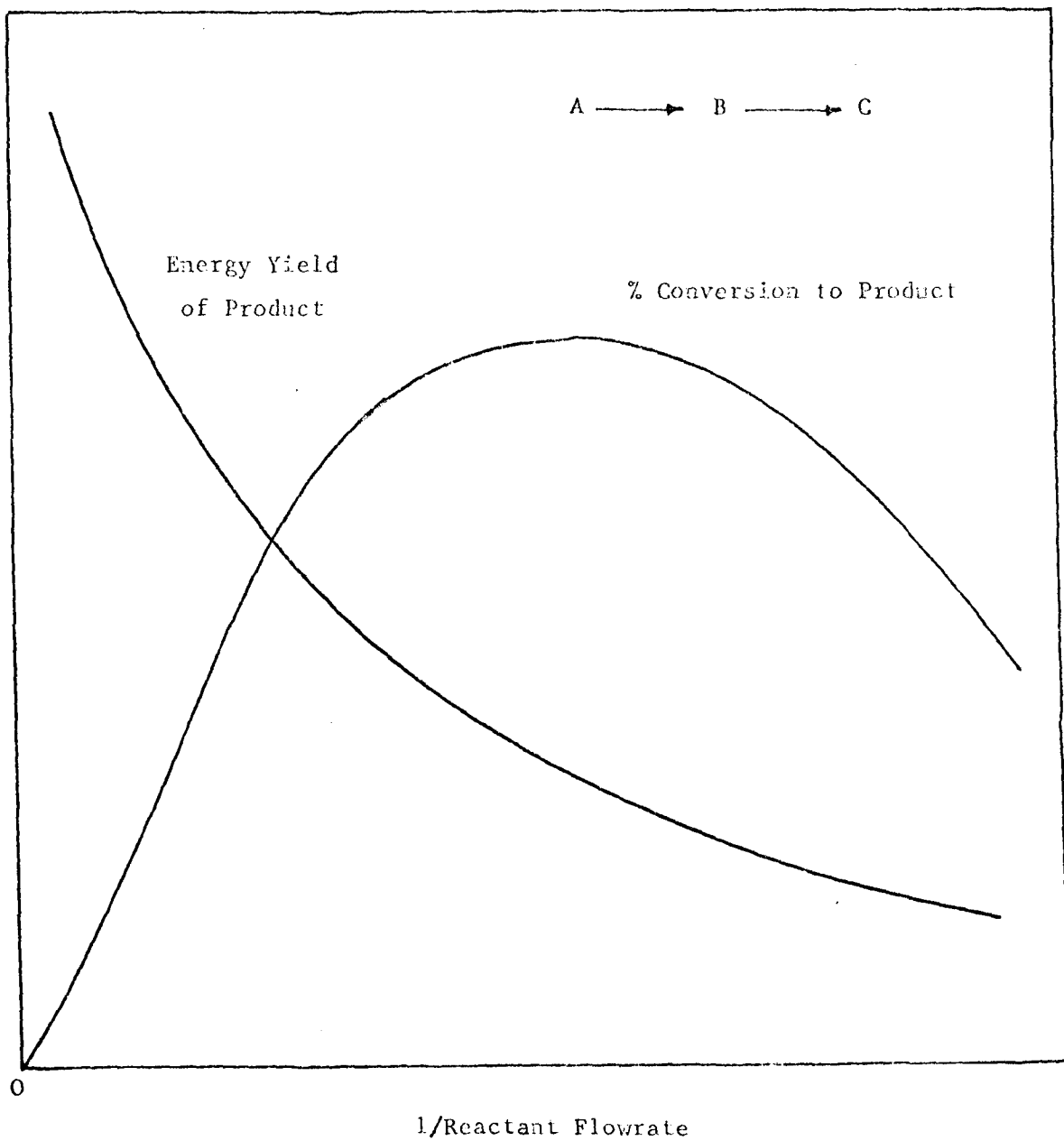


Figure 2.2. Influence of Reactant Flowrate on Product Yield.

A = Reactant; B = Product; C = By-Product

BREDIG, KOENIG and WAGNER<sup>(47)</sup>, some of the first pioneers of hydrazine synthesis in the electric discharge, found that the conversion of ammonia to hydrazine went through a maximum with flowrate, but the total conversion was as low as 0.016 wt% although about 80% of decomposed ammonia was converted to hydrazine. The best energy yield was not greater than 4.0 gm/kWh. DIXON<sup>(64)</sup> in his work on the decomposition of ammonia suggested that in order to achieve appreciable reduction in back reactions a residence time of not more than 10 msec. should be used.

The most comprehensive study on the effect of ammonia flow rate on the production of hydrazine was carried out by ANDERSON, ZWOLINSKI, and PARLIN<sup>(73)</sup>. They decomposed ammonia in a spherical discharge tube with 1.5 - 7.0 Mhz power. Typical conditions were 91 mm Hg, 100 mA discharge current and 5.1 mm electrode gap distance with gas flowrate ranging from 300-1400 cc/min(STP). Their results showed that hydrazine was formed in amounts from 4.7 - 37.1% of ammonia decomposed. The higher percentages were achieved at the higher flowrates. The maximum energy yields corresponding to these high flowrates were 4 - 6 gms/kWh. Based on total ammonia flowing through the cell, the conversion to hydrazine went through a maximum at 0.335 molar %. Similar results showing the effect of ammonia flowrate on hydrazine production have been reported by others<sup>(53,55,63,71,74)</sup>.

Expansion nozzles could be used as an alternative to increasing the gas velocity and thus overcoming the pumping limitations. ROUY et al<sup>(75)</sup> have pointed out the advantages that can be drawn by

matching the electric field distribution with the velocity, pressure, and temperature profiles set in this venturi type reactor. Expansion nozzles have also been proposed as means for rapidly withdrawing active species from a moderately high pressure discharge into a secondary reactor where the reaction product is protected from the action of the discharge<sup>(76)</sup>. Although these reactors seem to have some attractive features, their application<sup>(77,78)</sup> gave low conversions to hydrazine and were not developed commercially.

A much more flexible device for reducing the gas residence time was thought of by OUCHI<sup>(22)</sup>, and this was the operation of an intermittent or pulsating discharge. OUCHI compared the results from normal 50 Hz A.C. discharge with an intermittent discharge formed by the half-wave rectification of a 50 Hz A.C. voltage. This gave a discharge with an ON-time of 8 msec. and an OFF-time of 2 msec. and 12 msec. respectively. He found that both the energy yield and conversion to hydrazine benefited in the intermittent discharge. He attributed this to the shorter residence time in the latter. These results were later confirmed by JOGARAO and SASTRI<sup>(79)</sup> who used a cell similar to that of OUCHI'S for carrying out their investigation. Their results showed that under semi-wave discharge, the hydrazine concentration was improved to nearly double its value under ordinary A.C. discharge.

The success of the intermittent discharge led OUCHI to attempting longer OFF-times with the expectation of obtaining even higher energy yields. For this a high voltage rectangular wave generator was built giving pulses of 10 msec. long and OFF-times of 20 - 600 msecs. With this arrangement he was able to get energy

yields of up to 9.5 gm/kWh. By increasing the pulse OFF-time still further to about 0.700 second with the ON-time being 2 - 3.5 msec. using an impulse generator, OUCHI was able to achieve energy yields of up to 47 gm/kWh. However, the conversion to hydrazine was very low at only 0.013%. This prohibitively low concentration was attributed to the fact that at these very long OFF-times and short On-times, about 70 - 80% of the total ammonia passed through the discharge cell without even being irradiated. Allowing for this by-passing effect the actual conversion to hydrazine would have been about 0.45%.

An extension on OUCHI'S work was carried out by I.C.I. of Great Britain<sup>(80,81)</sup>. They used pulse ON-times ranging from 20 - 500  $\mu$ sec (c.f. OUCHI'S 2 - 3.5 msec) and OFF-times of 20 - 44 msec. Even with these short ON-times, the energy yields of hydrazine were much lower reaching a maximum value of only 20 gm./kWh. compared with OUCHI'S 47.0 gm./kWh. No explanation was given for this discrepancy, but careful examination of the two systems would reveal some answer. In all of I.C.I.'s work a liquid phase was introduced into the discharge reactor to act as an absorbent for hydrazine and it is this fact together with the lack of information on the level of power densities which make the quantitative comparison between these two studies rather impossible. The latter in particular is thought to have a major influence on hydrazine synthesis<sup>(21)</sup>. Another uncertainty stems from the fact that all the calculation of energy yields was based on the assumption that all the hydrazine was removed by the liquid absorbent. Now, if a substantial proportion of the hydrazine

was to have been carried away by the gas stream due to incomplete absorption, then its consequent effect will account for the difference.

The most up to date study on the effectiveness of the pulsed discharge on hydrazine synthesis was carried out by SAVAGE<sup>(21)</sup> and later by BROWN, HOWARTH, and THORNTON<sup>(25)</sup>. With a pulse ON-time of 5  $\mu$ sec and an OFF-time of 10 msec. and a power density of 1.5 watt/cc reactor volume, SAVAGE was able to obtain energy yields of hydrazine as high as 56.5 gms/kWh. However, the conversion to hydrazine corresponding to this energy yield was only 0.1 wt.%. He also found that the conversion to hydrazine reached a maximum with pulse ON-time with the position of the maximum depending upon the particular pulse OFF-time being used. Unfortunately the conditions for high energy yields were found to give low conversions to hydrazine and vice versa. This is consistent with OUCHI'S<sup>(22)</sup> findings.

An interesting feature of the pulsed discharge emerged when comparison between the results of direct current and pulsed discharges was made at the same active residence time. The latter being defined as the total cumulative activation time. For a continuous DC discharge it will be equivalent to the flight time of the molecule through the discharge space whereas for a pulsed discharge it is given by:

$$\text{Active Residence time (ART)} = \frac{\text{Pulse ON-time} \times \text{Gas Residence time}}{\text{Pulse ON-time} + \text{Pulse OFF-time}}$$

Figure 2.3. shows the effect of A.R.T. on energy yield and conversion to hydrazine. It can be seen that for an A.R.T. of less than 0.35 sec. the energy yield can be over 400% higher and conversions up to ten

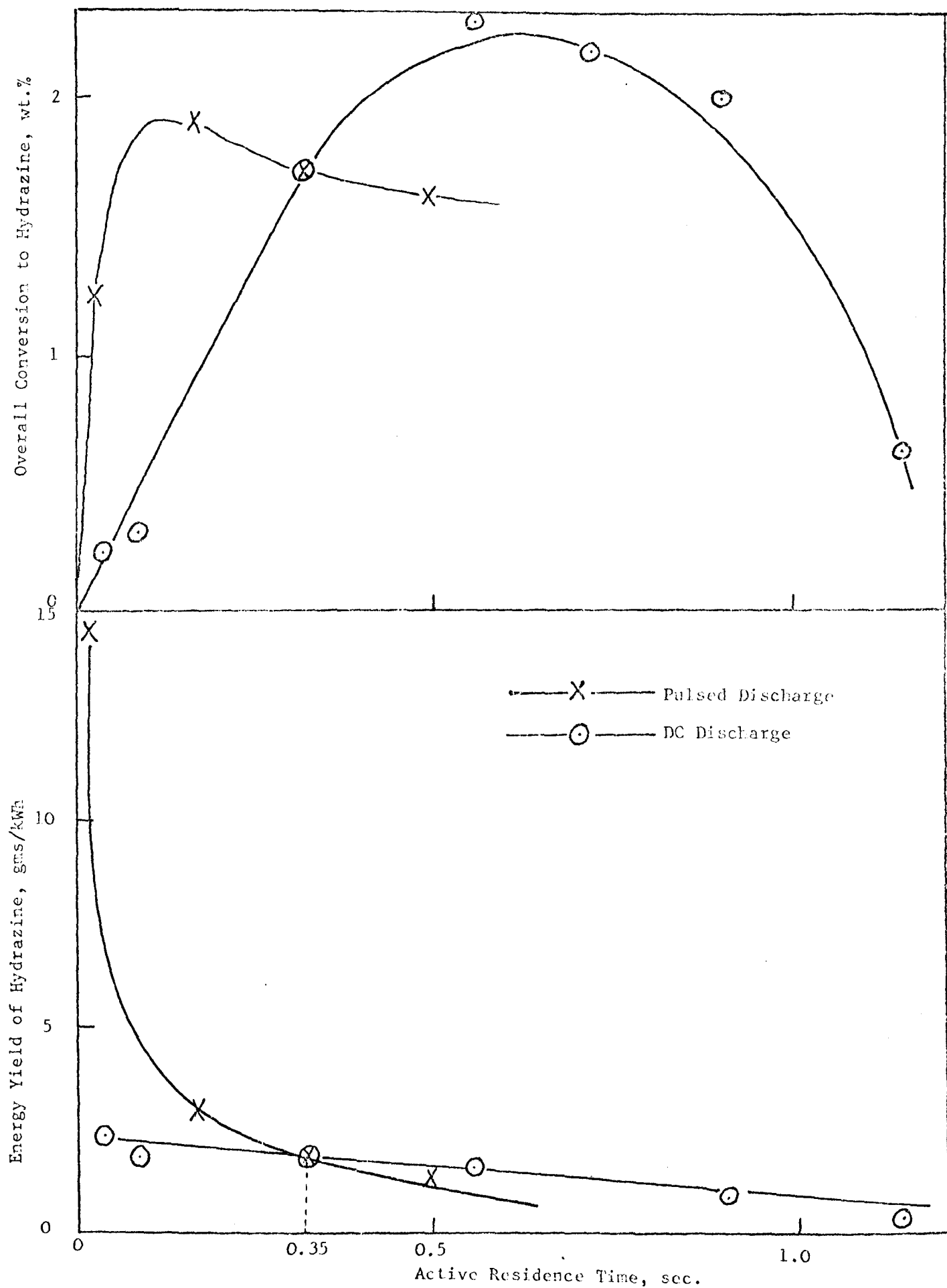


Figure 2.3. Effect of Active Residence Time on Yield and Conversion to Hydrazine (After Savage)

times higher for the pulsed discharge than for the continuous D.C. discharge. It therefore follows that a pulsed discharge possesses some attribute over and above residence time considerations which enhances the net rate of hydrazine production.

Later BROWN, HOWARTH and THORNTON<sup>(25)</sup> showed that when operating with pulsed discharges, the peak voltage was higher than the operating voltage under steady state conditions of a continuous D.C. discharge, and could be maintained as high as the striking potential by the correct manipulation of the operating variables such as pulse ON and OFF-times and even the gas flowrate. The consequence of this high peak voltage will be reflected in the value of the reduced electric field ( $E/p$ ) which is a measure of the mean electron energy. They showed that for an electrode separation of 26.8 cm. the reduced electric field in the positive column of a D.C. discharge was only 6 - 10 volt.  $\text{cm}^{-1}.\text{mm Hg}^{-1}$  in the pressure range 4 - 10 mm Hg corresponding to a mean electron energy of only 0.5 - 1.0 e.v. By contrast the corresponding figures for a pulsed discharge were 23 - 52 volt. $\text{cm}^{-1}.\text{mm Hg}^{-1}$  giving a mean electron energy around 2.2 e.v. The consequence of this increase in electron energy will be an enhancement in the rate of primary excitation of ammonia.

As well as reducing the active residence time and improving the mean electron energy, the pulse technique is found to have an effect on the free radical reactions<sup>(21)</sup>. Due to the intermittent nature of the pulsed discharge, the gas is either not ionized or at a low level of ionization at the commencement of each pulse. This will necessitate the requirement for a higher operating voltage in order to

provide those extra electrons needed for breakdown. This will result in an increase in the rate of the primary process of ammonia decomposition as mentioned earlier. As a consequence, free radicals are formed more rapidly in such a system and even though no hydrazine is formed while the pulse is on, the free radicals will react to give hydrazine even when the discharge is off. In this way, electron-induced decomposition of hydrazine and its precursors is reduced substantially. It can also be seen from the kinetic model proposed by SAVAGE<sup>(21)</sup>, that after the discharge is switched off, H-atoms decay much faster than the  $\text{NH}_2$  radicals and hence a lesser degree of hydrazine attack by hydrogen atoms will result as a consequence. The degradation of the hydrazine produced in the first pulse caused by electrons at the onset of the second pulse will not be so significant due to the much smaller concentration of hydrazine compared to that of ammonia and one can assume that it will escape the discharge without considerable decomposition. However, if the gas suffers a large number of pulses before the hydrazine is being removed, the situation will approach that of a D.C. discharge and further decomposition of the hydrazine will result in lower energy yields. This is shown to be so by SAVAGE<sup>(21)</sup> and BROWN and HOWARTH<sup>(27)</sup>. They found that decreasing the pulse OFF-time, i.e. increasing discharge pulse number, resulted in a decrease in the energy yield of hydrazine.

(b) Minimization of hydrazine decomposition by reducing the electron density

This is another classical method for the minimization of the back reactions. As a consequence of this method, both the energy yield and the fraction of ammonia decomposed which is converted to

hydrazine are increased<sup>(21,26,55)</sup>. The relationship between the power input (proportional to electron density) and the overall conversion to hydrazine is similar to the gas flowrate effect on conversion. It therefore follows that any improvement on the process in terms of energy yields of hydrazine is coupled with a corresponding fall in the hydrazine concentration, hence making this method rather unattractive. The effect of power input on energy yield of hydrazine can be well described by the empirical formula,

$$\ln Y = A - BW_d \quad \dots\dots\dots(2.19)$$

where,

Y = energy yield

$W_d$  = power density

A,B = constants.

If the operating pressure is also a variable the empirical formula takes the form,

$$\ln Y = \ln a + \dots(-bP - cW_d) \quad \dots\dots\dots(2.20)$$

where P is the operating pressure and a,b,c are constants. THORNTON, CHARLTON, and SPEDDING<sup>(26)</sup> used equation (2.20) to correlate their experimental results, but although straight line relationship existed the values of a,b,c were found to be dependent on the reactor geometries as well as <sup>the</sup> operating conditions. SAVAGE<sup>(21)</sup> on the other hand, used only one reactor geometry at one operating pressure (10 mm Hg) and hence did not observe these oddities but found that both A and B decreased with increasing residence time. Typical values of A were 1.6 at zero residence time to about 0.4 at a residence time of 0.9 sec.

B, on the other hand, decreased from 1.0 at zero residence time to 0.5 at 0.5 sec. after which any further increase in residence time resulted in a slight increase in the value of B.

The equation relating the effect of power input on the overall conversion to hydrazine is of a much more complicated nature. This is given in SAVAGE'S work as,

$$X_{N_2H_4} = \frac{2.8 \times 10^{-5}}{M_f} W \exp.(A - BW_d) \dots\dots\dots(2.21)$$

$X_{N_2H_4}$  is the overall conversion to hydrazine,  $M_f$  is the mass flowrate of ammonia in gm./sec., and W is the power in watts. Careful examination of this formula shows that  $X_{N_2H_4}$  will pass through a maximum with power input with the position and the value of the maximum depending on the flowrate of ammonia. In fact he found that the value of the maximum increased with increasing flowrate.

### (c) Absorption of hydrazine in an inert liquid

Interest in the design of these reactors, in which the decomposition of hydrazine is minimised due to its rapid removal by the liquid absorbent, was stimulated by HIKLING'S investigations on the synthesis of hydrazine by the glow discharge electrolysis of liquid ammonia<sup>(86-8)</sup>\*. This was later followed by a more detailed study carried out by I.C.I. of Great Britain<sup>(80)</sup>. In their early work I.C.I. used liquid ammonia (- 50°C to - 78°C) as an absorbent. But, due to the high vapour pressure of liquid ammonia at these temperatures (50 mm Hg) in comparison to the optimum pressure for hydrazine synthesis suggested by DEVINS and BURTON<sup>(10)</sup> (5 - 10 mm Hg), this technique not only gave poor energy yields (3 - 5 gas./kWh) but also demanded a very

\* This technique has been applied in other glow discharge syntheses such as ozone<sup>(83)</sup>, hydrogen peroxide<sup>(84)</sup> and hydrocarbons<sup>(85)</sup>.

precise temperature control. This difficulty was later overcome by replacing the ammonia with aqueous ammonia and later by ethylene glycol<sup>(81)</sup>. The latter was preferred to other absorbents due to its low volatility and its chemical inertness. Using these absorbents gave more flexibility on the operating pressures and improved the energy yields to up to 20 gm./lsh. In order to increase the rate of gas absorption, they introduced the liquid phase in the form of one or more jets, falling films, and sprays produced by rotating discs, vibrating surfaces or atomisation in a gas stream. The drop size produced by these techniques was found to vary from 0.2 - 2.0 mm in diameter.

In order to substantiate I.C.I.'s claims and to help clarify the mechanisms taking place in these gas-liquid reactors, THORNTON, CHARLTON and SPEDDING<sup>(26)</sup> have carried out a further investigation on this system using ethylene glycol as the liquid absorbent. This work provides a direct comparison between energy yields with and without the liquid absorbent. I.C.I.'s results lacked this information as no experiments were done without the absorbent. The various types of reactors used in THORNTON'S work are illustrated schematically in Figure 2.4. Reactors A and B are of the barrier type with a 1.2 MHz radio frequency power as the source of chemical activation. The central electrode in A is a rotating drum through which a spray of ethylene glycol is admitted while reactor B employs a central wire electrode with the absorbent being admitted in the incoming ammonia as a spray. Dispersion of the liquid was achieved ultrasonically using a vibratory generator. Reactor C, on the other hand, employs a pair

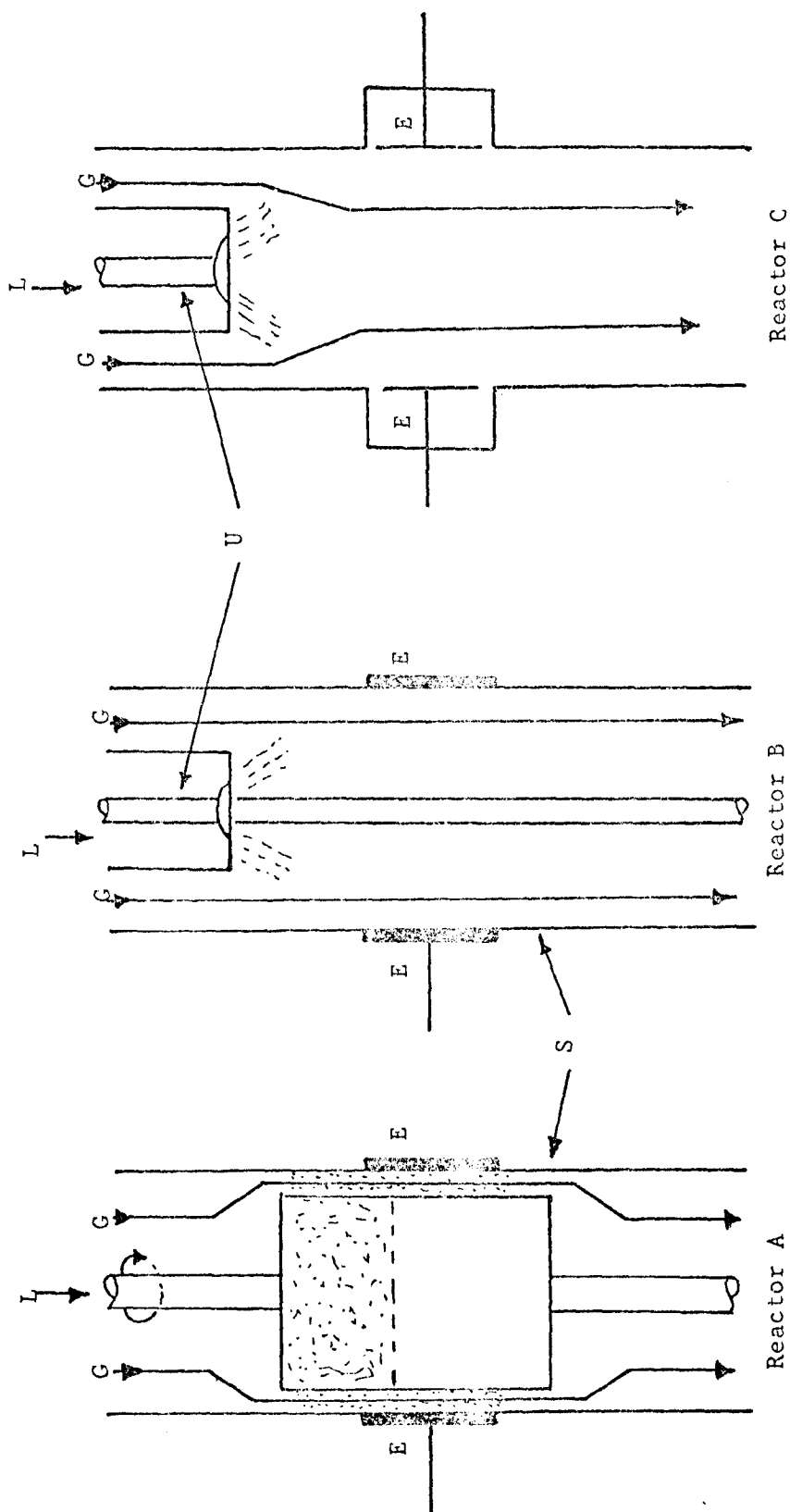


Figure 2.4. Schematic Diagram of Reactors used for Hydrazine Synthesis by Thornton, Charlton and Spedding

E = Electrodes      L = Liquid Inlet      G = Gas Flow  
S = Silica Barrier      U = Ultrasonic Vibrator

of rectangular electrodes so set in the gas flow as to avoid reactant by-passing. Dispersion of the liquid was done by the same method of reactor B. In reactor C pulsed D.C. power was used instead of the radio frequency power.

Experiments with reactor A showed that there was a fivefold increase in the energy yield when the liquid absorbent was in use, giving it a maximum value of about 10 gms./kWh. An interesting feature of this reactor emerged when the energy yields were plotted against the power inputs using equation (2.20). This showed that the slopes of the straight lines were less negative when using the absorbent, which is indicative of the role of the ethylene glycol as a means for reducing the degradative reactions. However, the fact that this slope was still negative emphasised that there was still a significant loss of hydrazine due to secondary processes in the gas phase. Had all the hydrazine being removed before any decomposition taking place, the slope of this line would have been either independent of discharge power or possibly positive. It therefore follows that if a more efficient absorption process was used, more hydrazine could be recovered. In order to substantiate this supposition experiments with reactor B were carried out where a more intimate contact between the liquid droplets and the gas was expected. Unfortunately, their results showed that yields were slightly below that of the film reactor A. This was attributed to the dissimilarities in the construction of these two reactors which led to radically different discharges being obtained. When discharge pulsing was used in conjunction with reactor C, energy yields of up to 15 gms./kWh were obtained but introduction of the liquid absorbent did not result in any improvement. No possible

explanation has been forwarded, but if their pulse conditions were such that degradation was negligible then introduction of the ethylene glycol will have little or no effect on reactor performance.

The use of liquid absorbents has the distinctive advantage of minimizing the degradative reactions without affecting the rate of electric energy input necessary for reactant activation, thus giving increased energy efficiency without the adverse effects on the overall conversion to hydrazine associated with techniques relying on short residence times such as the physical removal of hydrazine using high ammonia flowrates or even the pulsed discharges. Also, since chemical equilibrium in the gas phase could not be established, it is possible to build up the concentration of the hydrazine in the absorbent to substantial values by liquid recycling before any considerable degradation. From an engineering point of view liquid absorbent has the added advantage of acting as coolant for the reactor when some unnecessary heat is being generated during the discharge. However, like any other engineering operation, this technique is not free from flaws. One of the major disadvantages of this method is that under certain conditions, decomposition of the absorbent by the discharge action might result, thus not only leading to power losses but also giving<sup>a</sup>/wide spectrum of unwanted products. This will make the detailed analysis of the reaction mechanism rather complicated as well as affecting purification procedures to a large extent. Although there are no reported side effects regarding the decomposition of ethylene glycol in the ammonia/hydrazine system, its occurrence has been <sup>reported</sup> ~~proven~~ by SERGIO<sup>(90)</sup> when working on the partial oxidation of methane.

(d) Insertion of a suitable catalyst in the discharge zone

The result of DEVINS and BURTON'S<sup>(10)</sup> work on the glow discharge synthesis of hydrazine from ammonia was a positive proof of the effectiveness of this method as a tool for cutting down the degradation of hydrazine. They found that hydrazine yield was not only a function of the reduced electric field ( $E/p$ ) but depended also on the reactor diameter. This suggested the influence of the walls on the chemical reactions, as well as the discharge characteristics. Further support for this came to light when coating the reactor walls with platinum rings resulted in an eight fold increase in the energy yield of hydrazine to 43 gms./kWh based on energy consumption in the positive column only, but oddly enough no apparent change in nitrogen yield was noticed. This they attributed to the catalytic recombination of hydrogen atoms which were believed to be the main ingredients for hydrazine losses in the discharge. However, since the source for nitrogen was believed to arise from the decomposition of hydrazine, then any reduction in the latter process should undoubtedly give less nitrogen. Because no such effect was observed, their experimental data failed to establish whether the improvement in hydrazine yield was due to the prevention of its destruction by hydrogen atoms or the catalysis of its formation.

DEVINS AND BURTON'S observations were later confirmed by RATHSACK<sup>(90)</sup> who carried out a series of experiments in vessels with the walls treated with phosphoric acid to retard the recombination of hydrogen atoms. He later repeated these experiments with untreated

walls and found a four fold increase in the yield of hydrazine, thus indicating the influence of wall reactions. RATHSACK also suggested that when using electrodes of different materials the increase in hydrazine yield was not due to the change in the work function of the metal but rather to catalytic effects. He found that platinum was the best electrode material. The effectiveness of platinum as a catalyst was proven by yet another investigation carried out by RUBSTOVA and ERZHIN<sup>(82)</sup> using an ozonizer discharge at 633 mm Hg. They found that coating the tube walls with nickel and platinum increased the overall conversion by 50% and 200 - 300% respectively. Regeneration of the catalysts reduced the efficiency of nickel but had no apparent effect on platinum.

It follows from what has been said that introduction of a catalyst in the reaction zone does improve hydrazine yields but the exact role of this catalyst in the overall kinetics of the process can not yet be assessed. Further basic research is therefore necessary in order to determine the mechanism of these catalysis reactions.

#### (e) Removal of hydrogen atoms with scavengers

The consequence of this technique is the reduction of hydrogen atoms concentration in the reaction vessel and by doing so minimizing their rate of reaction with hydrazine. The scavenger used could be any organic compound with a strong affinity towards hydrogen atoms. The first to investigate the effect of these additives was MANION<sup>(91)</sup>. His measurements were made at a pressure of 5 mm Hg using an electric discharge current of 40 mA passed between electrodes 20 cm apart in a vessel 2.4 cm in diameter and an ammonia linear velocity of 526 cm/sec

and sometimes at 5200 and 376 cm/sec respectively. His results showed that additives contributed to an increase in hydrazine yield by a factor of up to three. Of the additives investigated, allyl ( $\text{CH}_2 = \text{CHCH}_3$ ) compounds were particularly effective with allylamine giving the highest yields of hydrazine. Also, the additive became more effective when present in concentrations ranging from 0.1 - 1.0 molar %. Another point of interest is that the role of the additive as a scavenger became less important at higher ammonia flow rates. This could be explained if one realizes that under these conditions, the lower concentration of hydrogen atoms coupled with a rapid removal of hydrazine by the gas stream leaves little room for improvement on the part of the scavenger.

MANION reported energy yields of up to 30 gms/kWh with a hydrazine concentration of 0.7 wt.% in a single pass. If higher concentration could be attained by recycling the mixture of hydrazine, ammonia and additive, as he suggested, then this technique will be a fruitful commercial proposition. But, on the other hand, if the additive itself underwent decomposition, then the problems associated with it would be enormous and industrial utilization becomes doubtful.

Similar results regarding the effect of hydrogen atom scavengers were also reported by BARKER<sup>(63)</sup> using a microwave discharge at 10 mm Hg with allyl alcohol as the additive in concentrations of up to 0.5 molar %. BARKER found that addition of the scavenger increased both energy yields and conversion to hydrazine by 200%. He reported maximum energy yield of 40 gms./kWh with a concentration of hydrazine equivalent to 0.06 molar %. He also found that the role of the

scavenger became less significant at higher power inputs and lower ammonia flowrates in agreement with MANION'S<sup>(91)</sup> findings. This was attributed to other mechanisms of hydrazine decompositions taking place under these conditions, namely the electron-induced decomposition of hydrazine and its precursor.

### 3.0. SCOPE OF PRESENT INVESTIGATION

The purpose of this research programme was to develop novel reactors in which the problems associated with the phenomenon of beam constriction were to be eliminated. Firstly, attention was devoted to the application of COTTON'S crossed discharge technique. This study, however, constituted only a minor part of the programme and for this reason it is not included in the main body of this thesis but is relegated to Appendix 1. The investigation was abandoned after it became apparent that some considerable and unavoidable error was involved in the measurement of the high frequency power. Nevertheless, a limited number of experimental runs were carried out which not only indicated the ineffectiveness of this device but also helped to explain some of COTTON'S findings.

The second and main part of this thesis is concerned with the development of a new type of reactor embodying the principle of beam scanning. Here, the problems associated with beam constriction were overcome by allowing the discharge beam to scan the entire reactor cross-section. Mechanical scanning, as compared to other means such as electromagnetic scanning or electrical switching devices, was used because of its simplicity. Rotation of the discharge was achieved by enclosing the cathode of the cell by a rotating insulating tube which was provided with an aperture of appropriate dimensions.

The performance of this reactor was studied in depth using both continuous and pulsed power supplies at an ammonia pressure of 10 torr. The effects of scanning frequency, discharge current, ammonia flowrate and pulse repetition rate (in the case of the pulsating discharge) were fully investigated. Analysis for hydrazine as well as

other gaseous products, namely hydrogen and nitrogen, has been carried out and the influence of the operating variables on the degree of ammonia decomposed and hydrazine formed was established.

In the continuous DC discharge the field strength in the positive column was measured using a single electrical probe and subsequently an estimate of the mean electron energy has been made. The probe also served to identify areas in the plasma which hitherto had no mention in any published literature. These are now described as active dark zones and are found to be responsible for some chemical activation.

Another phenomenon which has escaped the attention of most investigators in this field, i.e. the deposition of a film on the anode, is reported and a possible explanation for its formation is also given.

#### 4.0. EXPERIMENTAL WORK

##### 4.1. The Beam Scanning Reactor

The reactor developed in this study consisted in principle of a stainless steel cathode rod (O) located axially within an annular anode (M). The latter was fabricated from stainless steel machined carefully to give it a smooth surface and curved periphery to minimise edge effects and sparks which might have been created due to some irregularities on the surface. The cathode was shielded by an insulating tube (L) containing a circular aperture which lay in the plane of the anode. When a potential difference was applied to the electrode, a discharge beam was established through the shield aperture, and by rotating the latter, the beam was made to scan the entire reactor cross-section. A detailed diagram incorporating the dimensions of the different components of this reactor is shown in Figure 4.1. A supplementary photograph of the assembled cell together with its two basic elements is shown in Figure 4.2.

The shell of the reactor consisted of a borosilicate tube (D) closed at the ends by Perspex end plates (G). The closures were maintained gas tight by Gaco gaskets (K) and mild steel tie bars (N). Gas entry (H) and exit ports (J) were provided at each end of the reactor. These were backed by chambers loosely packed with glass wool which served to establish a uniform gas flow through the reactor. Flow experiments with vacuum gauges upstream and downstream of the reactor showed that the pressure drop across the reactor was negligible.

The cathode shield (L) was fabricated from Syndenyo tube

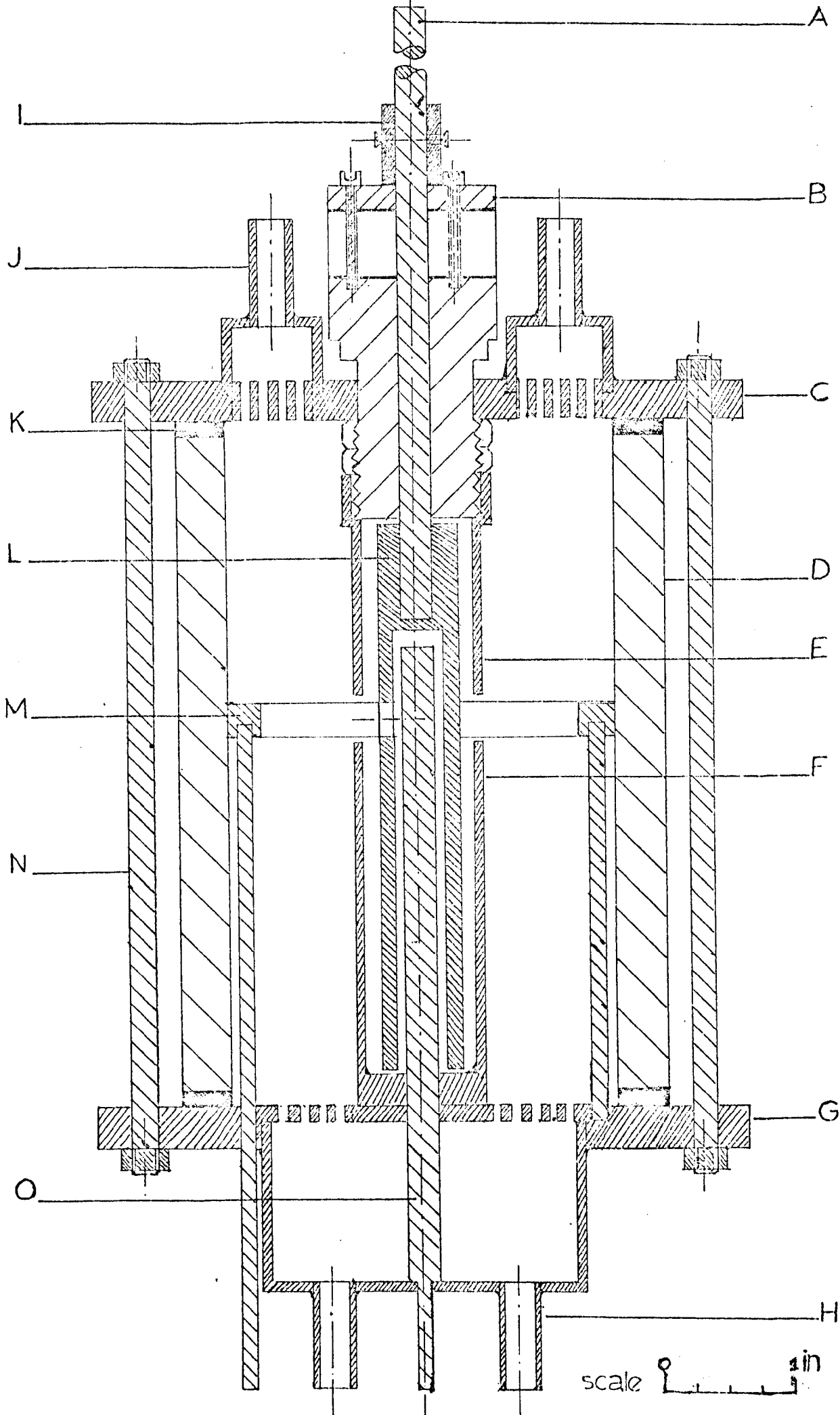
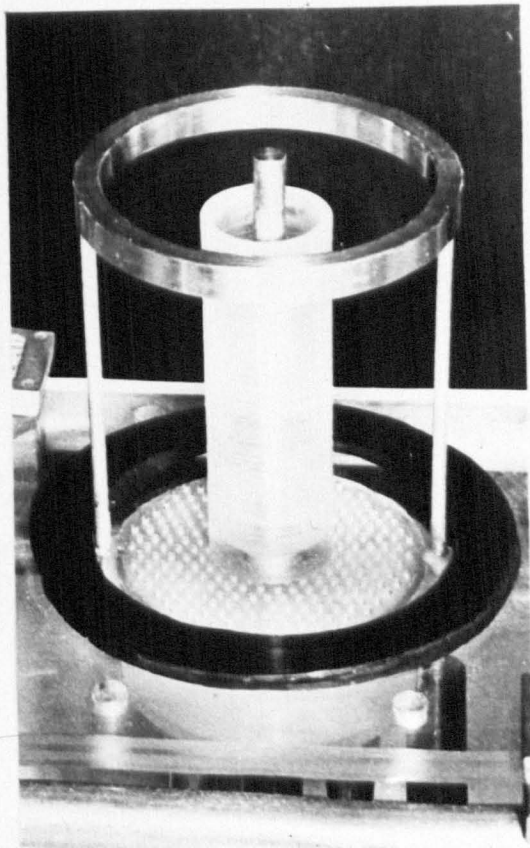
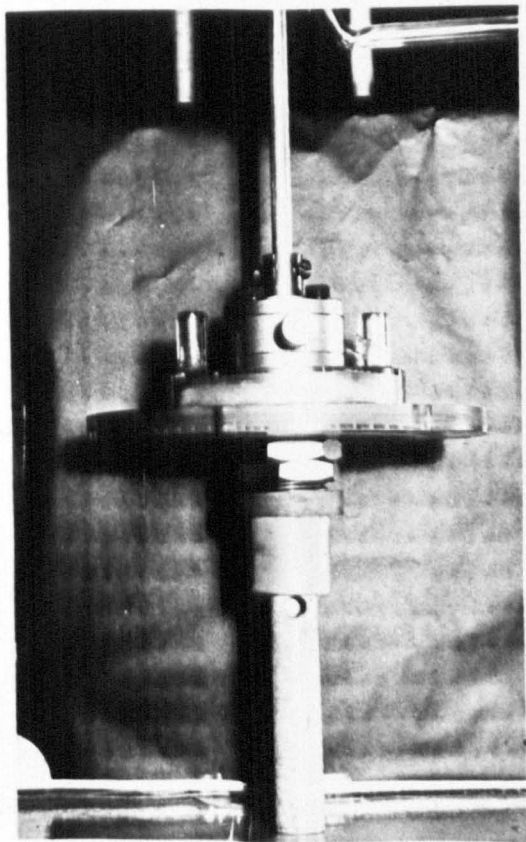
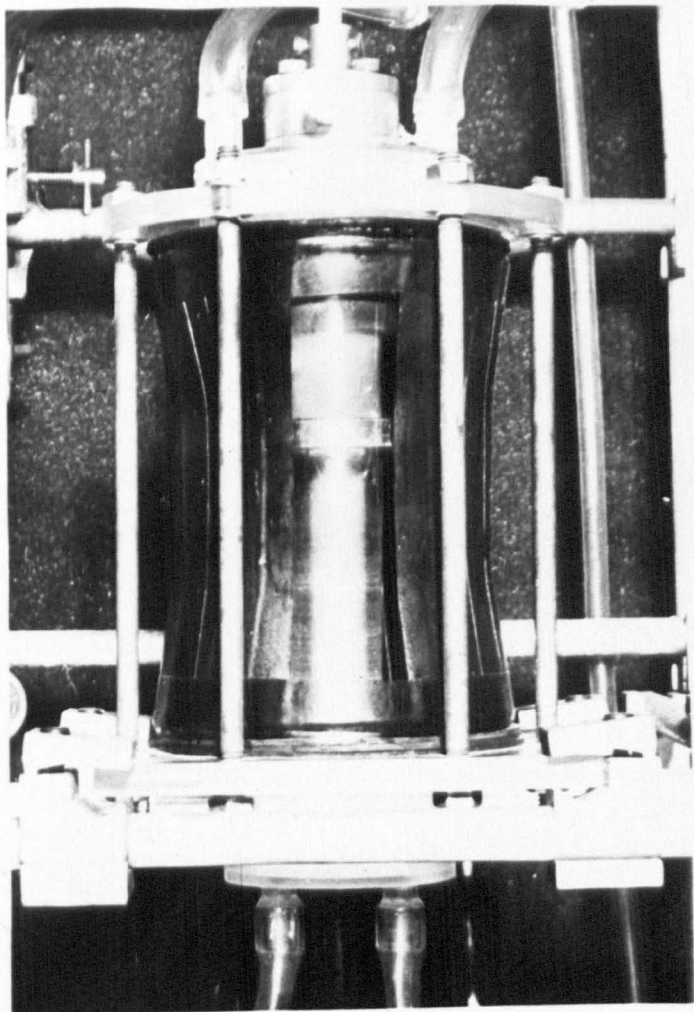


Figure 4.1 The Scanning Beam Reactor

Key to Figure 4.1

- A        Stainless steel shaft (diameter =  $\frac{1}{4}$ " )
- B        Rotary shaft seal
- C        Perspex end plate (thickness =  $\frac{5}{16}$ " )
- D        Borosilicate glass tube (internal diameter = 3";  
height = 5")
- E        Perspex sheath (bore =  $\frac{1}{4}$ "; wall thickness =  $\frac{1}{16}$ " )
- F        Perspex sheath (bore =  $\frac{1}{4}$ "; wall thickness =  $\frac{1}{16}$ " )
- G        Perspex end plate (thickness =  $\frac{5}{16}$ " )
- H        Gas inlet (bore =  $\frac{1}{4}$ "; wall thickness =  $\frac{1}{16}$ " ; height = 1")
- I        Brass bush and friction washer arrangement
- J        Gas outlet (bore =  $\frac{1}{4}$ "; wall thickness =  $\frac{1}{16}$ " ; height = 1")
- K        Gaco gasket seal (thickness =  $\frac{1}{8}$ " )
- L        Sindanyo tube (bore =  $\frac{1}{4}$ "; wall thickness =  $\frac{1}{8}$ "; aperture  
diameter =  $\frac{1}{4}$ " )
- M        Stainless steel anode (internal diameter =  $2\frac{1}{2}$ ";  $\frac{1}{2}$ " square  
cross-section)
- N        Mild steel tie bars (diameter =  $\frac{3}{16}$ " )
- O        Stainless steel cathode (diameter =  $\frac{1}{4}$ " )

Figure 4.2 SCANNING BEAM REACTOR



and was driven through a variable speed gear box by means of a  $1/30$  h.p. motor. This enabled speeds of up to 1000 r.p.m. to be attained without excessive heating of the shaft seal element (B). In order to stop the downward movement of the rotating shaft (A) during operation a brass bush (I) was incorporated. Friction between the latter and the rotary shaft seal (B) was cut to a minimum by the insertion of a PTFE washer between the two. Finally, the rotating cathode shield was surrounded by two stationary Perspex sleeves (E,F) above and below the beam aperture in order to minimize turbulence in the gas phase. In a later investigation using pulsed discharge techniques, the lower sleeve was substituted by a Perspex tube enclosing the cathode rod to within a distance of less than  $1/16$ " from the rotating insulator, and the upper sleeve was removed completely. The dimensions of the tube were  $2\frac{15}{16}$ " in length with an internal diameter of  $\frac{1}{4}$ " and a wall thickness of  $\frac{3}{32}$ ". The rotating Sydanoyo tube was  $1\frac{1}{2}$ " long with a wall thickness of  $1/16$ ". The clearance between the latter and the cathode was kept at  $1/32$ ". The aperture in this case was in the form of a rectangular slit measuring  $\frac{1}{4}$ " horizontally by  $\frac{1}{4}$ " vertically. This arrangement increased the cross-sectional area available for gas flow from  $26.6\text{ cm}^2$  to  $29.7\text{ cm}^2$ , i.e. an increase of 11.7%.

#### 4.2. Flow System

Figure 4.3 shows the flow system in a schematic form. Anhydrous ammonia, provided by I.C.I. with a minimum purity of 99.99%, was directly fed to the system from the supply cylinder without any further drying or purification. Its pressure was reduced to just above atmospheric with a Matheson stainless steel reducing valve. The pressure of ammonia at

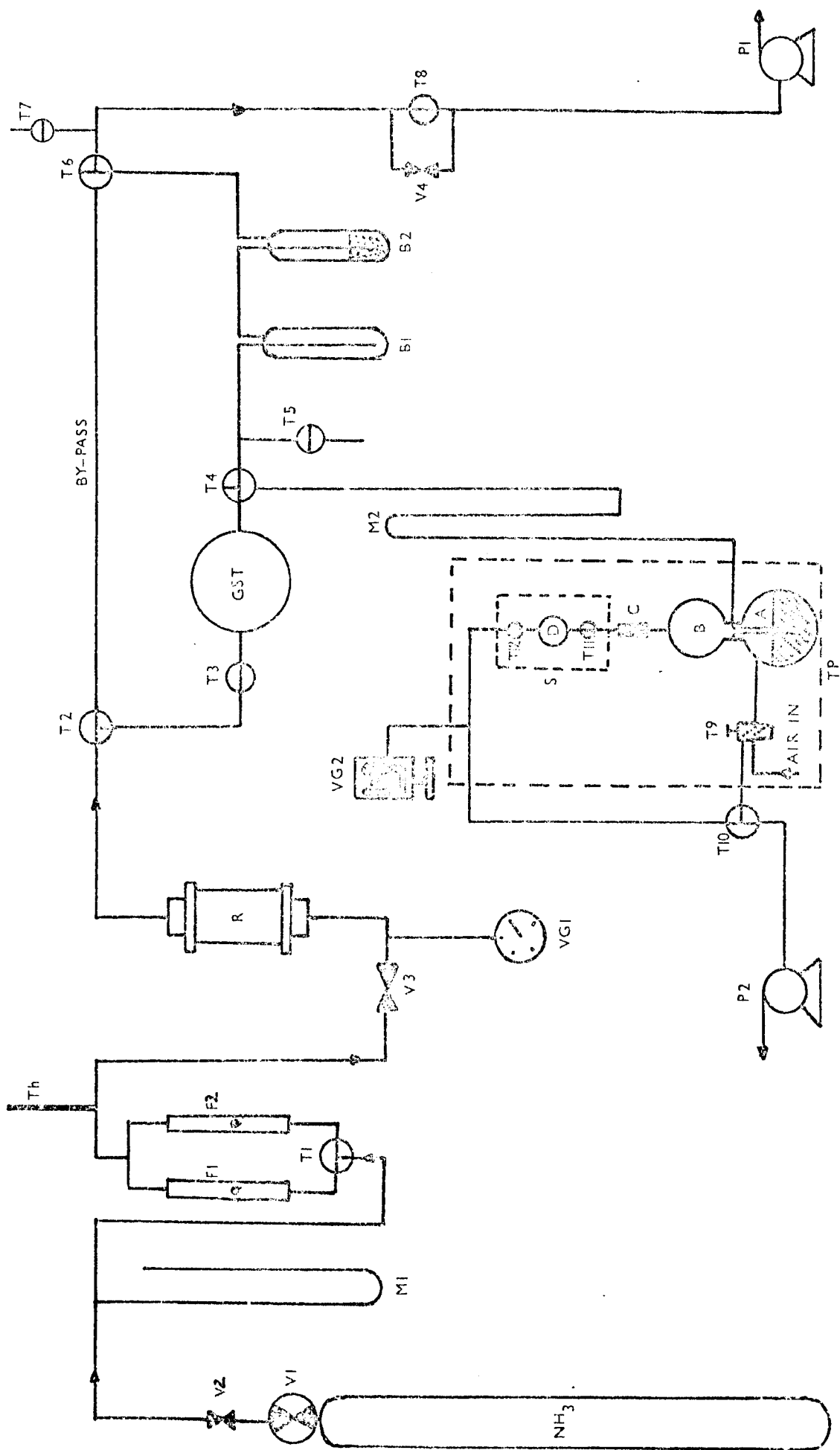


Figure 4.3 Schematic Diagram of The Flow System

Key to Figure 4.3

- V1 - Matheson stainless steel reducing valve model 12.240
- V2 - Stainless steel needle valve incorporated within the reducing valve
- M1,2 - Mercury manometers
- T1, 2, 4, 6, 9, 10 - 3-Way high vacuum stopcocks
- F1 - Fischer and Porter variable area flowmeter type OF -  $\frac{1}{16}$  - 10 -  $\frac{4}{36}$  with  $\frac{1}{16}$ " stainless steel float
- F2 - Fischer and Porter variable area flowmeter type FP  $\frac{1}{8}$  - 12 - C -  $\frac{5}{81}$  with  $\frac{1}{8}$ " sapphire float
- Th - -  $10^{\circ}\text{C}$  -  $110^{\circ}\text{C}$  mercury thermometer
- V3 - Ernid stainless steel needle valve
- VG1 - Speedivac dial gauge model CG3
- R - Reactor
- T3, 5, 7, 8, 11, 12 - 2-Way high vacuum stopcocks
- GST - Gas sample trap
- B1,2 - Absorption bottles
- V4 - Speedivac needle valve type OS1D with adjustable dial pointer
- P1,2 - Double stage Genovac rotary vacuum pumps
- VG2 - Speedivac Vacustat model 1B2
- TP - Toeppler pump unit
- A - 1 litre Pyrex flask containing 750 ml of mercury
- B -  $\frac{1}{2}$  litre Pyrex flask
- C - Magnetically operated valve
- D - Gas sample tube
- S - Gas sample tube unit

this stage was measured with a mercury manometer (M1).

At this pressure the ammonia flow rate was measured by one of two Fischer and Porter Tri-Flat variable area rotameters (F1,F2) and its temperature was monitored by a mercury thermometer (Th). The gas flow could be directed towards either of these flow meters with the aid of a three way high vacuum stopcock (T1). With this arrangement ammonia flowrate from as little as 10 cc/min to about 1300 cc/min (STP) could be measured. Since the pressure in this part of the system was above one atmosphere, there was no problem with air leaking in.

The pressure of the ammonia was reduced to the required level by a stainless steel needle valve (V3) and its pressure at this stage was monitored by a Speedivac dial gauge (VG1) having a range of 0 - 20 torr. The accuracy of this gauge was within 2.5% of the full scale deflection. The gaseous products leaving the reactor either flowed through the by-pass or through the gas sample trap (GST) followed by an absorption train (B1,B2). The second absorption trap (B2) contained 50 ml. of ethylene glycol to absorb the hydrazine whilst the first (B1) was kept empty and served to trap any liquid absorbent which might be inadvertently drawn back.

Fine control of the gas flow was achieved by the correct adjustment of the valve (V3) and a high vacuum stopcock (T8). When working with lower flowrates it was necessary to insert another stainless steel needle valve (V4) in parallel with T8 to give finer control of the flow.

The system was maintained at reduced pressures by a double stage Genevac rotating piston vacuum pump type GRD 2. This had a

displacement of 50 lit./min and a capability of reaching vacuums of up to  $2 \times 10^{-4}$  torr without gas ballast and  $5 \times 10^{-3}$  torr with gas ballast. A non-return valve was available to stop oil suck back. The maximum ammonia flowrate measured at  $20^{\circ}\text{C}$  and 760 mm Hg, achieved with this pump and the existing flow system did not exceed 200 cc/min. Also due to contamination of the oil by the ammonia, reconditions of the pump at regular intervals was necessary in order to keep its required efficiency.

The gas sampler (GST) was a round glass flask of 2 litre capacity and was enclosed in a wooden box for safety reasons. A gas sample could be trapped whenever necessary and then transferred to the Toepler pump unit (TP) via a high vacuum stopcock (T4). The Toepler pump consisted basically of two Pyrex flasks (A,B), a special valve (C), which could be operated magnetically when necessary, and a gas sample tube unit (S). Flask (A) was of one litre capacity and contained a pool of mercury (750 cc.) and flask (B) had a volume of  $\frac{1}{2}$  litre and was connected to the gas sample trap (GST) by a capillary tubing which also served as a manometer (M2). The valve consisted of a bundle of  $\frac{1}{16}$ " steel rods sealed in a glass envelope. The latter was positioned in the neck of flask (B) by a cone and socket assembly. The gas sample tube unit consisted of a 10 ml glass bulb with two high vacuum stopcocks (T11,T12), one at each end. The gas sample tube unit was connected to the Toepler pump by a socket and cone arrangement and could be removed and connected to a gas chromatograph for gas analysis whenever necessary.

Vacuum in the Toepler pump was maintained by another Genevac vacuum pump (similar to the previous one) and pressure stability at

high vacuums was observed on a vacustat gauge model 1B2. This gauge operates on the same principle as a McLeod gauge over the range  $10 - 10^{-2}$  torr.

As operations were at a pressure of 10 torr, strict attention was paid to the construction of the flow system to prevent air leakages. Glass tubes were used whenever possible. These were connected by means of Quickfit glass balls and sockets, and socket and cone joints smeared with Apelson high vacuum grease type M. Where these were impracticable such as connections to the reactor cell, rotameters etc., flexible PVC hoses were used to make connection between glass pipe lines and were kept as short as possible. Due to the highly corrosive nature of ammonia, all metal parts of the different instruments used in the flow system were fabricated from stainless steel. Flow meters and manometers were assembled on  $\frac{1}{4}$ " wooden panels and the whole apparatus was rigidly supported on a wooden bench by Lablox stands and retorts. All electrical switches were confined to one section of the rig and within easy reach. Power transmission was made through special high voltage cables and connections to the reactor were made through Belling and Lee high voltage single pole connectors. Where these could not be used, they were replaced by crocodile clips. Photographs showing the experimental rig in detail can be seen in Figures 4.4, 4.5.

### 4.3. Ancillary Equipment

#### 4.3.1. High Voltage Generators

A D.C. voltage of up to 4.0 kV could be obtained from a suitably built generator whose simplified circuit diagram is shown in

Figure 4.4 APPARATUS FOR CONTINUOUS DC OPERATION

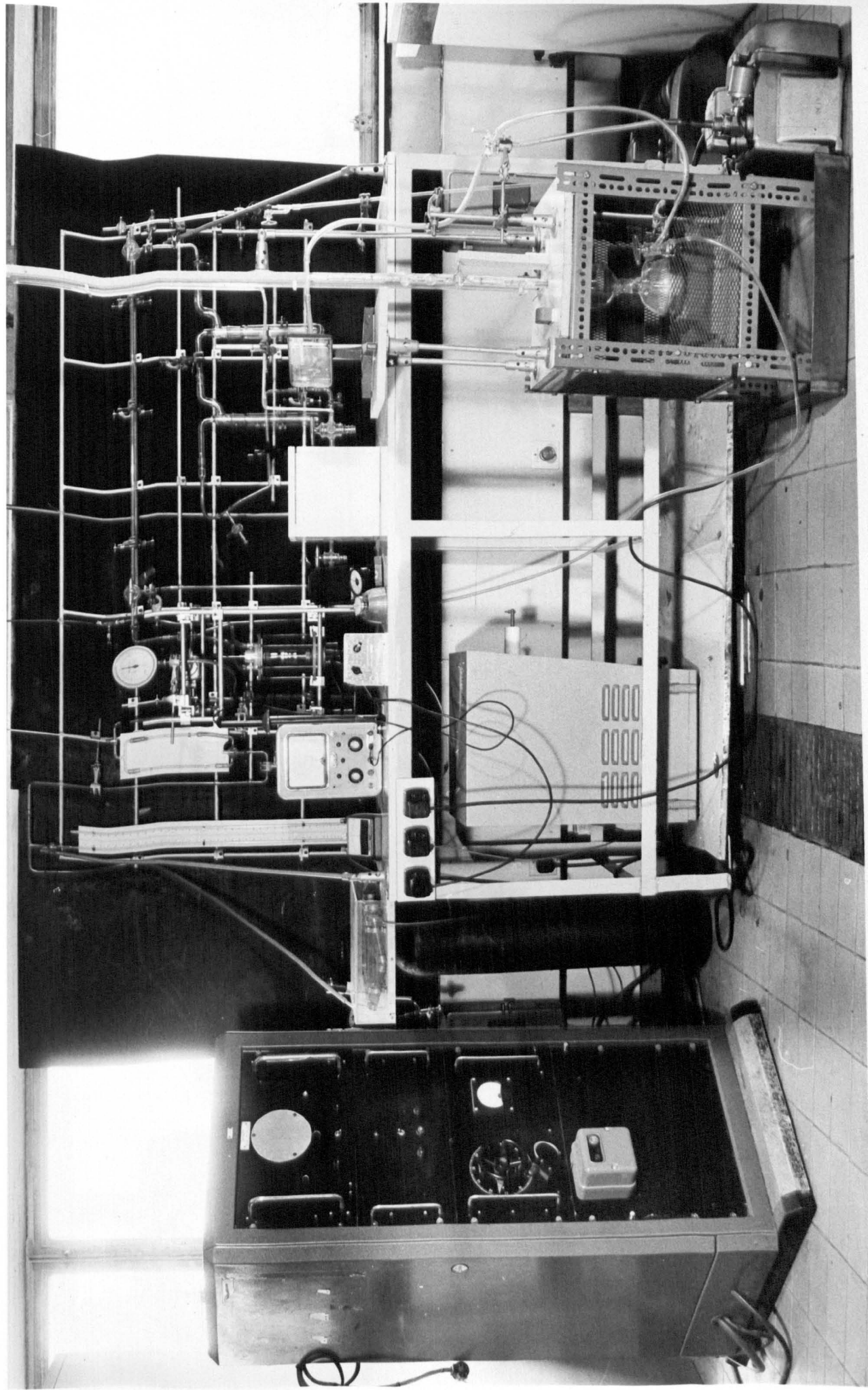


Figure 4.5 APPARATUS FOR PULSED DC OPERATION

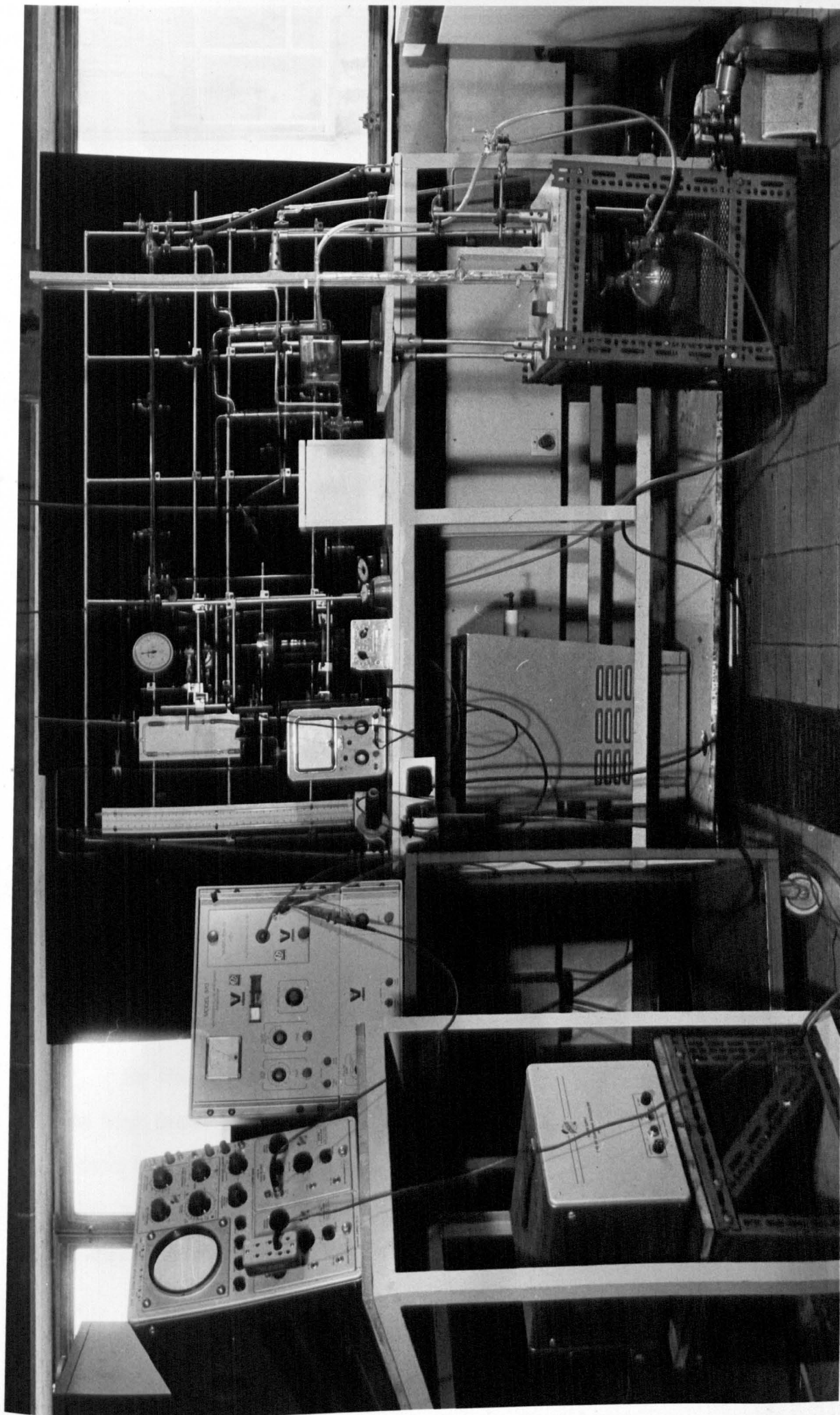


Figure 4.6. Mains voltage from 0 - 250 volts was supplied to the primary transformer and controlled by a Variac. The output from the secondary transformer was fully rectified and smoothing was achieved by a 10 Henry coil and a  $4\mu\text{F}$  high voltage capacitor. The generator had a negative output, and for this reason the cathode was the high tension electrode. To increase the safety of the equipment, micro-switches were provided on the supply cabinet doors and the Variac. Both the primary and secondary circuits were protected by fuses and thermal delay was provided on the H.T. to the rectifier valves. Any residual charges on the high voltage capacitor at the end of each experiment were discharged to earth by a heavily insulated high voltage cable through a series of resistors which constituted the ballast resistor. The latter was incorporated in the circuit between the output of the generator and the reactor cell and its existence was a necessity in order to limit the flow of current at the onset of the discharge and by doing so, sustain the non-disruptive nature of the glow discharge. A number of Welwyn type C47 enamel covered, wire wound resistors were used to make up the required ballast resistor. For the existing reactor geometry and operating pressure, a value of  $175\text{ K}\Omega$  was found to be suitable. The magnitude of this resistor could be knocked down to as low as  $5\text{ K}\Omega$ , if higher discharge currents were required.

In the pulsed discharge case, the power was provided by a Valonex high power pulse generator model 570. With this model pulse width from  $0.1 - 300\mu\text{ sec}$  with a repetition rate of  $3\text{ pps} - 10^5\text{ pps}$  were obtainable. Peak output voltages from as high as  $19\text{ kV}$  to as low as  $40\text{V}$  could be obtained by the insertion of special Plug-in Units.

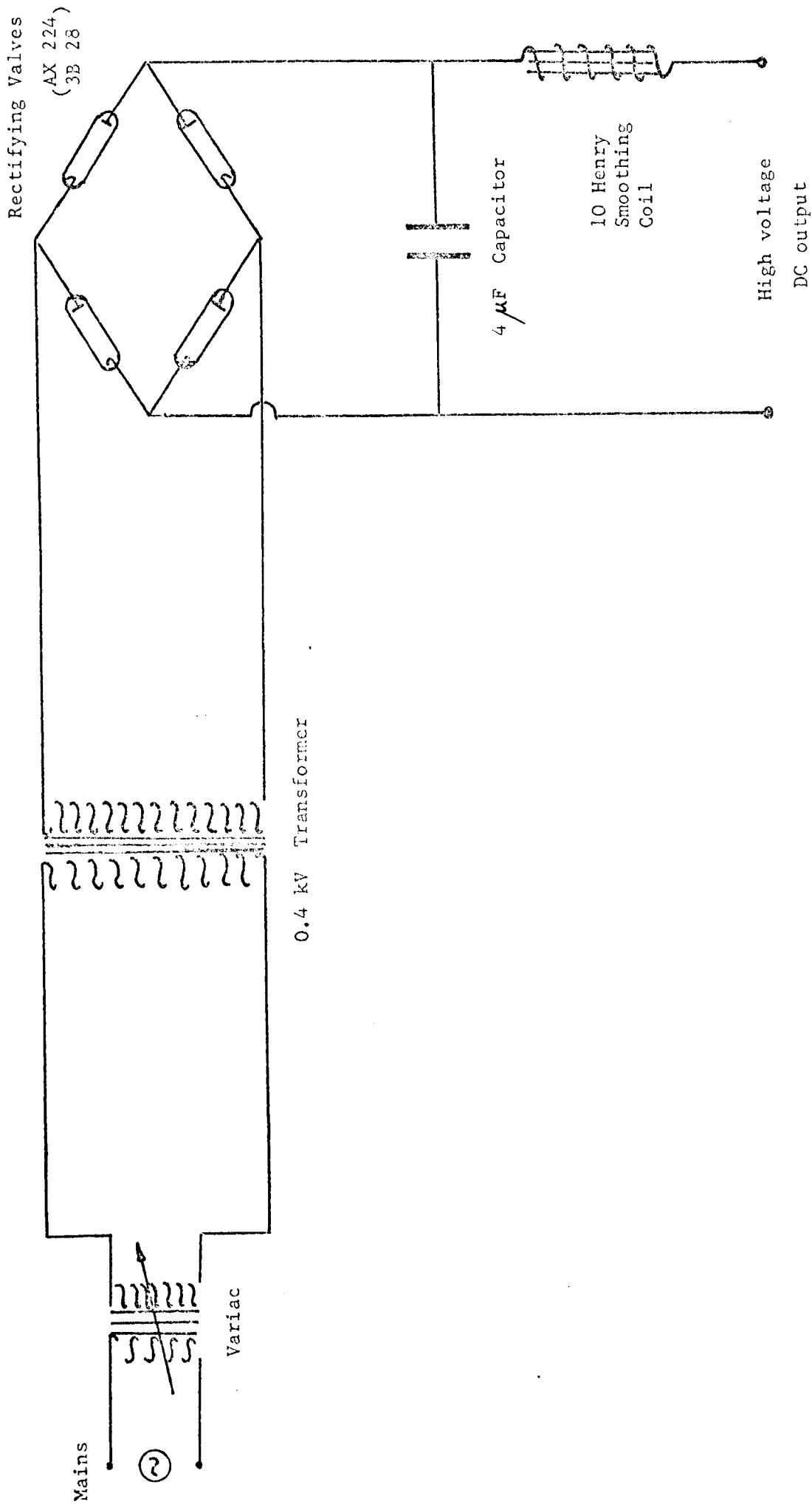


Figure 4.6 DC High Voltage Generator

For this particular investigation a direct output Plug-in Unit type V-1097 was used which gave voltages of up to 3 kV. When this output was fed into a nominal resistance of  $200\Omega$ , a square wave was obtained with a droop of less than 3%. The rise and fall times were 30 ns and 50 ns respectively. But when <sup>the</sup> discharge was in operation, delay in the rise and fall times together with a distortion of the wave-form resulted due to the dynamic impedance of the circuit. The generator had a duty factor of 1% at 22 kW peak, but greater for lower output levels. A ballast resistor of  $15\text{ k}\Omega$  was necessary and the output voltage was again negative. The model contained overload protection with reset if the duty cycle was exceeded or if the output was short circuited. A flashing red panel light advised the operator when the high voltage was on.

#### 4.3.2. Measuring Equipment

##### (a) Valve Voltmeter

An Airmac valve voltmeter type 314 incorporating a 1000:1 D.C. attenuator probe type 372 with an input resistance of  $2 \times 10^3\text{ M}\Omega$ , was used to read the D.C. voltage. This instrument could be adjusted to read voltages ranging from 300 mV - 30 kV, however, for most discharge conditions the maximum running voltage was less than 1 kV accounting for a current loss in the probe of less than  $0.5\mu\text{A}$ . The accuracy of this meter was quoted by the manufacturers as  $\pm 5\%$  of full scale deflection.

##### (b) Milliammeter

The D.C. current was measured by a moving coil milliammeter incorporating four appropriate shunt resistances and a switching device.

With this arrangement the meter could read currents from 0 - 300 mA in the steps, 0 - 10, 0 - 30, 0 - 100, and 0 - 300 mA respectively. When this meter was checked against a standard Avometer, which had an accuracy of 1%, no discrepancies were observed.

### (c) Oscilloscope

In order to trace the current and voltage waveforms of the pulsed discharge a Tektronix type 551 dual beam oscilloscope, incorporating a Plug-in Unit type K preamplifier, was used. The oscilloscope had a sweep rate of  $0.1 \mu\text{sec/cm}$  to  $5 \text{ sec/cm}$ , and a continuously variable deflection factor from  $0.2 \text{ V/cm}$  to  $20 \text{ V/cm}$ . Continuously variable sweep rates were available from  $0.1 \mu \text{ sec/cm}$  to  $0.12 \text{ sec/cm}$ . Both the horizontal and vertical sweep amplifier were accurate to within 3% of the control setting.

The voltage signal from the discharge cell to the oscilloscope could be attenuated 1000 times by a Tektronix probe type P6015. The latter had an input resistance of  $100 \text{ M}\Omega$  and a capacitance of  $3 \text{ pF}$ . With this unit pulsed voltages of up to  $40 \text{ kV}$  could be displayed on the oscilloscope screen without any damage to the components inside the probe body. The probe had two input terminals, one had to be clipped to the voltage under investigation and the other to a selected ground point near the probe input connection.

In some instances a Shackman camera was mounted on the oscilloscope screen to photograph the voltage and current waveforms.

### (d) Tachometer

For measuring the speed of rotation or the discharge

beam scanning frequency, a hand type Smiths tachometer was used. This meter was graduated 0 - 200 rev./min, and a X10, X100 range switch enabled higher readings to be made.

#### 4.4. Experimental Procedures

##### 4.4.1. Flowmeter Calibration

The larger capacity flowmeter (FP4-12-G41) was calibrated using the soap film technique. A schematic diagram for this arrangement is shown in Figure 4.7. The glass tube was about one metre long and had a volume of 500 ml. Markings on the outside surface indicated the volumes at different positions. The flowrate for any set position of the float was calculated from the time taken by a soap film, produced by pressing the rubber bulb, to sweep a certain volume. The ammonia temperature and pressure were monitored by the thermometer and the mercury manometer assembled on the gas flow line. These flowrates were then corrected to standard conditions of 20°C and 760 mm Hg using the appropriate correlation between the gas flowrate and flowmeter characteristics.

The flowrate of a gas is related to the flowmeter conditions by :

$$F_1 = C_1 B (\rho_f - \rho_{g1} / \rho_{g1})^{1/2} \dots\dots\dots(4.1)$$

where,

- $F_1$  = gas flowrate calculated at operating conditions
- $C_1$  = flow coefficient given by the manufacturers as a function of tube dimensions, scale reading, and viscosity number

B = constant for each tube

$\rho_f$  = float density

$\rho_{g1}$  = gas density at operating conditions.

The flowrate at standard conditions will be given as:

$$F_2 = C_2 B (\rho_f - \rho_{g2} / \rho_{g2})^{\frac{1}{2}} \dots\dots\dots(4.2)$$

$$F_2 = F_1 \frac{C_2}{C_1} \left[ \rho_{g1} (\rho_f - \rho_{g2}) / \rho_{g2} (\rho_f - \rho_{g1}) \right]^{\frac{1}{2}} \dots\dots(4.3)$$

But for small changes in pressure and temperature,

$$\rho_f - \rho_{g1} \approx \rho_f - \rho_{g2} \text{ and } C_1 \approx C_2$$

$$F_2 = F_1 (\rho_{g1} / \rho_{g2})^{\frac{1}{2}} \dots\dots\dots(4.4)$$

$$F_2 = F_1 (T_2 P_1 / T_1 P_2)^{\frac{1}{2}} \dots\dots\dots(4.5)$$

where,

$F_2$  = flowrate at 20 c and 760 mm Hg

$F_1$  = flowrate at operating conditions

$T_1 P_1$  = temperature and pressure at operating conditions

$T_2 P_2$  = temperature and pressure at standard conditions (i.e. 20°C and 760 mm Hg respectively). The calculated flowrates at 20° and 760 mm Hg together with the calibration curve are shown in Figure A3.1, Appendix 3.

The flowrates were also evaluated for different float positions at 20°C and 760 mm Hg, using the manufacturer's data (Fisher and Porter Co. Handbook 10 A9010) and the results agreed well within experimental error. For this reason and due to some practical difficulty in maintaining a

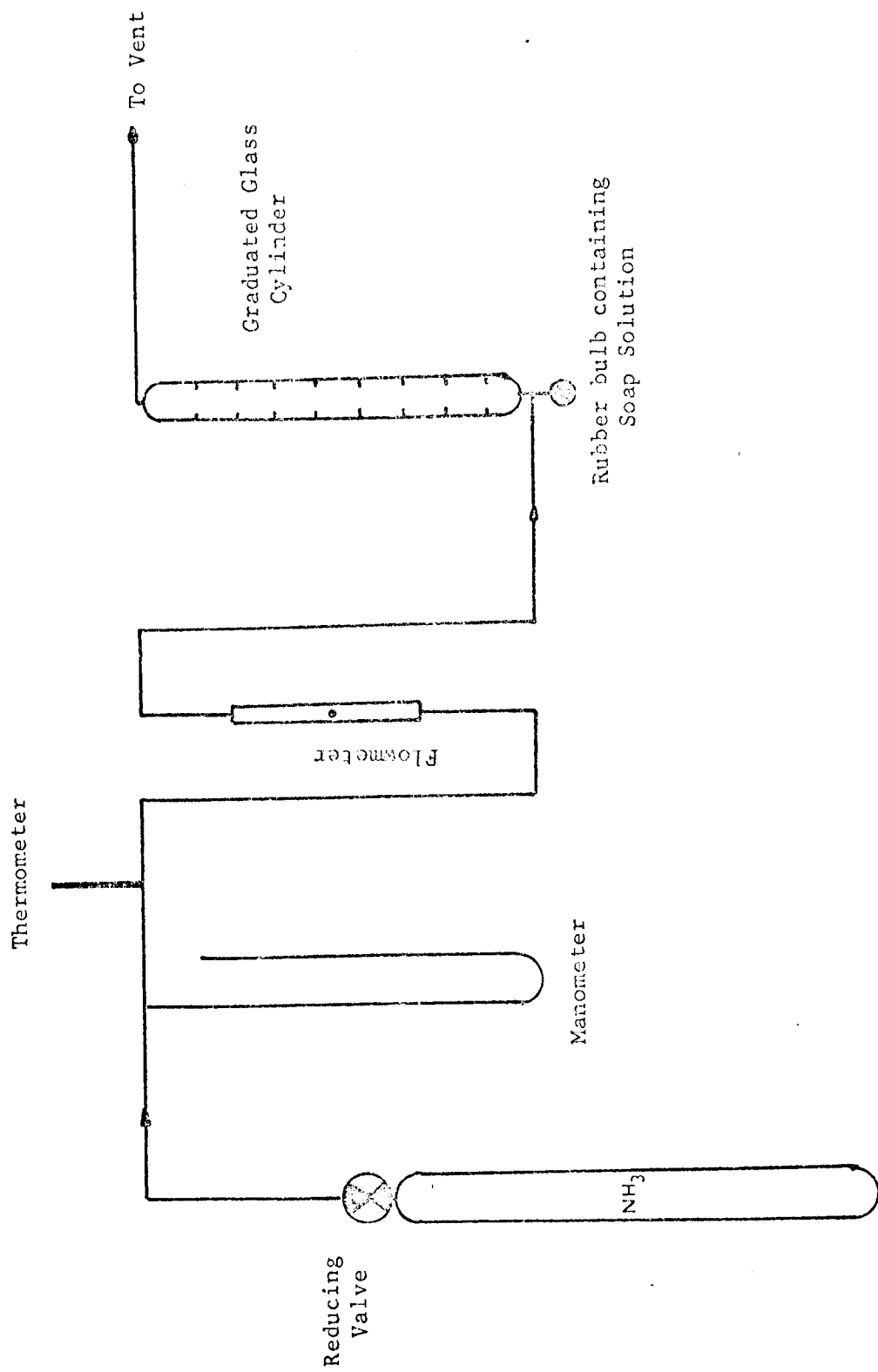


Figure 4.7 Flowmeter Calibration

soap film at lower flowrates, the latter method was adopted to calibrate the second flowmeter (OBF-<sup>1</sup>/16-10-4/36). The calibration curve for this flowmeter is shown in Figure A3.2, Appendix 3.

#### 4.4.2. Analysis of Products

##### (a) Hydrazine

Quantitative analysis of hydrazine can be carried out using gas chromatography<sup>(92)</sup>, titration<sup>(93)</sup> or colourimetric method of WATT and CHRISP<sup>(94)</sup>. However, due to the small amount of hydrazine produced, it was felt that the colourimetric analysis was the most sensitive.

This technique used the 458 m $\mu$  absorption band of the complex formed by the reaction of hydrazine with acidified p-dimethylamino-benzaldehyde. The orange colour of the complex develops fully in about 10 minutes and stays stable thereafter for a period of not less than 12 hours. Beers Law holds for up to 0.77 p.p.m. and ammonia does not interfere with hydrazine analysis. Absorptiometric measurements were carried out using a Unicam SP600 spectrophotometer which had a wavelength range of 340 - 1000 m $\mu$ . The instrument incorporated a tungsten filament lamp as the light source, two vacuum photocells (blue and red) and two light filters (clear glass and OX7 filter). The setting of the required wavelength (458 m $\mu$ ) was achieved by using the blue photocell in conjunction with the glass filter.

The spectrophotometer was calibrated using mixtures with known hydrazine concentrations. Solutions of 0.5 to 1.0 gm of hydrazinium chloride in one litre of distilled water were first prepared and then standardised by titration with standard potassium iodate solution

using chloroform as an indicator. The standardised solution was then carefully diluted with distilled water to give concentration of hydrazine of typically  $10^{-3}$  gm/litre. The colour reagent employed had the following composition: p-dimethylaminobenzaldehyde, 20.0 gms; ethanol, 1000 ml; distilled water, 500 ml; ethylene glycol, 500 ml; and concentrated hydrochloric acid, 188 ml. This mixture had a molarity of one with respect to hydrochloric acid and served as the blank for the absorptiometric measurements. Bunks of this solution were prepared and kept for periods of up to one month without any deterioration. Twenty ml of this mixture were added to aliquots of the diluted standardised hydrazine solution, selected so that the final concentration of hydrazine would be within 0.03 - 0.8 p.p.m. After the colour was fully developed, the % absorptancy of the liberated complex was measured against that of the blank mixture, and calibration curve relating the % absorptancy to the concentration of hydrazine was produced. This is shown in Figure A3.3, Appendix 3. The sensitivity of the spectrophotometer was checked at regular intervals with freshly prepared and standardised hydrazine solutions, and reproducibility was found to be well within  $\pm 0.5\%$ .

#### (b) Other Gaseous Products

The gaseous products from the glow discharge decomposition of ammonia are hydrogen and nitrogen as well as hydrazine, and in order to give an estimate of the extent of the decomposition process and also the fraction of the decomposed ammonia which is converted to hydrazine, analysis of the permanent gases ( $N_2$  and  $H_2$ ) was a necessity.

A Perkin-Elmer gas-liquid chromatograph model 452 was used for this purpose. The unit was equipped with a thermal conductivity

detector coupled to a Kent chart recorder. The signal generated by the detector drove a potentiometric recorder to produce a graphic display on a strip chart which could then be related to the concentration of the gas sample. A range control attenuated the signal fed to the recorder by successive accurate factors of two so that each sensitivity setting was half that of the previous setting.

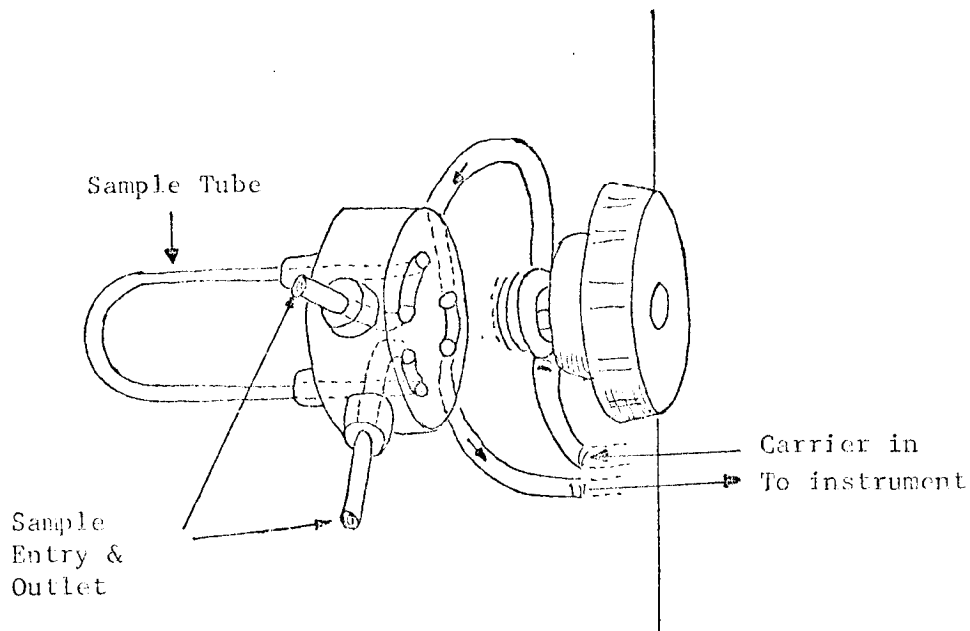
Hydrogen, nitrogen and oxygen were separated using a seven foot 5A molecular sieve column at 50°C. Argon at an input pressure of 10 p.s.i.g. was used as the carrier gas. The choice of the carrier gas depended to a large extent on the best sensitivity achieved with the thermal detector. Nitrogen was ruled out, since it was itself one of the gaseous products, and helium, although it gave a very good response to nitrogen and oxygen, but poor response to hydrogen, was not used due to its high cost. Argon was used as it was cheaper and at the same time extremely sensitive to hydrogen and also gave a fair response to nitrogen and oxygen. The length and temperature of the column together with the carrier input pressure were determined experimentally to give the best possible separation coupled with the shortest possible elution times. With the existing conditions the elution times were 49 sec. for hydrogen, 90 sec. for oxygen, and 128 sec. for nitrogen when the column was fully activated.

The molecular sieve column employed failed to give any response to ammonia and analysis of the gases emerging from the chromatograph showed no traces of ammonia. In view of this observation, it was believed that the ammonia was absorbed permanently on the surface of the packing material constituting the column. For this reason, it was found that after constant operation, the thermal detector became less sensitive, elution times shortened, and sometimes overlapping of

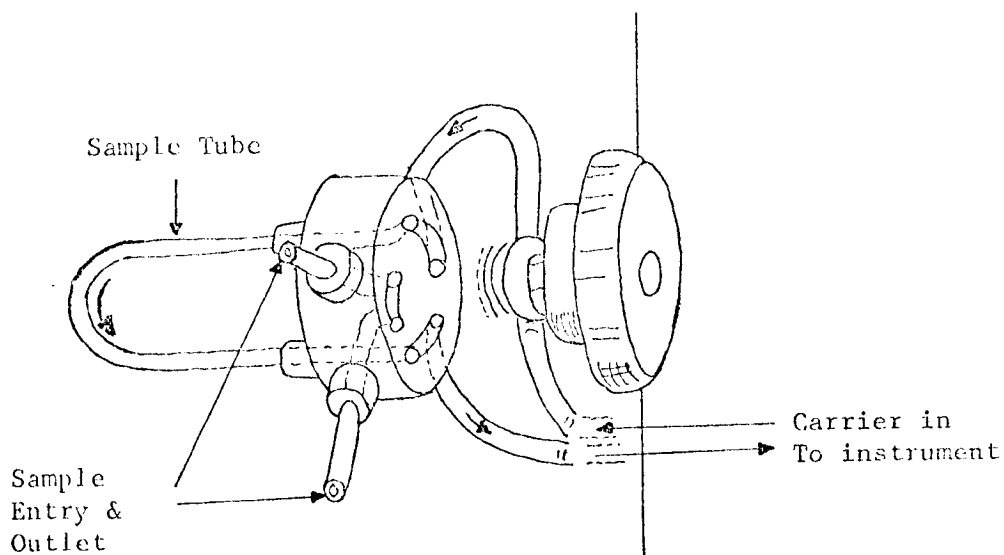
the oxygen and nitrogen peaks resulted. However, rejuvenation of the column was established by baking at 200°C for a period of not less than 12 hours. This was done regularly at weekly intervals.

The chromatograph was equipped with a special gas-sampling valve for injecting the gas samples into the stream of the carrier gas, see Figure 4.8. It can be seen that when the knob of the gas-sampling valve is in the fully clockwise position the sample tube is isolated from the instrument but is allowed to fill with the sample mixture. When the control knob is turned to the fully anti-clockwise position the sample tube is disconnected from the sample entry and exit connections and the retained sample is allowed to be swept into the instrument by the carrier gas. The gas sampling valve was fitted with  $\frac{1}{4}$ " diameter stainless steel tubing for connection to the sample tube which itself was a 5 foot stainless steel tube of the same diameter and made in the form of a coil.

The instrument was calibrated by injecting gas mixtures of known composition at different total pressures and measuring the response in terms of peak heights. Due to the sharp and well defined chromatograms, see Figure 4.9, it was found unnecessary to measure the area under each peak. Also, since the volume of the sample tube was the same in each case, the partial pressure of each component in the mixture was directly proportional to the mole fraction of that component. Calibration curves for nitrogen and hydrogen were then produced giving the peak height as a function of the partial pressure of each component in mm Hg. These are shown in Figures A3.4, A3.5 in Appendix 3. It can be seen that the response is linear in both



(a) Valve Fully Clockwise



(b) Valve Fully Counter-Clockwise

Figure 4.8 Gas Flow through the Chromatograph's Sample Valve

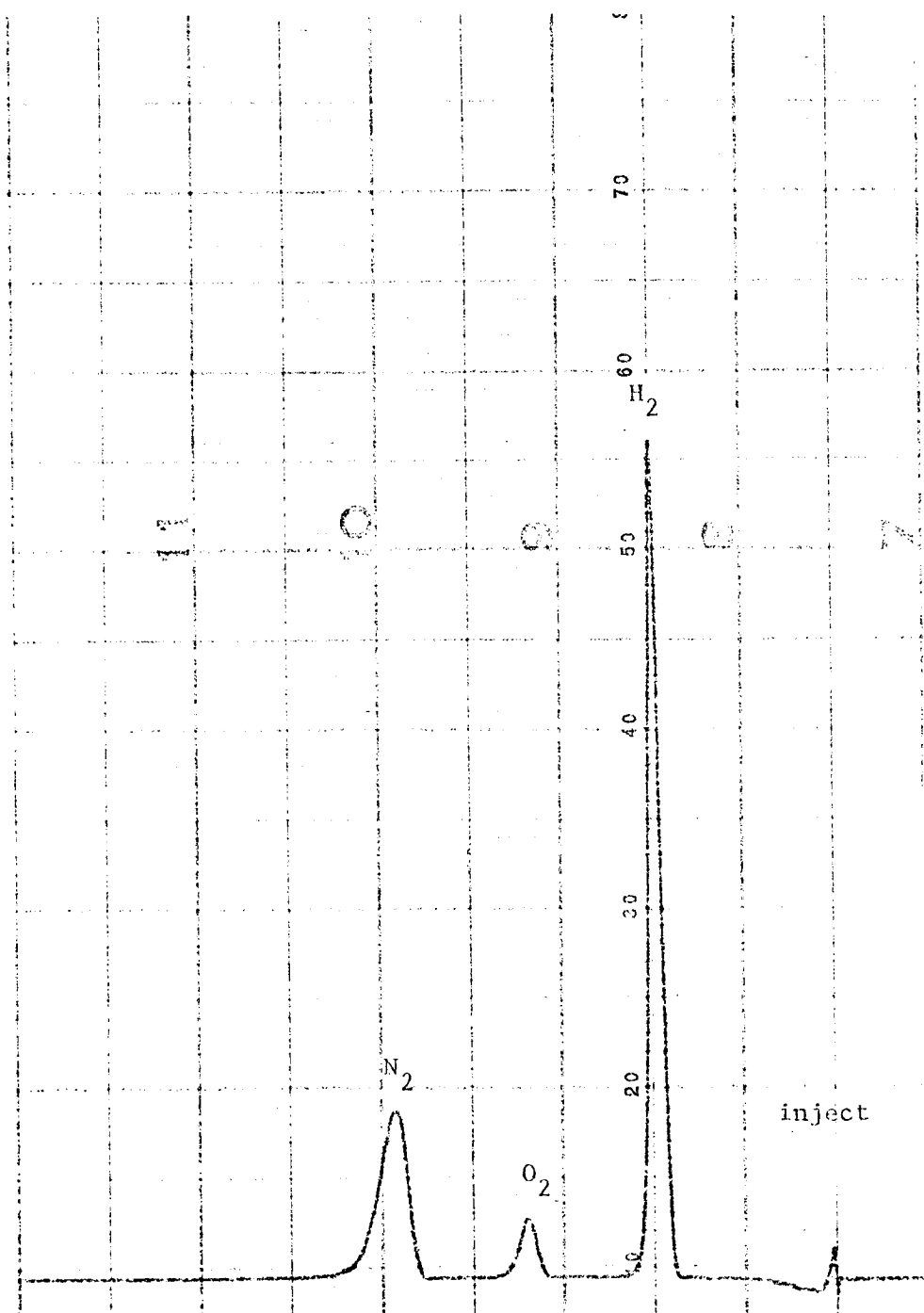


Figure 4.9 Typical Chromatograms using 7 ft. 5A Molecular Sieve Column at an oven temperature of 50 °C with Argon as carrier at 10 p.s.i.g.

cases and the straight lines pass through the origin. The performance of the instrument was checked daily by injecting only one sample and drawing a straight line through this point and the origin. For the calibration a gas mixture having the following composition: 95.42%  $\text{NH}_3$ ; 2.58%  $\text{N}_2$ ; 2.08%  $\text{H}_2$  on molar basis, was used. This was specially prepared and provided by Air Products.

A schematic diagram showing the arrangement for this calibration technique is shown in Figure 4.10. The general procedure was as follows:

- (1) The line down stream from the needle valve V1 was evacuated by the vacuum pump. With the knob on the gas-sampling valve in the fully clockwise position, this also included the evacuation of the incorporated gas sample tube.
- (2) With the stopcock T2 closed, argon was flushed into the system by turning the gas-sampling valve knob on and off for a number of times until the pressure indicated on the manometer was slightly above atmospheric.
- (3) Valve T2 was then opened and the system was again evacuated. When the pressure on the dial gauge was less than one torr V1 was slightly opened to let a stream of the gas mixture, from the cylinder, flush the flow line.
- (4) With V1 open, T2 was closed and when the pressure in the system built up to the required level, V1 was then closed. Any subsequent readjustment of the pressure could be achieved by slightly opening T2.
- (5) The pressure indicated on the manometer was then recorded and the knob on the gas-sampling valve was turned into the fully

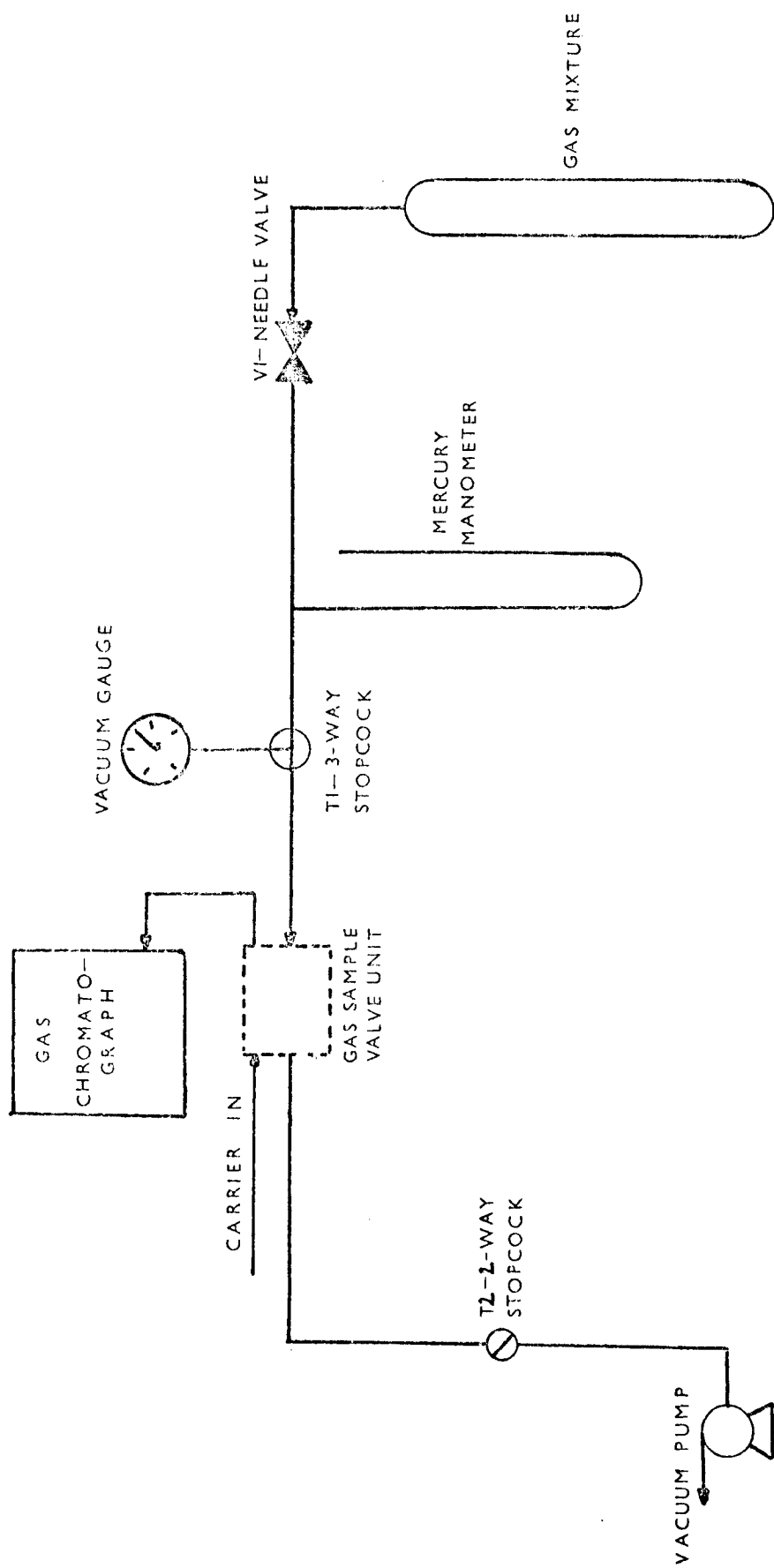


Figure 4.10 Flow Diagram for Chromatograph Calibration

anti-clockwise position to allow the retained gas in the sample tube to be swept by the carrier gas into the chromatograph.

The valve was kept in this position for a long enough interval, usually until all the peaks were obtained, to ensure that the sample volume was completely swept by the carrier.

- (6) The gas-sampling valve was then turned into the fully clockwise position and valve T2 was opened for the evacuation of the system.
- (7) Records of the peak heights were made and the procedure was repeated at exactly the same injection pressure to ensure reproducibility.
- (8) Steps 1 - 7 were repeated at a different pressure. The injection pressures were usually in the range of 20 - 200 torr.

The flow system depicted in Figure 4.10 had provisions for introducing a gas sample from an experimental run. Between the needle valve and the manometer there was a B14 cone and socket arrangement such that the gas line from the cylinder could be disconnected at any time and instead the sample tube from the Toepler pump unit inserted.

Since the molecular sieve column separated oxygen from hydrogen and nitrogen, it was easy to determine the amount of air in the system and hence the contribution of this to the overall peak height of nitrogen. The partial pressure of nitrogen was corrected by injecting pure air samples (0 - 5 torr) after each run and noting the peak height of oxygen. By comparing this with that obtained in the calibration procedure, it was possible to calculate exactly how much nitrogen was coming from the air and hence give the correct figure for

the partial pressure of nitrogen in the actual gas mixture with air being excluded. The presence of air was believed to have resulted from the incomplete evacuation of the gas lines or due to leakages into the gas-sampling valve during operation.

#### 4.4.3. Power Measurement

Power measurement in the DC discharge was relatively simple. The voltage and current were read from the voltmeter and milliammeter respectively, see Figure 4.11(a), and their product was taken as the power dissipated in the discharge. However, in the pulsed discharge its calculation was more complicated.

In the pulsed discharge the energy consumed between times  $t$  and  $t + dt$  is given by:

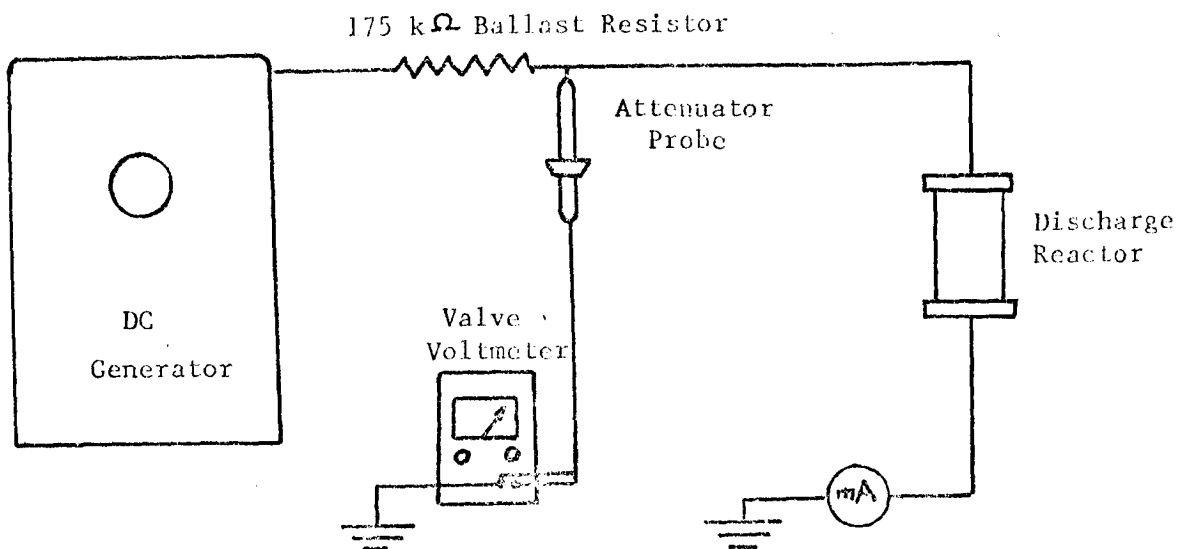
$$d E_t = V_t I_t dt \quad \text{.....(4.6)}$$

where,  $E_t$ ,  $V_t$  and  $I_t$  are the values of the energy, voltage and current respectively at time  $t$ . It therefore follows that the average power input,  $W$ , for a pulse duration  $T$ , will be :

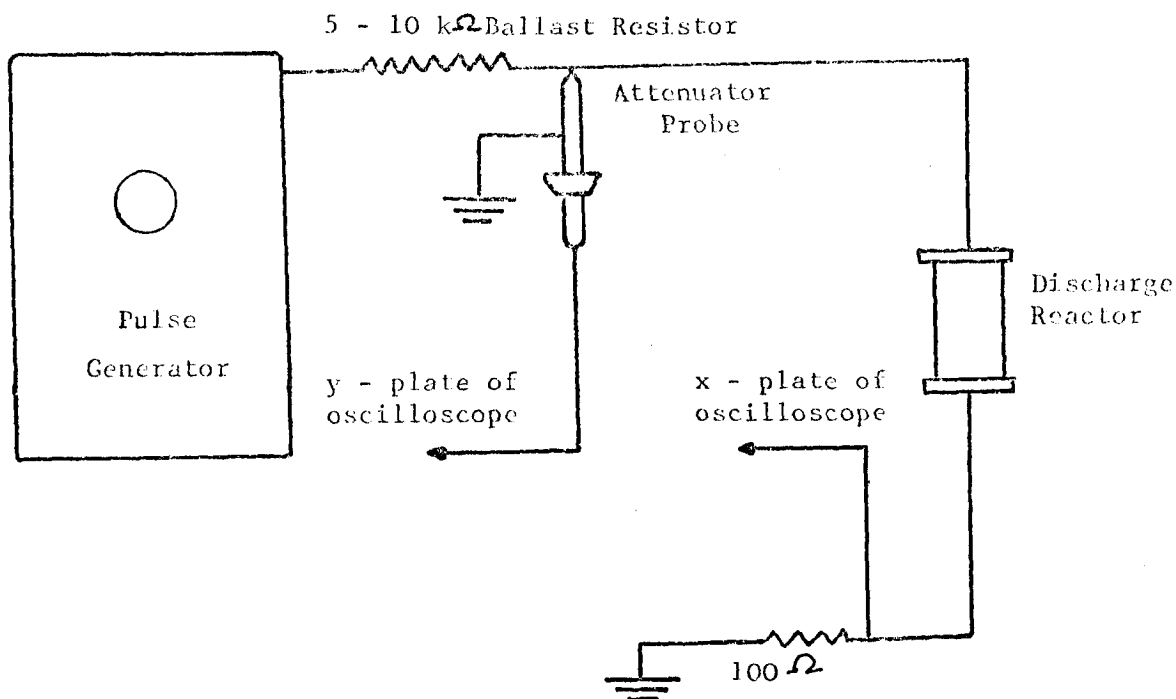
$$W = \frac{1}{T} \int_0^T V_t I_t dt \quad \text{.....(4.7)}$$

The integral will represent the amount of energy consumed in one pulse. In order to evaluate this integral, it is necessary to know the value of the product,  $(V_t I_t)$ , at every instant of time. This was achieved by displaying the voltage and current waveforms on an oscilloscope.

The current waveform signal was taken across a  $100\Omega$  high stability resistor while the voltage signal from the discharge was



(A) - Continuous DC Circuit Diagram



(B) - Pulsed DC Circuit Diagram

Figure 4.11 Circuit Diagrams for Power Measurement

attenuated 1000 times by an appropriate probe (see Section 4.3.2(c)) before feeding it to the oscilloscope. A circuit diagram showing this arrangement is depicted in Figure 4.11(b). The oscillograms were then traced on graph paper followed by evaluation of the integral using either Simpson's Rule of integration or by simply cutting and then weighing the area under the curve. Knowing the area density (gm/unit area) of the graph paper, the exact area under the curve was then calculated.

A more sophisticated technique was used by SAVAGE<sup>(20)</sup>. Here the oscillograms were first photographed then enlarged by a known factor onto a sheet of graph paper. A "Digitised Decoder Output Serialiser" machine was then used to trace the variables  $V_t$  and  $I_t$  on a screen. A special switching device would then punch the data onto a computer tape ready for subsequent processing. The multiplication and integration were then carried out using a computer programme based on Simpson's Rule. A comparison between the two techniques were made by treating a set of data. Results showed no significant difference ( $< \pm 5\%$ ) and for this reason the first method was adopted since it was less time consuming.

#### 4.4.4. Measurement of the Electric Field

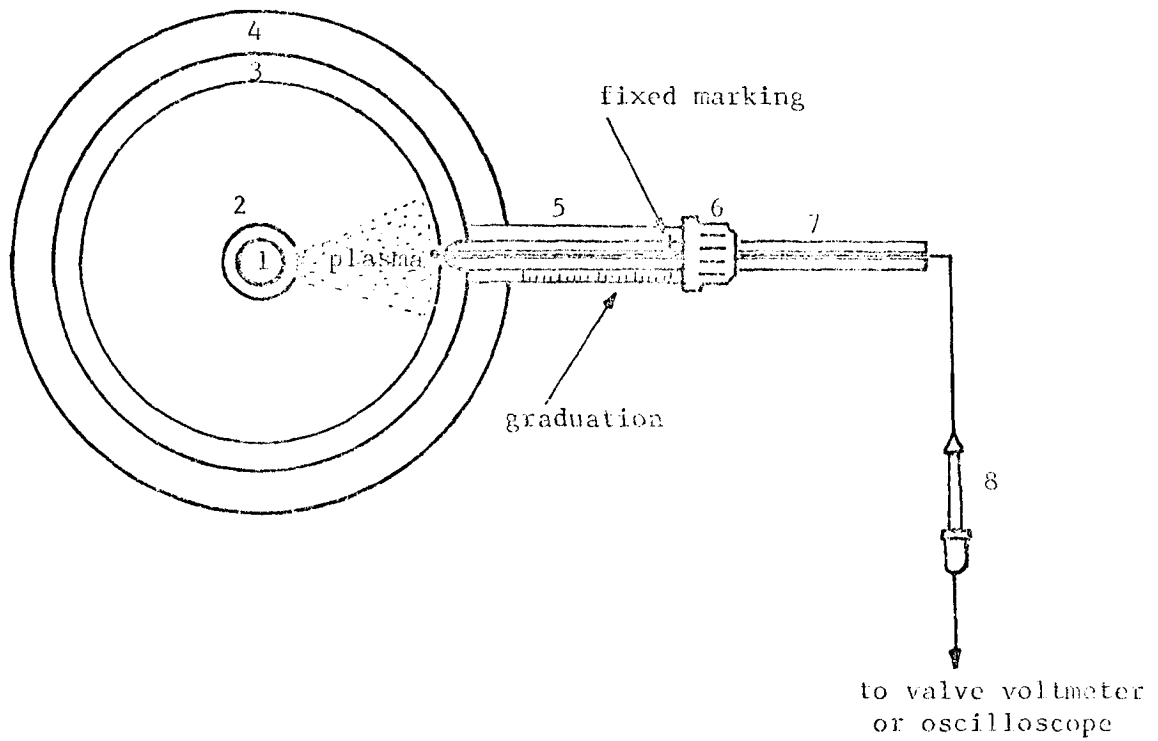
The field in the positive column of the continuous DC discharge was measured using a conventional single Langmuir probe. The latter consisted mainly of a  $1/32$ " platinum wire running through a length of a capillary tubing. The end of the latter was fused to the wire with one centimetre of the latter protruding from the fused junction. The capillary tubing was then positioned in a Quickfit screw thread

connector and secured by means of a screw down cap, silicone rubber compression ring and PTFE washer. The whole assembly was then fixed onto the borosilicate shell of the discharge reactor through a hole drilled at an appropriate position such that the tip of the probe could be placed in the centre of the plasma. With this arrangement it was possible to move the probe along the plasma quite easily and without disturbing the operating pressure inside the reactor cell. A schematic diagram of this arrangement is shown in Figure 4.12. The distance between the tip of the probe and the anode was measured with the aid of a fixed marking on the movable capillary tubing and a graduated scale on the fixed screw thread connector. The distance could be read accurately to within 0.25 mm.

Electrical connection to the probe was made via a crocodile clip and the output voltage signal was attenuated 1000 times before feeding it to either the valve voltmeter or the oscilloscope using the probes mentioned in Sections 4.3.2(a) and 4.3.2(c). All field measurements were carried out using the attenuator probe type 373 (Section 4.3.2(a)). The latter incorporated an input resistance of  $2 \times 10^3 \text{ M}\Omega$  and for this reason restricted the flow of current through the Langmuir probe to within a fraction of a  $\mu$  amp. It therefore follows that since no serious disturbances of the plasma were incurred, the reading of the probe could be interpreted as the actual plasma space potential.

#### 4.5. Routine Experimental Run

At the commencement of each run, 30 ml of pure (99.9%) BDH ethylene glycol was placed in the already cleaned and dried absorption



#### Key

- (1) cathode
- (2) insulating tube
- (3) anode
- (4) borosilicate glass
- (5) screw thread glass connector
- (6) screw down cap with silicon rubber compressing ring and PTFE washer
- (7) capillary tubing
- (8) Airmec attenuator probe type 372  
or Tektronix attenuator probe type P6015

Figure 4.12 Electric Field Measurement

trap B2, see Figure 4.3. Previous tests had shown that it was not necessary to employ two traps in series and that 50 ml of the absorbent was adequate to absorb all the hydrazine produced in a single run.

With V2 closed, V1 was adjusted carefully so that a pressure of about 1 p.s.i.g. was obtained. T5 and T7 were then closed and T4 positioned in order to disconnect the flow system from the Toepler pump unit. With all the other stopcocks and needle valves open (except V2), pump P1 was switched on to evacuate the system. At the same time P2 was switched on to evacuate the Toepler pump unit TP. T10 and T9 were carefully adjusted so that the pool of mercury in A was not disturbed. At this stage it was necessary to operate C magnetically in order to ensure complete evacuation of B.

When the pressure in the flow system, with TP excluded, was less than one torr, V2 was opened gradually and at the same time V3 was closed. By doing so the gas lines beyond V3 was isolated from the rest and it was possible to pressurise that part of the apparatus between V1 and V3 to above atmospheric. For all subsequent operations and experimental runs this section was kept above atmospheric pressure and hence the possibility of air leakages at this point was eliminated.

When the entire flow lines beyond V3 were completely evacuated, V4 and T8 were closed. The absence of air leaks was then confirmed by noting the pressure stability over a period of time. Leaks of up to 1 torr/15 mins. were regarded as tolerable, but if the rate exceeded this limit, the source of the leak was found using a Tesla coil leak detector, and rectified by blocking it with Araldite adhesive. Having established a satisfactory condition, V4 and T8 were again opened and

the system once more evacuated. T1 was then positioned such that the flow of gas was directed into either F1 or F2.

At this stage V3 was slightly opened and at the same time V1 adjusted so that the pressure indicated on M1 was still above atmospheric. Finally, the exact flowrate and pressure downstream of V3 were obtained by the correct manipulation of V3, V4 and T8. Having reached this stage the ammonia was allowed to flow for a period of 15 mins to purge any residual traces of air. T2 and T6 were then adjusted to allow ammonia to bubble through B2 in order to saturate the ethylene glycol. This usually required a period of 2.5 mins for a flowrate 200 cc/min. (STP) to up to 30 mins for a flowrate of 15 cc/min. (STP). For this reason, when operating at lower flowrates, the absorbent was first saturated with ammonia flowing at 200 cc/min. and then followed by readjustment of the flowrate to the required lower level.

On completion of the saturation procedure, T2 and T6 were repositioned to allow the gas to flow through the by-pass and the system was ready for experimental investigation.

The discharge was initiated by increasing the voltage gradually until breakdown occurred. The voltage, current, and scanning frequency were then set at the required levels and allowed to reach a steady state. Having done so the gas was then passed through the absorption trap for the duration of the experiment. Due to a slight pressure drop caused by the liquid, fine adjustment of V3 was necessary in order to bring back the pressure to the required level.

During a run which usually lasted from 2.5 - 30 mins, the gas pressure monitored by M1 and VG1, temperature on Th, current and

voltage readings, and scanning frequency were recorded. In the pulsed discharge case voltage and current waveforms were traced on graph paper, and records of pulse ON and OFF-times were made.

Before shutting down the run, T3 and T4 were closed such that a gas sample was trapped in GST. This was immediately followed by switching off the power supply and closing V3. V1 was then readjusted so that the pressure on M1 read only a few mm Hg above atmospheric. V4 and T8 were then closed and P1 was switched off. B1 and B2 were then pressurised by opening T5. This was followed by pressurising the rest of the flow system by first disconnecting B1 and B2 from the rest with T6 and then opening T7. In this way the possibility of unnecessary suck back of liquid absorbent from B2 into B1 was eliminated.

The gas sample trapped in GST was later transferred into D by pumping it with mercury using the Toepler pump principle. The procedure was as follows:

- (1) The pressure stability in TP was checked thoroughly, and when the pressure indicated on VG2 was less than 0.02 torr, T12 was closed and the magnet operating C was removed.
- (2) GST was connected to B by turning T4.
- (3) T9 was adjusted so that A was disconnected from P2 and instead compressed air was allowed to flow into A. This forced the gas in B to be compressed by the mercury via C into D.
- (4) When the level of mercury was just below T11, T9 was turned in such a manner that the air supply was cut off but at the same time A was connected to P2 via T10. This caused the level of the mercury to drop and the gas in D was completely isolated

from B by C. When A was fully evacuated, B would also be at vacuum and as a consequence more gas from GST will flow into the latter.

- (5) The whole pumping procedure was repeated until the pressure of the gas in D was above atmospheric, usually about 800 mm Hg. The pressure was taken as the difference between the mercury levels in M2 and S.
- (6) Having reached this stage, T11 was closed, GST was disconnected from TP by turning T4 and later pressurised by opening T3.
- (7) A was then evacuated and T9 closed. P2 was switched off and the gas sample unit (S) was then removed and connected to the gas chromatograph, see Figure 4.10, for analysis.

Since the gas sample tube of the chromatograph had to be evacuated, the final injection pressure of the compressed sample was reduced to about 150 torr. The procedure for analysis is described in Section 4.4.2(b).

Analysis of hydrazine was carried out by first removing B2 and then washing the side arms of the trap with 50 ml. of distilled water. 0.5 - 5.0 ml. of the final solution was added to 20 ml. of the coloured reagent and the % absorptancy of the liberated complex was measured using the spectrophotometer. The amount of hydrazine produced in the run was then calculated as shown in Appendix 2.

At the end of each experiment the absorption trap was thoroughly washed with hot water and I.C.I.'s Lissapol NDB detergent to remove traces of grease and ethylene glycol and later dried in a hot oven to remove the last traces of water and ethylene glycol.

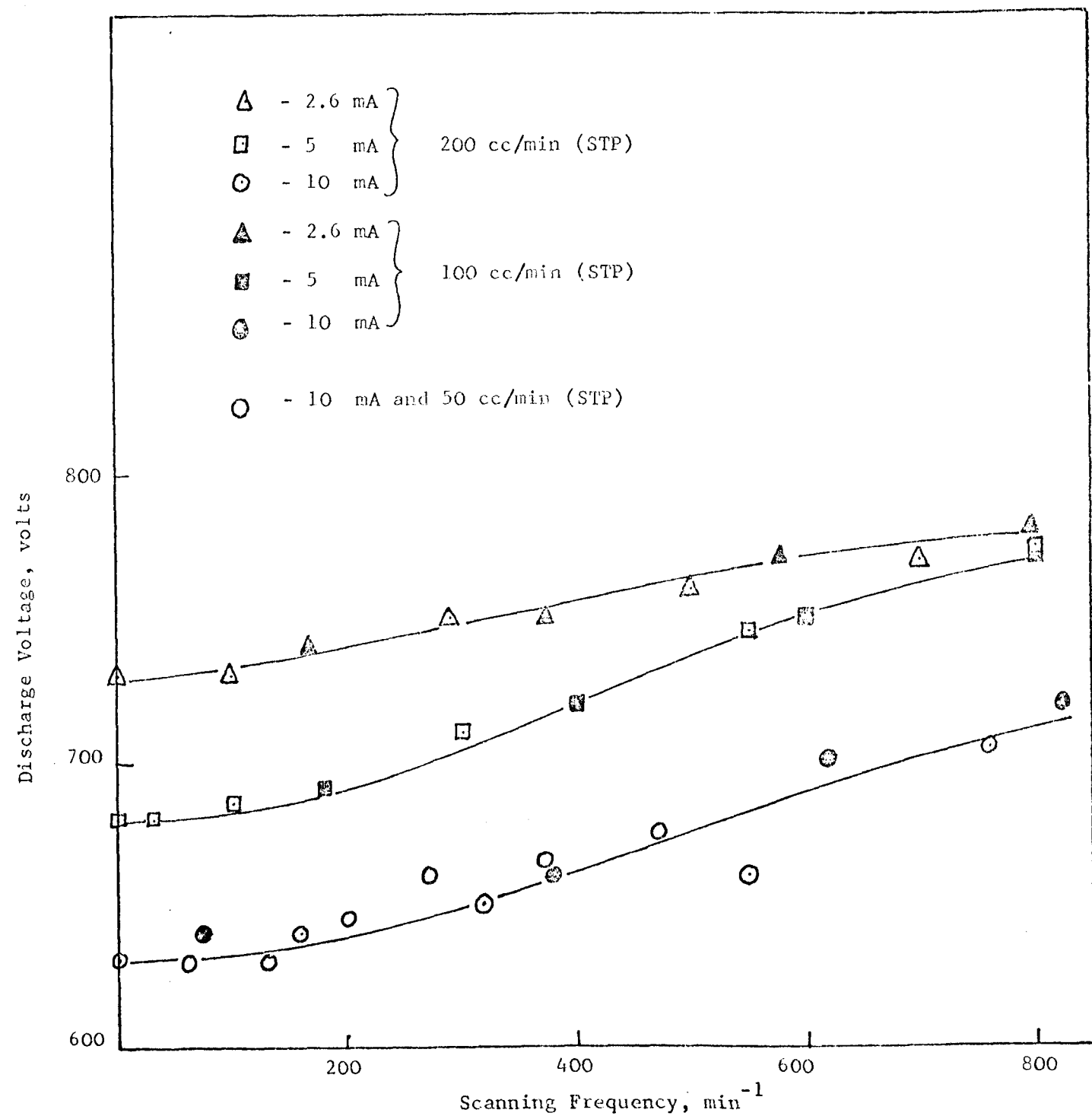
#### 4.6. Results

##### 4.6.1. Electrical and Physical Characteristics of the Discharge

For the continuous DC case a voltage of 1.6 kV was required to breakdown the ammonia at a pressure of 10 torr, but once the discharge was struck, it dropped to a value ranging from 630 - 730 volts depending on the discharge current. Under scanning conditions it was found that a slightly high<sup>er</sup>/voltage was required to sustain the same current level. Figure 4.13 shows the relationship between the scanning frequency and running voltage for three levels of current and ammonia flowrate. It can be seen that ammonia flowrate had no effect but the fractional increase in the running voltage at a particular scanning frequency is higher at the higher current. For a current of 10 mA and a scanning frequency of  $800 \text{ min}^{-1}$  an increase of about 14.3% is observed.

The glow discharge was operated under the subnormal region whereby a decrease in the current necessitated a higher applied potential. Currents of the order 2.6 - 10 mA could only be investigated due to the limitations imposed by the electrical circuitry and reactor design. At low currents it was found difficult to sustain the discharge continuously unless higher ballast resistors ( $>200 \text{ k}\Omega$ ) were incorporated in the circuit, whilst currents in excess of 10 mA caused excessive heating of the electrodes especially the cathode. During the period of an experiment, which usually took 2.5 - 5.0 mins, this heating effect resulted in a sudden change in the appearance of the discharge. The glow turned from its usual pale green colour into an intense white discharge followed by the formation of a striated positive column. These abnormalities in the glow characteristics were also accompanied by a rise in the running voltage.

FIGURE 4.13

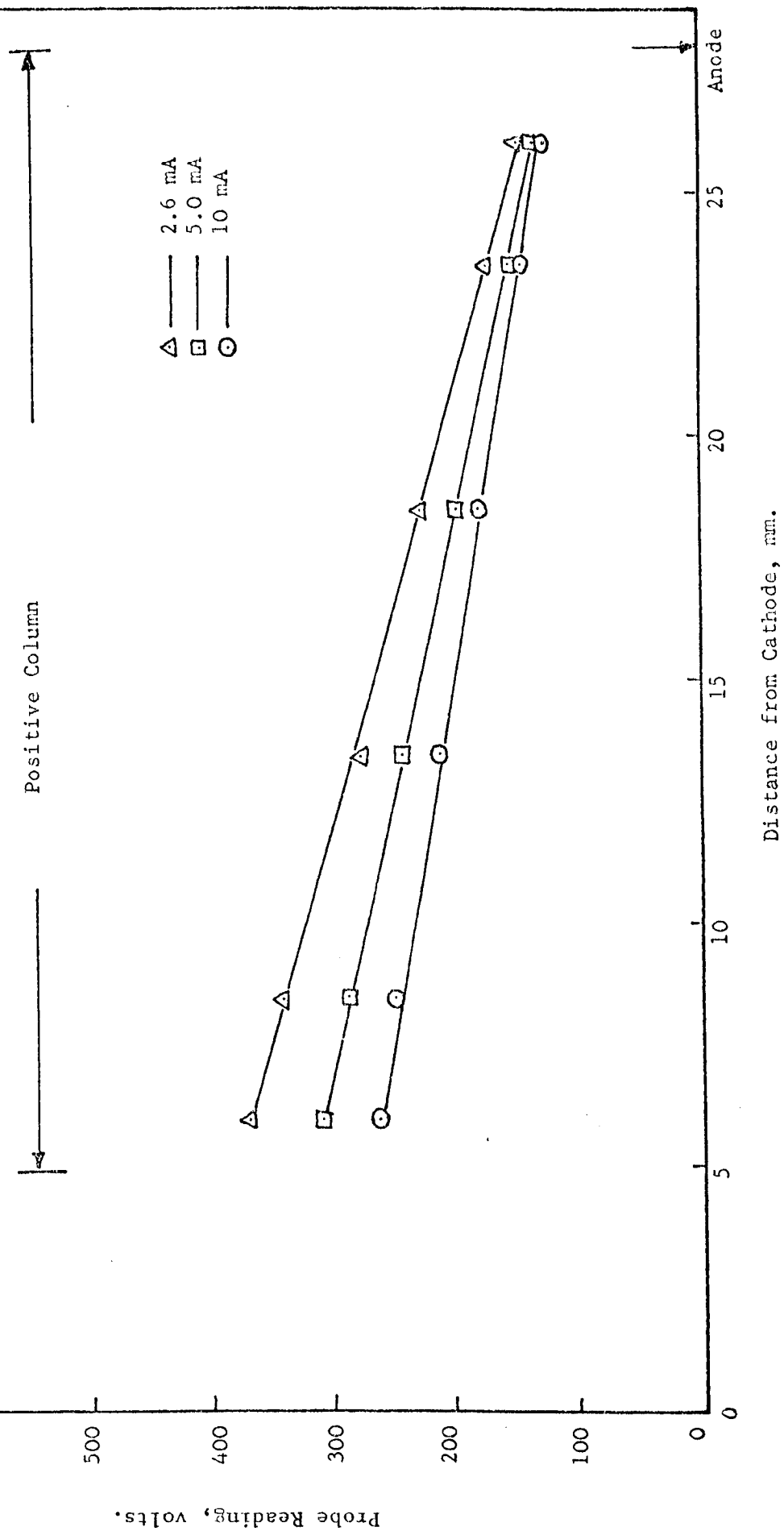


Under normal conditions the visible glow was recognised as wedge shaped with height equivalent to the anode depth, i.e. 6.35 mm ( $\frac{1}{4}$ " ), and width increasing from 6.35 mm ( $\frac{1}{4}$ " ) near the aperture to 25.4 mm (1 inch) at the anode. Its volume was calculated to be 12.75% of the effective reactor volume. The latter was taken as the overall volume contained between the anode and the insulator covering the cathode. However, probe measurements conducted on a later date indicated that the active discharge volume extended far beyond the visible glow boundaries. In some instances it represented over 70% of the effective reactor volume.

The breakdown procedure for the pulsed D.C. case was somewhat similar to the previous case except that in the former a high potential was necessary in order to initiate the discharge ( $\approx 3$  kV) and also the running voltage was higher ranging from 1.4 - 2.1 kV, depending on the pulse OFF-time. It was found that the running voltage did not change with scanning frequency, as was the case with <sup>the</sup> continuous D.C. discharge, but under stationary conditions it increased with longer OFF-times until a plateau was reached for OFF-times of 2 msec and over. Under the range of ON and OFF-times investigated in this study, the visible glow was found to be much narrower than that of the continuous D.C. discharge. At the anode surface its width was found to be 6.35 mm ( $\frac{1}{4}$ " ) thus giving it an apparent volume equivalent to 3.2% of the effective reactor volume.

The positive column of both discharges were seen to originate from the aperture in the insulating tube covering the cathode and its length was taken as the distance between this tube and the anode surface. For the continuous D.C. case this was 23.5 mm whilst for the pulsed discharge it was slightly longer at 26.2 mm.

Figure 4.14 Plasma Space Potential  
(Ammonia at a pressure of 10 torr)





**Figure 4.15**     **Film deposit on the anode**

The space potential at different points in the positive column of the continuous DC discharge was measured using the Langmuir probe. The results from these measurements, using an aged anode, i.e. an anode with a deposited film, are depicted on Figure 4.14. Figure 4.14 indicates that only a small proportion of the applied voltage existed across the positive column, the majority of it fell across the two electrode regions especially the cathode region. The anode and cathode falls were found by extrapolating the linear portions of the curves to zero and 23.5 mm from the anode. The space potential at zero distance from the anode was then taken as the anode fall, whilst that at 23.5 mm subtracted from the overall running voltage yielded the voltage drop across the cathode layers. Also, the difference between the overall voltage and the sum of these two falls, divided by the length of the positive column gave the average field strength,  $E$ , throughout the positive column. When the results from three sets of runs with current levels of 2.6, 5, and 10 mA were treated in this manner, the anode and cathode falls were found to be 115 and 360 volts respectively. However, the values of the electric field at the three current levels were calculated to be 108, 87.6, and 66 volts/cm respectively.

The rate of ammonia flow had no significant effect on the discharge characteristics such as running voltage, field strength, physical size, etc., but with the continuous DC discharge and at flowrates of less than 50 cc/min (STP), a dark brown film deposited on the inner surface of the anode as shown in Figure 4.15. The deposition took place at the onset of the discharge and persisted to cover the anode thereafter. Reversing the polarity of the electrodes did not bring about a similar deposition on either electrode, but when treating an

already covered anode in this manner, the deposit started to disappear slowly. This was possibly caused by local cathodic heating resulting in the disintegration of the deposited film.

The rate of film deposition was determined to be about  $8.4 \times 10^{-3}$  gms/hr at an ammonia flowrate of 50 cc/min (STP) and a discharge current of 10 mA. When the deposit was scraped off the anode surface, it proved to be a dark brown powder which was insoluble in water but readily soluble in concentrated hydrochloric acid. Qualitative chemical tests had shown the powder to be rich in ferric iron whilst a quantitative microanalytical technique gave a composition of 2.72% carbon, 1.84% hydrogen, and 5.96% nitrogen. The rest was assumed to be iron since the presence of other most likely elements such as oxygen was excluded. Support for this assumption came into light when a similar discharge in air produced no deposit. Also, X-ray diffraction technique indicated that the cell structure and lattice constant of the powder were different from that of any iron compound containing oxygen. The X-ray patterns showed the powder to have a cubic cell structure and lattice constant identical to the grade of steel from which the anode was fabricated.

#### 4.6.2. Decomposition of Ammonia in the Continuous DC discharge

##### (a) General

Ammonia was decomposed at a pressure of 10 torr and the gaseous product contained hydrazine as well as hydrogen and nitrogen. The relative concentrations of these products were dependant on the operating variables which were power input, ammonia flowrate, and

scanning frequency. The efficiency of hydrazine production may be described by the following parameters:

(i) Energy Yield, Y

This is a measure of the energy efficiency of the process and is given as grammes of hydrazine produced/Kilowatt-hour of electrical energy actually dissipated in the discharge.

(ii) Overall Conversion to Hydrazine,  $X_{N_2H_4}$

This gives the overall efficiency in terms of hydrazine production and is given as grammes of hydrazine/100 grammes of ammonia flowing through the reactor in one pass. This is a useful concept in reactor scale-up since it determines the degree of recycling necessary in order to achieve the required production rate.

(iii) Molar Conversion to Hydrazine,  $\bar{X}_{N_2H_4}$

This represents the fraction of the overall decomposed ammonia which is converted to hydrazine.  $\bar{X}_{N_2H_4}$  was calculated (see Appendix 2) using the overall stoichiometric equations for ammonia decomposition, viz.,



It can be seen from the above two equations that the molar conversion or  $\bar{X}_{N_2H_4}$  will be equal to the moles of hydrazine divided by the total moles of hydrazine and nitrogen. Since the latter can only arise from the decomposition of hydrazine and/or ammonia,  $\bar{X}_{N_2H_4}$  immediately affords a measure of the extent of any degradative reactions taking place in the

discharge. For no degradation,  $\bar{X}_{N_2H_4}$  should be 100%. Any figure which is  $< 100\%$  will be a direct consequence of these reactions.

The effectiveness of the discharge in decomposing ammonia is reflected in  $X_{NH_3}$ , which is the overall ammonia conversion. From equations 4.6 and 4.7 this is found to be twice the sum of hydrazine and nitrogen.

(b) Effect of power input and ammonia flowrate

The decomposition of ammonia was studied at flowrates ranging from 50 - 200 cc/min (STP) corresponding to a gas residence time across the discharge gap of 0.266 - 0.0665 sec. respectively. For each set of ammonia flowrates three current levels were investigated, namely 10, 5, and 2.6 mA, corresponding to an overall power input to the cell of 6.3, 3.4, and 1.9 watts respectively. The results from these runs are given in Tables 1, 2, and 3, located in Appendix 4 and are shown in Figures 4.16 - 4.20.

Figure 4.16 shows the effect of power input and flowrate expressed in terms of residence time, on the overall ammonia conversion. It is apparent that both longer residence time, i.e. lower gas flowrate, and higher power levels favour ammonia decomposition.

In the case of hydrazine production, increasing the residence time is accompanied by an increase in the concentration of hydrazine but no maximum is observed except for the 10 mA case where an ill defined maximum does occur at a residence time of 0.136 sec. (Figure 4.17). The dependence of the energy yield,  $Y$ , and molar conversion to hydrazine,  $\bar{X}_{N_2H_4}$ , on gas flowrate and power input are identical; both decreased

FIGURE 4.16

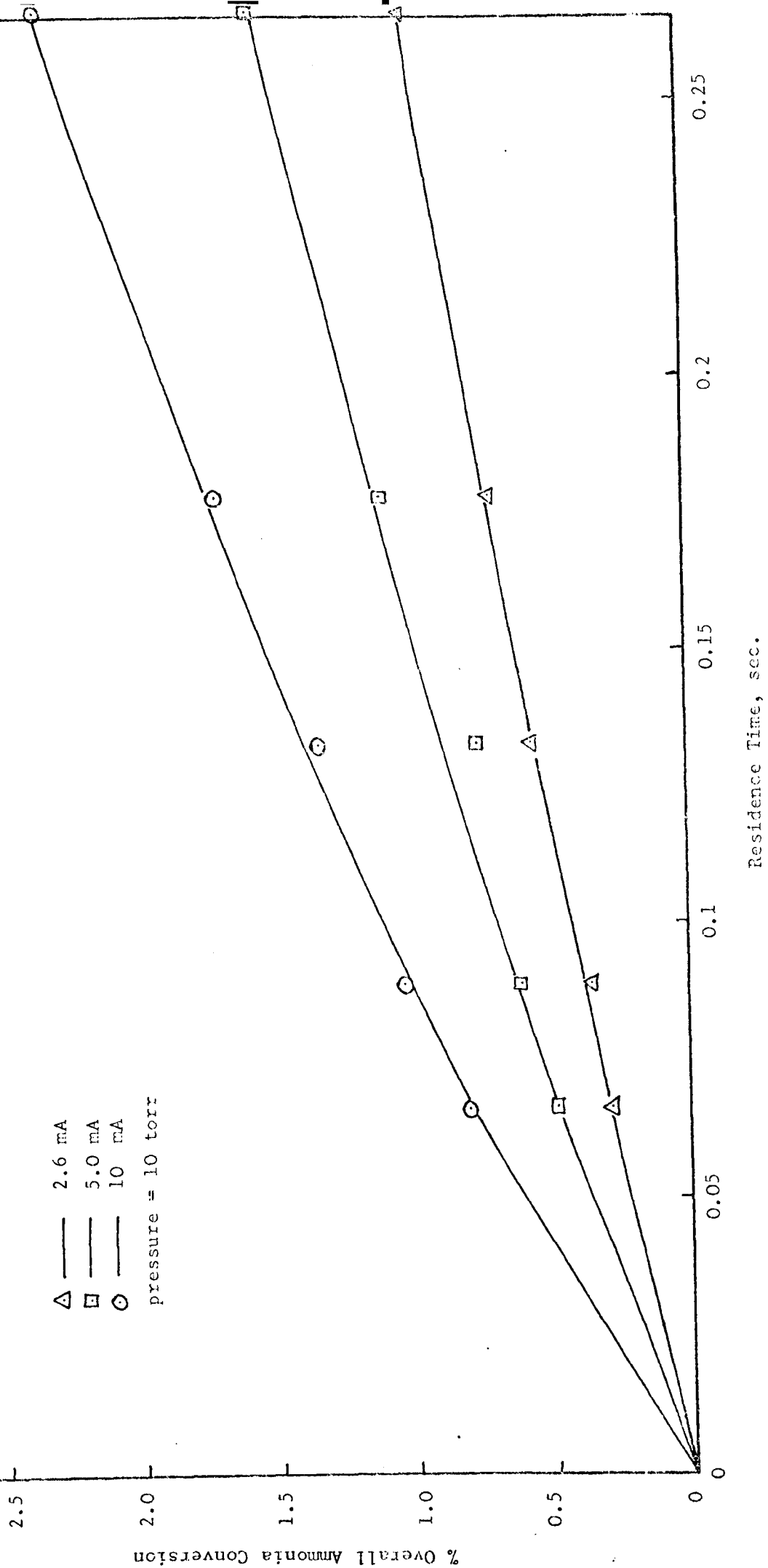


FIGURE 4.17

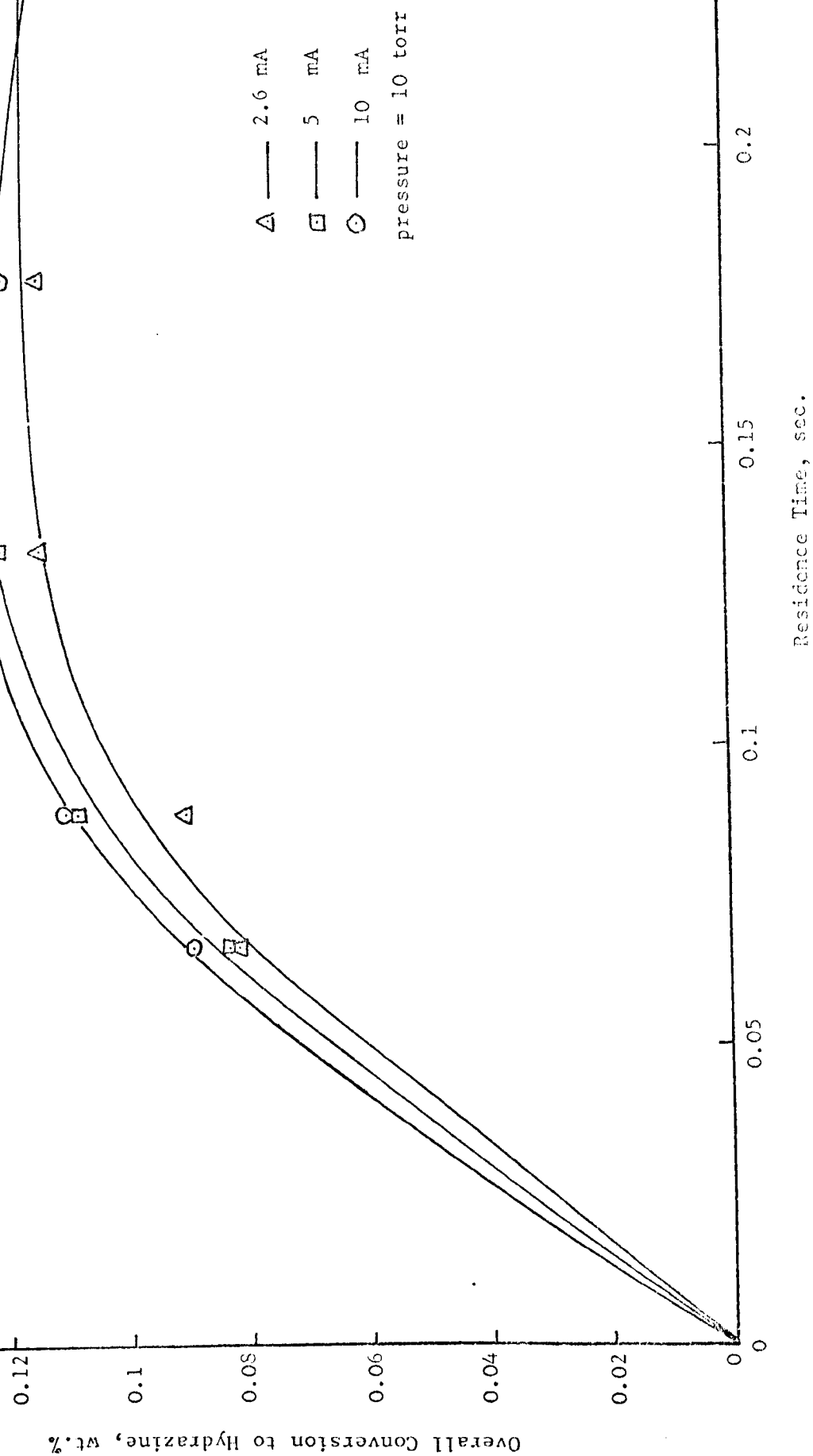


FIGURE 4.18

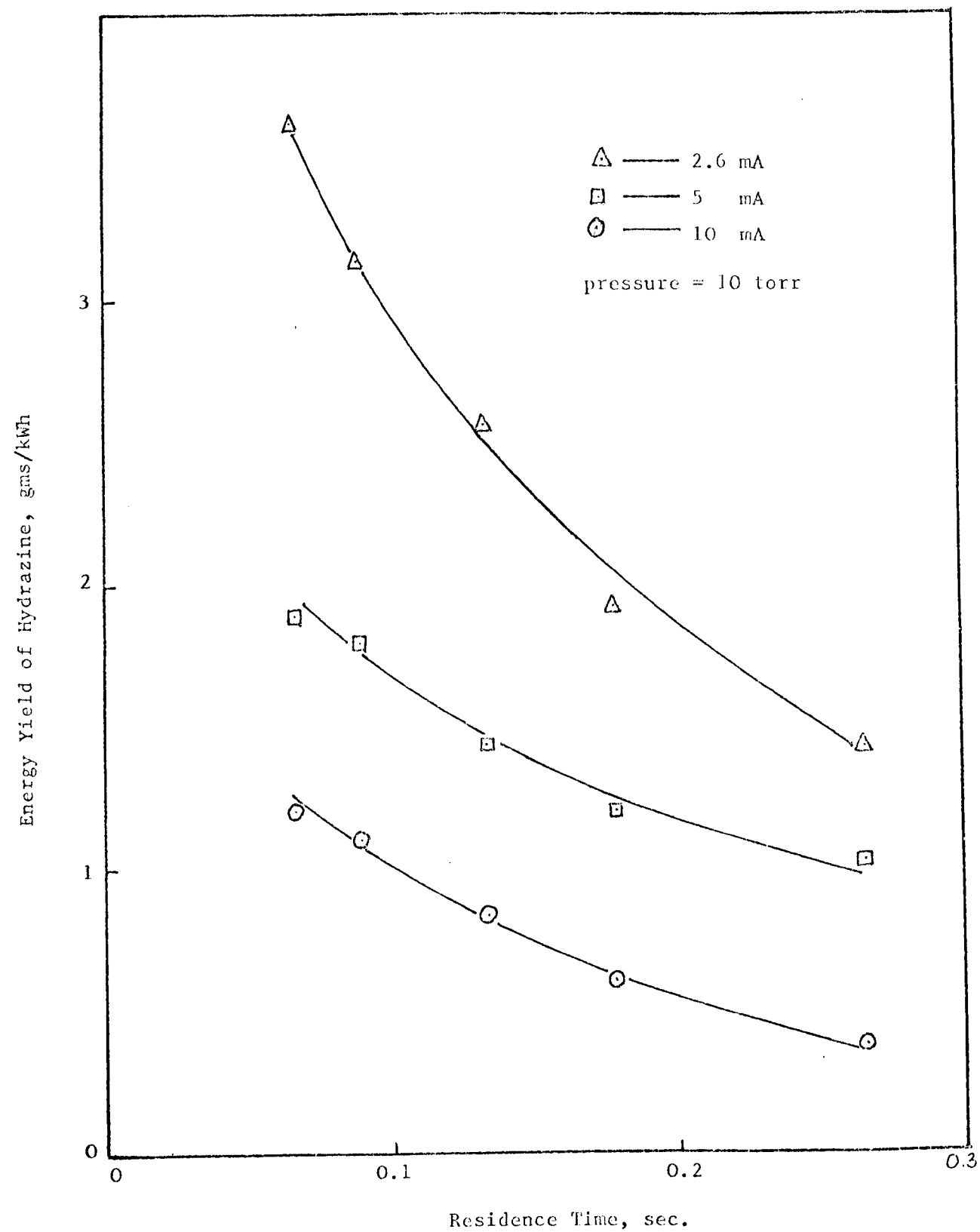
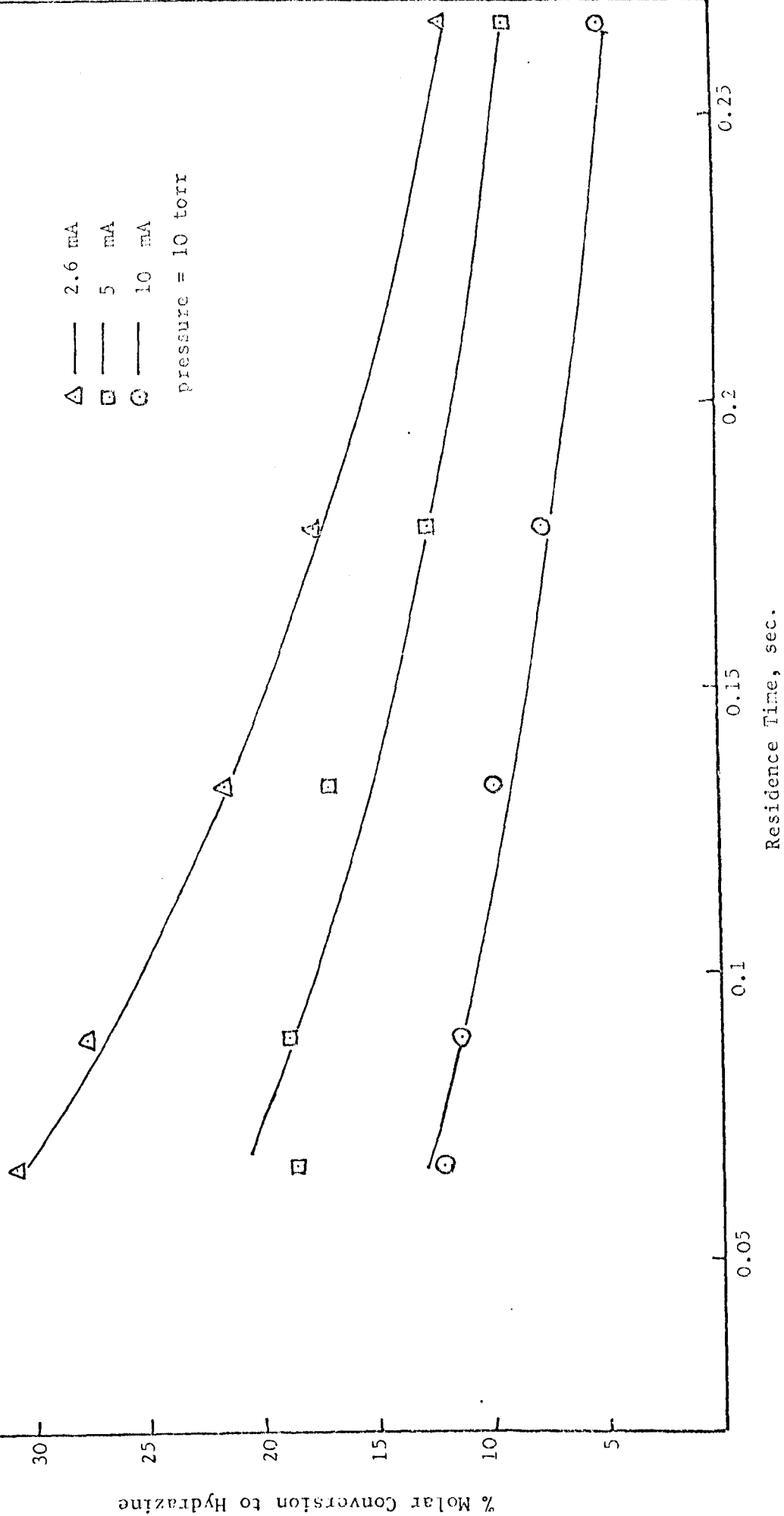


FIGURE 4.19

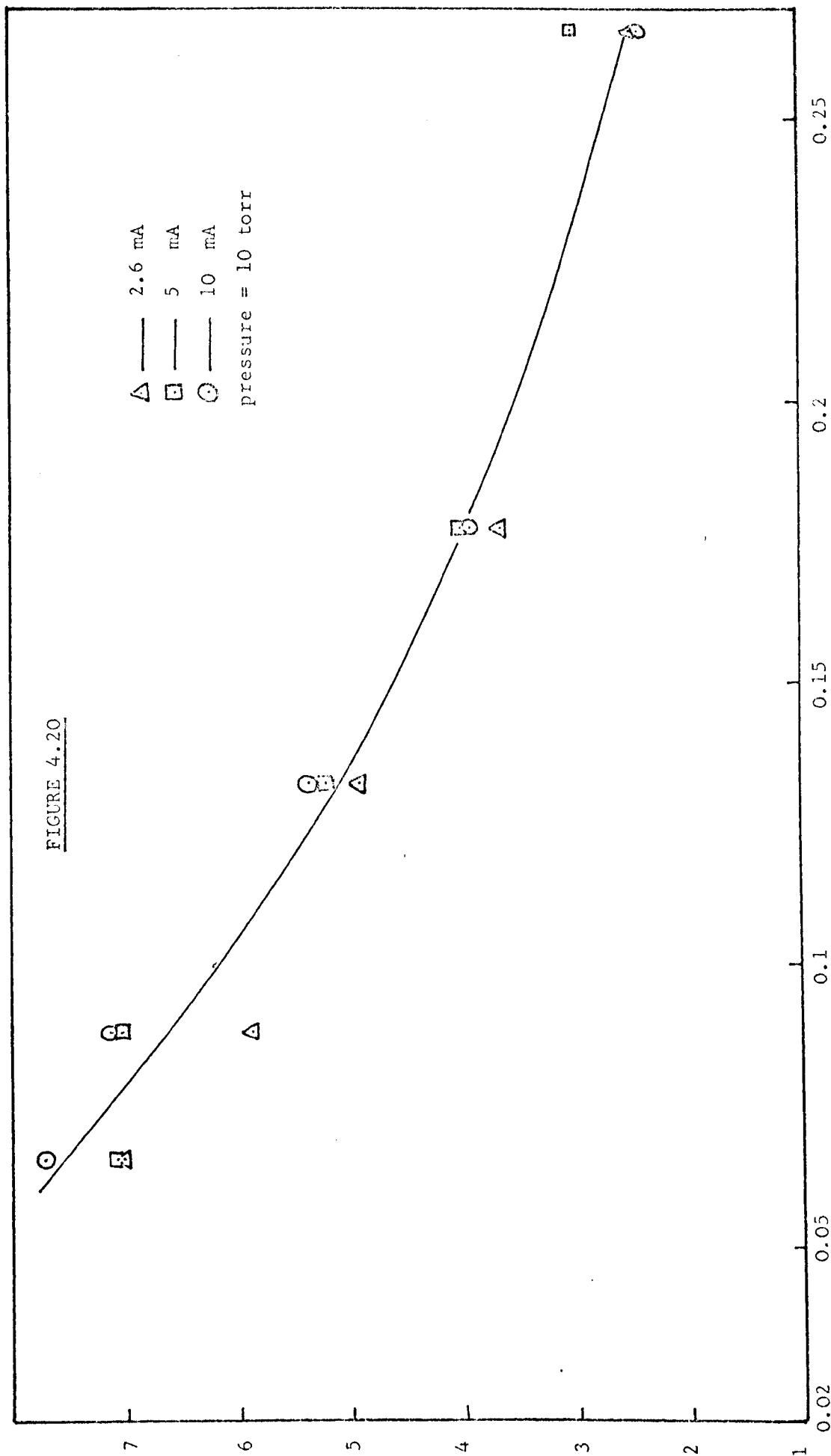


Overall Rate of Hydrazine Production,  $\text{gms/hr} \times 10^{-3}$

FIGURE 4.20

$\Delta$  — 2.6 mA  
 $\square$  — 5 mA  
 $\circ$  — 10 mA  
pressure = 10 torr

Residence Time, sec.



with increasing residence time (Figures 4.18 and 4.19). This is also true for the rate of hydrazine production expressed in gms/hr. Here more hydrazine is formed at higher flowrates, i.e. shorter residence times, but power input has little or no effect (Figure 4.20).

(c) Effect of Scanning Frequency

The influence of beam scanning on the decomposition of ammonia and formation of hydrazine was investigated at flow rates of 200, 100, and 50 cc/min (STP) and discharge currents of 10, 5, and 2.6 mA. In order to prevent excessive heating of the shaft seal element of the reactor (Figure 4.1), most of this work was carried out at frequencies ranging from 0 - 800  $\text{min}^{-1}$ . The optimum scanning frequency ( $\omega$ ), that is the minimum frequency necessary to give 100% irradiation of the ammonia is shown later to depend on both the ammonia flowrate and discharge width (Section 5.4.1). The calculated values at 200, 100, and 50 cc/min (STP), on the assumption that only the visible glow is responsible for chemical activation, are 787, 394, and 197  $\text{min}^{-1}$  respectively (Appendix 2). It therefore follows that the frequency range employed ensured at least one full scan situation in every case.

The results from these series of experiments are given in Tables 4 - 10 located in Appendix 4 and are plotted as performance of the reactor in terms of ammonia decomposition and hydrazine formation versus scanning frequency in Figures 4.21 - 4.32.

Figures 4.21 - 23 show the effect of scanning frequency on the fraction of ammonia decomposed, and it is apparent that an enhancement in the latter has resulted as a consequence of beam scanning.

FIGURE 4.21

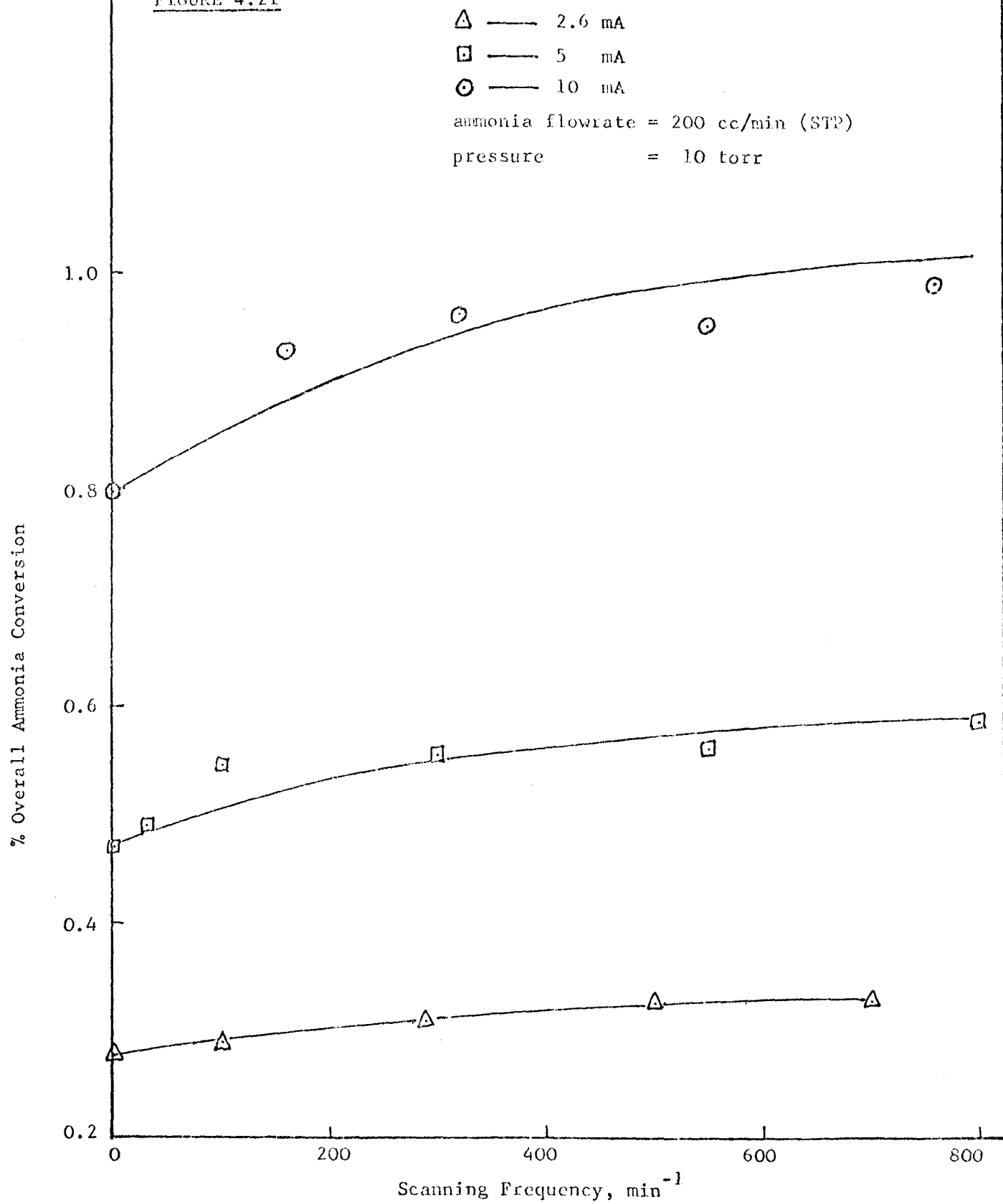


FIGURE 4.22

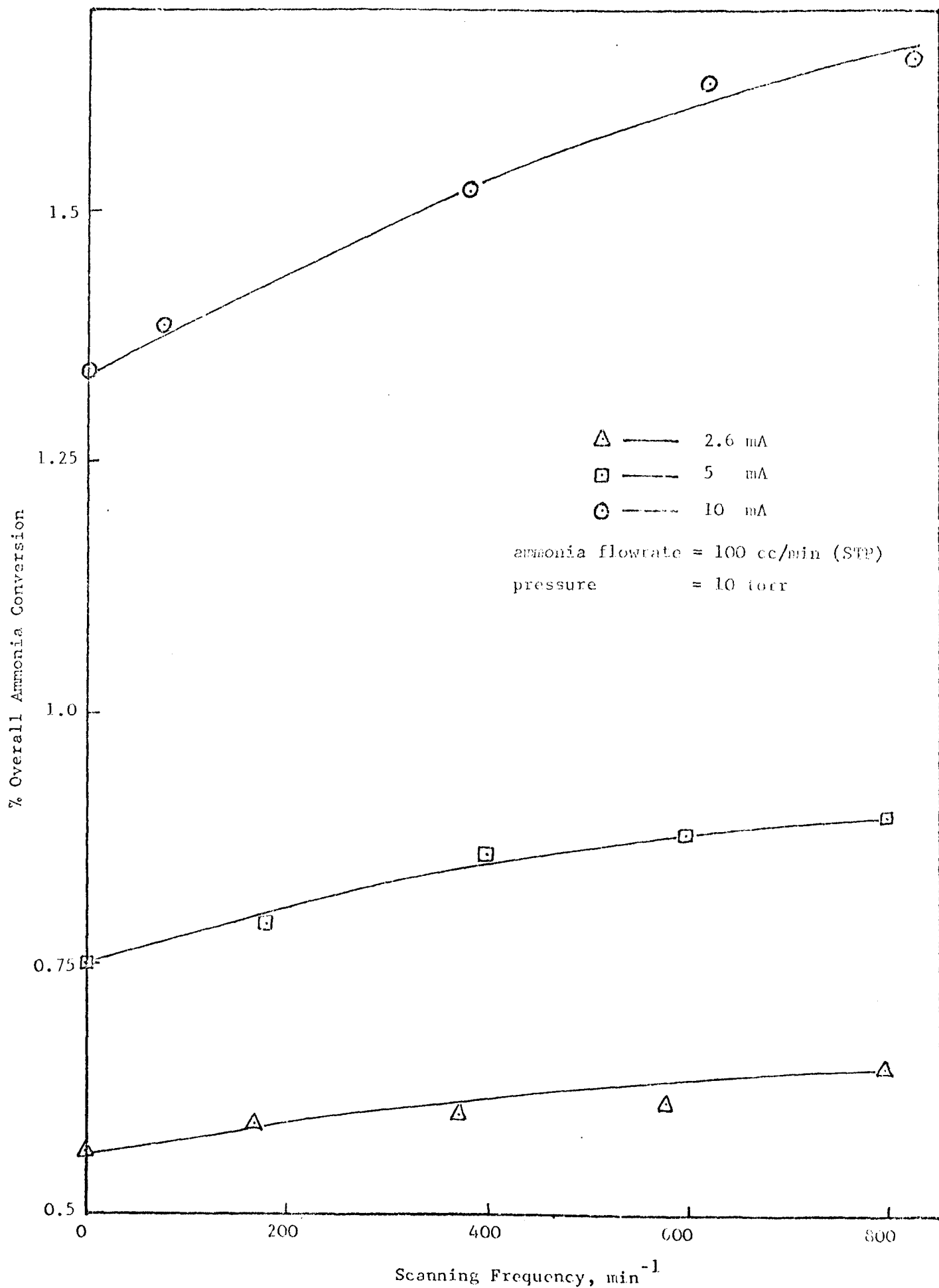


FIGURE 4.23

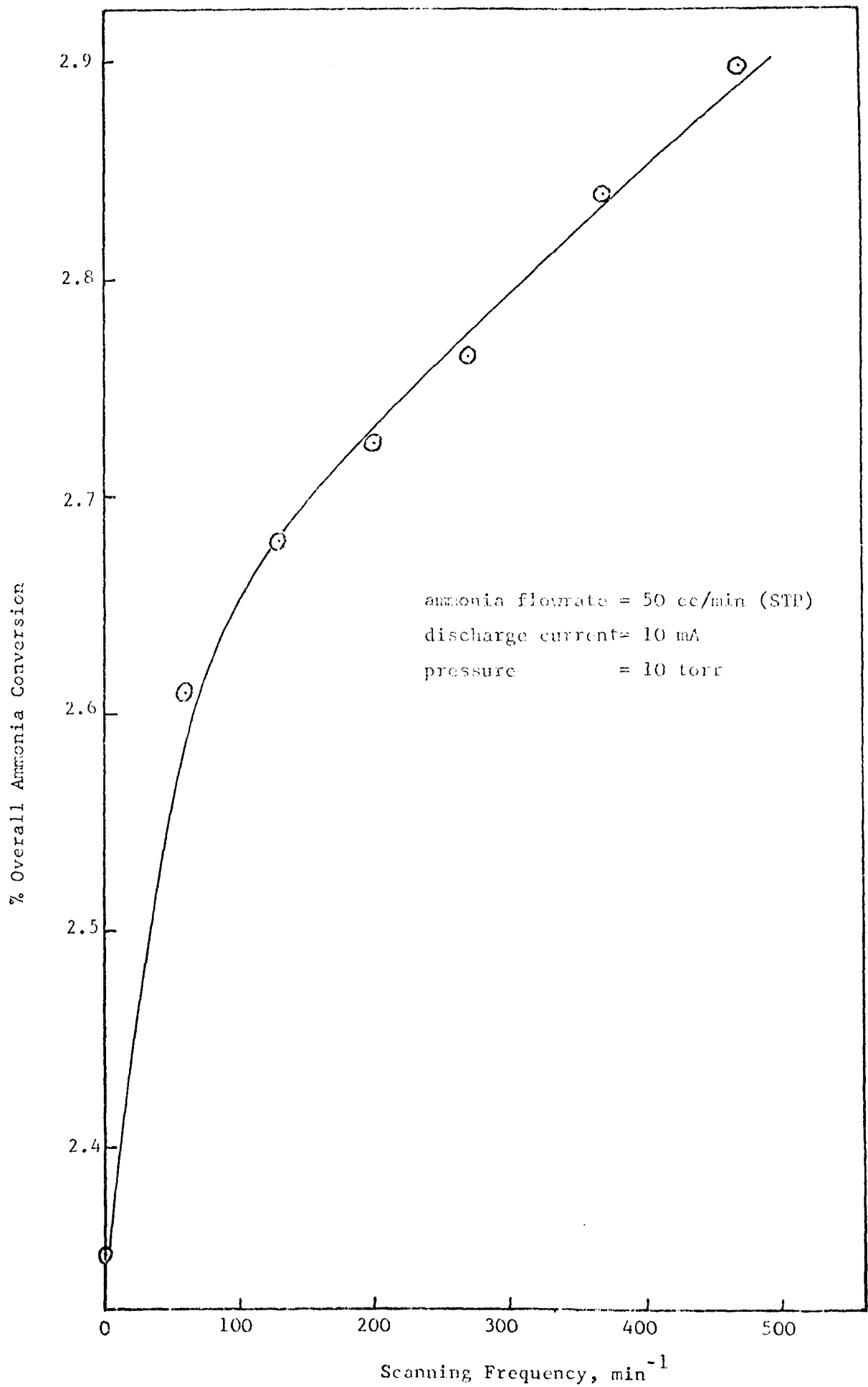


FIGURE 4.24

Overall Conversion to Hydrazine, wt. %

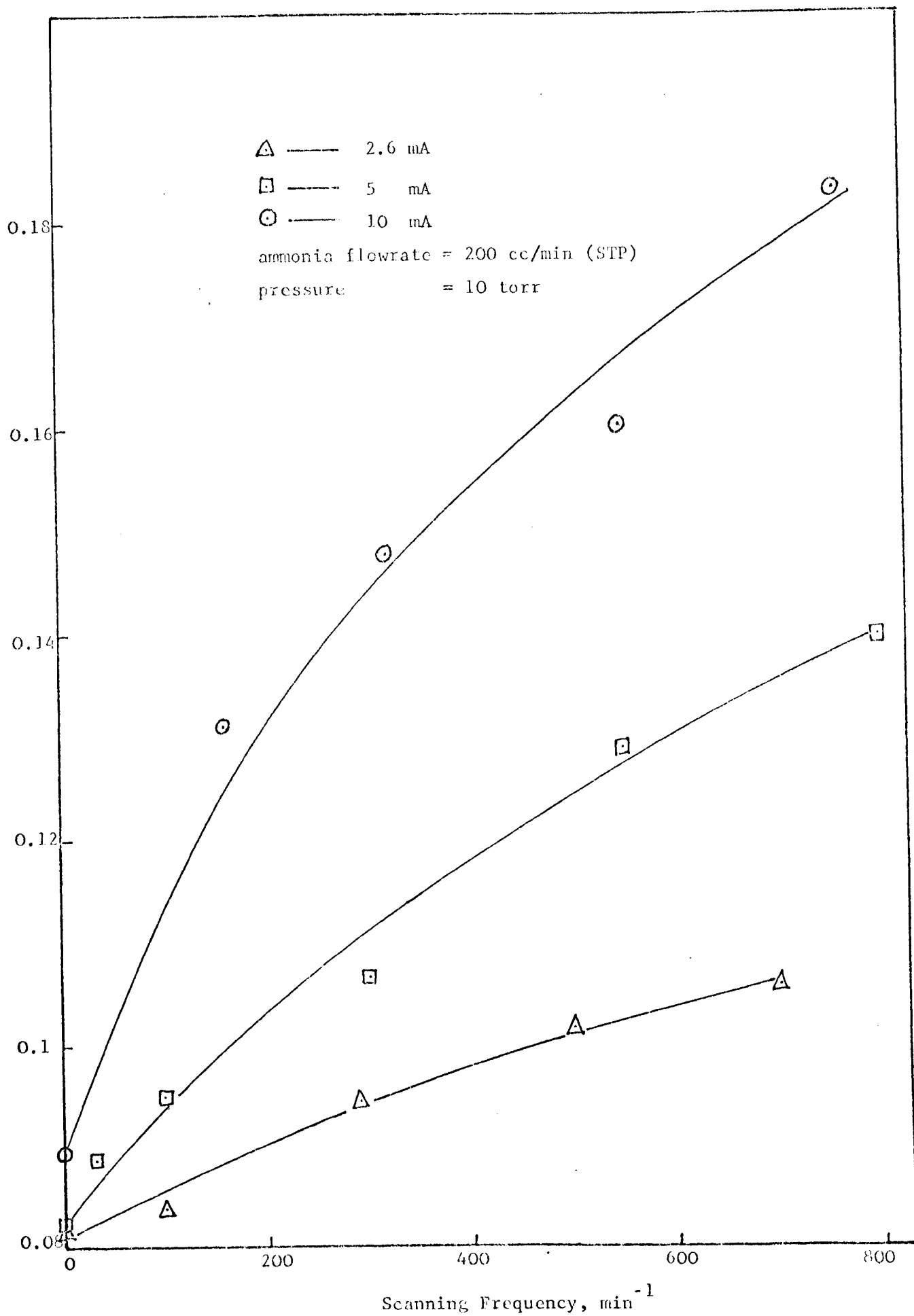


FIGURE 4.25

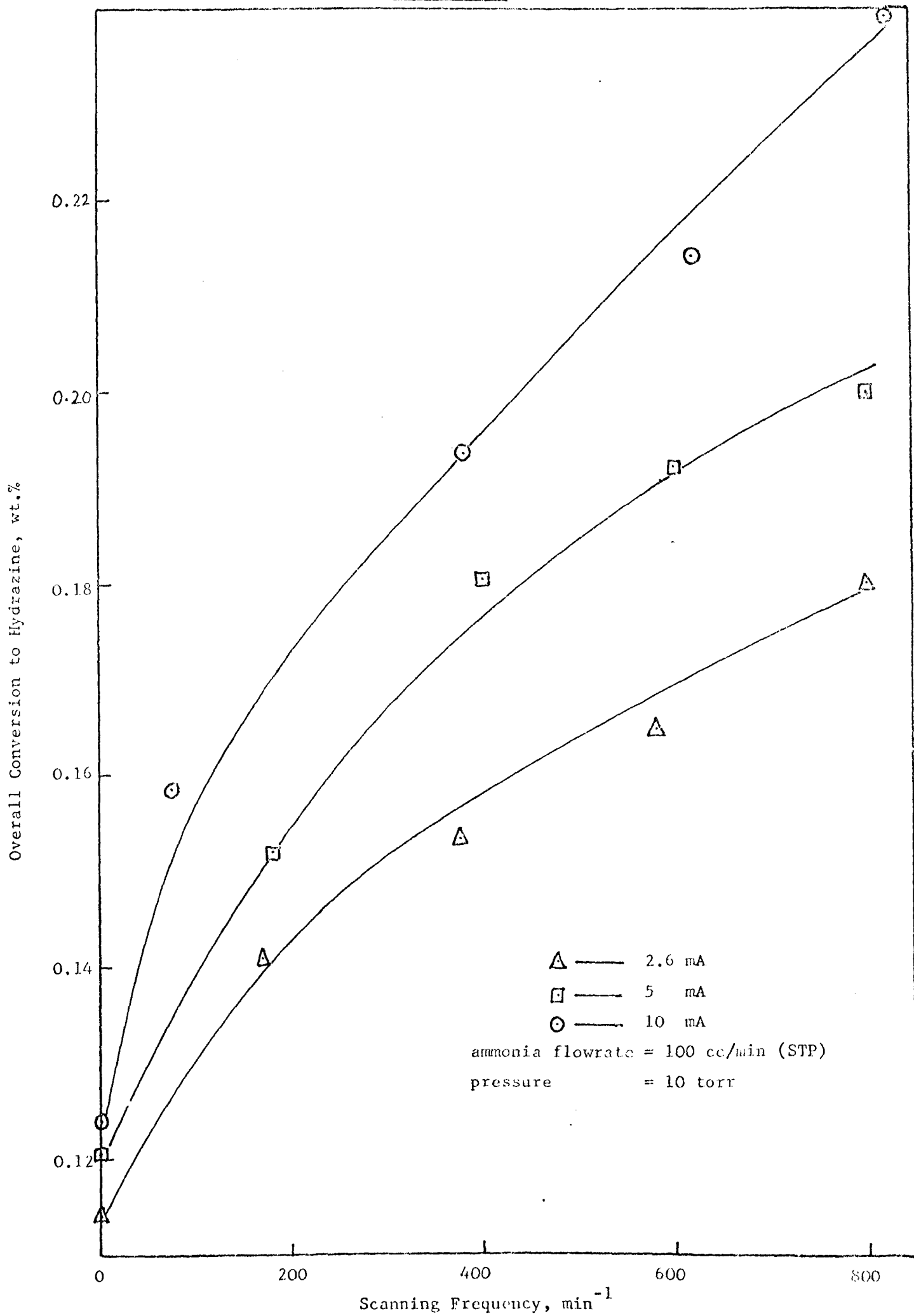


FIGURE 4.26

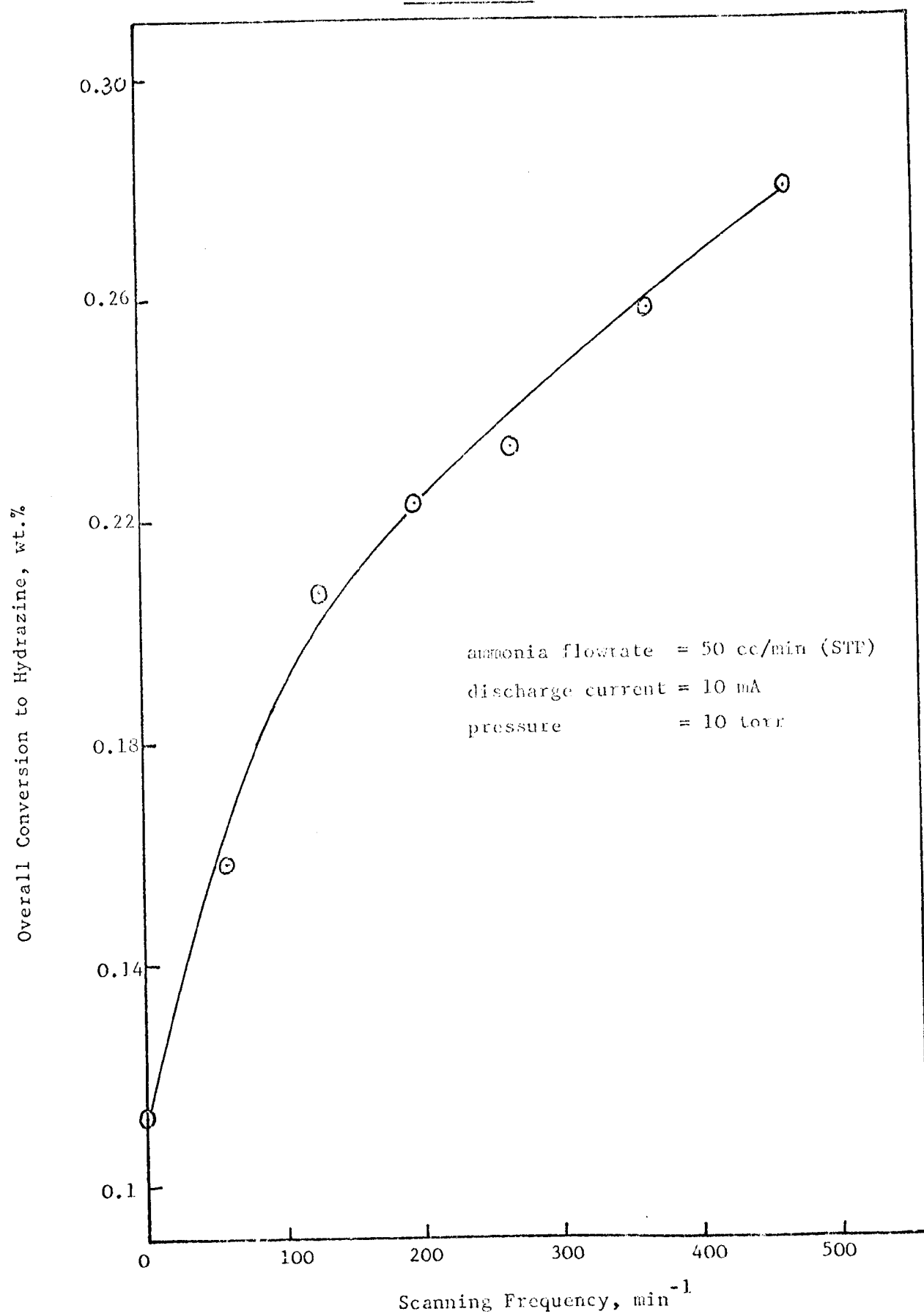


FIGURE 4.27

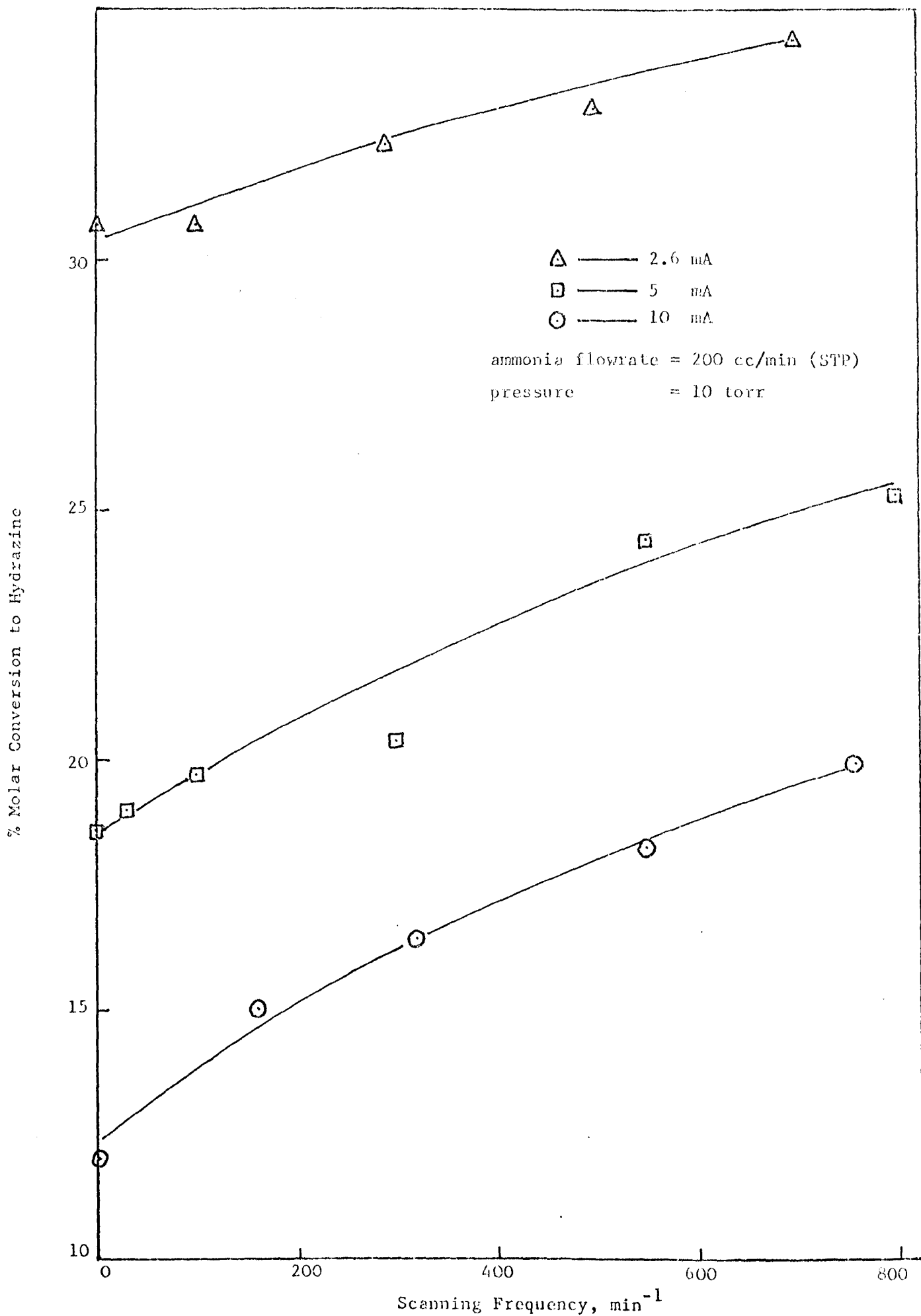


FIGURE 4.28

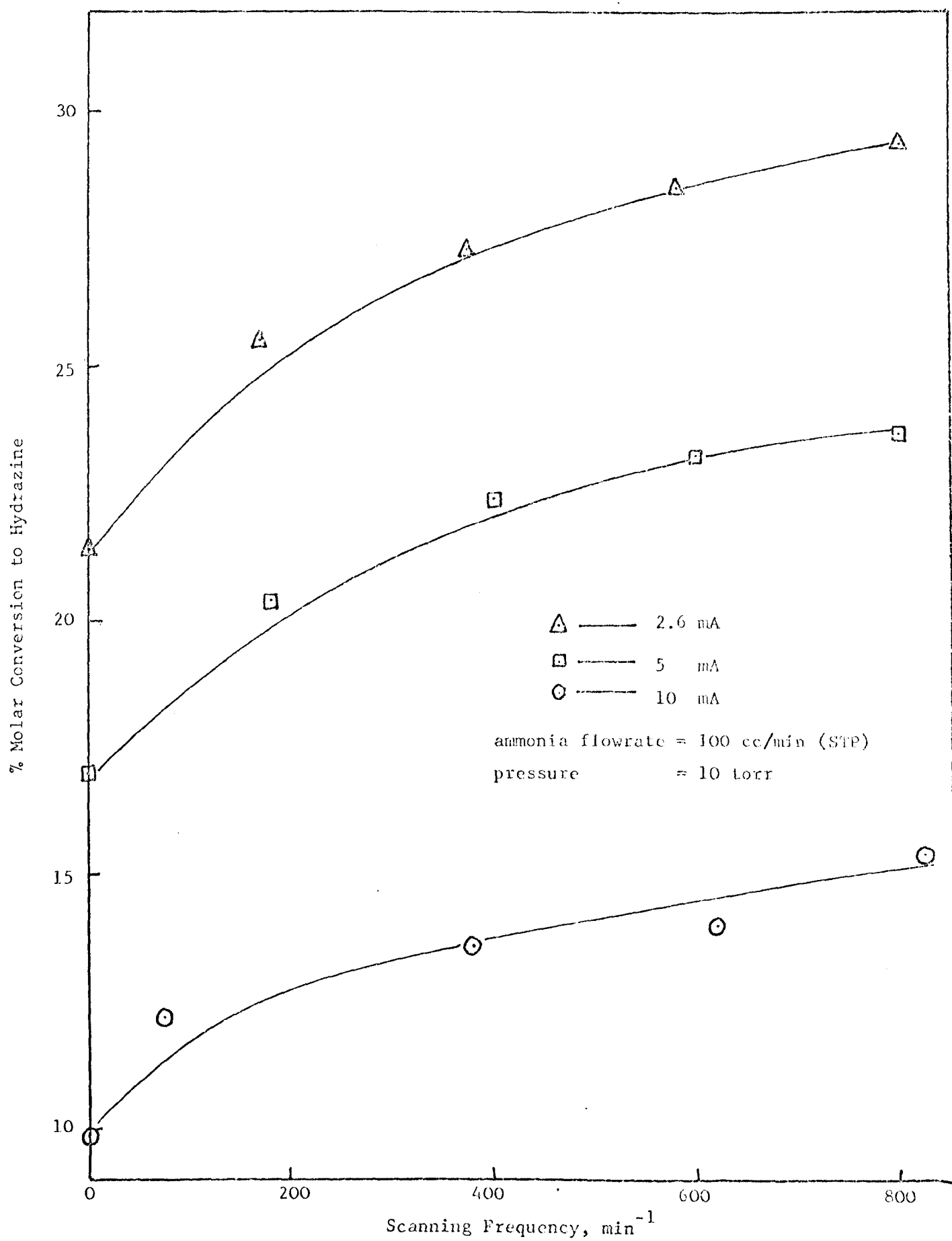


FIGURE 4.29

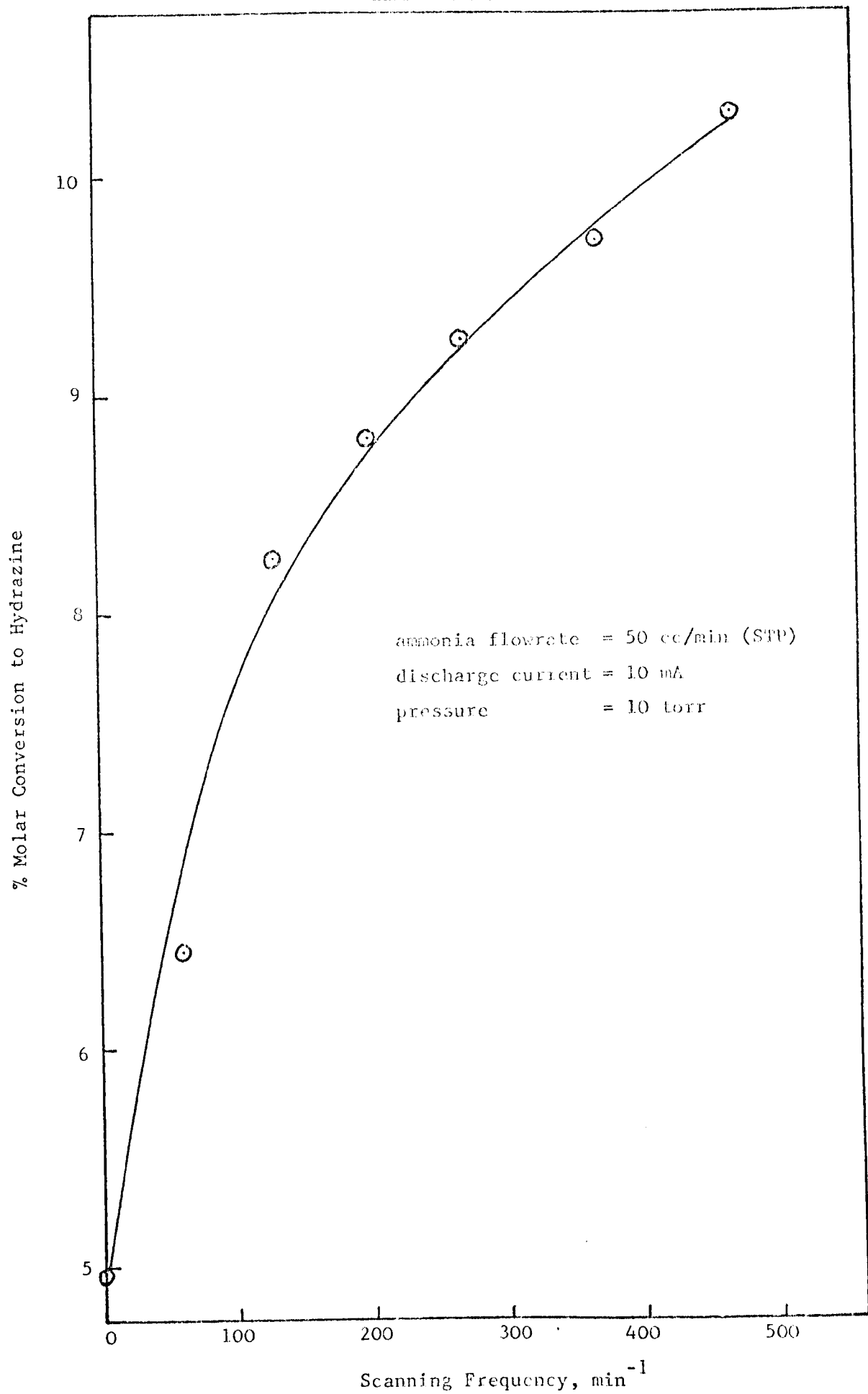


FIGURE 4.30

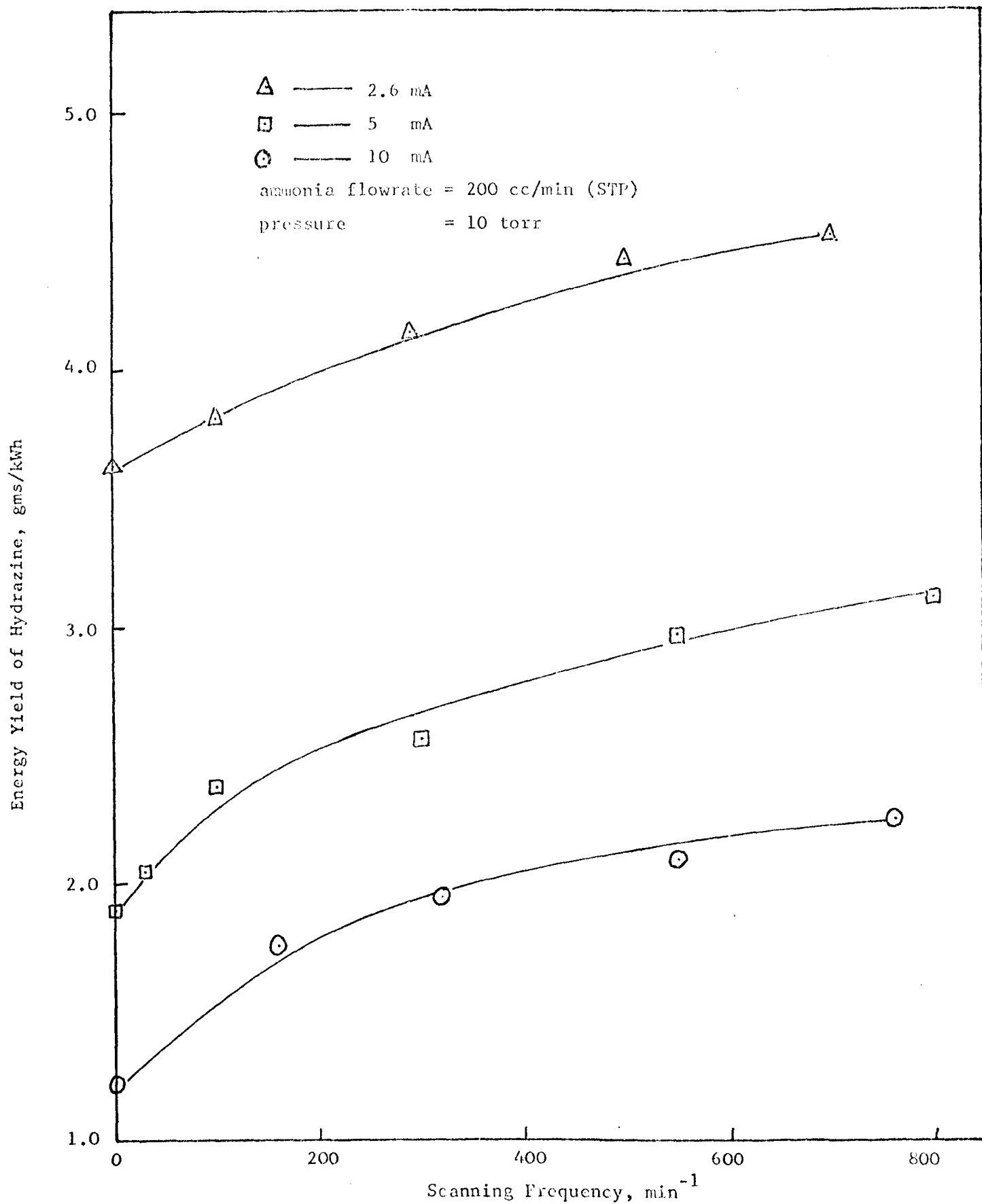


FIGURE 4.31

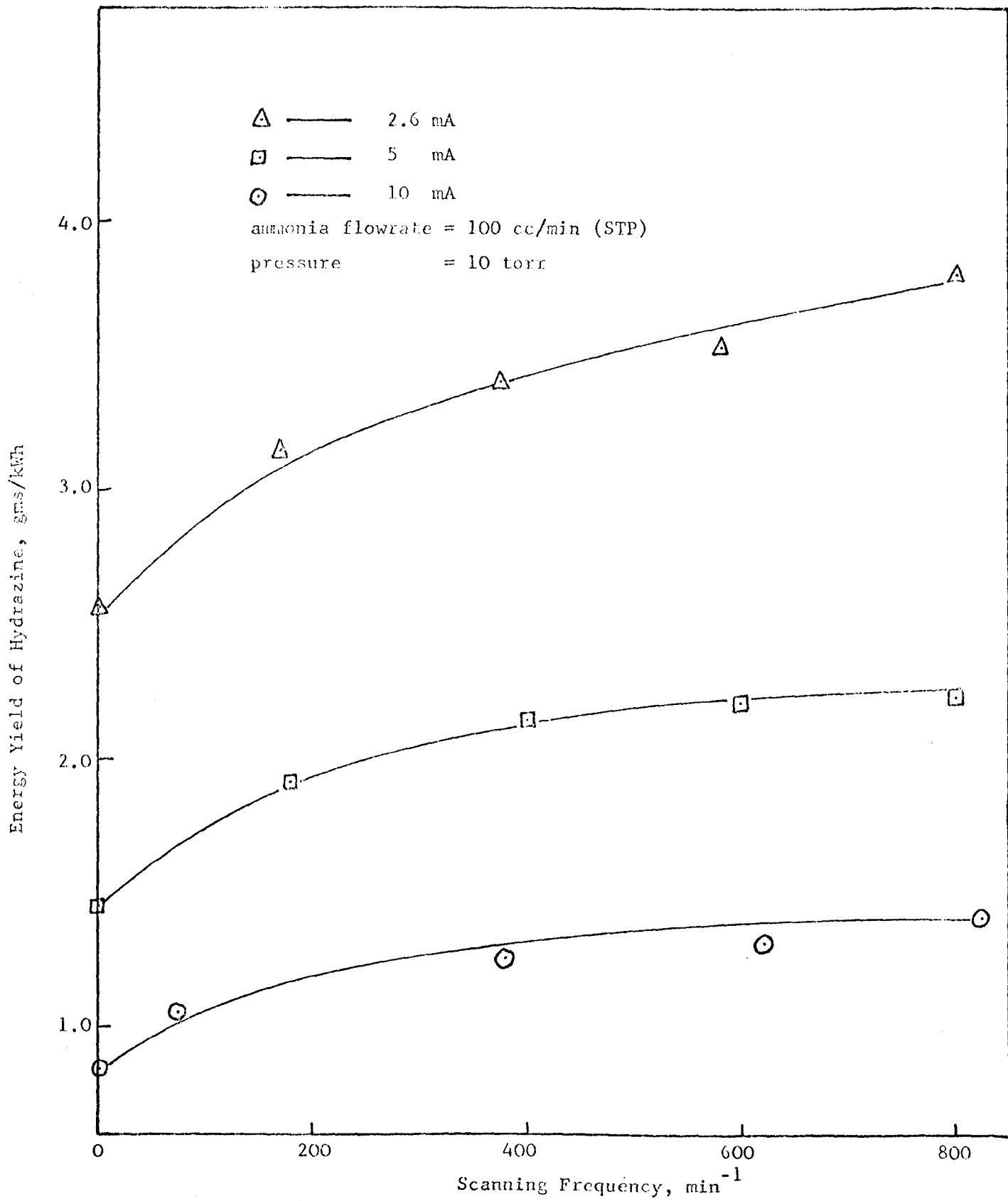
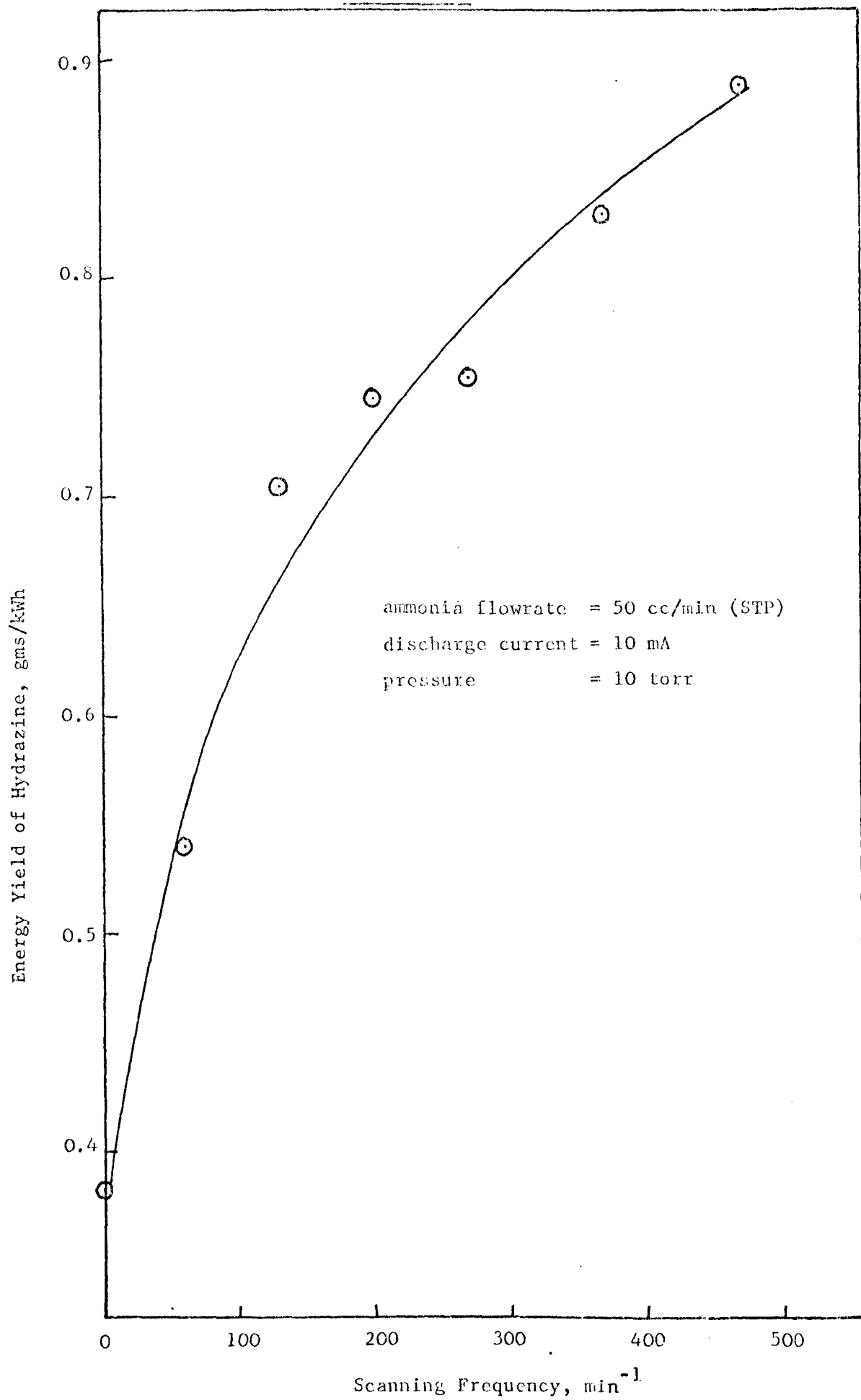


FIGURE 4.32



Comparison between Figures 4.21 - 23 at a fixed frequency shows that the percentage increase in overall ammonia conversion is higher at the lowest flowrate. Furthermore, in cases where more than one current level has been investigated, the dependence of  $X_{\text{NH}_3}$  on the scanning frequency becomes progressively less marked at lower currents.

The effect of scanning frequency on the overall conversion to hydrazine,  $X_{\text{N}_2\text{H}_4}$ , is shown in Figures 4.24 - 26. Here, the same trends in  $X_{\text{N}_2\text{H}_4}$  are apparent as in the case of  $X_{\text{NH}_3}$ . It is also interesting to note that scanning of the reactor cross-section seems to improve hydrazine production more significantly than overall ammonia conversion. Examination of Figures, 4.21 and 4.24 shows that for a frequency of  $800 \text{ min}^{-1}$  and a current of 10 mA the percentage increase in  $X_{\text{N}_2\text{H}_4}$  is 105% compared with 25% for  $X_{\text{NH}_3}$ .

The dependence of the energy yield and molar conversion on scanning frequency appears to follow a similar fashion as shown in Figures 4.27 - 32, i.e. both increasing with higher frequencies.

The best energy yields of hydrazine were obtained at the lowest current level, highest flowrate and highest scanning frequency. Figure 4.30 gives a maximum energy yield of 4.53 gms/kWh. The molar conversion to hydrazine is also the highest at 34.4% (Figure 4.27) but the concentration of hydrazine in the issuing gases does not exceed 0.11% by weight (Figure 4.24). Higher conversions of up to 0.28% are possible at 50 cc/min, 10 mA, and a scanning frequency of  $470 \text{ min}^{-1}$  (Figure 4.26), but unfortunately both the energy yield and the molar conversion are lower than the previous case at 0.89 gms/kWh and 10.3% respectively.

#### 4.6.3. Decomposition of Ammonia in the Pulsed DC discharge

##### (a) General

The decomposition of ammonia was studied at a pressure of 10 torr, with and without beam scanning. The same reactor as for the continuous DC case was employed, but with a slight modification in the design of the insulating barrier (see Section 4.1). It was found in practice that in order for the discharge beam to follow the displacement of the aperture in the insulator in an exact manner, it was necessary for that part of the cathode exposed by this aperture to be completely covered by the negative glow. Since the width of the visible glow in this case was only 25% of that of the continuous DC discharge, scanning of the beam at frequencies of  $100 \text{ min}^{-1}$  and over, using the original insulating tube, caused the anode glow to lag behind the aperture thus giving the glow an involute shape. This situation caused the glow to move in jumps rather than in a smooth manner over the anode surface, thus making the assessment of the fraction of the reactor cross-section scanned by the beam a very difficult task. This practical difficulty was overcome by using another insulating tube having a  $\frac{1}{4}$ " x  $\frac{1}{4}$ " rectangular slit (see Section 4.1).

The synthesis of hydrazine in the pulsed DC discharge has been shown to be strongly dependent on the pulse characteristics such as pulse ON and OFF-times<sup>(21,27)</sup>. Recently BROWN et al<sup>(27)</sup> has shown that hydrazine was best produced under conditions of very short ON-times (order of  $\mu\text{sec}$ ) associated with OFF-times in excess of 0.1 msec. For these reasons pulses of 3 - 6  $\mu\text{sec}$  duration were also used in this work.

A constant peak current of 150 mA was chosen since it was found to compare reasonably well with the optimum value used in most of BROWN et al work. Typical current and voltage waveforms adopted for this work are displayed in Figure 4.33.

(b) Effect of Ammonia Flowrate

Flowrates ranging from 15 - 200 cc/min (STP) were investigated corresponding to a molecule flight time across the height of the discharge of 0.99 - 0.075 sec. respectively. As mentioned earlier, only one current level was used. The pulse OFF-time was kept constant at 2 msec. The pulse duration or ON-time was found to be  $4.5 \mu\text{sec}$  with most of the current, however, decaying over the first  $0.5 \mu\text{sec}$ . The energy/pulse resulting from this pulse was computed to be  $24.4 \times 10^{-12}$  kWh. The results from these runs are given in Table 11 located in Appendix 4 and are graphically shown in Figures 4.34 - 36.

Figure 4.34 shows the effect of flowrate, interpreted as residence time, on the overall conversion of ammonia and molar conversion to hydrazine. It can be noted that as for the DC case, longer residence times favour the decomposition of ammonia but have an adverse effect on the chemical efficiency which is represented by the molar conversion to hydrazine. In addition to lower molar conversions longer residence time also produces less hydrazine per unit time (Figure 4.36). Many interesting features of the pulsed technique, such as the capability of reducing degradation of hydrazine by back reaction, is apparent from the relatively high molar conversions,  $> 90\%$  in some instances. This means that although very little ammonia is decomposed, a significant proportion of it is actually converted to hydrazine.

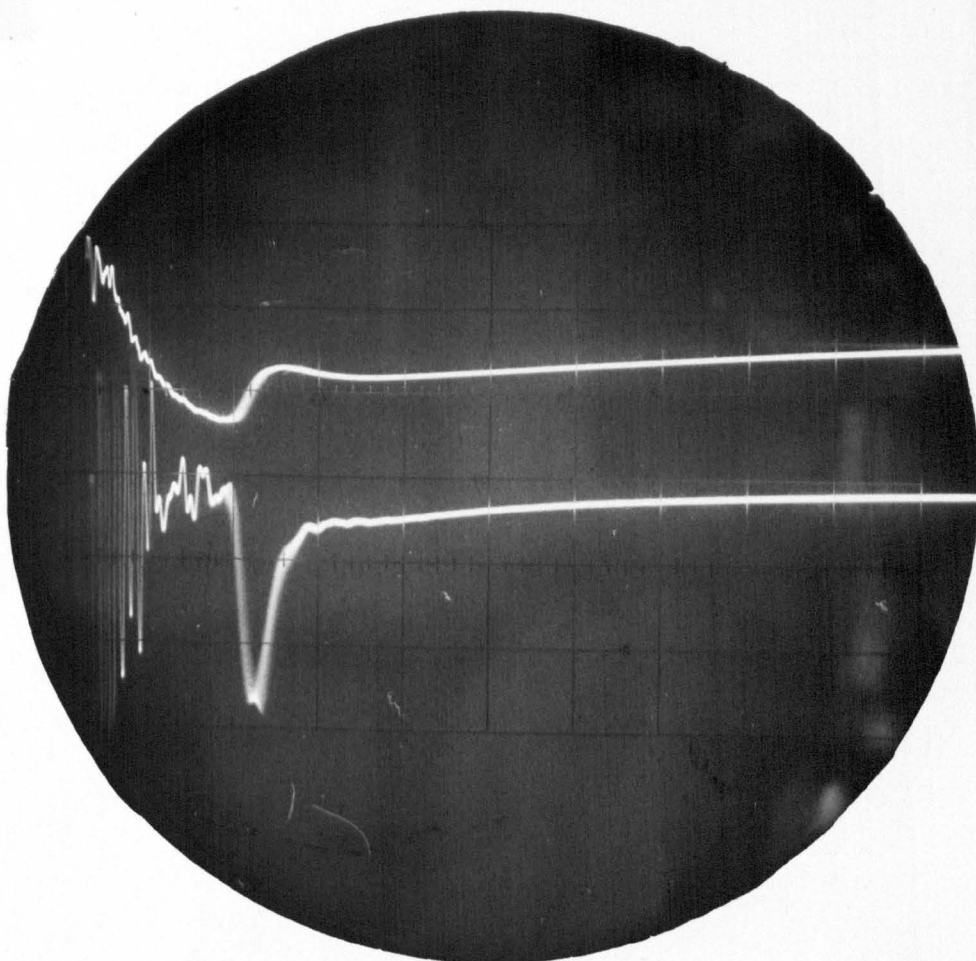


Figure 4.33 Typical voltage and current waveforms for the pulsed discharge.

- (a) upper trace - voltage, scale 1 kV/cm
- (b) lower trace - current, scale 50 mA/cm
- (c) sweep rate is 0.5  $\mu$ sec/cm

FIGURE 4.34

peak current = 150 mA  
 pulse OFF-time = 2 msec  
 pulse ON-time =  $4.5 \mu\text{sec}$   
 energy/pulse =  $24.4 \times 10^{-12} \text{ kWh}$   
 pressure = 10 torr

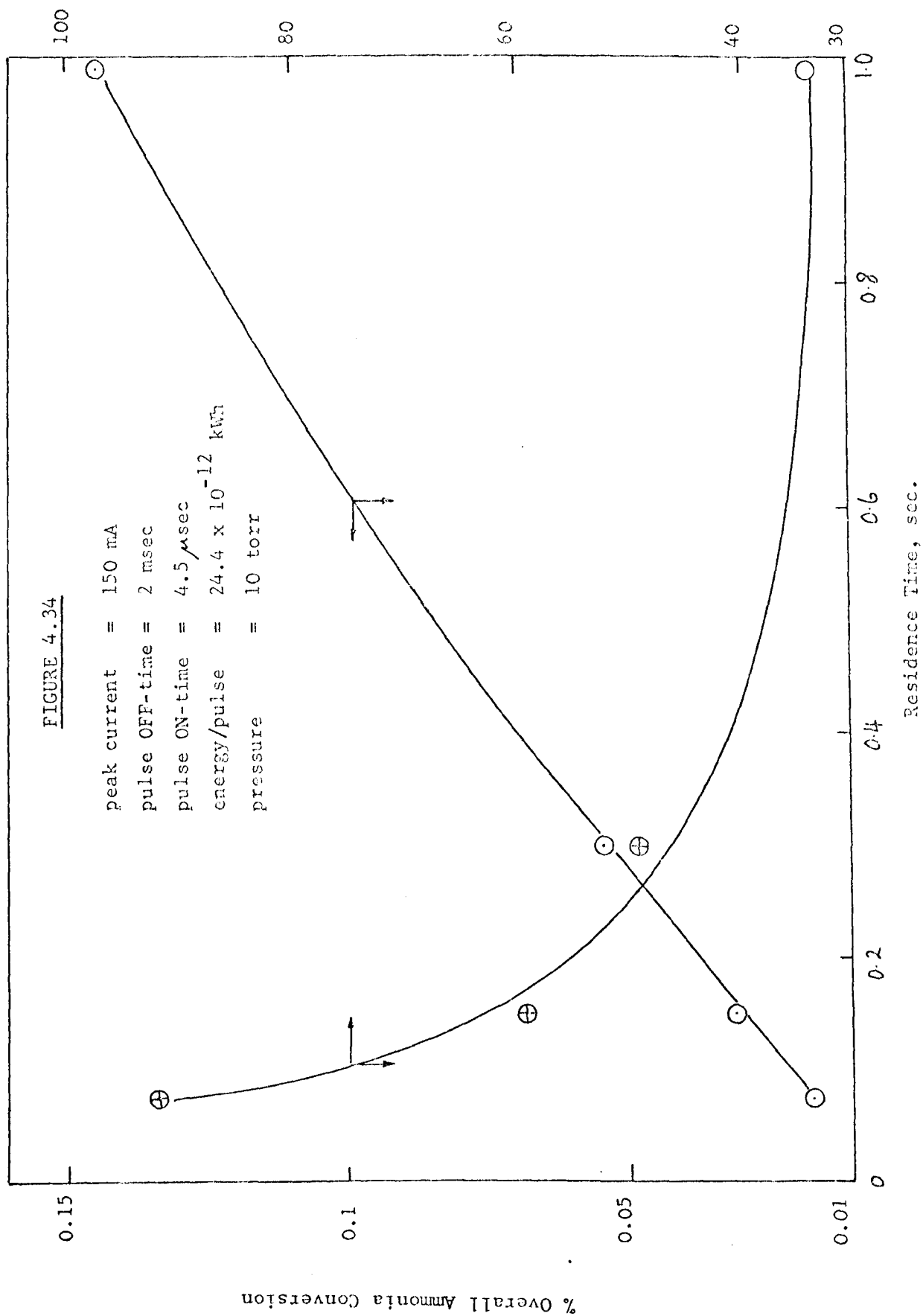
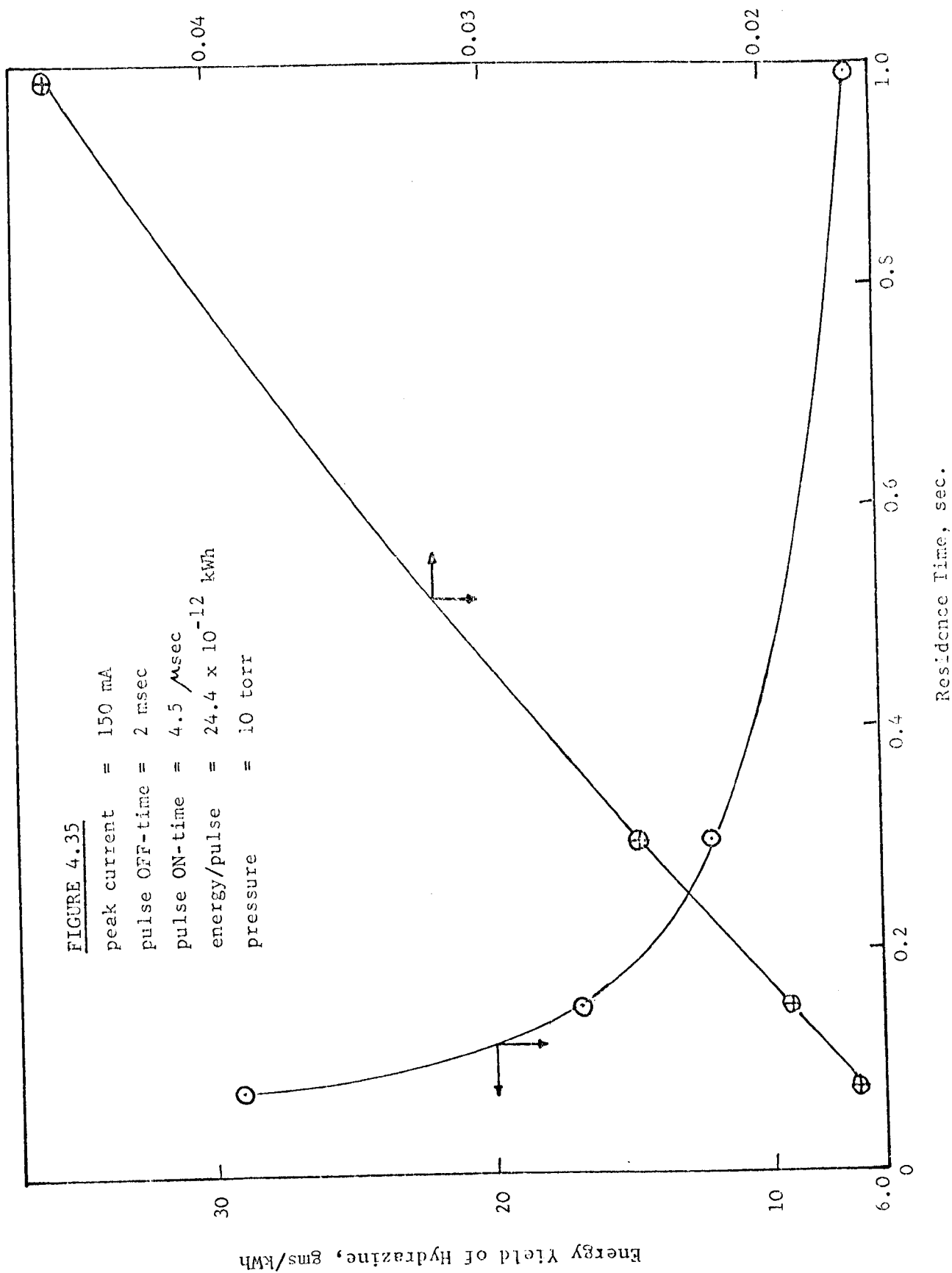
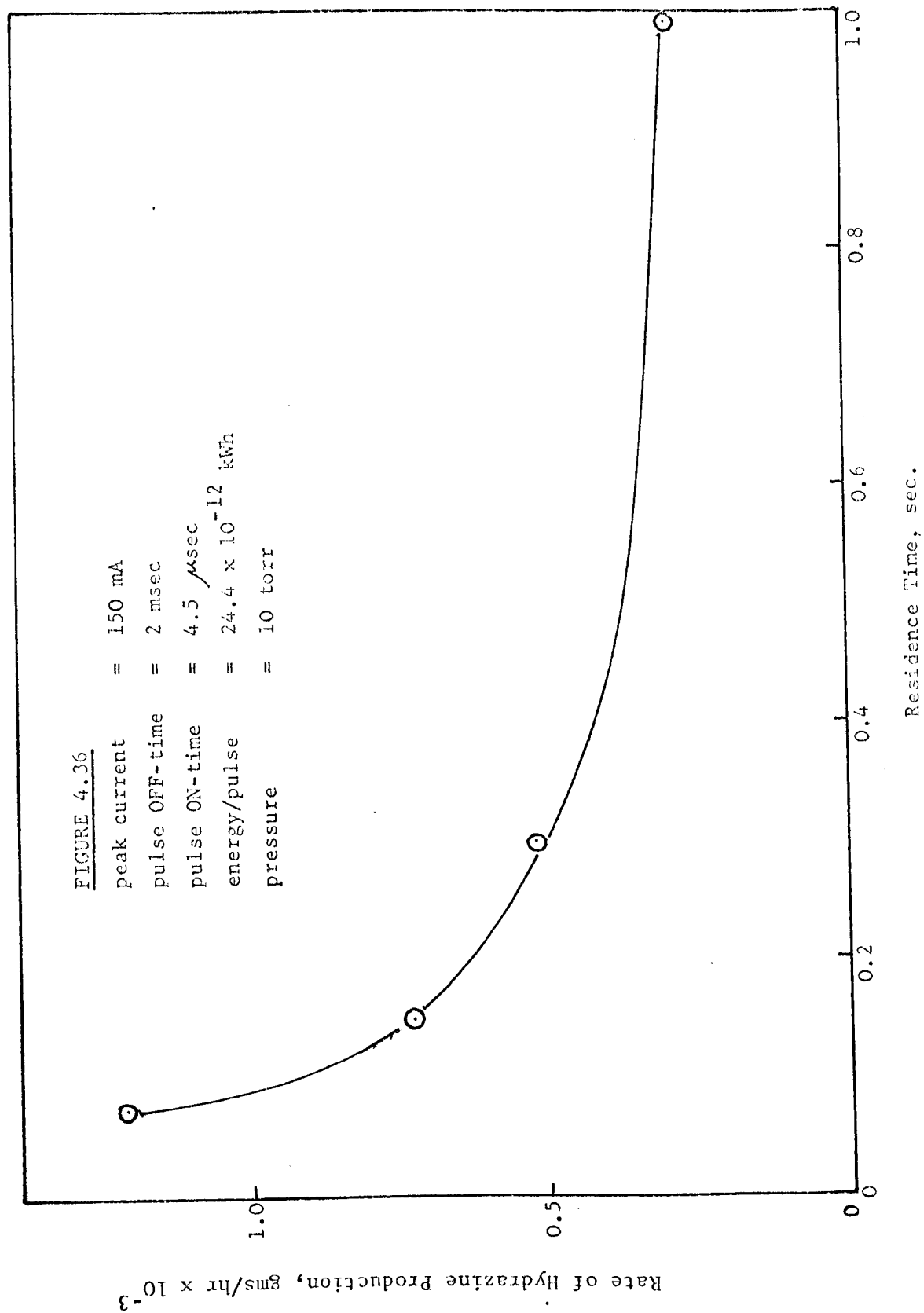


FIGURE 4.35

peak current = 150 mA  
 pulse OFF-time = 2 msec  
 pulse ON-time =  $4.5 \mu\text{sec}$   
 energy/pulse =  $24.4 \times 10^{-12}$  kWh  
 pressure = 10 torr





The effect of residence time on the energy yield and overall conversion to hydrazine is shown in Figure 4.33. Here, the trends observed in the DC discharge are also apparent with the pulsed discharge, i.e. higher energy yields and lower overall conversions at shorter residence times, but unlike the DC case yields of up to 30 gms/kWh are possible as compared to a maximum of just over 4 gms/kWh. However, the major drawback is that although higher energy yields are obtained the concentration of hydrazine in the gaseous mixture leaving the reactor is extremely small.

(c) Effect of Pulse OFF-time

The effect of pulse repetition rate was studied at a constant flowrate and peak current of 50 cc/min (STP) and 150 mA respectively. OFF-times ranging from 0.1 - 10 msec were investigated. Due to the different dynamic impedance of the discharge at these repetition rates, it was found difficult to keep the decay time of the pulse at a constant value for all cases. However, with every pulse OFF-time it was noticed that the main portion of the current decayed over the first  $0.5 \mu$  sec of the ON-time period. The actual ON-time ranged from 3 -  $6 \mu$  sec with decreasing OFF-times. This difference in the pulse duration meant that although a constant peak current was used in all cases, the actual energy/pulse was different. In fact the latter increased from  $18.6 \times 10^{-12}$  kWh/pulse for an OFF-time of 10 msec to  $33 \times 10^{-12}$  kWh/pulse for the shortest OFF-time, i.e. an increase of almost 100%.

The results from these runs are given in Table 12 located in Appendix 4. Graphs relating the effect of pulse OFF-time on ammonia

decomposition and hydrazine formation are shown in Figures 4.37 - 39. These indicate that although longer OFF-times, i.e. smaller repetition rates, result in higher energy yields and molar conversions, the overall conversion to hydrazine is very small. With an OFF-time of 10 msec, energy yields of up to 30 gms/kWh, corresponding to a molar conversion of just over 90%, are obtained. These figures would have been very encouraging had they not been associated with a low overall conversion of only 0.009%. These very low conversions are a direct consequence of the extremely low overall ammonia conversions as shown in Figure 4.37. In addition to low overall conversions, long OFF-times also result in a relatively low overall rate of hydrazine production as compared with the short OFF-times, (Figure 4.39).

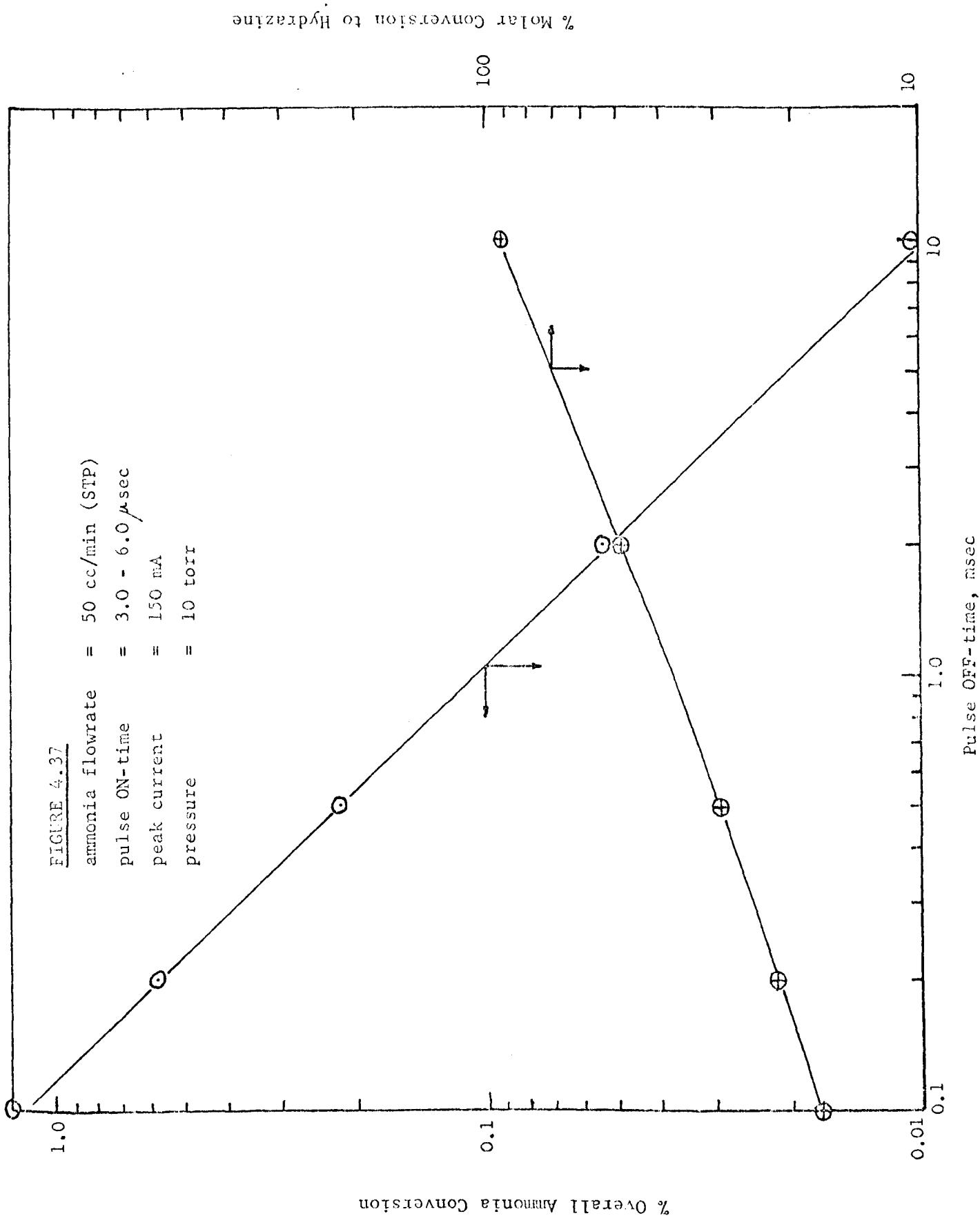
(d) Effect of Scanning Frequency

The effect of scanning frequency was studied at a flowrate of 50 cc/min (STP) and four sets of pulse OFF-times, namely 0.1, 0.2, 0.5, and 2.0 msec. Taking the observed discharge width to be  $\frac{1}{2}$ " (6.35 mm), the optimum frequency needed to give a full reactor cross-section scan at a pressure of 10 torr and ammonia flowrate of 50 cc/min, is  $195 \text{ min}^{-1}$  (Appendix 2). For this reason and due to lack of time, frequencies greatly in excess of this value were not investigated.

Results from these runs are given in Tables 13 - 16 located in Appendix 4. Only one set of graphs are produced from this data showing the effect of scanning frequency on the energy yield of hydrazine (Figure 4.40). As indicated in Figure 4.40, beam scanning has resulted in a slight improvement in hydrazine yield, especially at lower frequencies ( $< 100 \text{ min}^{-1}$ ). Higher frequencies have little or no effect.

FIGURE 4.37

ammonia flowrate = 50 cc/min (STP)  
 pulse ON-time = 3.0 - 6.0  $\mu$ sec  
 peak current = 150 mA  
 pressure = 10 torr



% Molar Conversion to Hydrazine

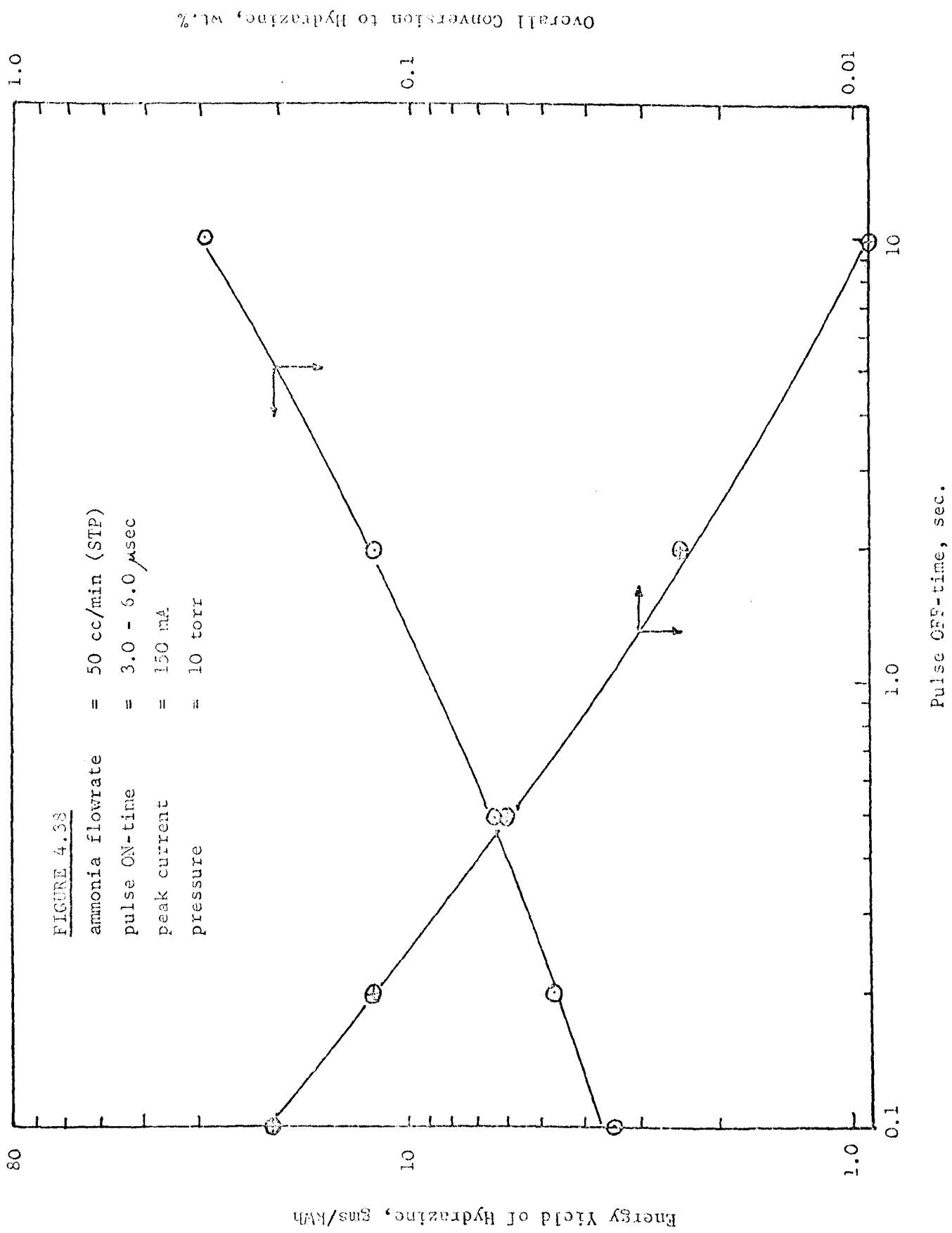


FIGURE 4.39

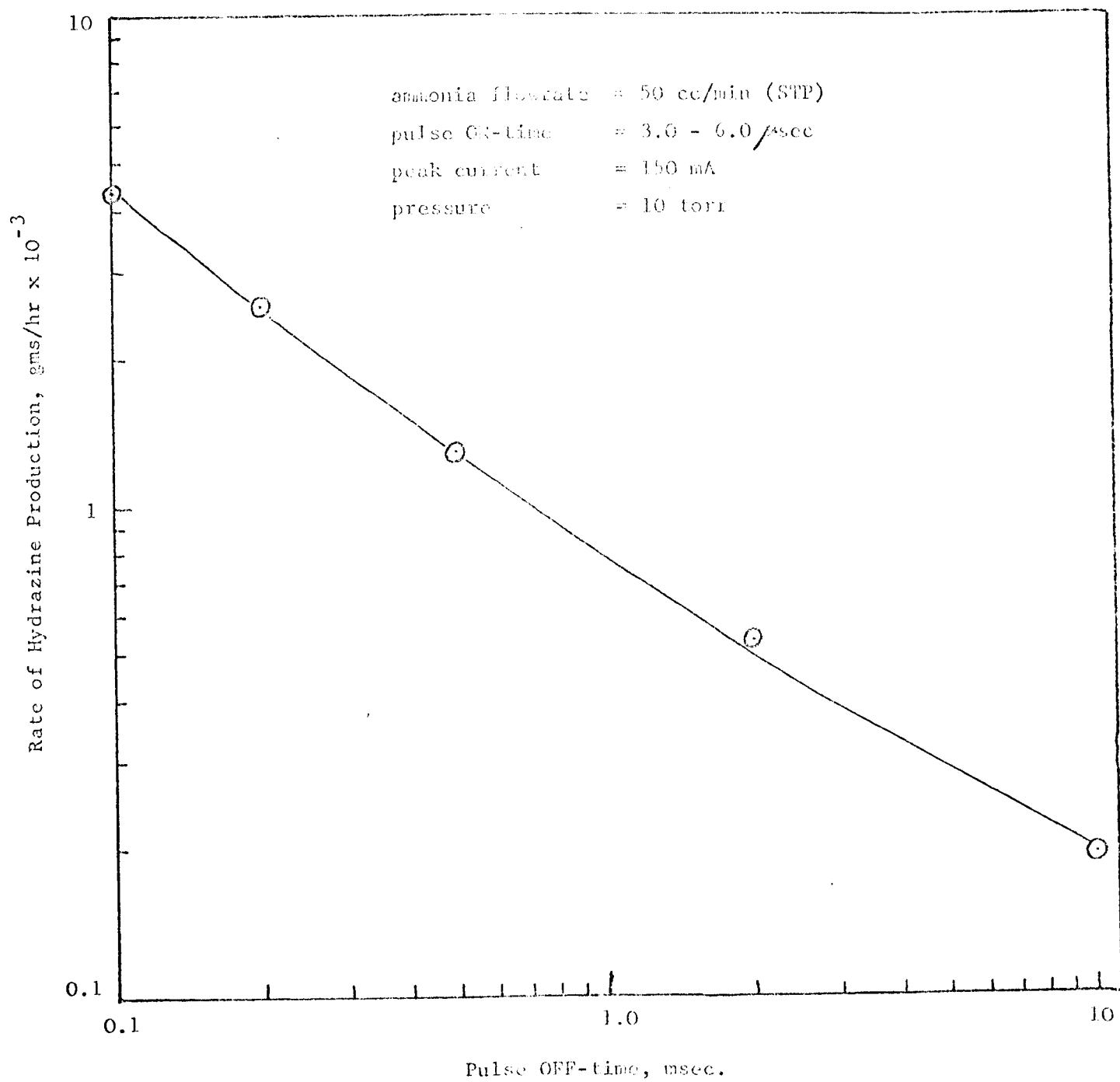
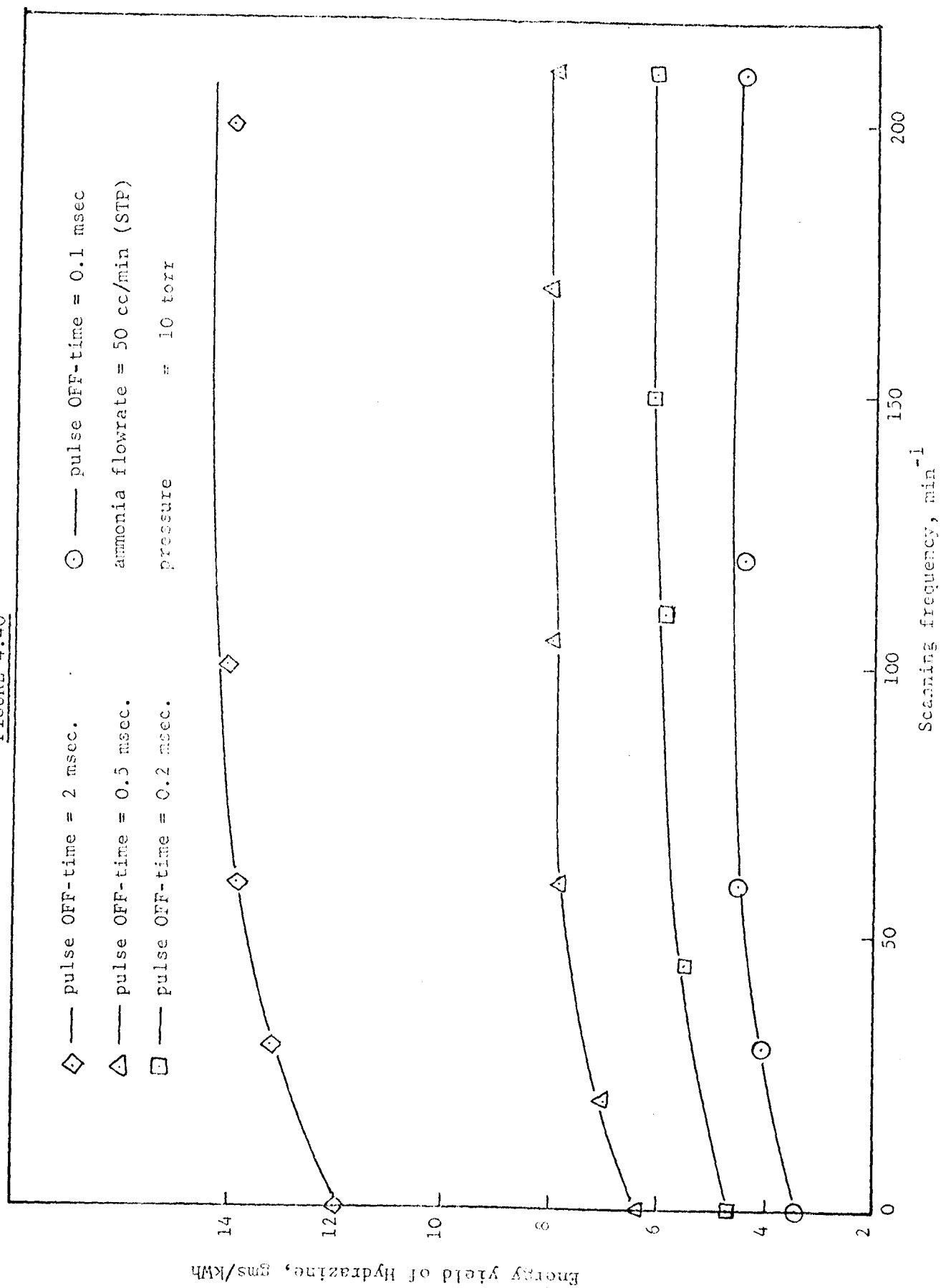


FIGURE 4.40



A glance at Tables 13 - 16 (Appendix 4) will reveal that this trend is also true for the amount of ammonia decomposed.

### 5.0. DISCUSSION AND INTERPRETATION OF RESULTS

#### 5.1. Anode and Cathode Fall Potentials and Mean Electron Energy.

The probe measurements indicate an abnormally high anode fall of 115 volts compared with the theoretical prediction. The anode fall is usually taken to be equal to the ionisation potential of the gas under consideration<sup>(30)</sup>, which for ammonia is 11.2 e.v., and any deviation from this value is due to disturbances caused by traces of gaseous impurities and dirty anode surfaces<sup>(95)</sup>. This discrepancy between the theoretical and measured values suggests that disturbances of this kind did exist and were probably caused by the deposit on the anode.

The observed value of 360 volts for the cathode fall compares reasonably well with those reported in the literature. DEVINS and BURTON<sup>(10)</sup> quote a cathode fall of 350 volts for their aged electrodes, whilst OUCHI<sup>(22)</sup> gives a slightly higher figure of 425 volts. In the latter case, the fact that OUCHI'S measurements were conducted under the abnormal region of the glow discharge will possibly account for the difference, because under these conditions the cathode fall is expected to be higher.

In the continuous DC discharge the reduced electric field,  $E/p$ , corresponding to the three current levels investigated, namely 10, 5, and 2.6 mA, and a pressure of 10 torr are 6.6, 8.7 and 10.8  $V.cm^{-1}.torr^{-1}$  respectively. Theoretical determination of the mean electron energy,  $\bar{\epsilon}_m$ , in the positive column using these reduced fields is not possible at present, because of a lack of the necessary data such as ionic mobilities, ionization cross-sections, ionization efficiency etc. The mean electron

energy was therefore determined from the experimental data of BAILEY and DUNCANSON<sup>(96)</sup> who carried out a detailed study on the behaviour of electrons amongst the molecules of ammonia, water vapour, and hydrogen chloride and their results for the mean energy of electrons in ammonia are shown in Figure 5.1 as a function of the reduced electric field. Unless the validity of this curve is disproved, we observe that the mean electron energy cannot be significantly improved beyond 2 e.v. by simply increasing the magnitude of  $E/p$ . This will mean that in cases where a substantial improvement in the electric field is envisaged by adopting new techniques such as the pulsed discharge, the resultant effectiveness in terms of electron energy will be very limited.

The mean electron energies in this work together with those reported by others<sup>(10,21,25)</sup> are shown in Table 5.1, and it is evident that a general disagreement exists. This is believed to be due to the misuse of Figure 5.1 by some<sup>(25)</sup> and unjustifiable assumptions by others<sup>(10,21)</sup>. BROWN et al<sup>(25)</sup> gave the reduced electric field in their discharge a value of  $6 - 10 \text{ V.cm}^{-1} \text{ torr}^{-1}$  and, referring to Figure 5.1, the corresponding values of  $\bar{E}_m$  should have ranged from 0.08 - 0.44 e.v. rather than the quoted 0.5 - 1.0 e.v. SAVAGE<sup>(21)</sup> on the other hand assumed a cathode fall of 350 volts taken from the glow discharge work of DEVINS and BURTON<sup>(10)</sup>, but failed to recognise that he was operating in the abnormal region which clearly meant a higher cathode fall. His data shows a lowest operative current of 15 mA, corresponding to a voltage of 850 volts. Taking this condition to be the start of his abnormal discharge, then the extra 100 volts required to sustain a current of 50 mA should have been added to the cathode fall rather than the positive column. Thus, assuming an overall anode fall of 115 volts, the

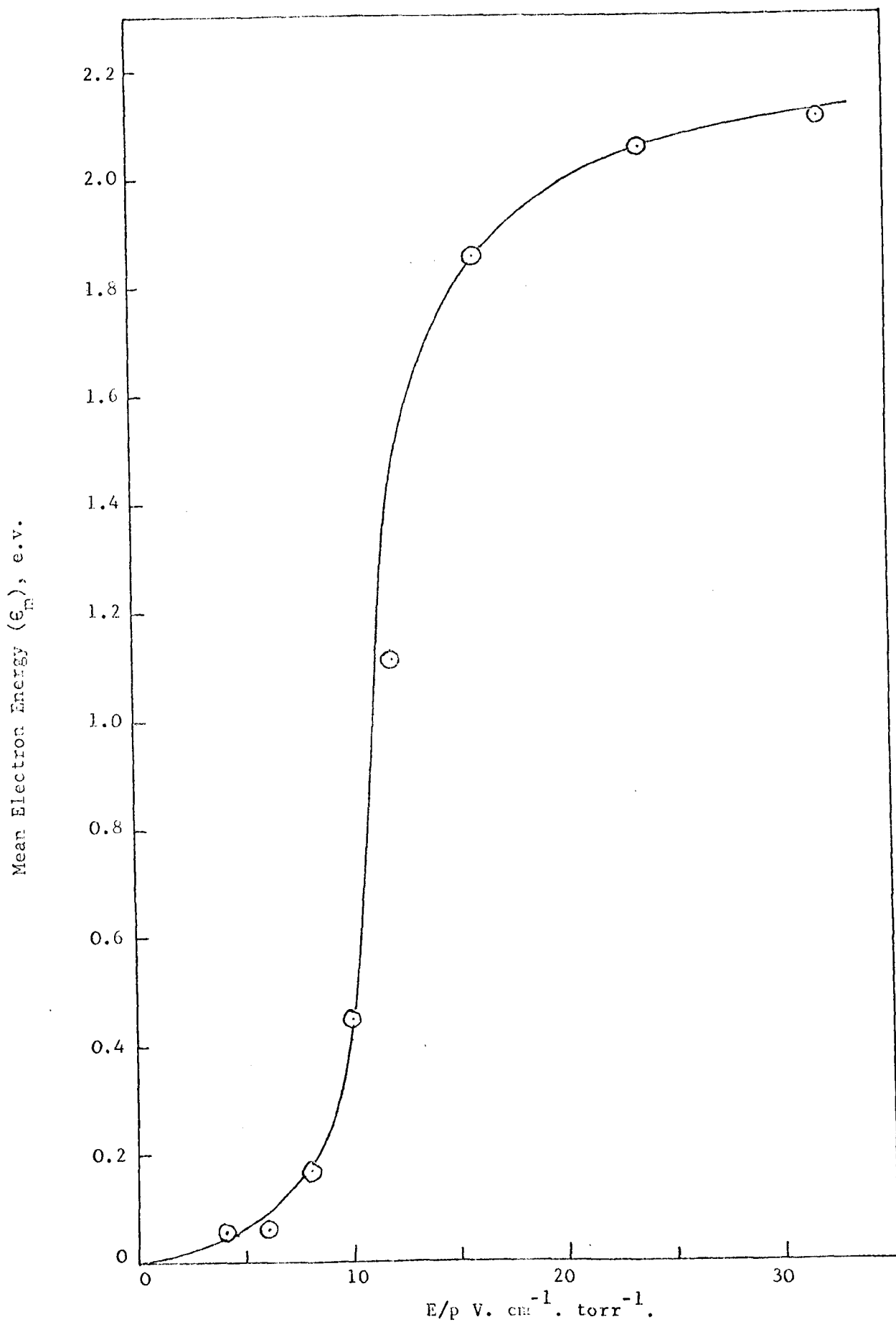


Figure 5.1 Mean Electronic Energy in Ammonia as a Function of Reduced Electric Field.

(After Bailey and Duncanson)

**TABLE 5.1**      **Reduced Field Strength and Mean Electron Energy in the Positive Column**  
**of a DC Discharge**

| Investigation        | Pressure<br>torr | Current<br>mA | Field Strength<br>(E)<br>V.cm <sup>-1</sup> | Reduced Field<br>Strength (E/p)<br>V.cm <sup>-1</sup> .torr <sup>-1</sup> | Mean Electron<br>Energy (ε <sub>m</sub> )<br>e.v. |
|----------------------|------------------|---------------|---------------------------------------------|---------------------------------------------------------------------------|---------------------------------------------------|
| Present              | 10               | 5             | 2.6    66    87    108                      | 6.6    8.7    10.8                                                        | 0.1    0.2    0.74                                |
| Brown et al          | -                | -             | -                                           | 6 - 10                                                                    | 0.4 - 1.0                                         |
| Savage               | 10               | 50            | 120                                         | 12                                                                        | 1.23                                              |
| Devins and<br>Burton | -                | -             | 63                                          | -                                                                         | 1.4                                               |

resultant potential difference across the positive column should have been 385 volts instead of the reported 600 volts. At a pressure of 10 torr and with a reported positive column length of 3 cm, the reduced electric field,  $E/p$ , will be  $7.7 \text{ V cm}^{-1} \text{ torr}^{-1}$  corresponding to a mean electron energy of 0.16 e.v.

In DEVINS and BURTON'S<sup>(10)</sup> work,  $\epsilon_m$  was evaluated by balancing the energy the electrons gain from the field and the energy they lose by collisions. LOEB<sup>(97)</sup> gives the following relationship,

$$e E v_d = \alpha (m \bar{c}^2 / 2) (\bar{c} / \lambda_e) \quad \dots\dots\dots(5.1)$$

But,  $m \bar{c}^2 / 2 = \epsilon_m$  and  $v_d / \bar{c} = (\frac{\alpha}{2})^{1/2}$  MASSEY<sup>(98)</sup>  
& BURNOP

$$\epsilon_m = e E \lambda_e / (2\alpha)^{1/2} \quad \dots\dots\dots(5.2)$$

where,

- $v_d$  = electron drift velocity
- $\alpha$  = fraction of electron energy lost in a collision
- $\bar{c}$  = average random velocity of electrons
- $\lambda_e$  = electron mean free path.

$e$ ,  $m$ ,  $E$ , and  $\epsilon_m$  have their usual designation.

DEVINS and BURTON used equation 5.2 for the evaluation of  $\epsilon_m$  and the reported high value (1.4 e.v.) was a consequence of a combination of unfounded values for  $E$ ,  $\lambda_e$ , and  $\alpha$ . Thus for example, they used a field strength of  $63 \text{ V cm}^{-1}$ , a conservatively low value for  $\alpha$  (0.024), and a value for  $\lambda_e$  of  $6.7 \times 10^{-2} \text{ cm}$  which was taken from BAILEY and DUNCANSON'S data at a pressure of 1 torr.

Accepting the validity of BAILEY and DUNCANSON'S data and

assuming a Maxwellian distribution of electron energies, it can be shown (Appendix 2) that the number of electrons with energies in excess of 4.5 e.v. ( $\text{NH}_2\text{-H}$  bond energy) and at mean electron energies of 0.1, 0.2, and 0.74 e.v. are less than  $10^{-10}$ ,  $10^{-9}$ , and  $10^{-2}$  respectively. With the exception of the last value, it appears that virtually no electrons are available to rupture the ( $\text{NH}_2\text{-H}$ ) bond by a single collision but, nevertheless, breakdown of the ammonia does take place. This implies that unless some other mechanism is responsible for the dissociation of ammonia, then the validity of BAILEY and DUNCANSON'S data and consequently the values of  $\epsilon_m$  evaluated for this study may be in doubt.

### 5.2. Film Deposition on the Anode

This is an observation which has no precedent in any published literature on ammonia decomposition in the glow discharge and it is not easy to establish why it has been so completely overlooked. Undesirable operating conditions could be a common cause but reluctance to account for such unexpected surface phenomenon in a generally accepted gas phase system might be a better reason. It must be emphasised that the exact nature of this deposit and the processes leading to its formation are still not completely understood.

A survey of some recent literature<sup>(99)</sup> regarding alloys of iron containing traces of non-metals failed to identify any alloy containing the three non-metals, namely hydrogen, nitrogen and carbon, together. This observation coupled with the fact that the x-ray diffraction patterns showed the cell structure and lattice spacing of the deposit to be almost identical to those for the steel from which the

anode was fabricated, and yet have a very different physical appearance, suggests only one possible explanation for its formation. During the course of the discharge, re-orientation in the structure of the steel may have occurred which caused some of the iron atoms to be replaced by hydrogen, nitrogen, and carbon atoms and this re-arrangement inevitably led to the complete breakdown of the nature of the steel (D.P. THOMPSON<sup>(100)</sup>). The reason why such deposition should only take place at the lower ammonia flowrates could be attributed to the fact that under these conditions the concentration of the species responsible for the formation of this product are higher than those at the higher flowrates. Furthermore, if one assumes that the migration of these species towards the anode is a diffusion controlled process, then the higher flowrates will hinder such a process due to the upward displacement of these species by the momentum of the gas. Support for this argument comes from the observation that at the highest flowrates, only a faint deposit is produced covering the upper rim of the anode. Furthermore, when operating with the pulsed discharge for long periods ( $> 10$  hrs.), the amount of deposit was found to be very small in comparison with the continuous discharge. This again is possibly due to the much smaller concentration of species produced in the pulsed discharge.

The source of the carbon observed in the deposit in such large amounts (2.72% c.f. 0.06% in the steel) is questionable. One possible source is the small traces of carbon dioxide (40 p.p.m) which are present in the ammonia. If it is assumed that all the carbon dioxide is decomposed by the action of the discharge and that all the resulting carbon is being deposited on the anode, together with the other species required for the make up of the product, then at an

ammonia flowrate of 50 cc/min (STP), the amount of carbon resulting in the product will be  $2.34 \times 10^{-5}$  gms/hr. The percentage of carbon in the deposit was 2.72%; this will represent an overall deposition rate for the compound of  $8.6 \times 10^{-4}$  gms/hr. This is found to agree surprisingly well with the experimentally determined rate of  $8.5 \times 10^{-4}$  gms/hr, measured by weighing the total product after a long run.

Finally, it is necessary to show that the amount of hydrogen and nitrogen taken up by this compound is only a small fraction of that produced from the electron decomposition of ammonia. If this is not so, then most of the calculated results such as molar conversion to hydrazine, overall ammonia conversion, etc. may be in error. Table 5.2 is calculated from Run 1 (Appendix 4), in which ammonia is decomposed at the highest current (10 mA) and lowest flowrate (50 cc/min) resulting in the highest deposition rate of  $8.5 \times 10^{-4}$  gms/hr. It is evident from this table that the rate of generation of the gas phase products ( $N_2 + H_2$ ) is greatly in excess of the rate of adsorption by the steel.

### 5.3. Decomposition of Ammonia in the Continuous DC Discharge

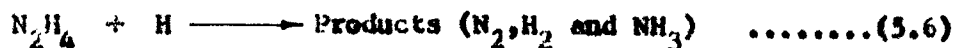
#### 5.3.1. Effect of Discharge Current and Gas Flowrate

Using simple kinetic consideration, it is possible to explain qualitatively the influence of these parameters on the course of the reaction and hence the product yield. The overall reactions leading to the formation and degradation of the hydrazine have already been discussed in Section 2.2 and have been taken to be:



**TABLE 5.2**      Comparison between the rate of generation of hydrogen and nitrogen in the  
gas phase and the rate of adsorption by the anode.

| $X_{NH_3}$<br>$Z$ | Equivalent<br>gas of $H_2$<br>/hr | Equivalent<br>gas of $N_2$<br>/hr | gas $H_2$<br>in deposit<br>/hr | gas $N_2$<br>in deposit<br>/hr | $\frac{H_2 \text{ in deposit}}{N_2 \text{ overall}}$ | $\frac{N_2 \text{ in deposit}}{N_2 \text{ overall}}$ |
|-------------------|-----------------------------------|-----------------------------------|--------------------------------|--------------------------------|------------------------------------------------------|------------------------------------------------------|
| 2.34              | $8.9 \times 10^{-3}$              | $41.5 \times 10^{-3}$             | $1.565 \times 10^{-5}$         | $5.06 \times 10^{-5}$          | $1.82 \times 10^{-3}$                                | $1.22 \times 10^{-3}$                                |



As in any kinetic scheme, the relative importance of each of the above reactions will depend on the operating variables and the rate constants. If we assume that the rate constants are not significantly influenced by the operating conditions, then the gas residence time, which is inversely proportional to the gas flowrate, and the electron density will determine the extent of ammonia decomposed and hydrazine formed.

In a gas discharge the electron density is taken to be a direct function of the discharge current. Accepting this fact and considering the reactions (5.3 - 6), we observe that at long residence times and high electron densities (higher currents), there is an increased probability that hydrazine decomposition will occur. According to reaction (5.3) these conditions should enhance the rate of the primary decomposition reaction to give a higher overall ammonia decomposition whilst the energy yield of hydrazine, which is considered to be a measure of these degradative reactions, will be adversely affected as shown in Figures 4.16 and 4.18. As the products from these degradative reactions will be nitrogen, hydrogen and ammonia (see Chapter 2) then a smaller percentage of the decomposed ammonia will be converted into hydrazine at higher currents and longer residence times (Figure 4.19). These findings are consistent with the photolysis work of McDONALD et al<sup>(53)</sup> and the gas discharge works of CARBAUGH et al<sup>(55)</sup> and ANDERSON et al<sup>(73)</sup>.

The observed dependence of the overall conversion to hydrazine on the discharge current and ammonia flowrate, as depicted in Figure 4.17, is also a consequence of the postulated kinetic scheme. Figure 4.17 shows

that there is no hydrazine at zero residence time but as the latter is increased, at a constant current, some hydrazine is formed and consequently some will be simultaneously degraded. Since the concentration of hydrazine at this stage will be very small, the rate of the forward reaction will be greater than that for the backward reactions and as a result some hydrazine will escape the discharge zone. At higher residence times, the concentration of both the hydrazine and the hydrogen atoms is increased and the effect of the back reactions becomes appreciable. This will eventually give a maximum in the conversion curve. At still longer residence times, comparable with those obtained in a batch reactor, most of the hydrazine will inevitably be converted to hydrogen, nitrogen, and ammonia. The position of the maximum will be dependant on other operating variables such as current, pressure, etc. In this present work, Figure 4.17 shows that only at a current of 10 mA was there a maximum. There are, however, few examples in the literature where these curves were fully established such as the work of ANDERSON et al <sup>(73)</sup> and SAVAGE <sup>(21)</sup>.

The overall conversion to hydrazine together with the energy yields obtained without beam scanning are prohibitively low, but nevertheless, they seem to be in reasonable agreement with most published data <sup>(21,73)</sup>. It has been customary to relate the inefficiency of hydrazine production in the glow discharge to the degradative back reactions, but careful study of the present data shows that there are two other factors contributing significantly to this effect:

(i) Energy Wastage in the electrode layers:-

It was mentioned earlier that the combined potential drop across the electrode layers (mainly the cathode) was 475 volts. Since

the normal discharge voltage lay between 630 - 730 volts, some 65 - 75% of the total energy was consumed in these regions of which about 49 - 57% was dissipated in the negative glow. This region contributes neither to hydrazine formation nor to ammonia decomposition since as well as being a region of high energy intensity, it was completely by-passed by the ammonia flow.

(ii) Inefficient energy transfer between electrons and ammonia molecules:-

Since the electrons have an energy distribution (probably Maxwellian) around a mean value that is much smaller than the ( $\text{NH}_2\text{-H}$ ) bond energy (4.5 e.v.), a very small fraction of the electrons will be able to dissociate the ammonia through a single impact. The exact value of this mean energy was shown to be somewhat questionable but even if we assume an upper limit of 1.5 e.v., we find that only about 12% of the electrons have energies in excess of 4.5 e.v. (see Figure A2.1, Appendix 2). This will imply that the majority of electrons undergo diverse impacts with the ammonia leaving the latter with an excitational energy less than 4.5 e.v. These partially excited molecules can either be fully excited by further collisions with electrons or return to their ground state energy level with the subsequent emission of light. It is the latter process which accounts for some energy loss.

The foregoing energy loss processes will undoubtedly have an adverse effect on the energy efficiency of the discharge. Excluding the energy losses in the electrode layers and taking the maximum theoretical yields of hydrazine and ammonia to be 133 and 141 gms/kWh (see Appendix 2) respectively then,

$$\text{energy efficiency, } \eta = \frac{\text{observed yield}}{\text{theoretical yield}}$$

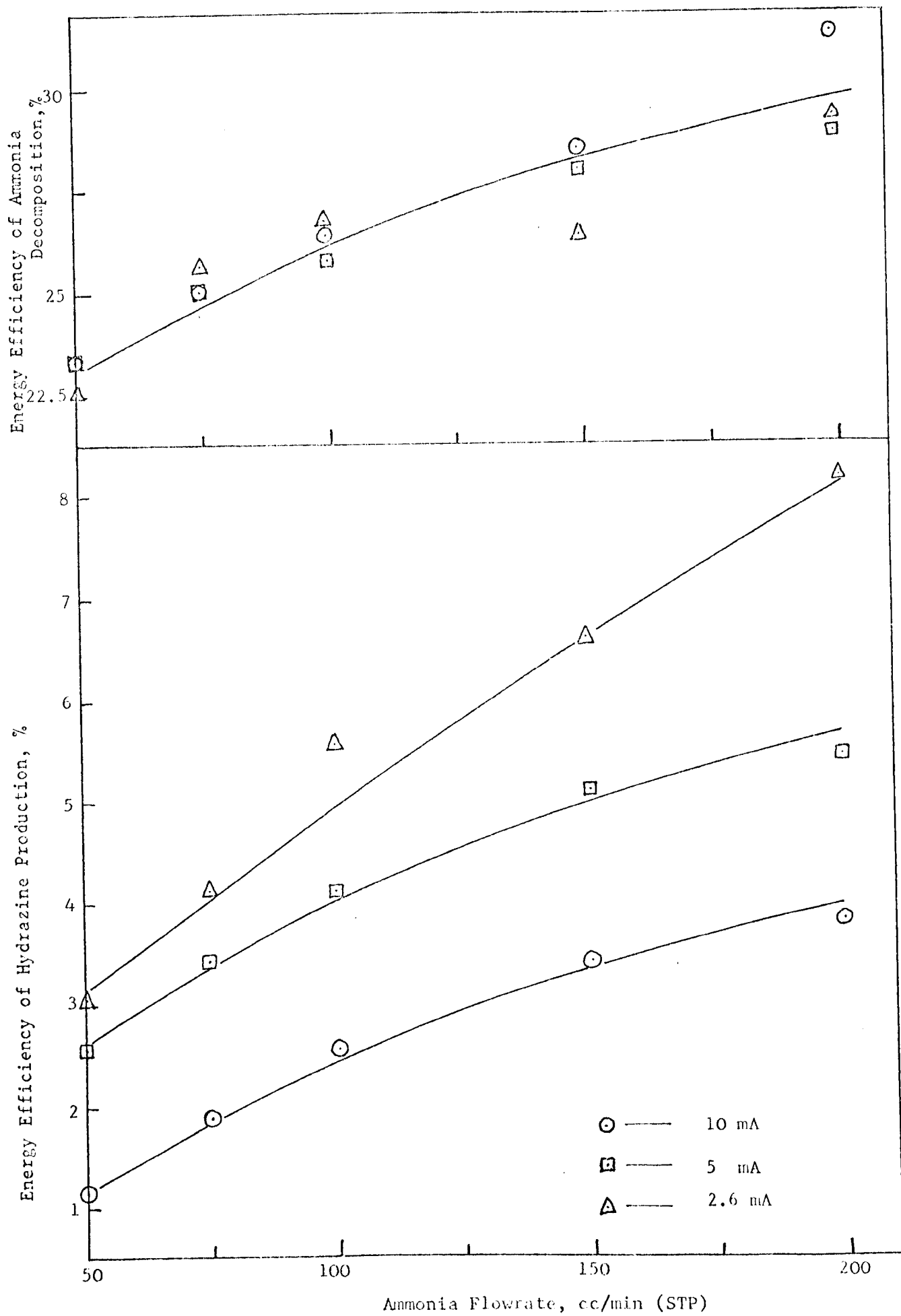
$\eta$  was calculated for both hydrazine and ammonia (based on power

dissipation in the positive column only) and are shown graphically in Figure 5.2 as functions of discharge current and ammonia flowrate.

Figure 5.2 indicates that the maximum energy efficiency for ammonia decomposition does not exceed 32%. This will imply that even if no hydrazine is to be degraded, the energy efficiency for its production will not be expected to exceed this value and the fact that it is lower than 32% (maximum 8%) is a direct result of degradative reactions. The extent of these reactions will be expected to be minimal at the highest flowrates (shortest residence time) and lowest currents, and hence the reason for higher efficiencies under these conditions. In the case of ammonia,  $\eta_{\text{NH}_3}$  seems to be independent of the discharge current. Strictly speaking one would expect  $\eta_{\text{NH}_3}$  to be higher at the lower currents due to the higher reduced electric fields, E/p. Higher E/p values will mean higher mean electron energies and consequently greater number of electrons with energies in excess of 4.5 e.v. The fact that  $\eta_{\text{NH}_3}$  does not vary with the discharge current, suggests that multiple electron collisions could be as important, in dissociating ammonia, as single excitational collisions. At higher currents, the fact that fewer energetic electrons are available for single excitational impacts is compensated for by the greater probability of multiple collisions due to the larger electron density. Therefore, it could be concluded that in these discharges, the extent of the primary reaction is much more influenced by the current than the voltage.

Another point of interest which stems from Figure 5.2 is the adverse effect of lower ammonia flowrate on  $\eta_{\text{NH}_3}$ . The reason for this observation is apparent from the postulated kinetic scheme. At

FIGURE 5.2



longer residence times, i.e. lower flowrates, the higher concentration of the H-atoms will enhance the rate of hydrazine decomposition which will subsequently reform some of the decomposed ammonia and hence reduce  $\eta_{\text{NH}_3}$ .

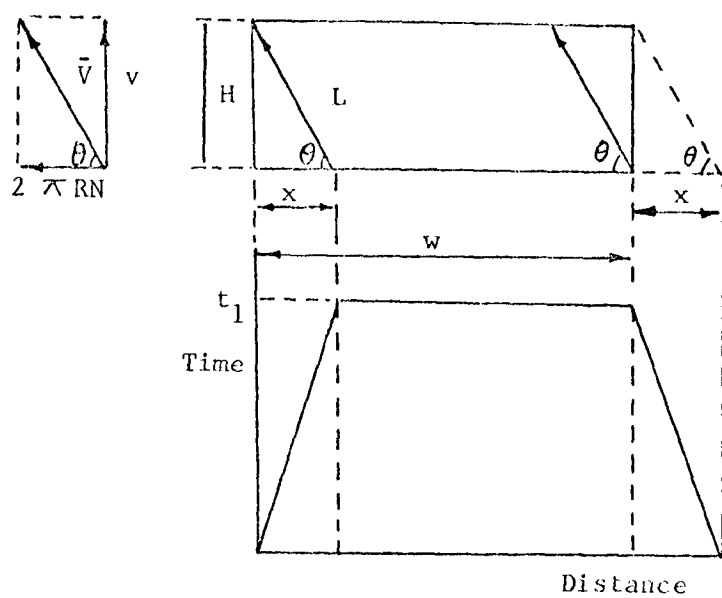
### 5.3.2. Effect of Scanning Frequency

#### (a) Evaluation of Activation Residence Time and Fraction of Ammonia Subjected to the Discharge

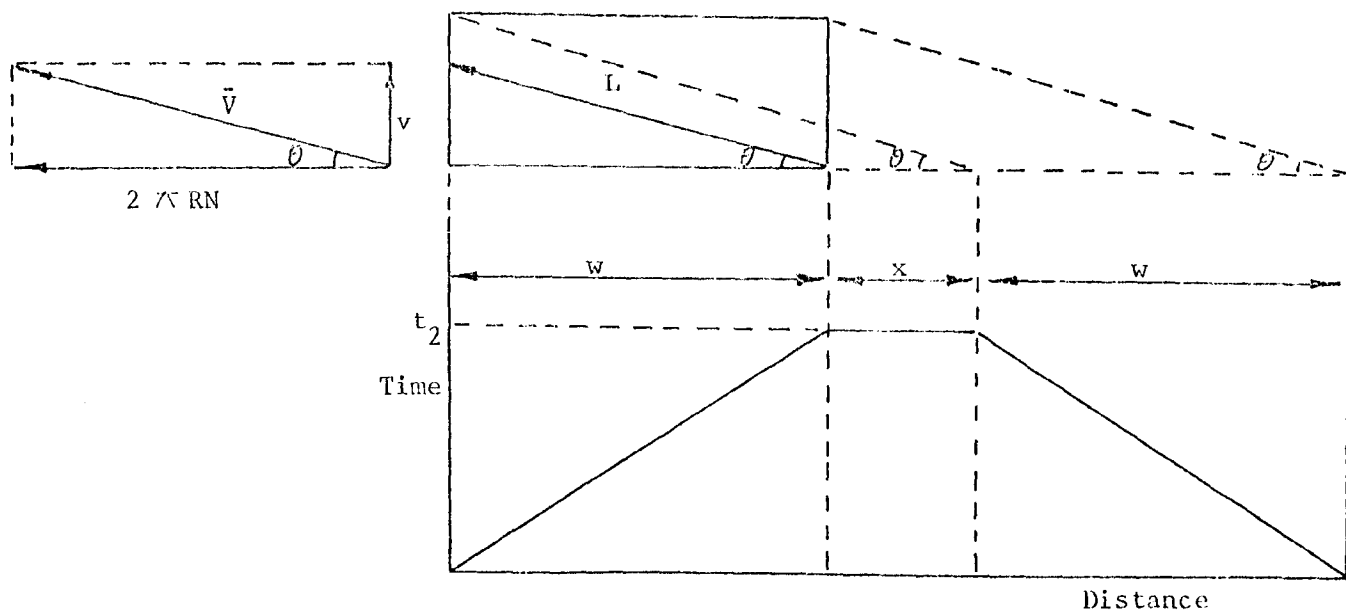
In order to quantify the effect of scanning frequency on activation residence time and fraction of ammonia irradiated or subjected to the discharge, it is necessary to make a number of basic assumptions:-

- (i) the flow pattern in the reactor is approximated by a plug-flow model. This is not an unreasonable assumption as the Reynolds Numbers did not exceed a value of 10.
- (ii) only the visible glow of the discharge is responsible for chemical activation.
- (iii) the physical size of this glow is unaltered by scanning.
- (iv) all those runs which involved multiple scans of the molecules are omitted.

The residence time ( $\tau$ ) is governed by both the axial gas velocity as well as the horizontal scanning velocity. As mentioned earlier the discharge beam was wedge shaped and of rectangular cross-section, so that at any radius (R), the discharge dimensions may be taken as height (H) and width (w) as depicted in Figure 5.3. At this radius the gas will flow axially with a velocity (v) whilst the



(A)



(B)

Figure 5.3 Evaluation of Mean Residence Time.

discharge plane moves at right angles with a velocity  $(2 \pi RN)$ , where  $N$  is the speed of rotation or scanning frequency. The resultant velocity of the gas relative to the discharge is then represented by the vector  $(\vec{V})$  in a direction  $(\theta)$  relative to the lower edge of the discharge plane. Two cases are now of interest.

$$(1) \quad \underline{t_1} < \underline{t_2}$$

This corresponds to the situation where the gas velocity is high relative to the scanning velocity. It is clear from Figure 5.3(A) that those molecules entering the discharge along the width  $(w - x)$  will have a constant residence time given by  $(L/\vec{V})$  where  $L$  is the path length at an angle  $(\theta)$ . However, since,

$$\sin \theta = H/L = v/\vec{V}$$

it follows that the residence time  $(L/\vec{V})$  is given by  $(H/v)$  which is equal to  $t_1$ , i.e. the molecular flight time across the discharge height. Similarly, gas molecules entering the discharge through plane section  $(x)$  will have residence times ranging from  $0 - t_1$ . Thus defining a mean residence time  $(\bar{\tau})$ :

$$\bar{\tau} (w + x) = t_1 (w - x) + 2 \left( \frac{x}{2} \right) t_1 \quad \dots\dots\dots(5.7)$$

Defining  $x$ :

$$\tan \theta = H/x = v/2 \pi RN$$

$$\text{so that,} \quad x = 2 \pi RNH/v = 2 \pi RN t_1 \quad \dots\dots\dots(5.8)$$

Substituting for  $x$  in equation (5.7) and rearranging,

$$\bar{\tau} = t_1 t_2 / t_1 + t_2 \quad \dots\dots\dots(5.9)$$

where,  $t_1 = H/v$  ;  $t_2 = w/2 \wedge RN$

$$(ii) \underline{t_1 > t_2}$$

This situation is depicted in Figure 5.3(B). Again all molecules entering the discharge via the plane (x) will have a constant residence time ( $L/\bar{V}$ ) where L is the path length in the discharge at angle  $\theta$ . Since in this case,

$$\cos \theta = w/L = 2 \wedge RN/\bar{V}$$

it follows that the residence time ( $L/\bar{V}$ ) is equal to ( $w/2 \wedge RN$ ), i.e.  $t_2$ . All other molecules entering the discharge will have residence times ranging from 0 -  $t_2$ . Hence again:

$$\bar{\tau} (2w + x) = t_2 x + 2(\frac{w}{2}) t_2 \dots\dots\dots(5.10)$$

Defining x:

$$\tan \theta = H/w + x = v/2 \wedge RN$$

$$\text{so that, } x = 2 \wedge RN t_1 - w \dots\dots\dots(5.11)$$

Substituting for x in equation (5.10) and rearranging gives:

$$\bar{\tau} = t_1 t_2 / t_1 + t_2 \dots\dots\dots(5.12)$$

which is identical with equation (5.9) as expected. In the special case where  $t_1 = t_2$ , equation (5.9) indicates that,

$$\bar{\tau} = t_1/2 = t_2/2$$

Two limiting conditions are immediately apparent from the foregoing:

(a)  $\underline{t_2 \longrightarrow \infty}$

This is the case corresponding to  $N = 0$ , i.e. no scanning. From equation (5.9) this situation will give,  $\bar{t} = t_1$

(b)  $\underline{t_2 \ll t_1}$

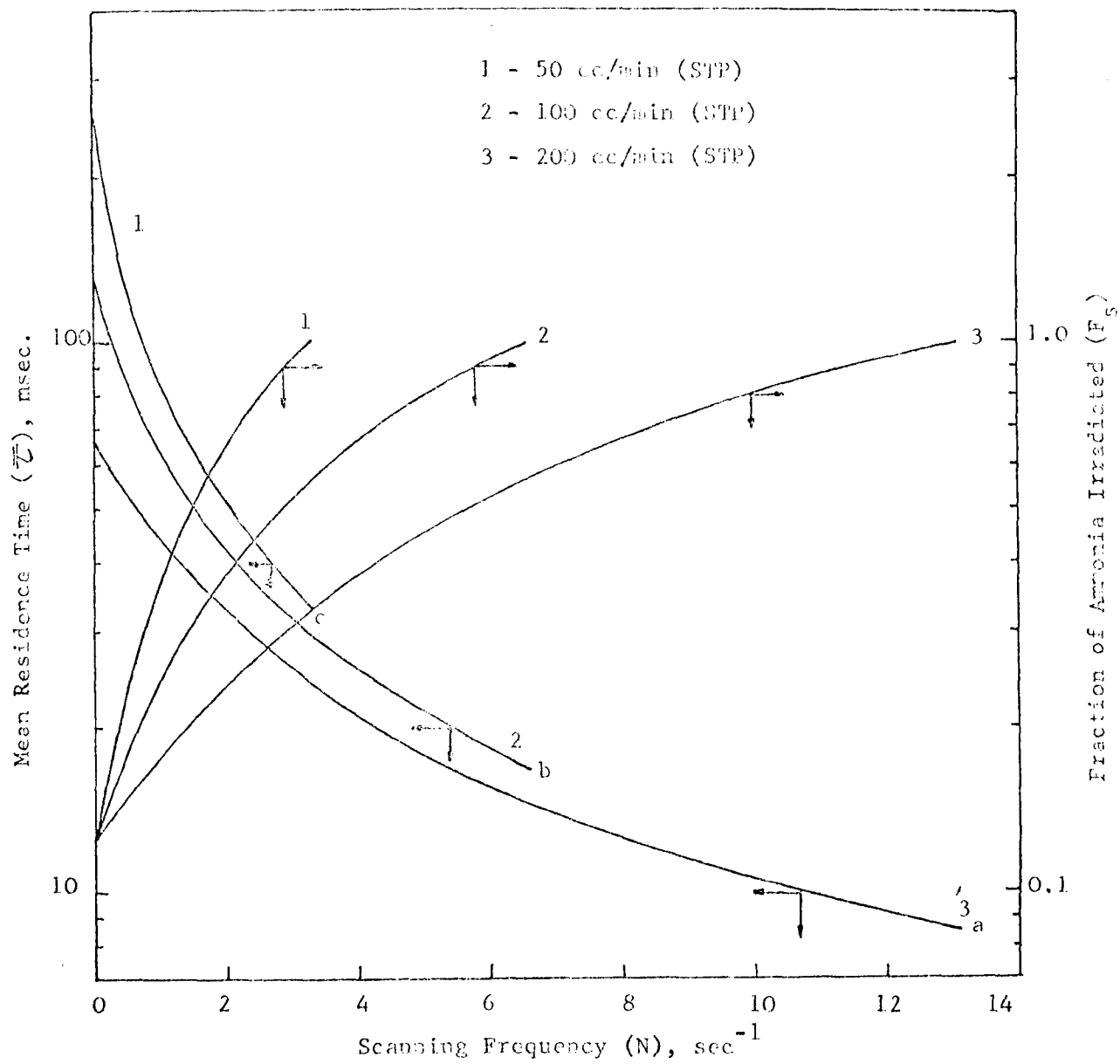
This is the case where the discharge width is very small or the scanning velocity is much higher than the gas axial velocity. According to equation (5.9),  $\bar{t} \longrightarrow t_2$ .

Since the discharge beam had a finite width (w), the fraction of the reactor cross-section scanned by the discharge during the time taken for the gas to pass through height (H) is:

$$\begin{aligned} F_s &= \frac{w}{2 \pi R} + N t_1 \\ &= N(t_1 + t_2) \end{aligned} \quad \text{.....(5.13)}$$

Assuming that only the visible glow is responsible for chemical activation, equations (5.9) and (5.13) were used to calculate both  $\bar{t}$  and  $F_s$  at ammonia flowrates of 200 cc/min, 100 cc/min, and 50 cc/min (STP), using the discharge profile at the anode surface. The result of this computation is shown graphically in Figure 5.4. It is apparent from Figure 5.4 that increasing the scanning frequency (N) will increase  $F_s$  but at the same time a reduction in  $\bar{t}$  is incurred. Also, at a given N, both  $F_s$  and  $\bar{t}$  are higher for lower gas flowrates. Points a, b, c represent cases where the whole of reactor cross-section is scanned by

FIGURE 5.4



the discharge during the time the gas takes to pass through the discharge height. Beyond a, b, c further increase in N will lead to multiple scanning of the gas molecules but the mean residence time will remain constant. This implies that if a molecule scanned once, twice or n times, the cumulative residence time will be the same in each case. It follows that for very high scanning frequencies this device will be identical to the pulsed discharge in some aspects. The pulse ON-time will be given by  $(w/2 \pi R N)$  while the pulse OFF-time will be equivalent to  $(2\pi R - w/2 \pi R N)$ . The only difference between this device and the pulsed technique is that in the latter the pulse ON and OFF-times can be varied independently whilst in the former the ratio of the (ON-time/OFF-time) is always a constant.

(b) Effect of Scanning Frequency on Ammonia Decomposition and Hydrazine Formation

The observed improvement in the energy yield (Figures 4.30 - 32) and molar conversion to hydrazine (Figures 4.27 - 29) is merely an attribute of a reduction in the activation residence time during beam scanning. Interpreting the effect of scanning on the overall ammonia conversion ( $X_{\text{NH}_3}$ ) is not as straight forward since a reduction in the residence time and the degree of by-passing will both have a bearing on  $X_{\text{NH}_3}$  but in an opposing manner. Analysis of the results of zero scanning frequency (Figure 4.16) will show that  $X_{\text{NH}_3}$  decreases with decreasing residence time and it follows that the advantages of beam scanning in terms of increasing total irradiation will be largely offset by the decrease in activation time. It is the net result of these two opposing factors which accounts for the slight increase in  $X_{\text{NH}_3}$  when

the discharge beam is made to rotate (Figures 4.21 - 23). In certain circumstances, particularly at low discharge current, these two factors tend to compensate and as a result no apparent increase in  $X_{\text{NH}_3}$  is observed. At higher currents, however, there is an increased possibility of ammonia decomposition arising from electron-molecule collisions and so the amount of ammonia decomposed would be more dependent upon the number of molecules irradiated than the active residence time.

The observed improvement in the overall conversion to hydrazine or  $X_{\text{N}_2\text{H}_4}$  is the result of two factors; one is the increase in the fraction of ammonia decomposed and the other is the reduction in residence time. The latter will ensure that more of the decomposed ammonia will be converted to hydrazine. It follows that even if no more ammonia is decomposed during scanning, then the reduction in the residence time alone will suffice to increase  $X_{\text{N}_2\text{H}_4}$ . However, since in most cases more ammonia did decompose as a result of beam scanning, the effect of scanning frequency on  $X_{\text{N}_2\text{H}_4}$  was more pronounced than on  $X_{\text{NH}_3}$  (Figures 4.21 - 26).

### 5.3.3. Comparison of reactor performance with and without beam scanning

It has been shown earlier that increasing the scanning frequency will reduce the average activation residence time,  $\bar{\tau}$ . It follows that if one eliminates the effect of reactant by-passing, i.e. base performance on the fraction of ammonia actually subjected to the discharge, then this will be almost identical to increasing the gas

flowrate at no scanning. In both cases more ammonia is irradiated per unit time but at the expense of a reducing residence time. The only difference between the two techniques is that, with scanning the concentration of hydrazine in the gaseous mixture leaving the reactor will be greater because a substantially smaller ammonia throughput is required to give the necessary activation time. Therefore if we have a situation where the same amount of ammonia is subject to the discharge, either by scanning or increasing flowrate, then we should expect the amount of hydrazine produced and ammonia decomposed per unit electrical energy to be the same in both cases. If this is so, then it would be possible to predict the reactor performance for simultaneous changes in both the scanning frequency and ammonia flowrate.

In order to justify the validity of this argument, the energy yield of hydrazine ( $Y_{N_2H_4}$ ) together with the amount of ammonia decomposed/kWh ( $Y_{NH_3}$ ) are plotted, as shown in Figures 5.5 and 5.6, against the amount of ammonia subjected or irradiated by the discharge ( $M_s$ ). The data at a discharge current of 10 mA were used but all those runs which involved multiple scans were omitted. The energy yields were based on overall power consumption rather than the power dissipated in the positive column because the latter could not be assessed accurately during scanning. The amount of ammonia irradiated was taken as the product of the mass flowrate and the fraction of the reactor cross-section which is scanned by the discharge, that is,

$$M_s = M_f \times F_s \quad \dots\dots\dots(5.14)$$

where,

$$M_s = \text{gms } NH_3 \text{ irradiated/hr}$$

FIGURE 5.5

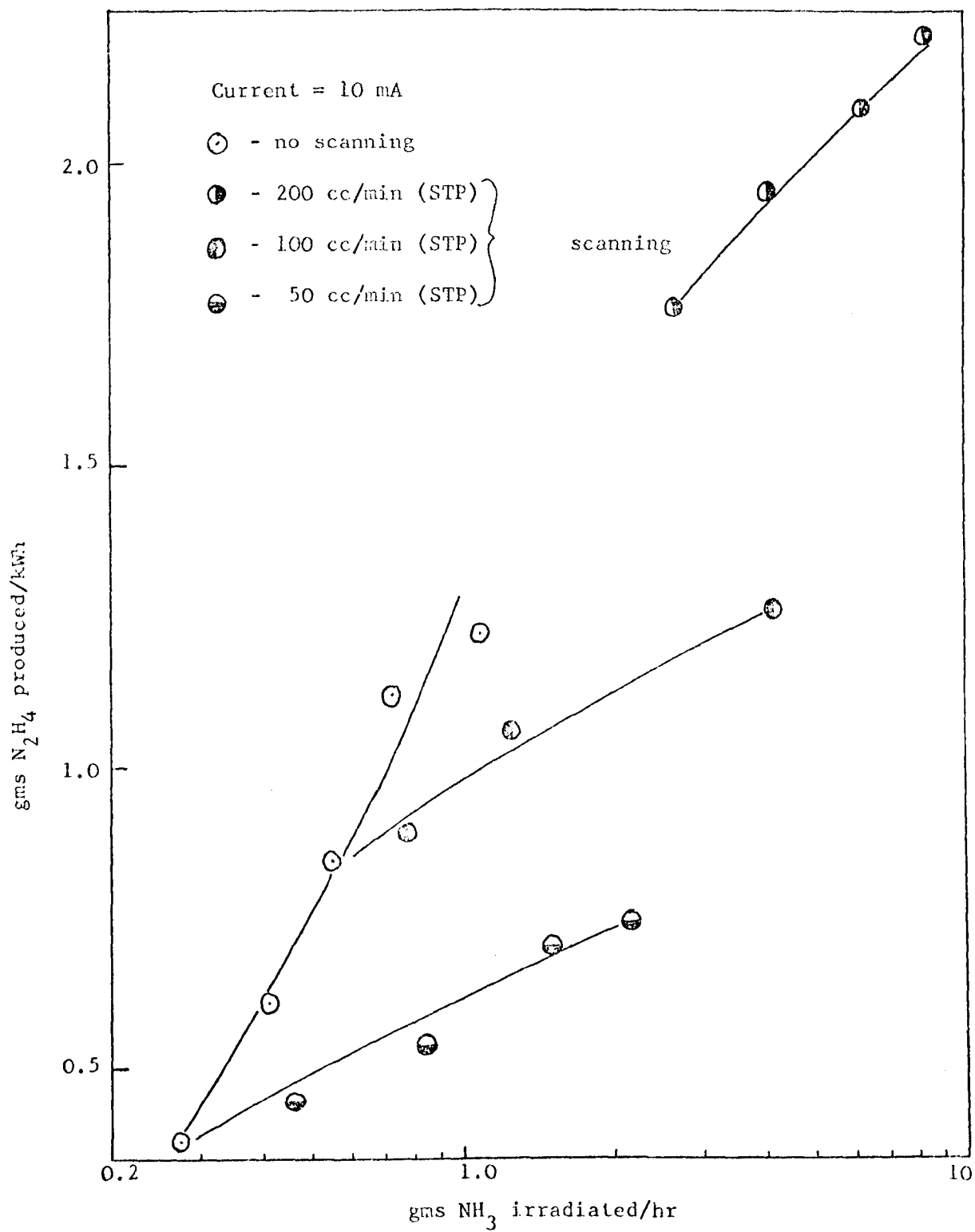
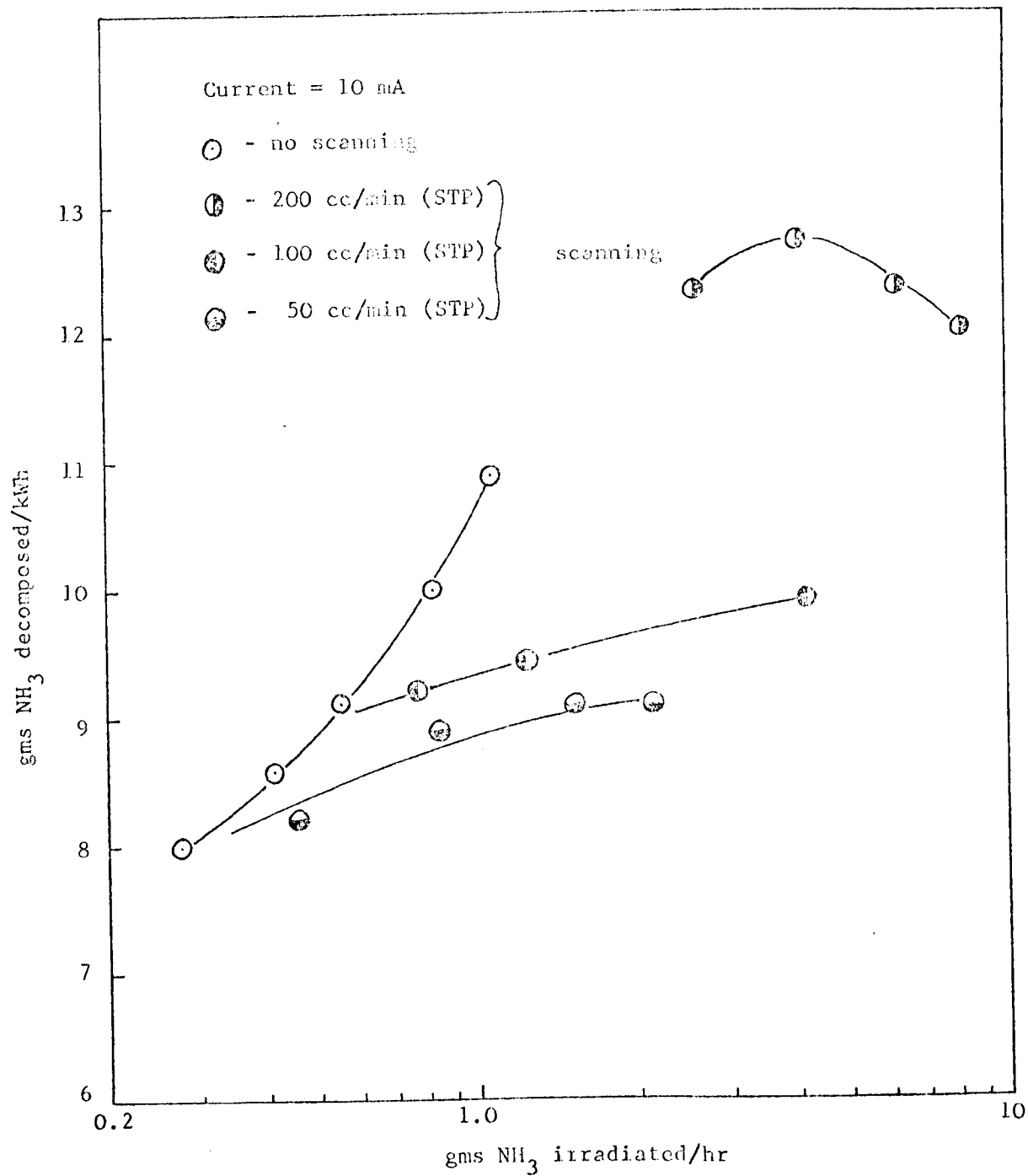


FIGURE 5.6



$M_f$  = mass flowrate, gms/hr

$F_s$  = fraction of reactor cross-section scanned by the  
discharge

$$= N(t_1 + t_2) = N\left(t_1 + \frac{W}{2\pi RN}\right) \dots\dots\dots(5.13)$$

Figures 5.5 and 5.6 indicate that at a particular value of  $M_s$  both  $Y_{N_2H_4}$  and  $Y_{NH_3}$  appear to be higher for the case of no scanning. This implies that it is more beneficial to increase the amount of ammonia irradiated by virtue of higher mass flowrate than by fixing the flowrate and increasing the scanning frequency. Now, if we assume that the physics of the discharge, and in particular the positive column, is not seriously affected by beam scanning then it is not unreasonable to expect this apparent discrepancy to be a direct result of some invalid assumptions which were made in the evaluation of  $F_s$ .

The first of these assumptions was the absence of turbulence in the reactor. This was justified by the low Reynolds numbers ( $< 10$ ) which suggested a plug-flow regime. Further substantiation was obtained by conducting a simple experiment in which a stream of air was injected into the ammonia flow from a fine nozzle (I.D. = 1.5 mm) positioned on the lower endplate of the reactor. The pressure of the air reservoir was kept just above the operating pressure of 10 torr, thus ensuring a steady and slow stream with the least pressure disturbances in the reactor. It was observed that when the discharge in ammonia was struck and made to rotate, it was only when the beam was vertically above the nozzle that there was a significant change in the colour of the glow. This observation was considered as a positive proof for the absence of turbulence in the reactor.

The evaluation of  $F_g$  also assumed no changes in the physical size of the glow as a result of beam scanning. If a contraction had taken place then this would have resulted in lower values of  $F_g$  than those predicted by equation (5.13) and consequently the amount of ammonia irradiated would have been lower than those given by equation (5.14). Contraction of the visible glow would have also had an adverse effect on the energy yield of hydrazine as a result of higher power densities.

In order to test whether this factor was contributing to the observed deviation from the expected reactor performance (Figures 5.5 and 5.6), a few experimental runs were carried out at low scanning frequencies ( $\leq 40 \text{ min}^{-1}$ ). At this speed it was possible to identify visually the absence of such contraction. These runs were expected to give energy yields of hydrazine consistent with those predicted from Figure 5.5 for the case of no scanning and at the same values of  $M_s$ . Ammonia at a very slow rate of 10 cc/min (STP) was used in order to give high values of  $F_g$  at these low scanning frequencies.

The results from these runs are given in Table 5.3 and it is evident that the observed yields are an order of magnitude lower than those predicted from Figure 5.5. These observations clearly justify the assumption that scanning does not alter the physical dimensions of the visible glow. It follows that the discrepancies in Figures 5.5 and 5.6 are probably a consequence of some other reason.

The third and the most significant assumption made in the evaluation of  $F_g$  was that the plasma was made up of a single primary reaction zone which occupied the same volume as the visible glow. If

TABLE 5.3

Ammonia flowrate = 10 cc/min (STP)  
 = 0.429 gms/hr  
 Optimum scanning frequency = 40 min<sup>-1</sup>  
 Discharge current = 10 mA  
 Discharge voltage = 630 volts

| Scanning<br>frequency<br>min <sup>-1</sup> | F <sub>s</sub><br>from equ <sup>n</sup> 5.13 | M <sub>s</sub><br>gms/hr | Observed Y <sub>N<sub>2</sub>H<sub>4</sub></sub><br>gms/kWh | Expected Y <sub>N<sub>2</sub>H<sub>4</sub></sub><br>from Fig. 5.5 |
|--------------------------------------------|----------------------------------------------|--------------------------|-------------------------------------------------------------|-------------------------------------------------------------------|
| 0                                          | 0.1275                                       | 0.0547                   | 0.0299                                                      | -                                                                 |
| 25                                         | 0.67                                         | 0.288                    | 0.0324                                                      | 0.41                                                              |
| 40                                         | 1.00                                         | 0.429                    | 0.0342                                                      | 0.64                                                              |

this premise is not true and in fact it is possible for the primary reaction zone to extend laterally to regions far beyond the visible zone due to unhindered electron diffusion, then the evaluated values of  $F_s$  are in error.

The existence of a zone beyond the visible region was established using the electrical probe described earlier (Section 4.4.4). The tip of the probe was positioned parallel and a few millimeters from the surface of the anode. By rotating the discharge beam through  $360^\circ$ , the probe was made to experience different plasma regions and thus produced a series of voltage pulses which were displayed on the oscilloscope and later photographed (Figure 5.7). Each pulse in Figure 5.7 is made of:-

- (i) a flat portion or zero probe reading corresponding to regions where no plasma exists.
- (ii) the remainder of the pulse corresponds to regions where the probe is experiencing the existence of the plasma and thus produces voltage signals corresponding to the position of the probe in the plasma.

If the pulse ON and OFF-times are  $t_1$  and  $t_2$  respectively then the ratio of the effective plasma volume to the overall effective reactor volume will be  $t_1/(t_1 + t_2)$ . Figure 5.7 was used to evaluate  $t_1/(t_1 + t_2)$  at discharge currents of 10, 5, and 2.6 mA and found to be 0.625, 0.69, and 0.72 respectively. These figures indicate that the majority of the plasma appears to be invisible to the eye and it is for this reason that no account has been taken of its existence and

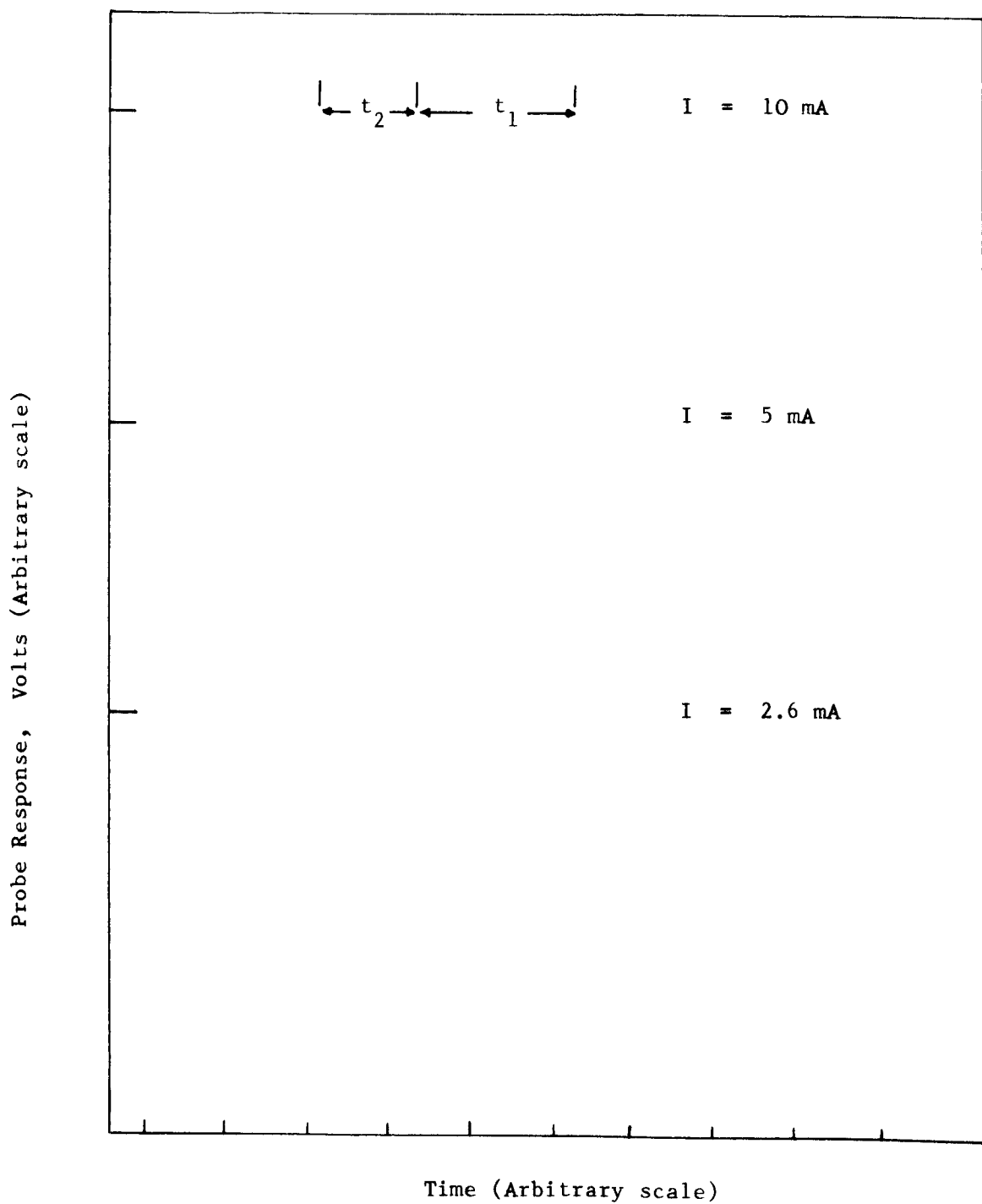
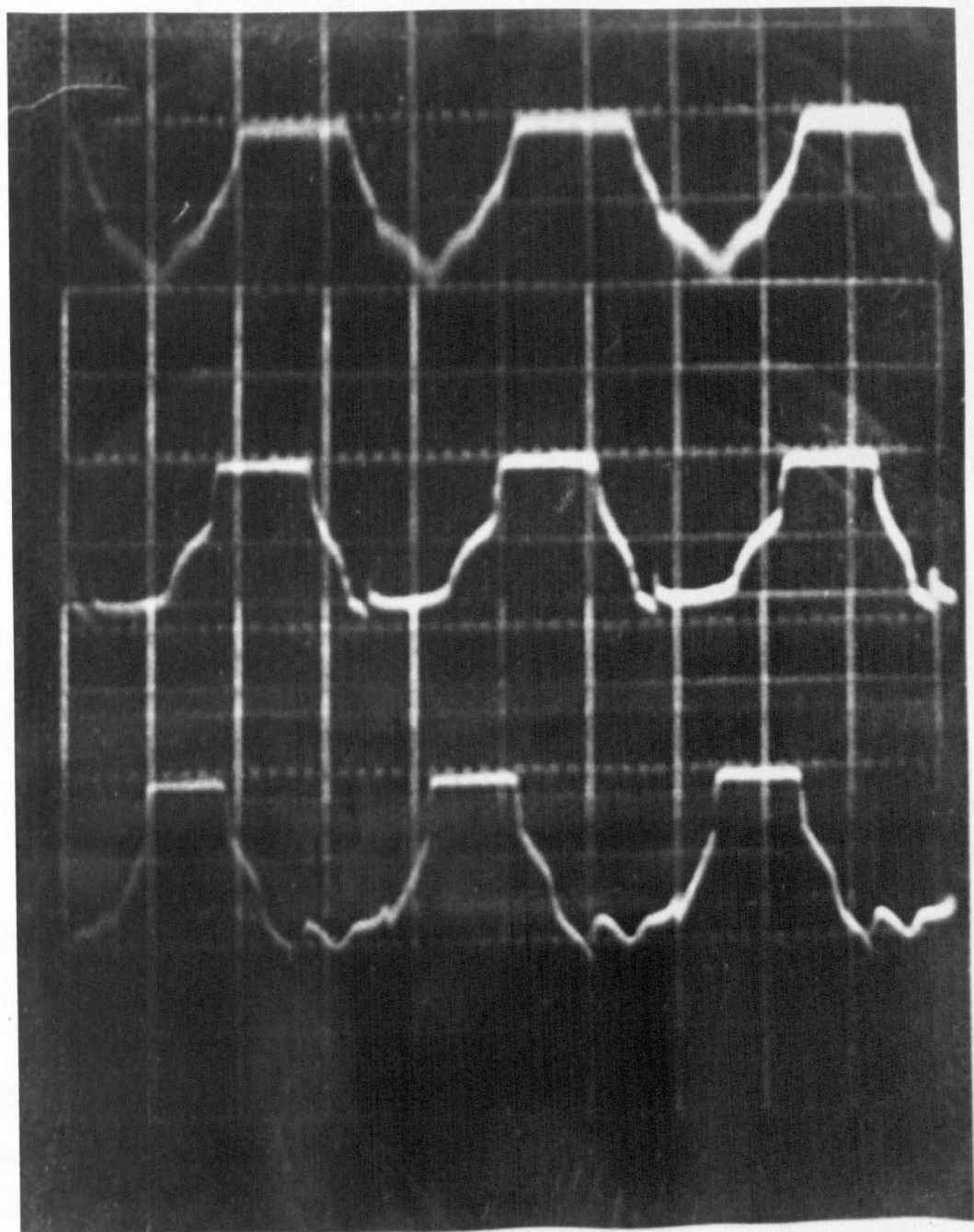


Figure 5.7 Probe Response to Positions in Plasma

(Ammonia at a pressure of 10 torr)



Probe Response, Volts (Arbitrary scale)

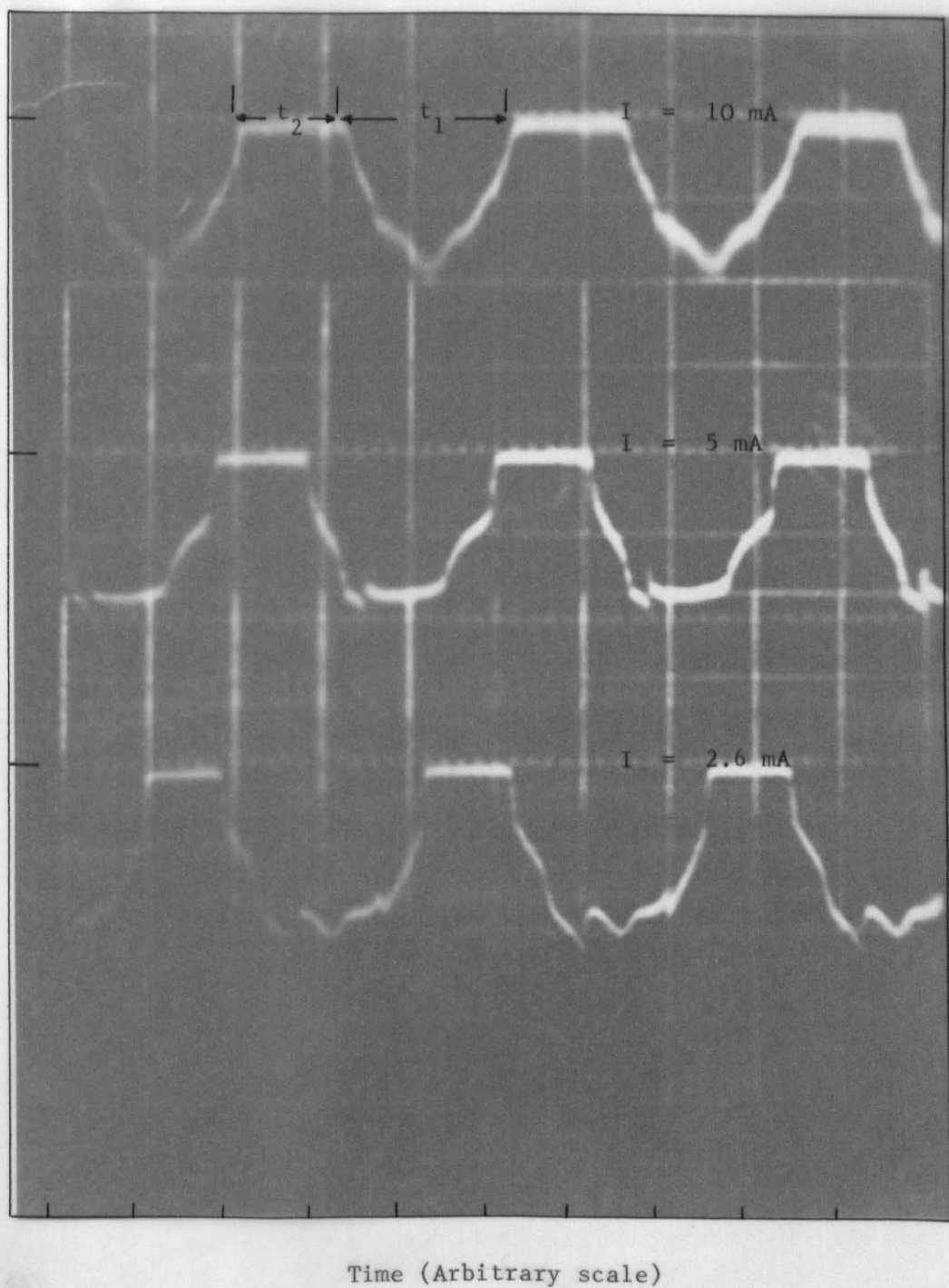


Figure 5.7 Probe Response to Positions in Plasma

(Ammonia at a pressure of 10 torr)

effectiveness in any published literature. Here, these regions are believed to be responsible for some chemical activation and are consequently called the Active Dark Zones (ADZ). It follows from what has been said that any correlation which does not take into consideration the ADZ will inevitably lead to discrepancies of the kind depicted in Figures 5.5 and 5.6.

Accepting the new plasma volume (visible + ADZ) then the optimum scanning frequency, necessary to ensure irradiation of all the ammonia molecules at least once, will be substantially smaller than the previous case. These scanning frequencies have been evaluated at the operating conditions of interest and are shown below:-

|                                          | 10 mA                                             | 5 mA           | 2.6 mA         |
|------------------------------------------|---------------------------------------------------|----------------|----------------|
| NH <sub>3</sub> flowrate<br>cc/min (STP) | Optimum scanning frequency<br>N <sup>o</sup> /min | N <sup>o</sup> | N <sup>o</sup> |
| 200                                      | 335                                               | 280            | 253            |
| 100                                      | 168                                               | 140            | 127            |
| 50                                       | 84                                                | 70             | 64             |

It is apparent from the above table that most of the experimental data given in Appendix 4 correspond to cases of multiple scanning, that is the case where every ammonia molecule is subjected to the discharge more than once. In this case, although the cumulative residence time can be evaluated, the fact that the amount of ammonia decomposed and hydrazine formed are not additive with the number of scans, a comparison between the data with and without beam scanning will

not be possible. In order, therefore, to establish a correlation between  $Y_{N_2H_4}$ ,  $Y_{NH_3}$  and  $M_s$  when the ADZ are taken into consideration, it was found necessary to predict some values of  $Y_{N_2H_4}$  and  $\chi_{NH_3}$ , at scanning frequencies corresponding to the case of partial irradiation, from Figures 4.30 - 32 and Figures 4.21 - 23 respectively. For every scanning frequency  $M_s$  was calculated and  $Y_{N_2H_4}$  and  $Y_{NH_3}$  were then replotted against  $M_s$  as shown in Figures 5.8 and 5.9. It is evident from Figures 5.8 and 5.9 that a much better correlation is obtained thus substantiating the hypothesis regarding the effectiveness of the ADZ as regions of chemical activation. Figures 5.8 and 5.9 suggest that the effect of increasing  $M_s$  by an increase in the scanning frequency is indistinguishable from the case where the change is brought about by an increase in the ammonia flowrate.

#### 5.3.4. Correlation of Experimental Data with and Without Beam Scanning

Unfortunately a rigorous kinetic analysis of the data has not been possible because all the factors necessary for this line of attack (such as the concentration of different species and their energy distributions and the rates and cross-sections of the processes involved) were totally lacking. Furthermore, the uncertainty regarding the concentration of electrons and other species in the dark areas of the plasma made this kind of analysis even more difficult. For these reasons the influence of the operating variables on the reactor performance was found to be best presented empirically in the form of a grouped parameter.

Grouped parameters have been widely used in gas discharge work and the most common of these is VASILEV'S<sup>(101)</sup> specific energy or the

FIGURE 5.8

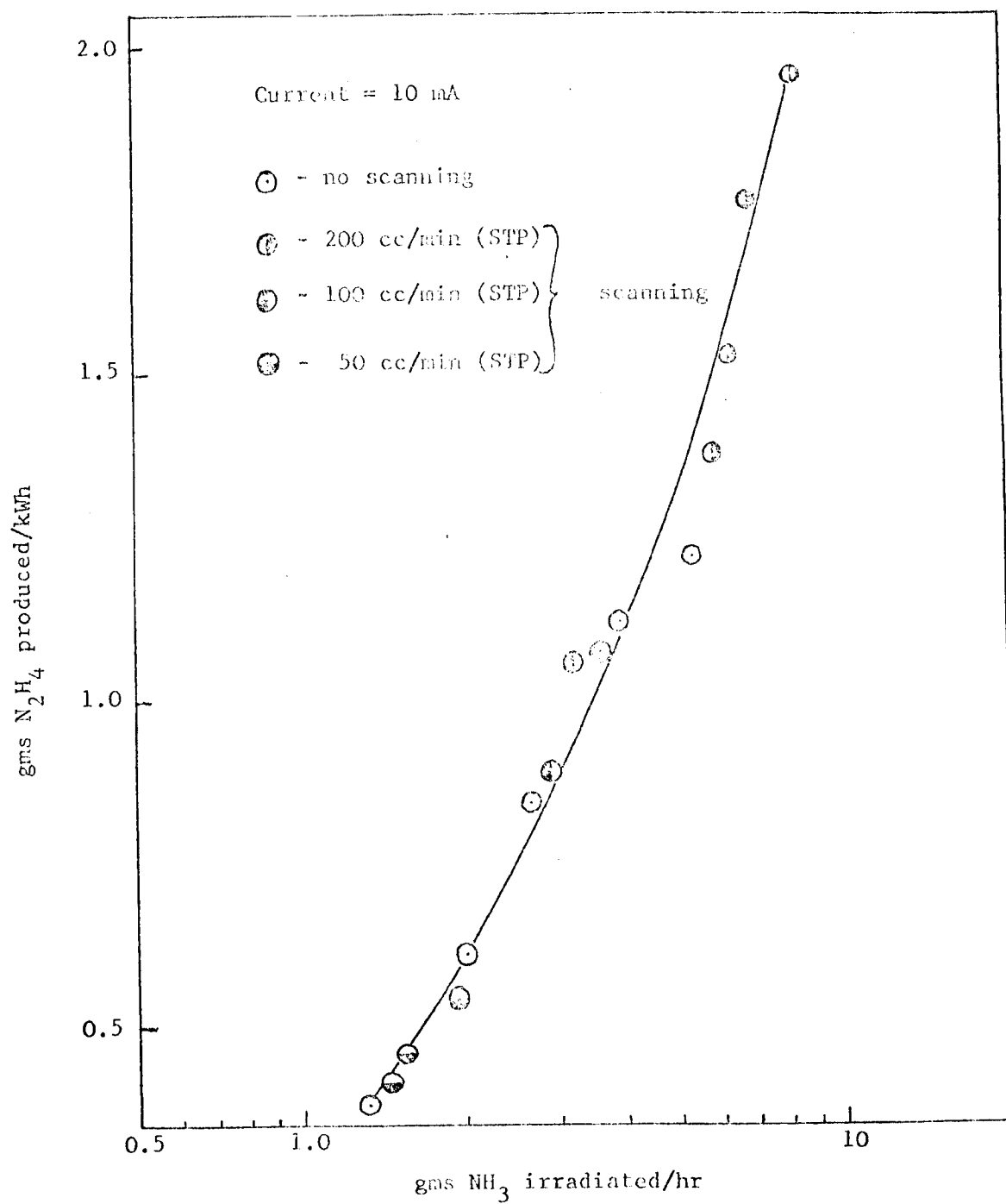
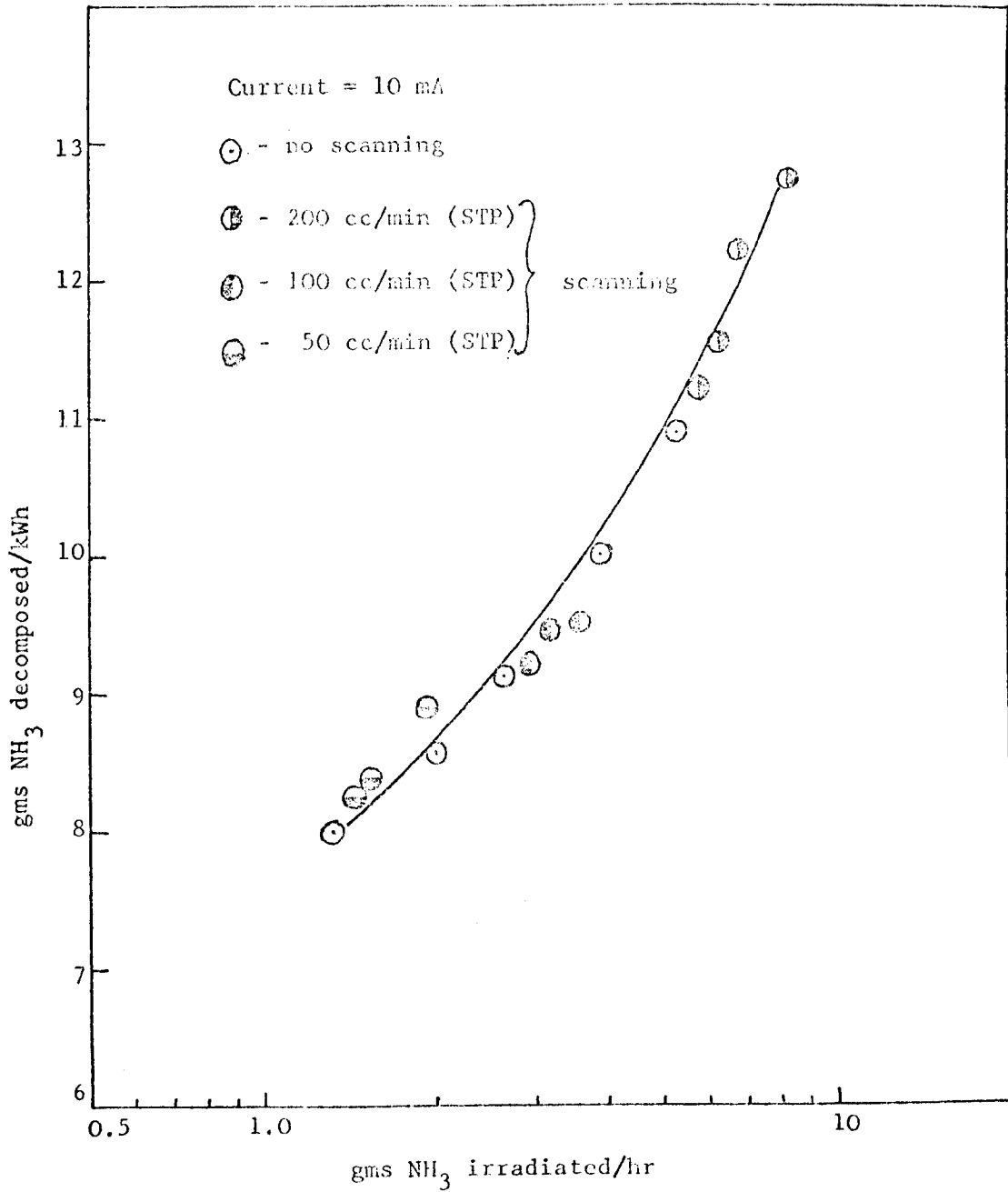


FIGURE 5.9



ratio of power input to the gas flowrate ( $W/F$ ). The theoretical justification for using  $W/F$  has been recently dealt with by DECKERS<sup>(102)</sup> but in most of its application the limitations ~~adequate~~ of the theory have been grossly overlooked. For instance, theoretically  $W/F$  should only be applied under conditions of constant electric field and electron current density, such as the case in the positive column of a DC discharge, but in almost every application<sup>(18,21,22,89)</sup> the overall power input has been used which clearly implies the inclusion of the very much higher field in the negative glow. This will not only give a higher hypothetical average field but is also quite unnecessary in cases (ammonia/hydrazine) where the negative glow is known not to contribute to product formation.

In cases where the reaction pressure is also a variable, modified versions of VASILEV'S specific energy have been adopted such as  $W/P$  used by WALLER<sup>(18)</sup> and SERGIO<sup>(89)</sup> and  $WP/F$  used by SKOROKHODOV et al<sup>(103)</sup>. CARBAUGH<sup>(104)</sup> on the other hand successfully correlated his data for ammonia decomposition using the product of discharge current and residence time ( $I\tau$ ). The latter is a simplified version of VASILEV'S parameter where the reciprocal of the gas flowrate ( $1/F$ ) is replaced by the residence time ( $\tau$ ) and the voltage is eliminated by replacing the power ( $W$ ) by the discharge current ( $I$ ). This treatment will only be valid if the influence of discharge current on reactor performance is more significant than that of the voltage. This has been shown to be so for the present study (Section 5.3.1) and for this reason and due to the failure of  $Wp/F$  (where  $Wp$  is the power in the positive column) to correlate the data satisfactorily, the product ( $I\tau$ ) was also used to correlate the present data. Here  $\tau$  is replaced by the mean residence time,  $\bar{\tau}$ , and since the latter is related to the gas flowrate as well as

the scanning frequency, the product ( $I\bar{\tau}$ ) will include all the operating variables studied.

In order to demonstrate the significance of  $I\bar{\tau}$  as a correlating parameter, the overall ammonia conversion,  $X_j$ , is plotted as shown in Figure 5.10 against  $I\bar{\tau}$  using all the data except those which involved multiple scans.  $\bar{\tau}$  is calculated from equation (5.9) using the plasma profiles given by the probe.  $X_j$  is the conversion based on the fraction of reactor cross-section scanned by the discharge and is given by,

$$X_j = \frac{X_{NH_3}}{F_s} \quad \text{.....(5.15)}$$

It is evident from Figure 5.10 that  $I\bar{\tau}$  correlates the data satisfactorily and it appears that higher conversions are obtained at higher  $I\bar{\tau}$ . It therefore follows that in order to keep  $X_j$  constant when the discharge beam is made to rotate, it is necessary to increase the discharge current by such an amount so as to compensate for the reduction in the mean residence time and by doing so keep the value of  $I\bar{\tau}$  at a constant level.

As far as hydrazine formation is concerned, the fact that  $I\bar{\tau}$  is shown to determine the extent of the primary decomposition reaction suggests that the energy yield of hydrazine, (Y), the molar conversion to hydrazine ( $\bar{X}_{N_2H_4}$ ) and the overall conversion to hydrazine ( $X_1$ ) should also be functions of the parameter  $I\bar{\tau}$ . Again  $X_1$  is the conversion based on fraction of reactor cross-section scanned by the discharge beam and is given by.

$$X_1 = \frac{X_{N_2H_4}}{F_s} \quad \text{.....(5.16)}$$

FIGURE 5.10

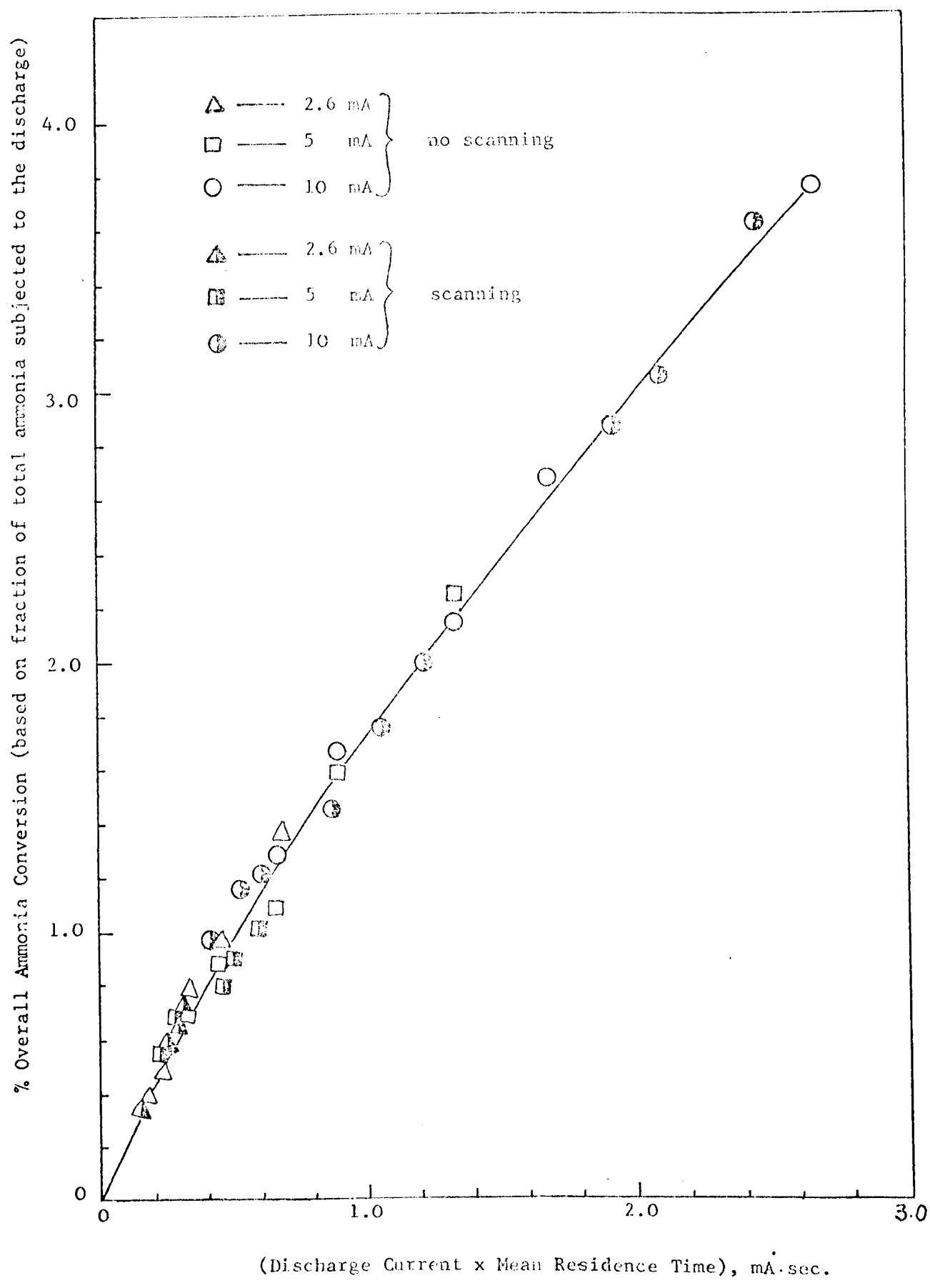


FIGURE 5.11

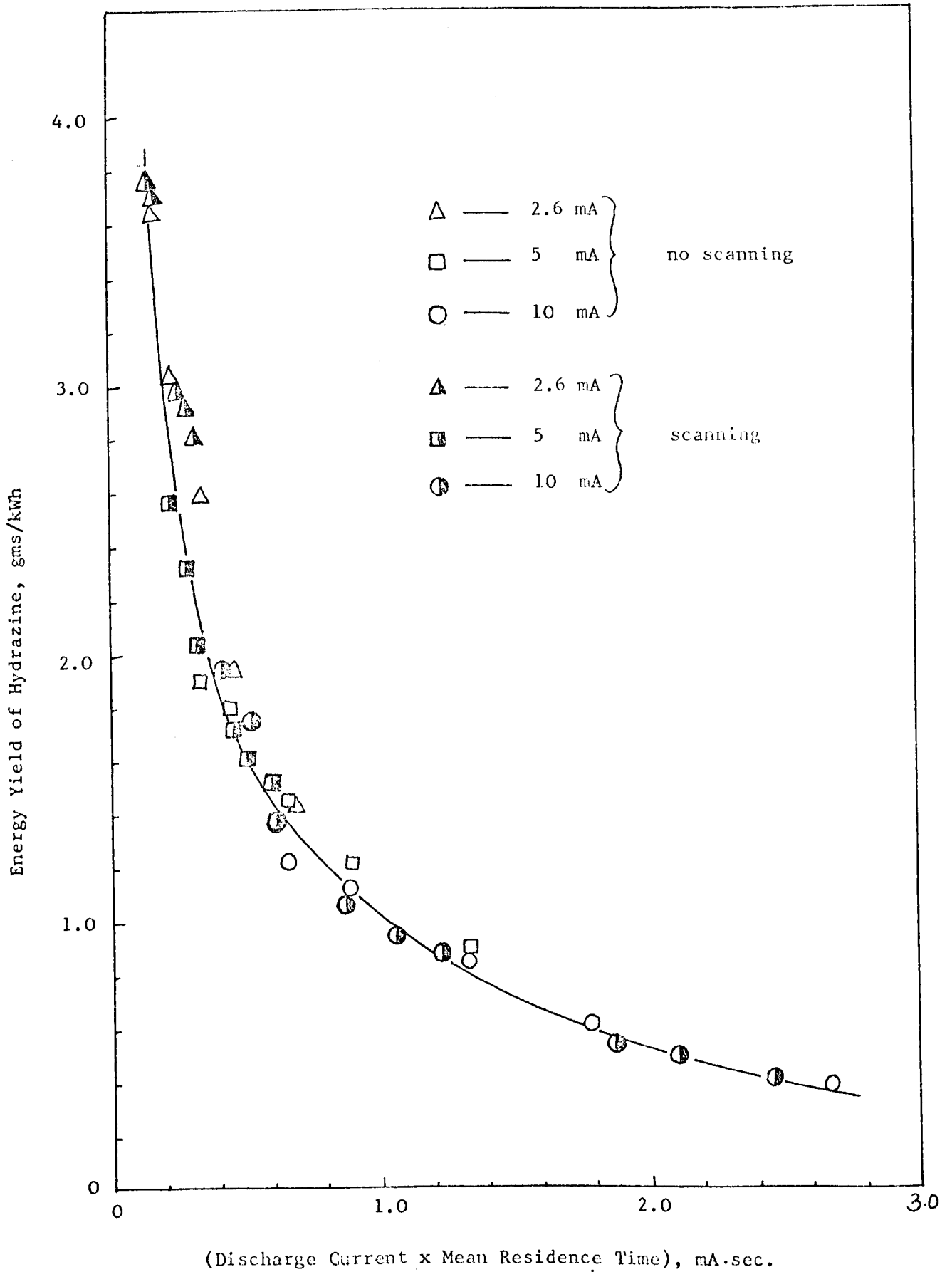


FIGURE 5.12

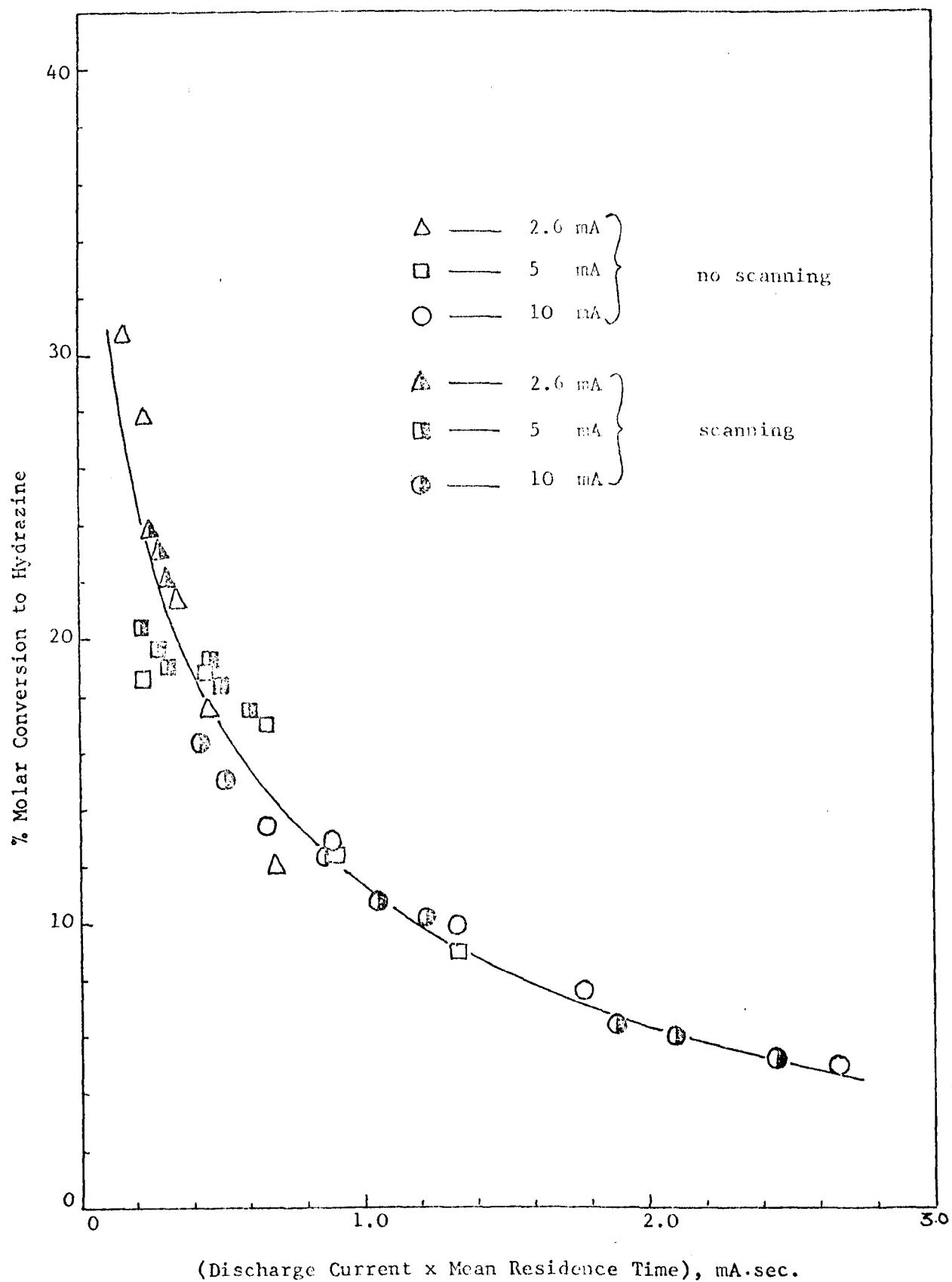
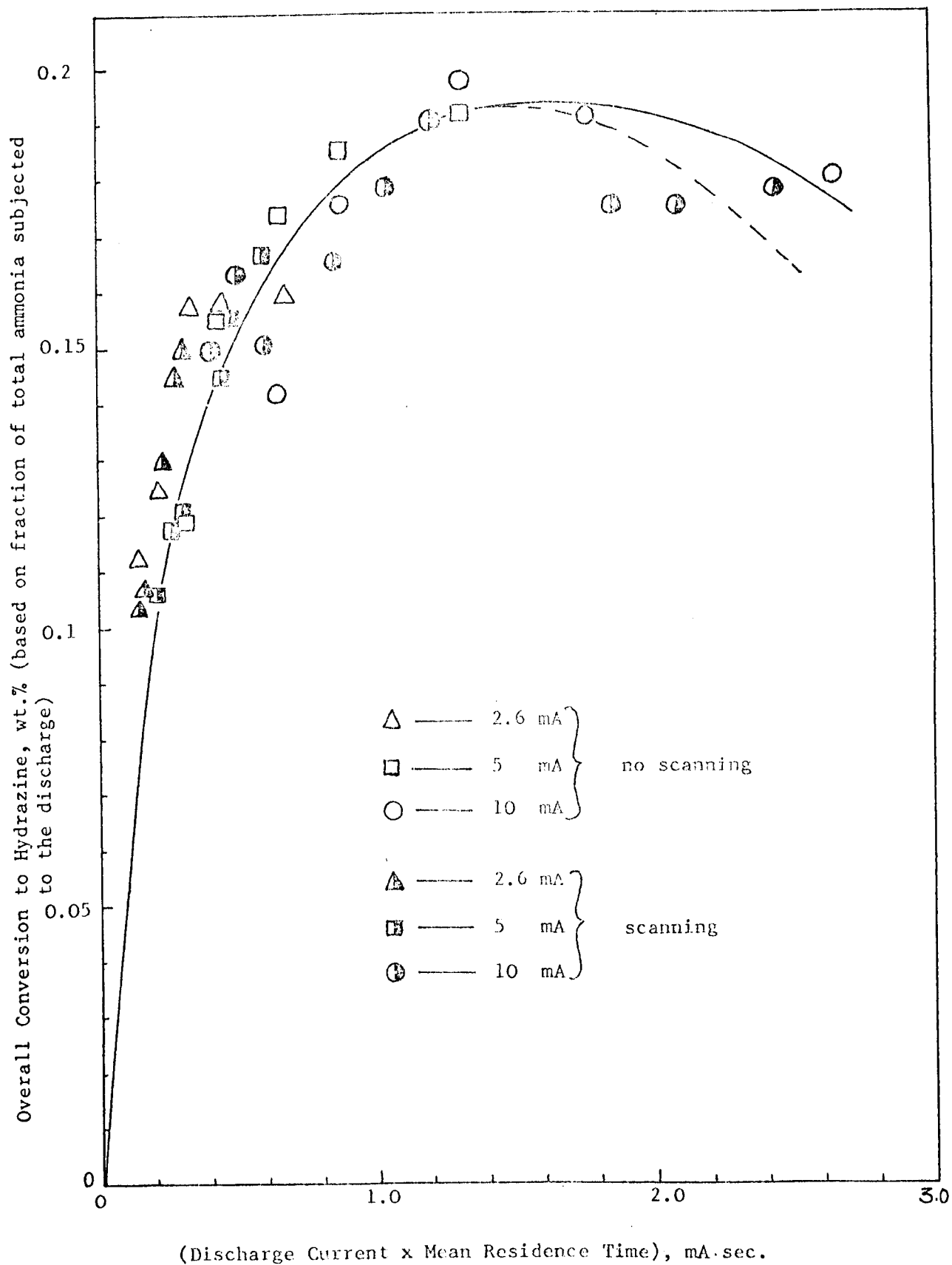


FIGURE 5.13



The parameters  $Y$ ,  $\bar{X}_{N_2H_4}$ , and  $X_1$  are plotted against  $I\bar{t}$  as depicted in Figures 5.11 - 13 and it is evident that apart from a slight scatter in Figure 5.13, the parameter  $I\bar{t}$  seems to correlate the data reasonably well. Figures 5.11 - 13 indicate that both  $Y$  and  $\bar{X}_{N_2H_4}$  bear an exponential relationship with  $I\bar{t}$  whilst in the case of  $X_1$  the curve is typical of a product being formed and then degraded reaching a maximum conversion of 0.195 wt.% at an  $I\bar{t}$  value of 1.6 mA.sec. The corresponding values of the energy yield and molar conversions are about 0.7 gms/kWh and 6.8% respectively but higher values are possible at lower values of  $I\bar{t}$ . The maximum conversion in Figure 5.13 is by no means the highest obtainable with this device; indeed conversions of up to 0.26% are possible (Figure 4.26) but these were not included in the correlation because multiple scans were involved. It therefore follows that Figures 5.10 - 5.13 must not be considered as representative of the efficiency of the beam scanning device. They merely show  $I\bar{t}$  as a significant correlating parameter for that part of the experimental data which fell in the category of partial scanning.

#### 5.4. Decomposition of Ammonia in the Pulsed DC Discharge

##### 5.4.1. Effect of Pulse OFF-Time and Ammonia Flowrate

The observed energy yields and overall conversion to hydrazine (Figures 4.35,38) agree qualitatively with those reported by SAVAGE<sup>(21)</sup> and BROWN et al<sup>(27)</sup> but quantitative comparison is not possible due to the wide differences in the reactor designs and to differences in the range of operating variables studied. Neither of these groups of workers considered the degree of ammonia by-passing the discharge zone which would also contribute to the lack of quantitative agreement.

The higher energy yields obtainable from a pulsed discharge have been usually considered to be a result of two factors:-

- (a) a much shorter activation residence time,
- (b) a substantially higher reduced electric field resulting in higher electron energies.

In this study the reduced electric field at the onset of the discharge is found to vary from  $37.4 \text{ V.cm}^{-1}.\text{torr}^{-1}$  for an OFF-time of 0.1 msec to  $62 \text{ V.cm}^{-1}.\text{torr}^{-1}$  for an OFF-time of 10 msec. These values have been corrected for the combined cathode and anode falls of 475 volts estimated for the DC discharge. It follows from the extrapolation of Figure 5.1 that the corresponding mean electron energies are around 2.2 e.v. The fraction of electrons with energies greater than 4.5 e.v. is around 20% (Appendix 2). This may be compared with a maximum value of less than 1% for the continuous DC discharge. This comparison suggests that, regardless of whether the decomposition of ammonia is single or multiple collision controlled, the energy efficiency of the pulsed discharge must be far greater than that in the continuous case.

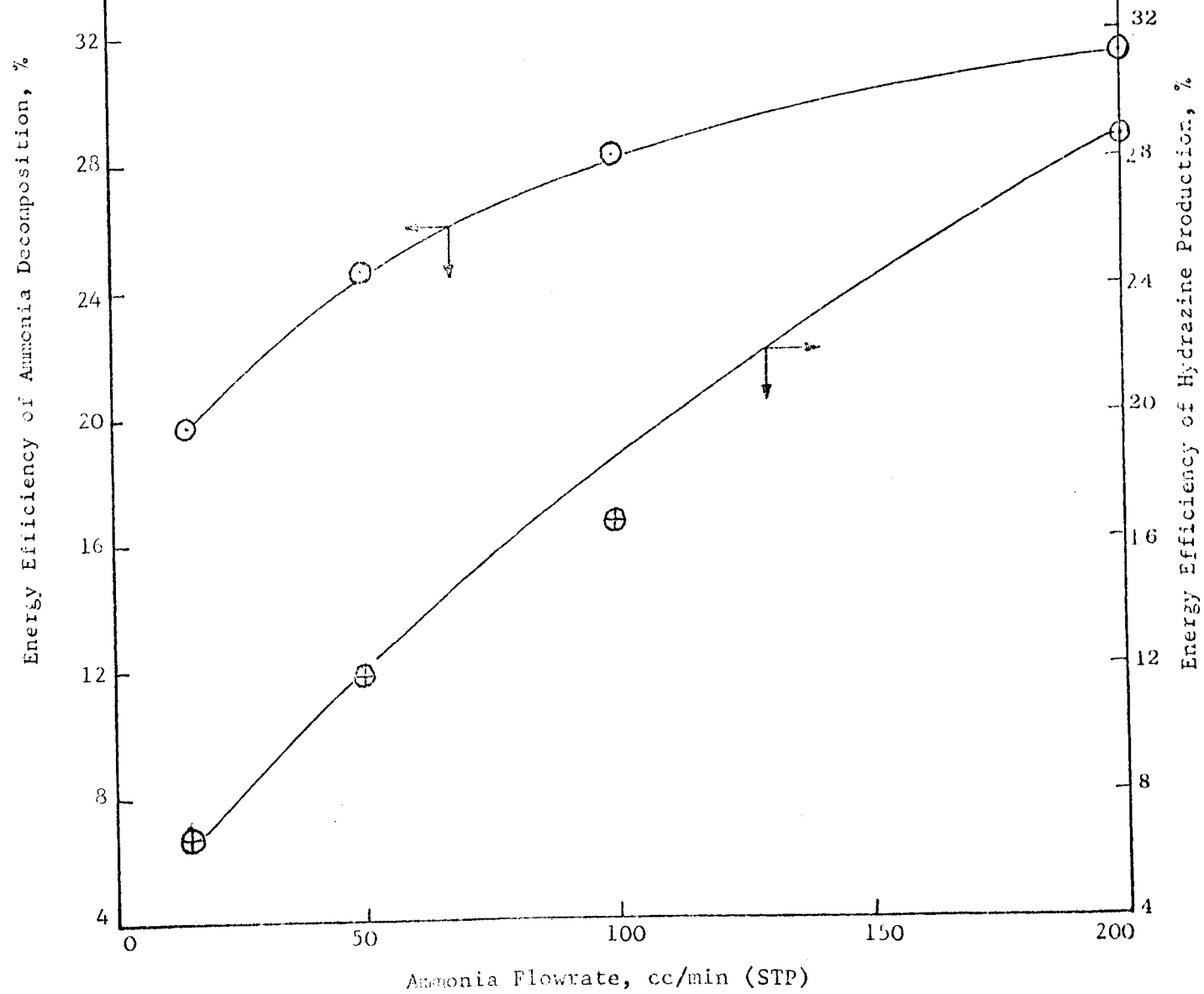
In order to verify this point, the energy efficiency of ammonia decomposition,  $\eta_{\text{NH}_3}$ , and hydrazine formation,  $\eta_{\text{N}_2\text{H}_4}$ , were calculated (Appendix 2) for the range of ammonia flowrate investigated and are shown in Figure 5.14. A comparison with Figure 5.2 (continuous DC) shows that although  $\eta_{\text{N}_2\text{H}_4}$  is greater for the pulsed discharge, no significant improvement in  $\eta_{\text{NH}_3}$  is observed. A likely factor which is believed to be responsible for this discrepancy between the expected and actual efficiencies of ammonia decomposition is the very short pulse duration used in this study. As mentioned earlier (Section 4.6.3(b)) the overall pulse ON-time was  $4.5 \mu\text{sec}$  but the majority of

FIGURE 5.14

pulse OFF-time = 2 msec.

pulse ON-time = 4.5  $\mu$ sec.

peak current = 150 mA



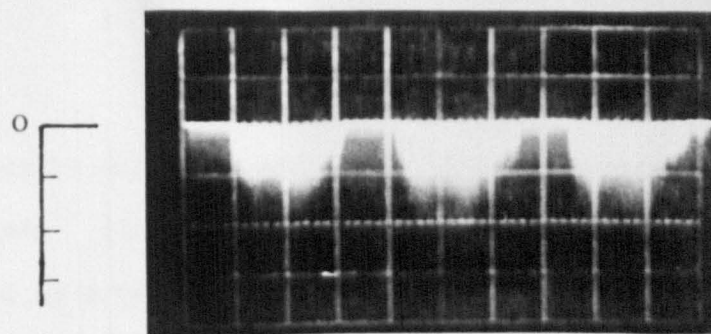
the current was found to decay over the first 0.5 sec of the pulse. It follows that if the decomposition reaction is multiple collision controlled then, because of the availability of such short a time, the probability of fully energising an ammonia molecule will be reduced. Consequently, those molecules which are only partially excited after the completion of the pulse will be deactivated by collision with other ground state molecules. It is this deactivation process which accounts for some energy loss and subsequently lower values of  $\eta_{\text{NH}_3}$ .

It follows from what has been said that despite the presence of more energetic electrons in the pulsed discharge, the fact that  $\eta_{\text{NH}_3}$  is unchanged seems to suggest that the apparent increase in  $\eta_{\text{N}_2\text{H}_4}$  over that for the continuous DC discharge is a result of less hydrazine degradation rather than the enhancement of the electric field as claimed by BROWN et al<sup>(27)</sup>.

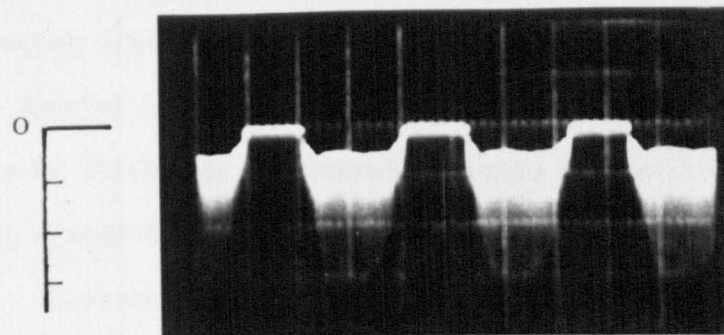
#### 5.4.2. Effect of Beam Scanning

The reason for the limited improvement in hydrazine formation as a result of beam scanning can be explained in the light of the proposed hypothesis regarding the effectiveness of the active dark zones of the plasma in promoting chemical reaction. Using a similar method to that employed in the continuous DC discharge, the effective plasma volume (visible + dark) was estimated to be 70.5% of the total effective reactor volume (Figure 5.15) at a pulse OFF-time of 2 msec and 67% of the total effective reactor volume at pulse OFF-times of 0.5, 0.2, and 0.1 msec. This implies that the optimum scanning

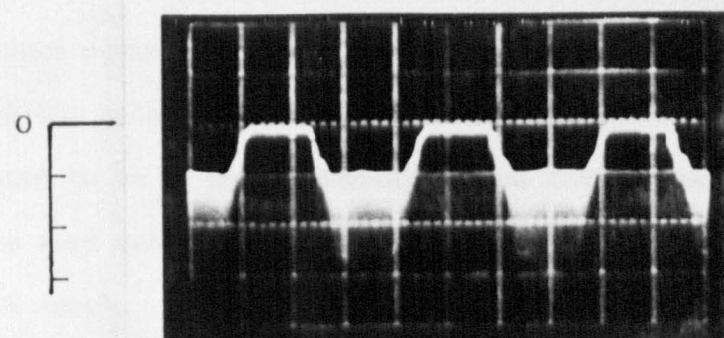
Probe Reading, Volts (Arbitrary scale)



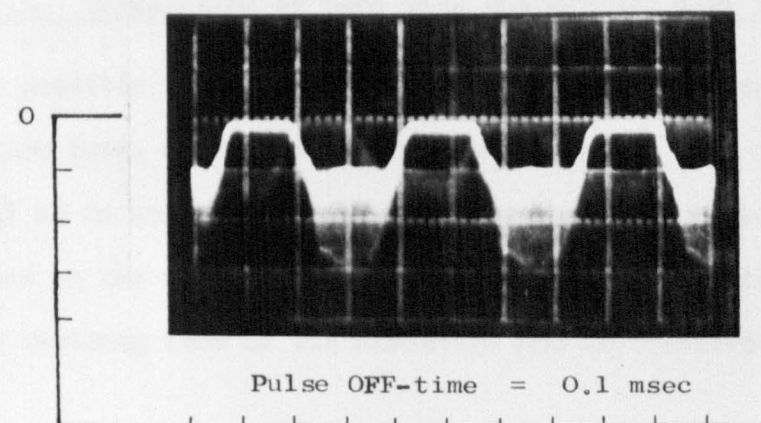
Pulse OFF-time = 2 msec



Pulse OFF-time = 0.5 msec



Pulse OFF-time = 0.2 msec



Pulse OFF-time = 0.1 msec

Time (Arbitrary scale)

Figure 5.15 Probe Responses to Positions in Plasma.

(Ammonia at a pressure of 10 torr  
peak discharge current = 150 mA).

frequencies are  $60 \text{ min}^{-1}$  and  $67.5 \text{ min}^{-1}$  respectively instead of the reported  $195 \text{ min}^{-1}$  (Section 4.6.3(d)), when only the visible glow was considered as a region of primary reactions. In other words, the majority of the data fell in the category of multiple scanning. Here, although the cumulative active residence time remains constant, the average activation residence time of a molecule per scan gets progressively shorter with increasing scanning frequency. Hence, for the continuous DC discharge the overall picture may well be analogous to a pulsating system having a relatively long pulse duration (order of few msec). Nevertheless, even with such long pulse duration, some advantages over a purely continuous discharge will be expected and hence the reason for the continual increase in hydrazine formation after the optimum scanning frequency has been exceeded (Figures 4.26,32). In the case of the pulsed discharge, however, these scanning frequencies are not expected to be of much advantage since the discharge is itself pulsating at a very much faster rate and with a very much shorter pulse duration ( $< 6 \mu\text{sec}$ ).

#### 5.4.3. Correlation of Data with and without Beam Scanning

One possible way of describing the effect of ammonia flowrate, pulse repetition rate, and scanning frequency (for the case of partial scanning) will be to use a parameter known as the pulse number,  $n^*$ . This is defined as the average number of pulses a molecule is subjected to during its residing time in the discharge and is therefore given by:-

$$n^* = \text{mean residence time} \times \text{pulse repetition rate}$$

or 
$$n^* = \bar{\tau} \times \frac{1}{\text{pulse OFF-time}} \quad \dots\dots\dots(5.17)$$

where  $\bar{\tau}$  is the mean residence time given by equation (5.9). Since  $\bar{\tau}$  takes into account the effect of both the flowrate and scanning frequency, then  $n^*$  will contain all the variables studied. Now, since  $n^*$  represents the number of irradiations per unit time, then it is not unreasonable to expect that higher values of  $n^*$  will inevitably increase the chances of hydrazine degradation whilst at the same time increase the probability of ammonia decomposition.

In order to verify this point of view, the parameters describing the performance of the reactor, namely  $Y$ ,  $\bar{X}_{N_2H_4}$ ,  $X_i$ , and  $X_j$ , are plotted against  $n^*$  as shown in Figures 5.16 - 19.  $X_i$  and  $X_j$  are conversions based on actual ammonia subjected to the discharge and are evaluated from equations (5.16) and (5.15) respectively. As expected, Figures 5.16 - 19 indicate that although higher values of  $n^*$  favour ammonia decomposition, both the energy yield and molar conversion to hydrazine are adversely affected. The effect on the overall conversion to hydrazine, however, is again analogous to that on a product first formed and then degraded by back reactions. The absence of a maximum in Figure 5.18 suggests that higher concentrations of hydrazine are still possible at higher pulse numbers. These findings are again in qualitative agreement with those of BROWN et al<sup>(27)</sup> who first introduced the use of the pulse number as a correlating parameter.

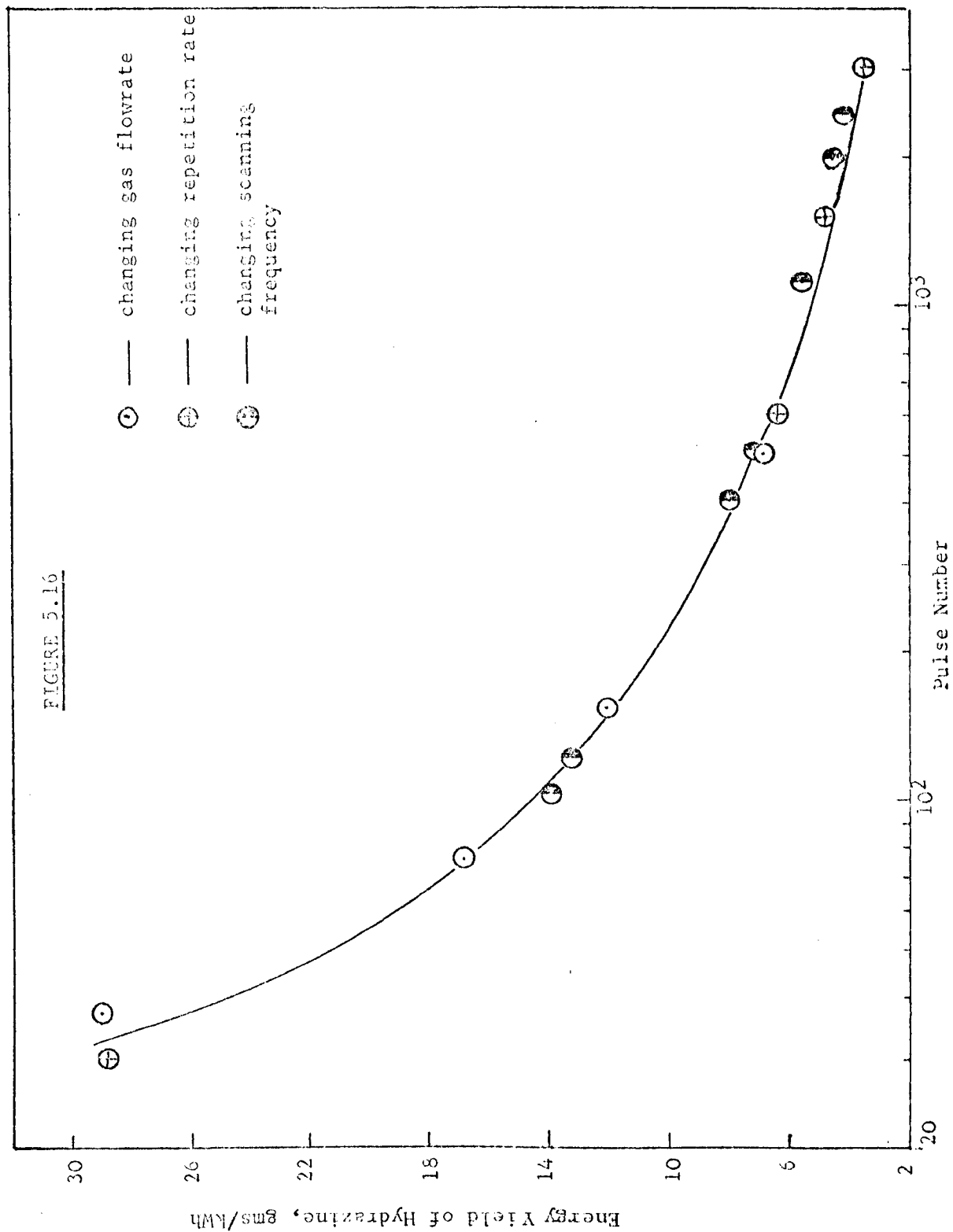


FIGURE 5.17

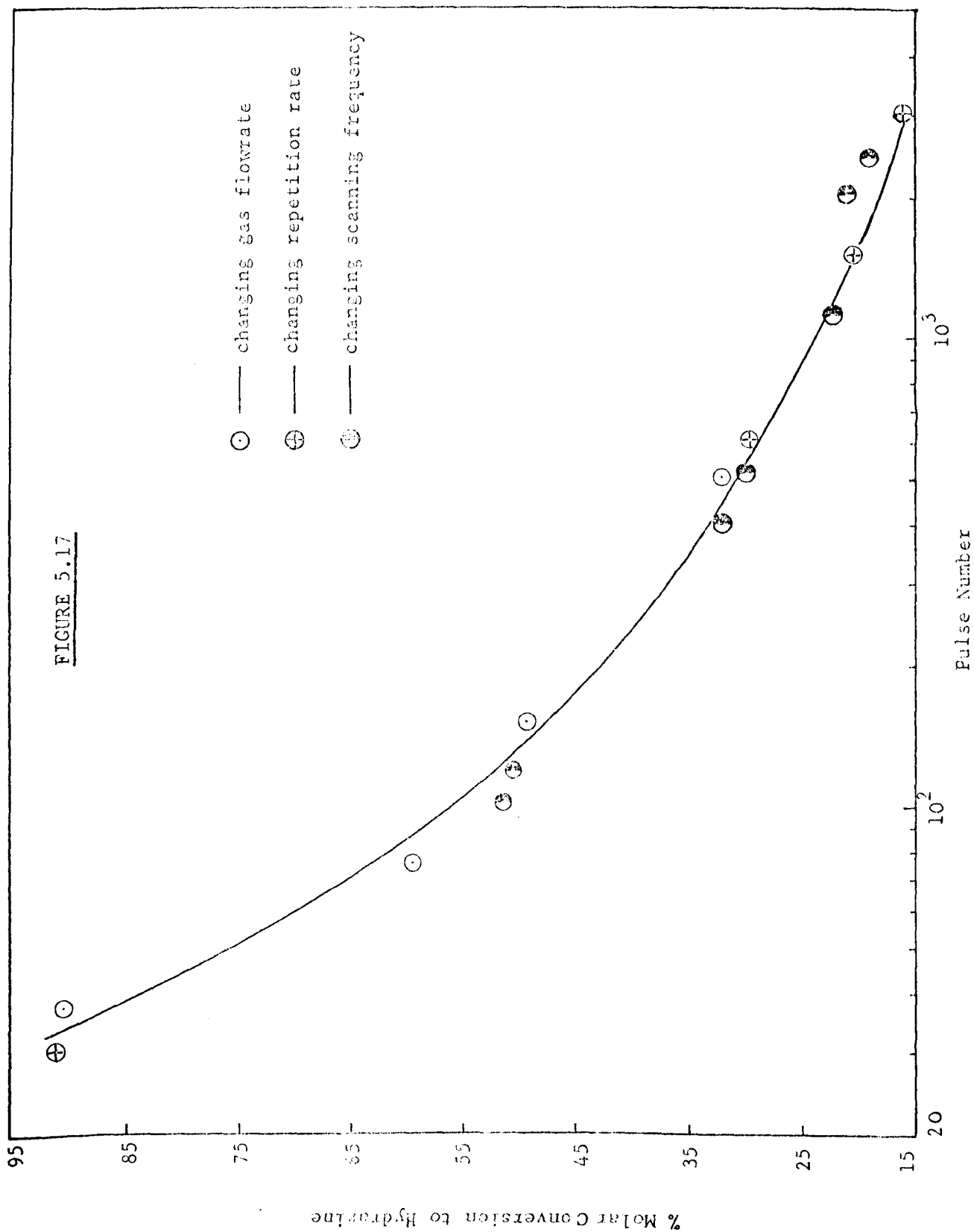
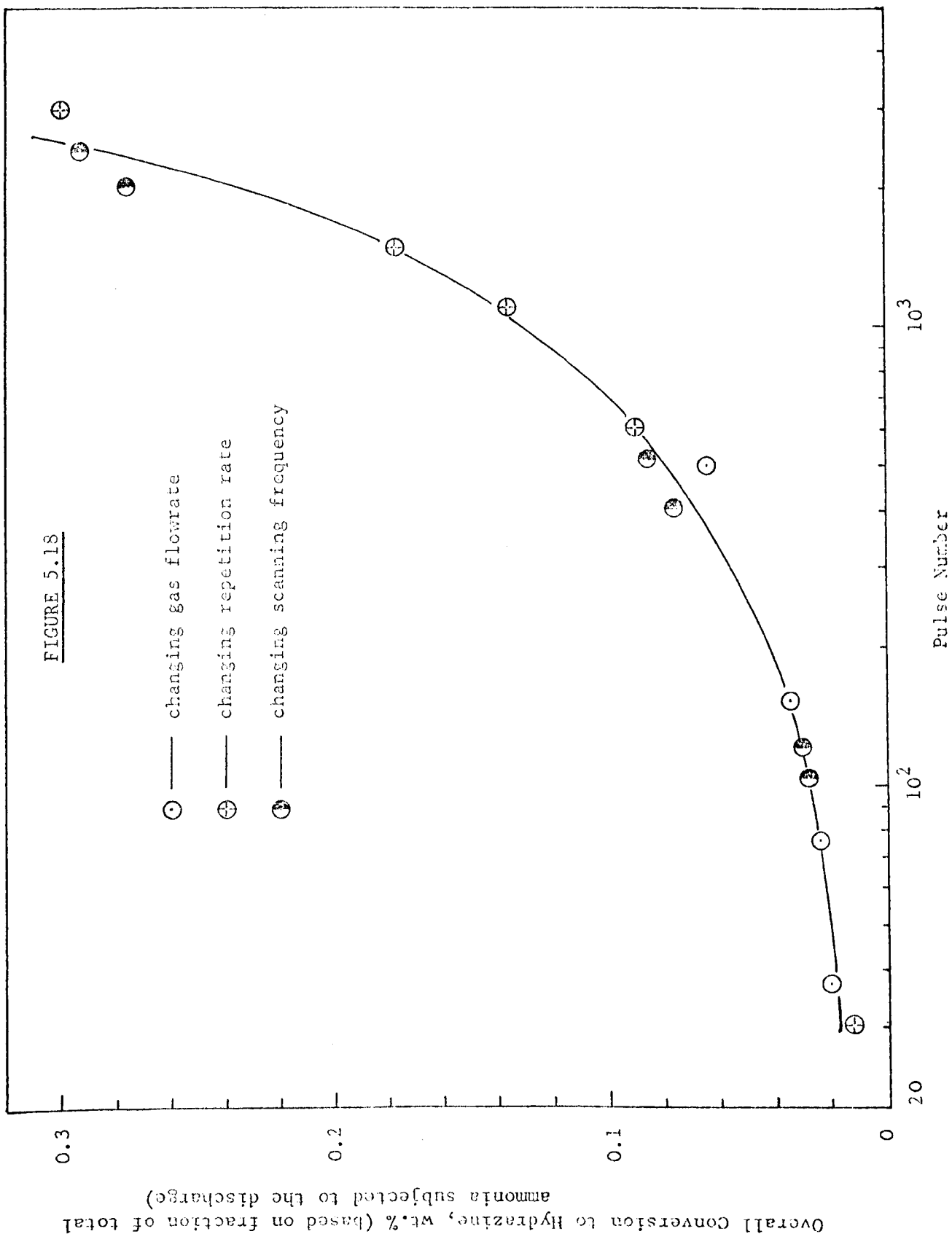


FIGURE 5.18



% Overall Ammonia Conversion (based on fraction of total ammonia subjected to the discharge)

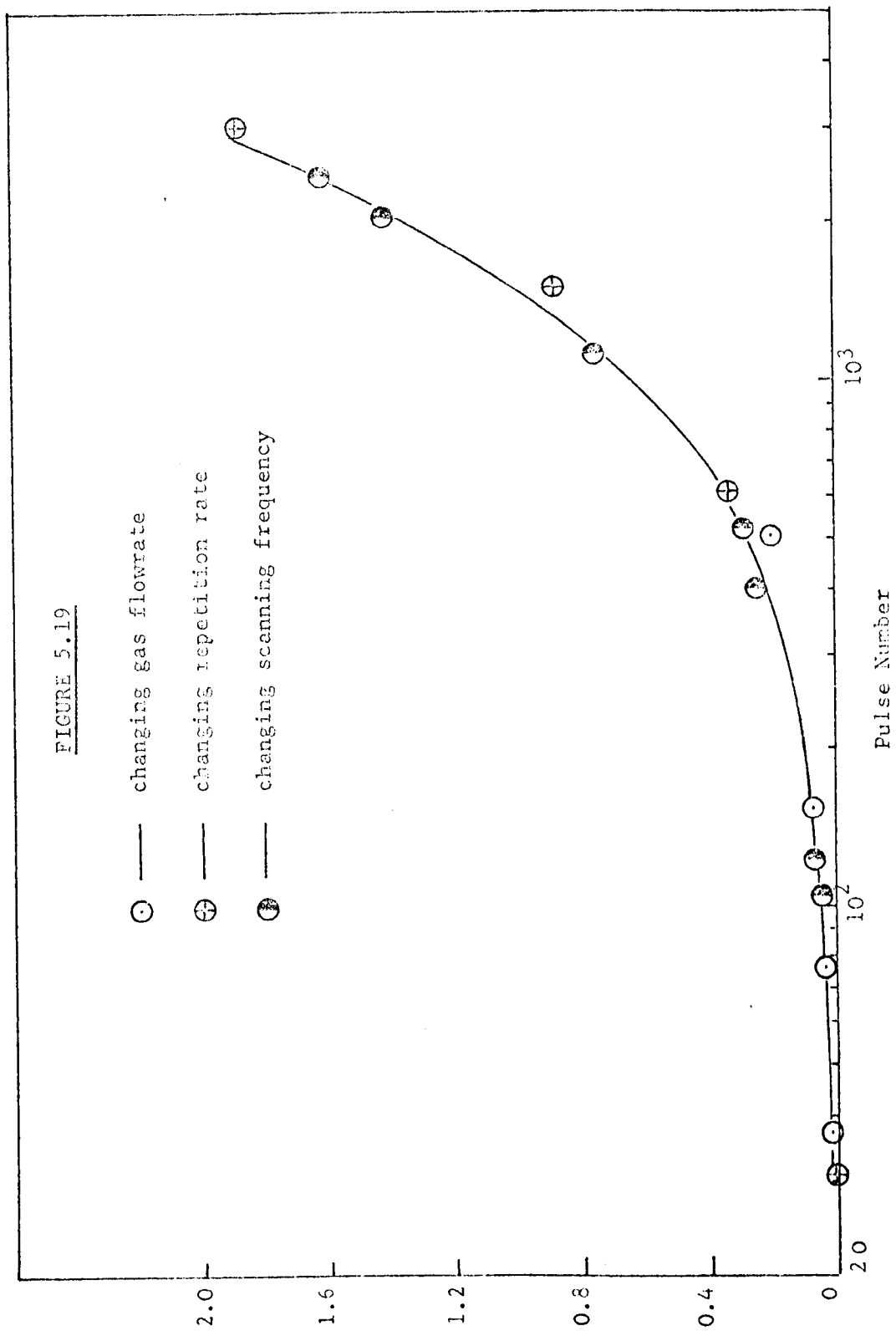


FIGURE 5.19

#### 6.0. RECOMMENDATION FOR FUTURE WORK

The present work has shown that by using a scanning beam reactor it was possible to eliminate completely any ammonia by-passing the discharge zone. Unfortunately, the benefit of this device in terms of hydrazine production, and in particular with the pulsed discharge, has not been fully appreciated. This has been so because a substantial proportion of the reactor volume was occupied by what is described as active dark zones. Although analysis of the experimental data have indicated that these regions contributed to hydrazine formation, their full significance is still not understood. It is therefore recommended that some work aimed at establishing the physics and chemistry of these plasma regions should be carried out. Such work should establish information regarding the electron density, energy distribution, and whether or not hydrazine is formed preferentially in these regions. Furthermore, the effect of electrode separation on the physical size of these regions, in relation to the visible glow, should be determined.

The scanning beam reactor could be utilized in fields other than hydrazine synthesis. One possible application would be in the laying down of organic films. This device has few advantages which will encourage such application,

- (a) It provides a much larger substrate surface area,
- (b) As electrode heating will be less severe, the adverse effect of high temperatures on the rate of film lay-down will be reduced.

## 7.0. CONCLUSIONS

### 7.1. Continuous DC Discharge

#### 7.1.1. Electrical Effects

- (i) The discharge was operated in the subnormal glow region where a decrease in current was accompanied by an increase in the discharge voltage. At a fixed current, an increase in the voltage was also incurred by beam scanning. It was found that the higher the current and scanning frequency, the greater was this increase.
- (ii) Using an electrical probe, it was established that a substantial proportion of the active discharge plasma was invisible to the naked eye. These areas are believed to be responsible for some chemical activation and are consequently called active dark zones.
- (iii) With the discharge beam stationary, the potential drops across the cathode and anode layers were found to be 360 and 115 volts respectively. The abnormally high value for the anode potential drop was believed to be the result of the deposited film on the anode.
- (iv) The reduced electric fields at 10, 5, and 2.6 mA were found to be 6.6, 8.7, and 10.8  $\text{V.cm}^{-1}.\text{torr}^{-1}$ . Using BAILEY and DUNCANSON'S data, the mean electron energies at these three current levels were found to be 0.1, 0.2, and 0.74 e.v. respectively. These very low mean energies suggested that the decomposition of ammonia took place via multiple rather than single excitational collisions.

7.1.2. Chemical Effects

- (i) At low ammonia flowrates ( $\leq 50$  cc/min) a brown deposit was formed on the anode which had the following composition:-  
88.48% iron; 5.96% nitrogen; 2.72% carbon; 1.84% hydrogen.
- (ii) The effect of operational variables on hydrazine synthesis was found to follow the same trends as those reported by other investigators in this field, namely high discharge currents and lower ammonia flowrates although favouring ammonia decomposition, were found to have an adverse effect on the energy yield and molar conversion to hydrazine. The effect of current and flowrate on the overall conversion to hydrazine was similar to that on a product which is first produced and then degraded by back reaction. The rate of hydrazine product<sup>ion</sup> on the other hand, was found to be independent of the discharge current but<sup>to</sup> increase with increasing ammonia flowrates.
- (iii) The energy yields and overall conversion to hydrazine were found to be prohibitively low; maximum (without beam scanning) were 3.63 gms/kWh and 0.124 wt.% (based on total ammonia flow) respectively. This is believed to be the result of not only the degradative back reactions but also the energy wasted in the electrode layers as well as losses due to inefficient energy transfer between electrons and ammonia molecules. Of the total electrical energy some 65 - 75% was dissipated in the electrode layers and of the remainder over 68% was lost, probably as light and heat, due to diverse electron impacts with the ammonia molecules.
- (iv) It was established analytically that an increase in the scanning frequency was accompanied by a decrease in the mean residence

time ( $\bar{t}$ ) and an increase in the fraction of reactor cross-section scanned by the discharge ( $F_g$ ). At a given frequency both  $\bar{t}$  and  $F_g$  increased with decreasing flowrate. At frequencies in excess of the optimum value (frequency when  $F_g = 1$ ), the cumulative residence time remained the same but the average residence time of a molecule per scan got progressively shorter as the scanning frequency was increased.

- (v) At a fixed discharge current and ammonia flowrate, both hydrazine formation and ammonia decomposition were found to increase with scanning frequency. However, the influence on the former was found to be more significant. Furthermore, the effect of beam scanning on ammonia conversion was found to become progressively less marked at lower currents. The maximum increase in hydrazine formation was over 100% whilst that of ammonia conversion about 25%.
- (vi) The effect of discharge current, ammonia flowrate, and scanning frequency was represented empirically in terms of a grouped parameter which was the product of the discharge current and mean residence time or  $I \bar{t}$ . It was found that although higher values of this parameter favoured ammonia decomposition, both the energy yield and molar conversion to hydrazine were adversely affected. The overall conversion, however, increased with increasing values of  $I \bar{t}$  reaching a maximum of 0.195% at 1.6 mA.sec. Beyond this point further increase in  $I \bar{t}$  resulted in lower conversions.

## 7.2. Pulsed DC Discharge

### 7.2.1. Electrical Effects

- (1) The operating voltage for the pulsed discharge was much greater than that for the continuous discharge; 1.5 - 2.1 kV as compared

to 0.63 - 0.73 kV. Also, the voltage was found to be higher for the longer pulse OFF-times.

- (ii) The reduced field strength in the positive column was found to range from  $37.4 - 62 \text{ V.cm}^{-1}.\text{torr}^{-1}$  giving a mean electron energy of around 2.2 e.v.
- (iii) Although the visible channel of the discharge was found to be much narrower than that for the continuous discharge, the overall volume of the plasma (visible + dark) was not found to be as widely different.

#### 7.2.2. Chemical Effects

- (i) Higher energy yields and molar conversions to hydrazine were obtained at longer pulse OFF-times and higher ammonia flowrates. These conditions, however, gave low overall ammonia conversions and overall conversions to hydrazine. The rate of hydrazine production was found to be higher for the shorter pulse OFF-times and higher flowrates.
- (ii) Although the energy yields of hydrazine obtained were considerably greater than those obtained with the continuous discharge (maximum: 29 c.f. 3.63 gas/kWh) the energy efficiency of ammonia decomposition was found to be unaltered. This was contrary to what was expected and the reason was attributed to the very short pulse duration used in this work.
- (iii) Unlike the continuous case, beam scanning was found to improve hydrazine formation and ammonia conversion only marginally. The increase was observed for scanning frequencies of less than  $70 \text{ min}^{-1}$ .

- (iv) The effect of pulse repetition rate, ammonia flowrate, and scanning frequency was described through a parameter called the pulse number. High values of the latter were found to increase ammonia conversion and overall conversion to hydrazine but both the energy yield and molar conversion to hydrazine were decreased.

NOMENCLATURE

Throughout this thesis the symbols used have been explained locally to avoid confusion and repeated reference to this section. However, a complete list of these symbols is as follows:

|           |                                                            |
|-----------|------------------------------------------------------------|
| A         | Constant in equation (2.19)                                |
| a         | Constant in equation (2.20)                                |
| a         | Linear dimension of a reactor                              |
| B         | Constant in equation (2.19)                                |
| B         | Constant in equation (4.1)                                 |
| b         | Constant in equation (2.20)                                |
| $C_{1,2}$ | Constant in equation (4.1)                                 |
| c         | Constant in equation (2.20)                                |
| $\bar{c}$ | Mean random velocity of electrons                          |
| E         | Field strength                                             |
| $E_t$     | Energy in a pulse                                          |
| $E(t)$    | AC electric field strength                                 |
| $E_0$     | Peak AC electric field strength                            |
| e         | Electronic charge                                          |
| F         | Volumetric flowrate                                        |
| $F_s$     | Fraction of reactor cross-section scanned by the discharge |
| f         | Frequency of power supply                                  |
| H         | Height of discharge glow or anode depth                    |
| h         | Planck's constant                                          |
| I         | Discharge current                                          |
| $I_t$     | Instantaneous current                                      |

|                         |                                                                               |
|-------------------------|-------------------------------------------------------------------------------|
| J                       | Current density                                                               |
| K                       | Scale-up factor                                                               |
| K                       | Rate constant                                                                 |
| $K_{ob}, k_1, k_2, k_d$ | Rate constants                                                                |
| L                       | Projected molecular path length in the discharge                              |
| M                       | Mass of gas                                                                   |
| $M_f$                   | Mass flowrate                                                                 |
| $M_s$                   | Fraction of overall gas subjected to the discharge per unit time              |
| m                       | Electronic mass                                                               |
| N                       | Scanning frequency                                                            |
| $N^*$                   | Optimum scanning frequency                                                    |
| $n^*$                   | Pulse number                                                                  |
| $n_e$                   | Electron number density                                                       |
| $n_+$                   | Positive ion number density                                                   |
| P                       | Pressure of gas                                                               |
| R                       | Radial position of a point in the discharge with respect to the cathode       |
| r                       | Distance between a point in the electrode gap and an electrode                |
| S                       | Surface area on an electrode                                                  |
| T                       | Temperature                                                                   |
| T                       | Pulse duration                                                                |
| t                       | Time                                                                          |
| $t_1$                   | Molecular flight time across discharge gap                                    |
| $t_1$                   | Duration of a pulsed signal produced by probe response to positions in plasma |
| $t_2$                   | Time during which the probe is not experiencing the existence of the plasma   |
| $t_2$                   | Time of discharge sweep at the anode                                          |

|                    |                                                                                                                |
|--------------------|----------------------------------------------------------------------------------------------------------------|
| $t_d$              | Pulse decay time                                                                                               |
| $t_f$              | Pulse formative time lag                                                                                       |
| $t_p$              | Pulse width                                                                                                    |
| $t_r$              | Pulse rise time                                                                                                |
| $t_s$              | Pulse shoulder time                                                                                            |
| $V$                | Discharge voltage                                                                                              |
| $V_p$              | Peak discharge voltage                                                                                         |
| $V_s$              | Striking voltage                                                                                               |
| $V_t$              | Instantaneous voltage                                                                                          |
| $\bar{V}$          | Velocity of gas relative to sweeping plasma                                                                    |
| $v$                | Axial velocity of gas                                                                                          |
| $v$                | Velocity of an electron                                                                                        |
| $v_d$              | Drift velocity of an electron                                                                                  |
| $\dot{v}$          | Acceleration of an electron                                                                                    |
| $W$                | Total discharge power                                                                                          |
| $W_p$              | Power in the positive column only                                                                              |
| $w$                | Width of discharge glow at radius $R$                                                                          |
| $Y$                | Energy yield                                                                                                   |
| $X_{N_2H_4}$       | % Overall conversion to hydrazine                                                                              |
| $\bar{X}_{N_2H_4}$ | % Molar conversion to hydrazine                                                                                |
| $X_{NH_3}$         | % Overall ammonia conversion                                                                                   |
| $X_i$              | % Overall conversion to hydrazine based on fraction of ammonia subjected to the discharge                      |
| $X_j$              | % Overall ammonia conversion based on fraction of ammonia subjected to the discharge                           |
| $x$                | Angular distance moved by the discharge plane during the flight time of a molecule across the discharge height |
| $\epsilon$         | Electron energy                                                                                                |
| $\epsilon_m$       | Mean electron energy                                                                                           |

|              |                                                                                             |
|--------------|---------------------------------------------------------------------------------------------|
| $\alpha$     | Fraction of electron energy lost in a collision                                             |
| $\alpha_d$   | Rate coefficient for electron-ion recombination                                             |
| $\theta$     | Angle between the molecular path in the discharge and the lower edge of the discharge plane |
| $\rho$       | Space charge density                                                                        |
| $\rho_f$     | Density of float                                                                            |
| $\rho_g$     | Density of gas                                                                              |
| $\delta$     | Surface charge density                                                                      |
| $\lambda_e$  | Electron mean free path                                                                     |
| $\nu$        | Frequency of emitted light                                                                  |
| $\eta$       | Energy efficiency of the discharge                                                          |
| $\tau$       | Residence time                                                                              |
| $\bar{\tau}$ | Mean residence time                                                                         |
| $\omega$     | Angular velocity                                                                            |
| $\Omega$     | Ohms                                                                                        |

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## **APPENDICES**

## APPENDIX 1.

### THE CROSSED DISCHARGE

#### 1.0. INTRODUCTION

The application of the crossed discharge for gas discharge synthesis was first reported by COTTON<sup>(28)</sup> in 1947. Since then and apart from the work of CHARLTON<sup>(105)</sup> no further research has been conducted in this field. Charlton failed to substantiate Cotton's claims on the higher chemical activation provided by the crossed discharge and could not forward any possible explanation for Cotton's results, but merely concluded that they were peculiar to the apparatus. It was this complete contradiction which prompted the present study. It was felt that a further independent study was necessary in order to decide whether or not Cotton's claims were at all founded.

It should be pointed out that when this work was about to commence, the advantages of SAVAGE'S<sup>(21)</sup> pulsed discharge work on ammonia were not fully recognised. Consequently, it was natural to explore alternative ways of applying electrical energy such as the crossed discharge.

Ammonia at a pressure of 10 torr was used as the reactant gas. A continuous DC discharge was struck between two plate electrodes and a high frequency (1.54 MHz) field, in the form of a corona type double barrier discharge, was applied across the positive column of the DC discharge. By doing so, it was expected that the positive column will get activated due to an increase in the field strength and at the same time more diffuse. If this was so an improvement in both the energy yield and overall conversion to hydrazine was to be expected.

## A2.0. EXPERIMENTAL WORK

### A2.1. Discharge Reactor

The reactor consisted mainly of a 6" long silica tube (1) with two B19 sockets, one at each end. The external and internal diameters of this tube were 23 and 19 mm respectively. Around the centre of this tube was a stainless steel band (3) fitted closely to the surface and acted as the high tension electrode for the H.F. circuit. The band was cooled uniformly by a jet of compressed air from three coaxial glass rings which were drilled with small holes directed into the centre. Two B19 cones (3,4), each with a side arm to facilitate the flow of ammonia, were fitted on the silica tube as shown in Figure A1.1. One carried the cathode (2b) for the DC circuit whilst the other carried the anode (2a) for the same circuit, together with the earth terminal (8) of the H.F. circuit.

The cathode was in the form of a 15 mm diameter stainless steel plate with a smooth surface and curved periphery to minimise edge effects and to prevent the occurrence of sparks. It was secured in position by a  $\frac{1}{16}$ " stainless steel rod (10) which was itself enclosed in a capillary tubing (11). The latter was fused to the containing B19 cone (3) to ensure good vacuum. The anode was similar to the cathode except that the former had a 5 mm hole through its axis to allow for the earth terminal of the H.F. circuit. The latter was in the form of an  $\frac{1}{8}$ " aluminium rod enclosed in a 3 mm bore high precision silica tube (9). Without this shielding there would have been two earth terminals for the high tension DC electrode thus preventing the occurrence of a true crossed discharge. A glass to metal seal (6) was used to position the anode. Electrical connection to the anode was

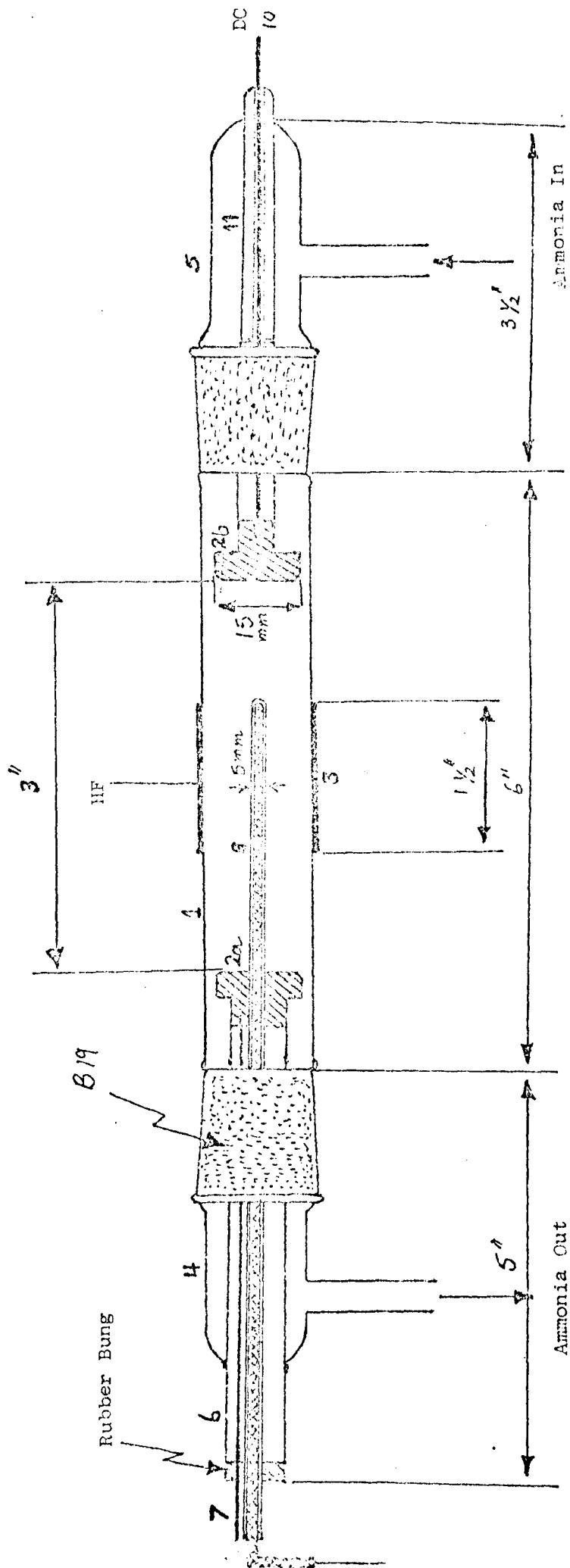


Figure Al.1 Crossed Discharge Reactor

made via a  $\frac{1}{16}$ " stainless steel rod (7). This and the silica shielding tube (9) passed through a rubber bung at the end of the tube (6) and sealed with Araldite adhesive for vacuum tightness.

## A2.2. Flow System and Electrical Equipment

Except for the omission of the Toepler Pump unit and the gas sample trap, the flow system was the same as that described in Section 4.2 (Page 62).

The H.F. power (1.54 MHz) was supplied by a 1 kW rated output Radyns generator and the generator described in Section 4.3.1 (Page 65) was used to provide the DC power. In addition to the measuring instruments listed earlier (Page 67), the following were also used,

### (a) Voltmeter

The DC voltage was measured using a moving coil meter with appropriate series resistances enabling voltages in the range 0 - 1 kV, 0 - 3 kV to be measured.

### (b) H.F. Milliammeter

This was a Cambridge Unipivot milliammeter incorporating six thermocouples. These enabled currents as low as 1.0 mA to be measured accurately. The instrument gave the R.M.S. value of the H.F. current.

### (c) Wave Analyser

An Airmec wave analyser type 853 was employed to determine the harmonic contributions of the tuned H.F. current. With this instrument, it was possible to measure harmonic frequencies of up to 30 MHz.

(d) Wayne Kerr Bridge

To measure the various circuit capacitances a Wayne Kerr Bridge B221 was used. The bridge had an operating frequency,  $f$ , such that  $2\pi f = 10^4$  Hz. The instrument was capable of measurement in the 0 - 10 pF range correct to 0.002 pF.

A2.3. Circuit Layout

In order to prevent the DC discharge arcing a ballast resistor of 15 k $\Omega$  was placed between the generator output and the reactor. Due to the high frequency of the applied AC power, care was taken to minimize the effect of stray capacitances and inductances of the loads. Earth loops were also eliminated by using one common earth point on the Radyne generator. In addition, the residual stray capacitance, between the circuit components and from each component to earth was cut to a minimum by not using screened leads except for the oscilloscope measurements. The milliammeter was placed in an earthed metal box to prevent the pick-up of stray currents. The inductances of the leads were kept to a minimum by using short connections between components and laying input and output lines in parallel wherever possible. Finally, in order to keep the H.F. current out of the DC circuit lines, two 20 mH high frequency chokes were used as shown in Figure A1.5.

A2.4. H.F. Power Measurement

Due to the capacitive nature of the discharge, the power measurement necessitated the evaluation of the power factor. This was first achieved by displaying the voltage and current waveforms on the oscilloscope and then measuring the angular displacement. This angle,

as depicted in Figure A1.2, was found to be too small for accurate measurement and consequently this method of power evaluation was abandoned. Instead the phenomenon of parallel resonance, proposed by WALLER<sup>(18)</sup>, was used. Here, the current and voltage were brought into phase by incorporating a variable air capacitor (7 - 130  $\mu$ F) and an 0.4 mH inductor in the circuit as shown in Figure A1.3.

At resonance the net current is composed of the fundamental and harmonic components and is given by:-

$$I = I_1 \sin(\omega t + \phi_1) + I_2 \sin(2\omega t + \phi_2) + I_3 \sin(3\omega t + \phi_3) \\ + \dots + I_n \sin(n\omega t + \phi_n) \quad \dots (A1.1)$$

where,

$I$  = net peak current

$I_1$  = fundamental peak current

$I_2, \dots, I_n$  = harmonic peak currents

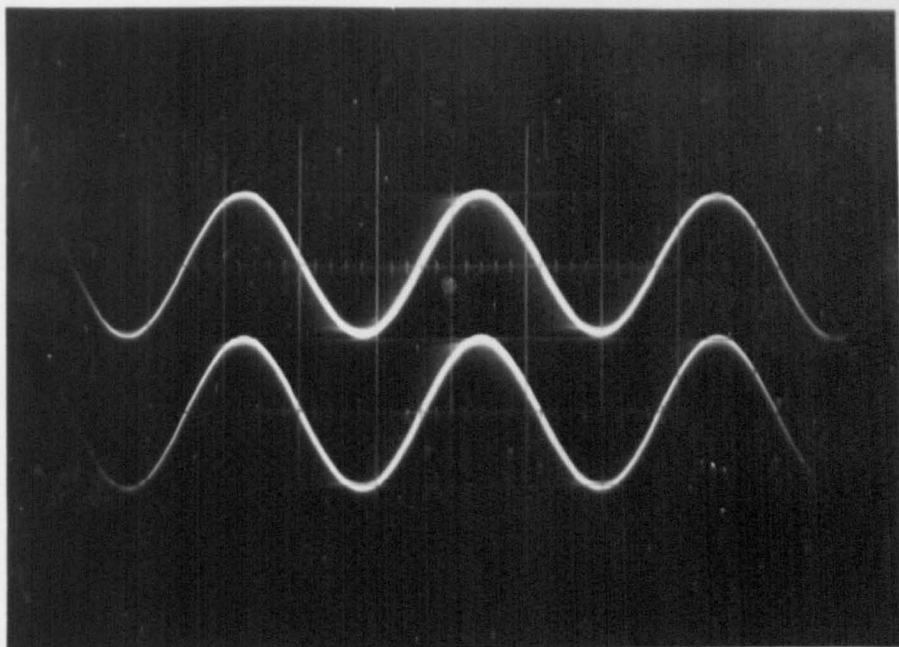
$\phi_1, \dots, \phi_n$  = phase lags

Squaring equation A1.1 we get,

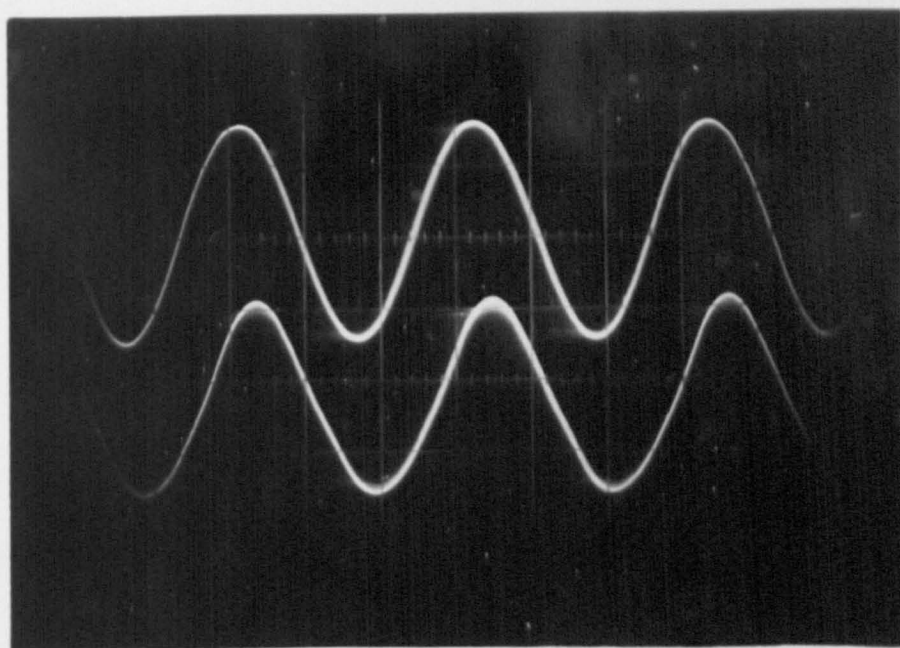
$$I^2 = (I_1 \sin(\omega t + \phi_1) + I_2 \sin(2\omega t + \phi_2) + I_3 \sin(3\omega t + \phi_3) + \dots)^2 \\ = I_1^2 \sin^2(\omega t + \phi_1) + I_2^2 \sin^2(2\omega t + \phi_2) + I_3^2 \sin^2(3\omega t + \phi_3) + \\ 2I_1 I_2 \sin(\omega t + \phi_1) \sin(2\omega t + \phi_2) + 2I_1 I_3 \sin(\omega t + \phi_1) \\ \sin(3\omega t + \phi_3) + \dots$$

Now, taking the average value of a  $\sin^2$  term between  $t = 0$  and  $t = 2\pi$  as  $\frac{1}{2}$  and that of each product of two dissimilar sines as zero, then:

$$I^2 = \frac{1}{2}(I_1^2 + I_2^2 + I_3^2 + \dots) \quad \dots (A1.2)$$



Before Discharge



During Discharge

Figure A1.2 Voltage & Current Oscillograms

(a) Upper trace-current; (b) Lower trace-voltage

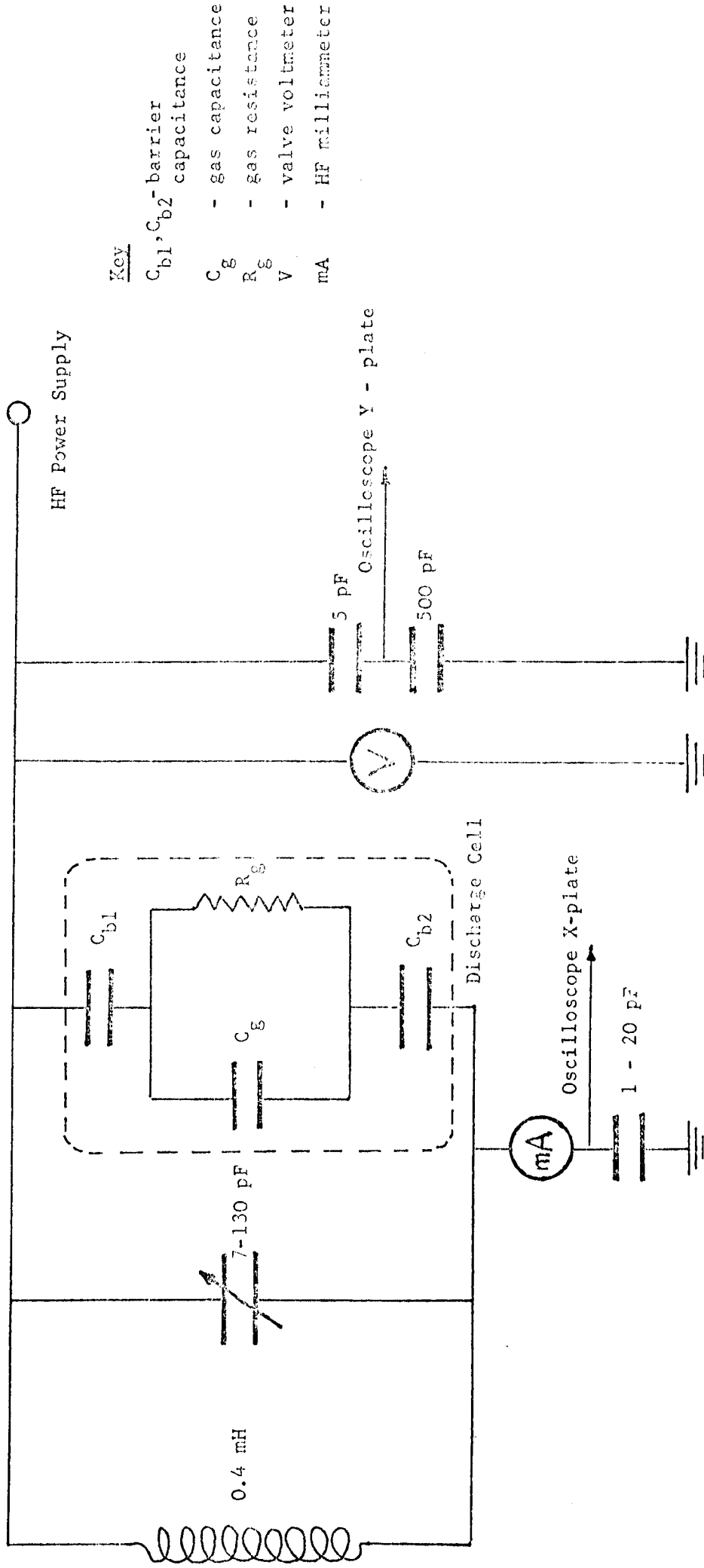


Figure A1.3 Network for Power Measurement by Parallel Resonance

But,  $I_{\max}^2/2 = I_{\text{R.M.S}}^2$

$\therefore I_{\text{R.M.S}} = (I_1^2 + I_2^2 + I_3^2 + \dots)^{1/2} \dots\dots\dots(\text{A1.3})$

where,  $I_1, I_2, I_3, \dots$ , are now in R.M.S. values. Now if we let  $I_2^2/I_1^2 = \alpha_2, I_3^2/I_1^2 = \alpha_3$ , etc. then:

$$I_{\text{R.M.S}} = I_1(1 + \alpha_2 + \alpha_3 + \dots)^{1/2}$$

or  $I_1 = \frac{I_{\text{R.M.S.}}}{(1 + \sum_2^n \alpha)^{1/2}} \dots\dots\dots(\text{A1.4})$

where,

$I_1$  = fundamental current (R.M.S.)

$I_{\text{R.M.S}}$  = net current measured by the milliammeter at resonance (R.M.S.)

The Airmec wave analyser was used to determine the values of  $\alpha$ . The signal from the tuned circuit was fed to the analyser by connecting the input lead across a 10 ohm resistor. By selecting the generator supply frequency (1.54 Mhz), the instrument was tuned and the corresponding attenuator readings recorded. On retuning at integral multiples of the fundamental frequency, a new set of attenuator readings were obtained for each harmonic component. For each selected frequency there was a calibration factor given by the manufacturer's data (see Table A1.1) and the value of  $\alpha$  in decibels, for a particular harmonic frequency, was then evaluated from the formula:-

$$\alpha = (\text{attenuator readings when tuned to harmonic} + \text{calibration factor for frequency of harmonic}) - (\text{attenuator readings when tuned to the fundamental} + \text{calibration factor for frequency of fundamental})$$

Four runs were carried out covering the operating range of H.F. voltages and the corresponding attenuations and values of  $\alpha$  are presented in Table A1.1. It is apparent from this table that the harmonic currents were very small and could therefore be neglected without incurring a serious error in the power measurement. This was further supported by the current and voltage oscillograms at resonance (Figure A1.4) which show a very slight deviation from actual sinusoidal waveforms.

#### A2.5 Procedure for H.F. Power Measurement

With the discharge cell at atmospheric pressure, so that spark breakdown was impossible, parallel resonance was achieved by tuning the variable air capacitor. It was found that the tuned current was nearly zero at voltages ranging from 550 - 900 volts. This showed that power losses in the tuned circuit due to the inductor and reactor cell geometry was negligible. The circuit was then returned at actual operating conditions and the power was taken as the product of the current and the voltage.

### A3.0. RESULTS AND DISCUSSION

#### A3.1. Electrical Characteristics of the Discharge

A crossed discharge of the type claimed by COTTON<sup>(28)</sup> could not be obtained. A tendency for cross coupling between the two DC electrodes and the H.F. high tension electrode always developed which resulted in a discharge comprising three distinct zones, as shown in Figure A1.5. Region A was considered as a true crossed discharge whilst regions B and C were DC superimposed H.F. discharges.

TABLE A1.1 Harmonic Analysis for the Tuned Circuit

| H.F. Voltage | Tuned Current | Fund. Attenuat <sup>n</sup> | 2nd Harmonic Attenuat <sup>n</sup> | 3rd Harmonic Attenuat <sup>n</sup> | 4th Harmonic Attenuat <sup>n</sup> | 5th Harmonic Attenuat <sup>n</sup> | 6th Harmonic Attenuat <sup>n</sup> | $\propto 2$ | $\propto 3$ | $\propto 4$ | $\propto 5$     | $\propto 6$     | $\frac{1}{(1+\sum \alpha)}$ |
|--------------|---------------|-----------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|-------------|-------------|-------------|-----------------|-----------------|-----------------------------|
| Volts        | mA            | db                          | db                                 | db                                 | db                                 | db                                 | db                                 |             |             |             |                 |                 |                             |
| 600          | 8.0           | 89.5                        | 76                                 | 73.5                               | 63.0                               | 49.0                               | 45.0                               | 0.05        | 0.0141      | 0.0015      | negl-<br>igible | negl-<br>igible | 1.03                        |
| 690          | 20.0          | 106.0                       | 86                                 | 84.0                               | 65.5                               | 63.0                               | 56.0                               | 0.014       | 0.0035      | -           | -               | -               | 1.01                        |
| 805          | 27.5          | 107.5                       | 89.5                               | 89.5                               | 74.0                               | 67.0                               | 60.0                               | 0.0178      | 0.0088      | 0.0003      | -               | -               | 1.015                       |
| 900          | 32            | 108.5                       | 84.5                               | 90.0                               | 70.0                               | 74.5                               | 60.0                               | 0.0070      | 0.0079      | -           | -               | -               | 1.01                        |

|                                             |      |      |       |       |       |      |
|---------------------------------------------|------|------|-------|-------|-------|------|
| Frequency<br>KHz                            | 1.54 | 3.08 | 4.62  | 6.16  | 7.70  | 9.24 |
| Calibrat <sup>n</sup> .<br>Chart<br>Reading | -9.0 | -8.5 | -11.5 | -10.7 | -10.0 | -9.2 |

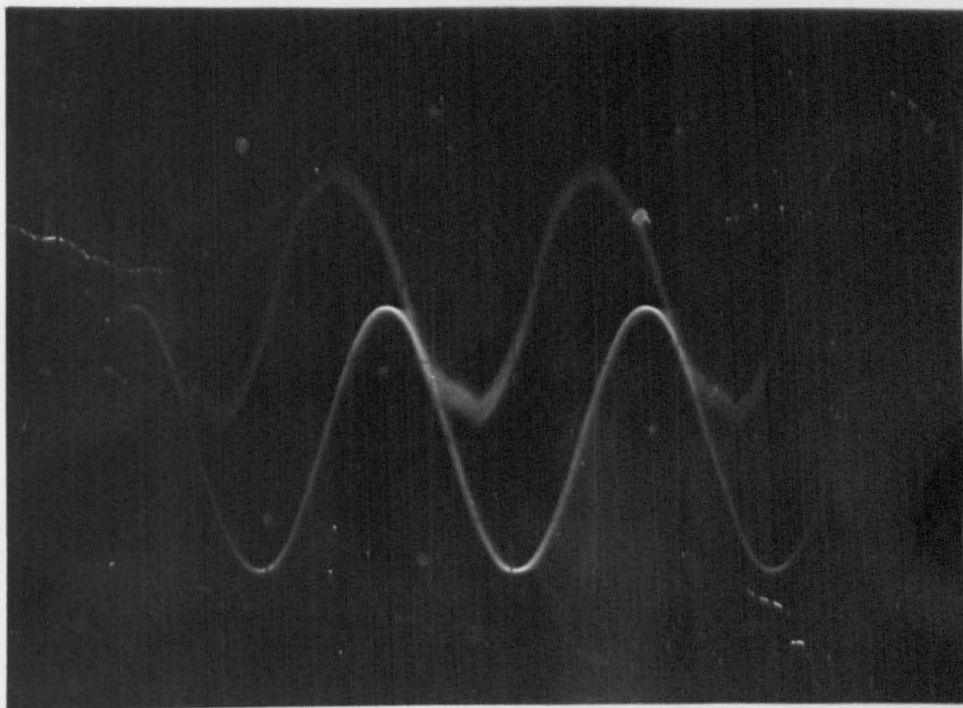


Figure A1.4 Voltage & Current Oscillograms  
at Resonance

(a) Upper trace-current; (b) Lower trace-voltage

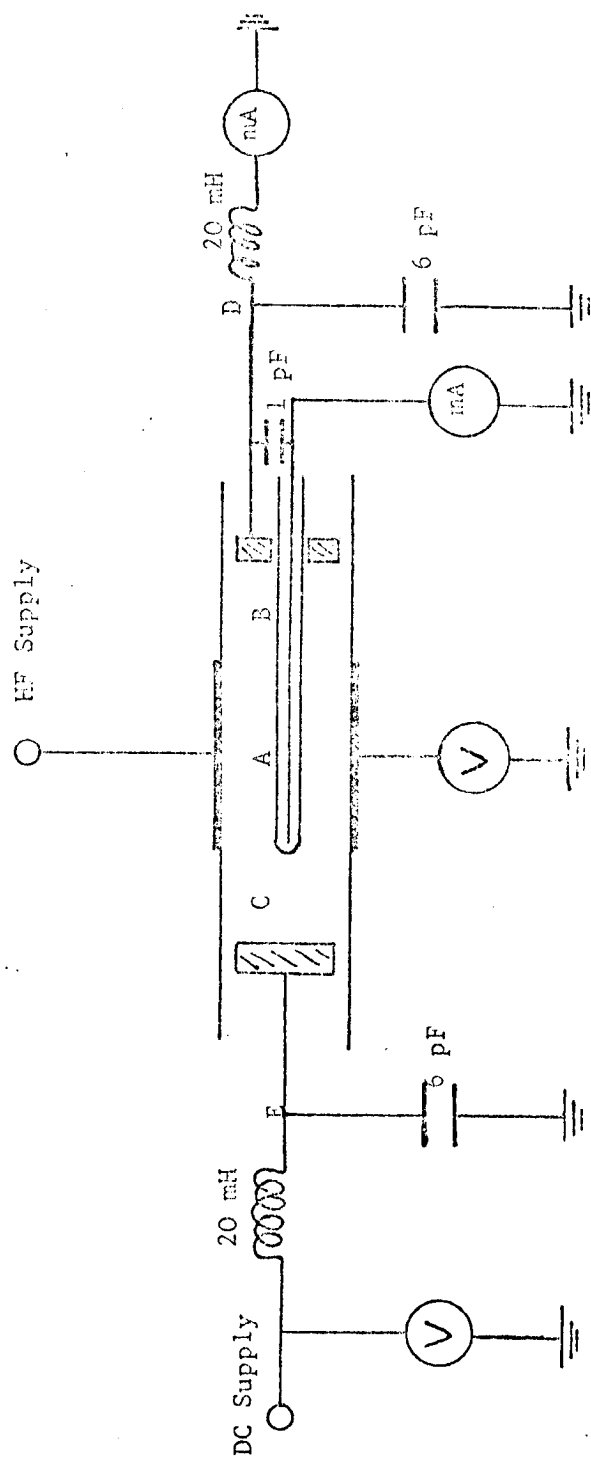


Figure A1.5 Schematic Representation of the Discharge Zones and  
The Associated Stray Capacitances

The flow of H.F. current down the DC circuit lines was restricted to a near zero by the insertion of the H.F. chokes. However, due to their high impedances ( $194 \text{ k}\Omega$  at 1.54 MHz) there always existed some potential (300 - 400 volts) at points D and E (Figure A1.5) which caused part of the current from region B to pass through the H.F. milliammeter and to be subsequently measured. The remainder of the current and the whole of that from region C passed to earth as stray currents. The relative magnitude of these currents depended on the capacitances of these different paths. These capacitances, as measured by the Wayne Kerr Bridge, are shown on Figure A1.5. On examination of these values we observe that only 70% of the current from region B is actually measured by the milliammeter whereas the rest and the whole of that from region C are not accounted for in the power measurement.

The phenomenon of cross coupling observed here has no mention in either COTTON'S<sup>(28)</sup> or CHARLTON'S<sup>(105)</sup> work. However, looking at their electrodes configuration (Page 17) one can see for certainty that such phenomenon was hardly avoidable. Therefore, it would be concluded that in both studies only part of the overall H.F. power was actually measured.

### A3.2. Effect of Measured H.F. Power on the Energy Yield and Conversion to Hydrating.

The purpose of this exercise was not to establish the effectiveness of the crossed discharge, since this was not possible because of erroneous H.F. power measurement, but rather to show whether it was possible to obtain a relationship similar to that claimed by Cotton.

Three sets of experimental runs were carried out at nearly constant total powers (DC + measured H.F.) of 12, 17, 23 watts. In every set only the percentage of the H.F. power was varied from 0 - 100%. In all runs, the operating pressure and ammonia flowrate was constant at 10 torr and 190 cc/min (STP) respectively.

The results from these runs are shown in Tables A1.2 - 4 and are plotted in Figures A1.6 and A1.7 as overall conversion to hydrazine and energy yield of hydrazine versus % H.F. power. Figures A1.6 and A1.7 indicate that in all cases the curves are similar in appearance to those reported by Cotton but in general the data became progressively more erratic at higher total powers. The slight improvement in both the energy yield and overall conversion at reduced % H.F. power could not be attributed to the effectiveness of the crossed discharge because, although the total power was assumed to be constant, its actual value could have been considerably higher. The nature of Figures A1.6 and A1.7 was therefore considered to be the result of power dissipation in region B and C of the discharge (Figure A1.5). The curves show the usual maxima associated with hydrazine formation as a function of power. The scattering of the data at higher total powers (17 & 23 watts) was probably the result of a more difficult power measurement as the discharges in regions B and C became progressively more predominant.

#### A4.0. CONCLUSIONS

It was found that under no circumstances could a true crossed discharge be obtained. The apparent improvement in hydrazine yield, as a result of increasing the % measured H.F. power, was merely the result of electrical energy being dissipated in the system but not

TABLE A1.2

Crossed Discharge with Tuned H.F. Current

Ammonia flowrate = 190 cc/min (STP)

Frequency = 1.54 Mc/s

Total discharge power 12.0 watts

Pressure = 10 torr

| Run No. | H.F. Voltage volts | H.F. Current mA | H.F. Power watts | DC voltage volts | DC current mA | DC Power watts | % H.F. power | Run duration mins | Dilution ratio | P.p.m. $N_2H_4$ wt. % | Overall Energy conv. to yield $N_2H_4$ gms/1000 |      |
|---------|--------------------|-----------------|------------------|------------------|---------------|----------------|--------------|-------------------|----------------|-----------------------|-------------------------------------------------|------|
| A1      | 0                  | 0               | 0                | 970              | 12.4          | 12.0           | 0            | 3                 | 5              | 0.199                 | 0.244                                           | 1.69 |
| A2      | 390                | 3.5             | 1.37             | 900              | 12.0          | 10.8           | 11.2         | 3                 | 5              | 0.22                  | 0.27                                            | 1.81 |
| A3      | 455                | 5.5             | 2.5              | 830              | 11.0          | 9.2            | 21.3         | 2.5               | 5              | 0.209                 | 0.307                                           | 2.14 |
| A4      | 515                | 8.4             | 4.32             | 820              | 9.5           | 7.8            | 35.6         | 3                 | 5              | 0.258                 | 0.316                                           | 2.13 |
| A5      | 535                | 9.4             | 5.03             | 750              | 9.0           | 6.75           | 42.8         | 3                 | 5              | 0.293                 | 0.359                                           | 2.29 |
| A6      | 595                | 10.7            | 6.37             | 690              | 8.0           | 5.55           | 53.5         | 3                 | 5              | 0.269                 | 0.33                                            | 2.26 |
| A7      | 625                | 13.5            | 8.44             | 520              | 6.5           | 3.38           | 71.0         | 3                 | 5              | 0.246                 | 0.302                                           | 2.08 |
| A8      | 655                | 15.7            | 10.3             | 340              | 4.5           | 1.53           | 87.0         | 3.5               | 5              | 0.266                 | 0.28                                            | 1.93 |
| A9      | 705                | 17              | 12.0             | 0                | 0             | 0              | 100          | 3                 | 5              | 0.179                 | 0.22                                            | 1.54 |

TABLE A1.3

Crossed Discharge with Tuned H.F. Current

Ammonia flowrate = 190 cc/min (STP)  
 Frequency = 1.54 MHz  
 Total discharge power 17 watts  
 Pressure = 10 torr

| Run No. | H.F. Voltage volts | H.F. Current mA | H.F. Power watts | DC voltage volts | DC current mA | DC Power watts | % H.F. power | Run duration mins | Dilution ratio | p.p.m. $N_2H_4$ | Overall conv.to $N_2H_4$ wt. % | Energy yield gms/kWh |
|---------|--------------------|-----------------|------------------|------------------|---------------|----------------|--------------|-------------------|----------------|-----------------|--------------------------------|----------------------|
| A10     | 0                  | 0               | 0                | 954              | 17.8          | 17.0           | 0            | 3                 | 5              | 0.222           | 0.272                          | 1.3                  |
| A11     | 400                | 5.0             | 2.0              | 880              | 17.0          | 15             | 11.75        | 2.5               | 5              | 0.252           | 0.371                          | 1.78                 |
| A12     | 490                | 8.0             | 3.92             | 840              | 15.5          | 13             | 23.2         | 2.0               | 5              | 0.185           | 0.34                           | 1.64                 |
| A13     | 555                | 11              | 6.1              | 800              | 13.5          | 10.8           | 36.1         | 2.5               | 5              | 0.252           | 0.37                           | 1.78                 |
| A14     | 605                | 13.8            | 8.35             | 700              | 12.5          | 8.75           | 49.0         | 3.5               | 5              | 0.328           | 0.344                          | 1.65                 |
| A15     | 660                | 16.8            | 11.1             | 540              | 11.0          | 5.95           | 65           | 3.0               | 5              | 0.228           | 0.29                           | 1.34                 |
| A16     | 715                | 19.6            | 14.0             | 380              | 7             | 3.04           | 82.5         | 2.5               | 5              | 0.164           | 0.242                          | 1.155                |
| A17     | 815                | 20.8            | 17.0             | 0                | 0             | 0              | 100          | 2.5               | 5              | 0.169           | 0.249                          | 1.19                 |

TABLE A1.4      Crossed Discharge with Tuned H.F. Current

Ammonia flowrate      = 190 cc/min (STP)  
 Frequency                = 1.54 MHz  
 Total discharge power    23 watts  
 Pressure                  = 10 torr

| Run No. | H.F. Voltage volts | H.F. Current mA | H.F. Power watts | DC Voltage volts | DC Current mA | DC Power watts | 2H.F. power | Run duration mins | Dilution ratio | p.p.m. $N_2H_4$ | Overall conv. to $N_2H_4$ wt. % | Energy yield gms/kWh |
|---------|--------------------|-----------------|------------------|------------------|---------------|----------------|-------------|-------------------|----------------|-----------------|---------------------------------|----------------------|
| A18     | 0                  | 0               | 0                | 950              | 24.2          | 23             | 0           | 2                 | 5              | 0.157           | 0.288                           | 1.03                 |
| A19     | 415                | 7.2             | 2.99             | 930              | 21.5          | 20             | 13.0        | 2                 | 5              | 0.164           | 0.301                           | 1.075                |
| A20     | 540                | 11.8            | 6.4              | 820              | 20            | 16.4           | 28          | 3                 | 5              | 0.23            | 0.283                           | 1.01                 |
| A21     | 592                | 15.0            | 8.87             | 780              | 18            | 14.05          | 38.5        | 2.5               | 5              | 0.19            | 0.279                           | 0.995                |
| A22     | 660                | 17.5            | 11.2             | 670              | 17.5          | 11.7           | 49.0        | 2                 | 5              | 0.154           | 0.283                           | 1.01                 |
| A23     | 730                | 21.0            | 15.45            | 530              | 14.0          | 7.42           | 67.5        | 2                 | 5              | 0.13            | 0.239                           | 0.85                 |
| A24     | 810                | 22.9            | 18.5             | 400              | 11.5          | 4.6            | 80          | 2                 | 5              | 0.105           | 0.193                           | 0.68                 |
| A25     | 940                | 24.5            | 23               | 0                | 0             | 0              | 100         | 2                 | 5              | 0.125           | 0.23                            | 0.81                 |

FIGURE A1.6

- (1) ○ — 12 watts  
 (2) □ — 17 watts  
 (3) △ — 23 watts

ammonia flowrate = 190 cc/min  
 (STP)

pressure = 10 torr

frequency = 1.54 MHz

Overall Conversion to Hydrazine, wt. %

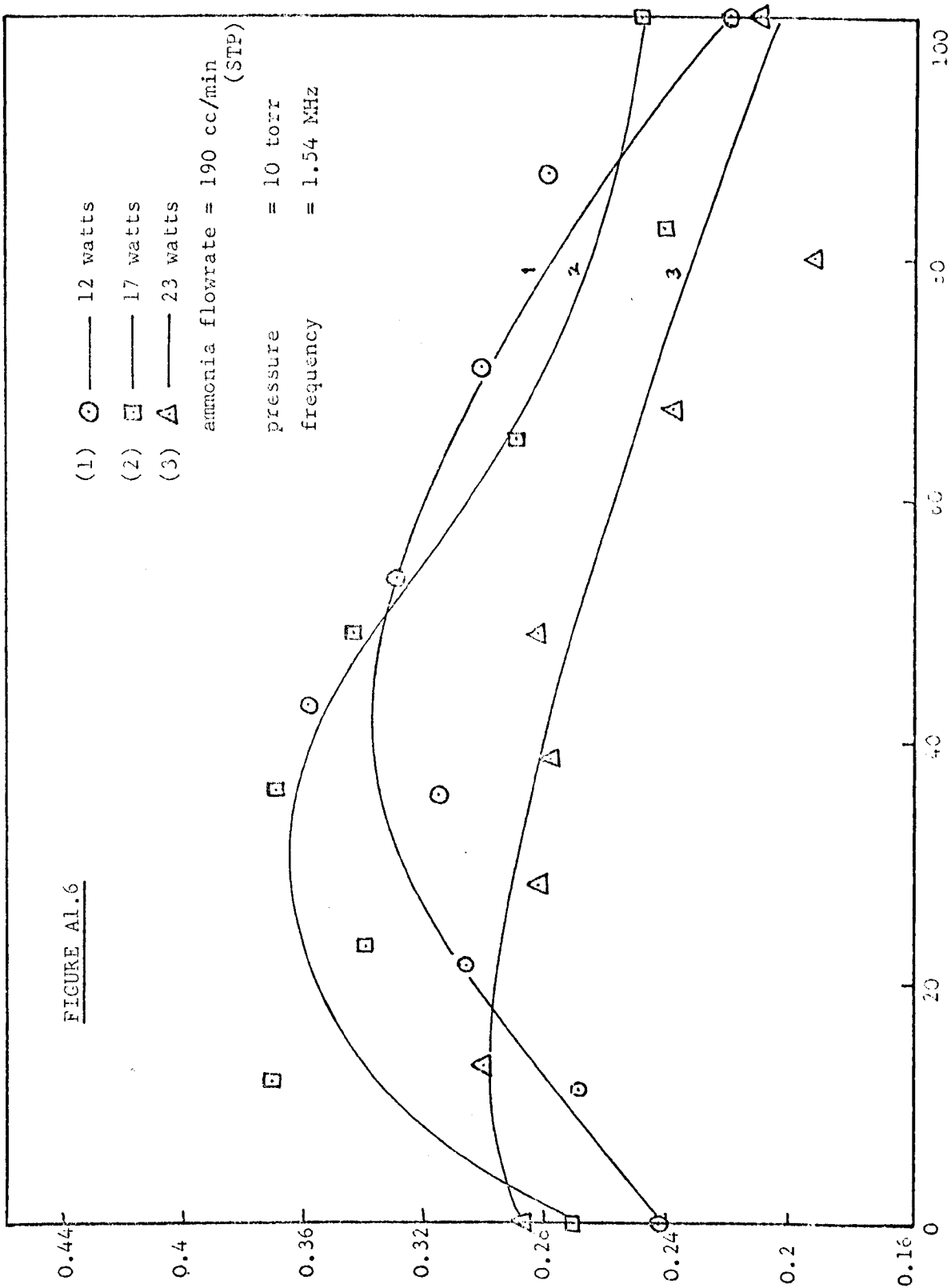
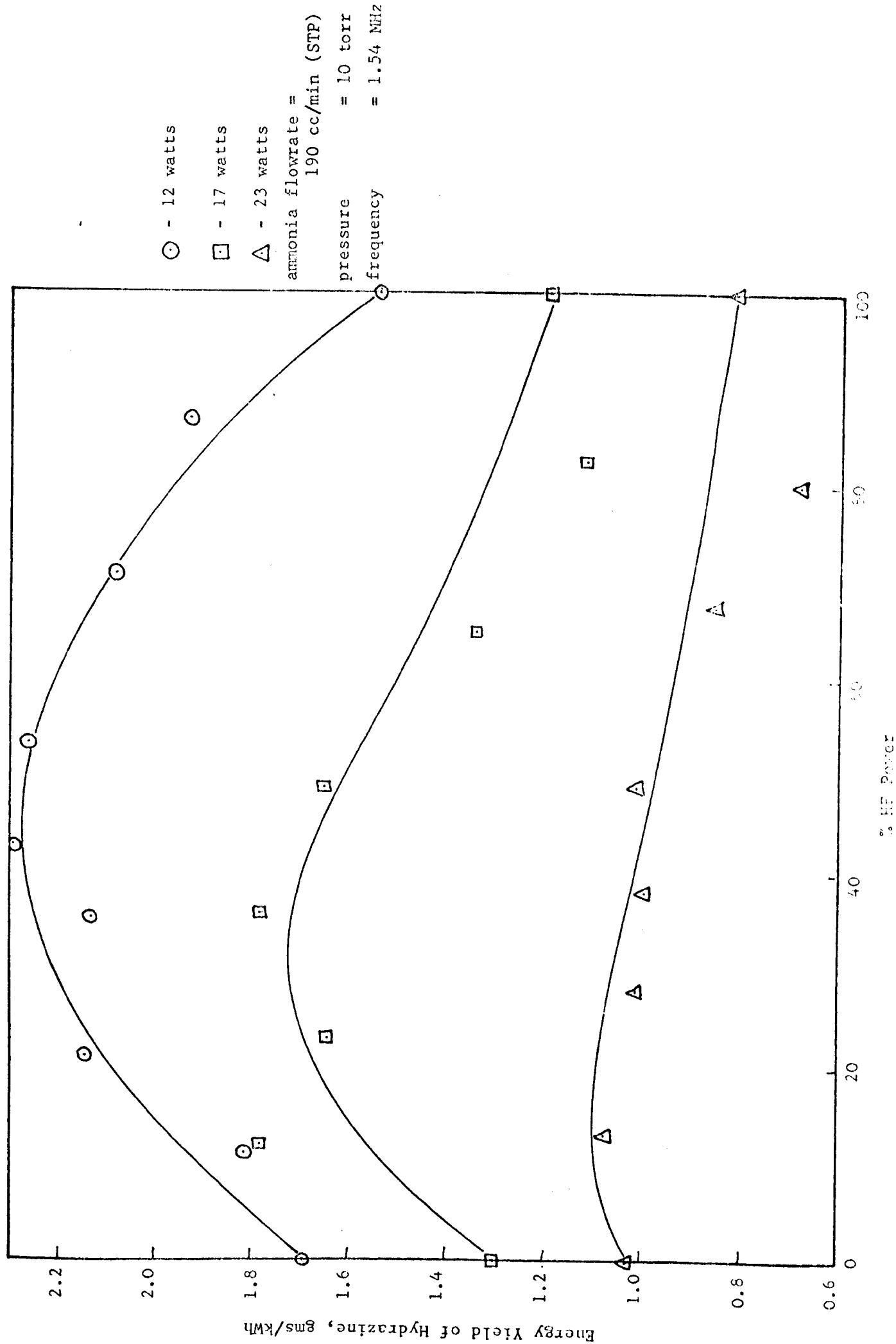


FIGURE A1.7



accounted for in the evaluation of the energy yield. Unfortunately, there was no way of establishing exactly the magnitude of this energy. It seems that Cotton's failure to recognise the existence of cross coupling, between the various electrodes, and its consequences to the power measurement, led to his misleading conclusions. It is concluded, therefore, that the crossed discharge is not a useful way of activating a discharge.

## APPENDIX 2.

### SPECIMEN CALCULATIONS

#### A2.1. Hydrazine Produced in a Run

In all runs hydrazine was absorbed in 50 ml of ethylene glycol. The latter was made up to 100 ml with distilled water after the completion of each run. 0.5 - 5.0 ml of this solution was added to 20 ml of coloured reagent for analysis. Let duration of each run be  $t$  mins and the volume of diluted product added to 20 ml of reagent be  $x$  ml then,

$$\text{dilution ratio} = \frac{x + 20}{x}$$

If the concentration of  $\text{N}_2\text{H}_4$  in the coloured complex was  $m$  p.p.m. then,

$$\text{total } \text{N}_2\text{H}_4 \text{ collected} = m \times 10^{-6} \times \frac{20 + x}{x} \times 100 \text{ gm.}$$

In order to evaluate the actual amount of  $\text{N}_2\text{H}_4$  produced in  $t$  mins, one has to realise that at the onset of each run, i.e. at the moment when the gas flow is directed towards the absorption train, the concentration of  $\text{N}_2\text{H}_4$  in the ammonia stream leaving the empty trap prior to the one containing the absorbent will be zero. The concentration will then rise exponentially to the steady state value. The time taken will be dependent on the ammonia flowrate and the combined volume of the empty trap and the gas sampling trap (see Figure 4.3). If the latter is considered to be  $V$  ml, then a mass balance on  $\text{N}_2\text{H}_4$  across  $V$  will give:

$$F\bar{x} = Fx + V \frac{dx}{dt} \quad \dots\dots\dots(A21)$$

where,

$F$  = ammonia flowrate at 10 mm Hg

$\bar{x}$  = steady state concentration of  $N_2H_4$

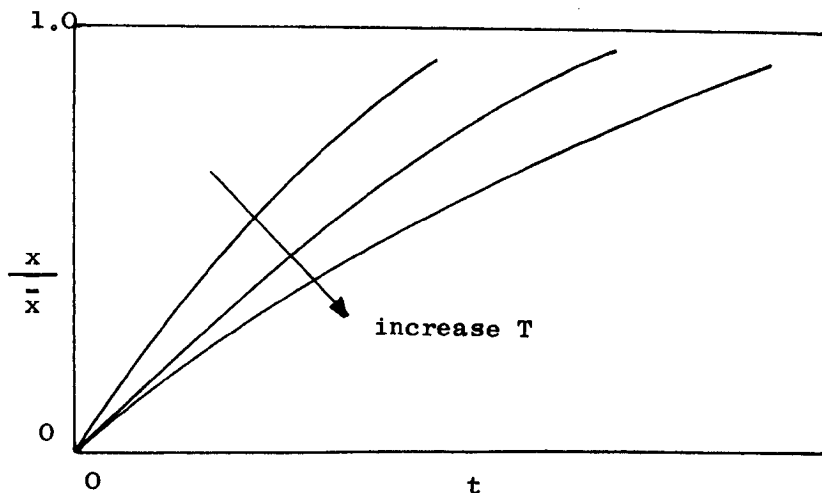
$x$  = concentration of  $N_2H_4$  in the stream leaving  $V$

Integrating equation (A21) and setting  $x = 0$  at  $t = 0$  will give,

$$\frac{x}{\bar{x}} = 1 - e^{-tF/V} \quad \dots\dots\dots(A22)$$

or 
$$\frac{x}{\bar{x}} = 1 - e^{-t/T} \quad \dots\dots\dots(A23)$$

The shape of the exponential curve will depend on the value of  $T$  as shown below,



It follows that for a run of  $t$  mins, the area under the curve (A) will be proportional to the amount of  $N_2H_4$  collected whilst the total area ( $A_t$ ) bounded by the asymptotes  $\frac{x}{\bar{x}} = 1.0$  and  $t = t$  will be proportional to the actual  $N_2H_4$  produced in  $t$  mins. Therefore, defining a correction factor,  $f_c$ , such that,

$$f_c = \frac{A}{A_t} = \frac{t}{\int_0^t (1 - e^{-t/T}) dt} \quad \dots\dots\dots(A24)$$

the actual amount of  $N_2H_4$  produced in t mins will be,

$$\text{gms } N_2H_4 = \frac{t}{\int_0^t (1 - e^{-t/\tau}) dt} \left( m \times 10^{-6} \times \frac{20 + K}{K} \times 100 \right) \dots\dots\dots(A25)$$

Typical Case (Run 1)

In all cases V was estimated to be 2300 ml.

$$F = 50 \text{ cc/min (STP)} = 50 \times 76 = 3800 \text{ cc/min at 10 torr}$$

$$t = 5 \text{ mins.}$$

$$\therefore f_c = 1.135$$

$$m = 0.084$$

$$K = 1.0 \text{ ml}$$

$$\begin{aligned} \therefore \text{gms } N_2H_4 \text{ produced} &= 1.135 \times 0.084 \times 10^{-6} \times 21 \times 100 \\ &= \underline{2.0 \times 10^{-4}} \end{aligned}$$

$$\begin{aligned} \therefore \text{rate of } N_2H_4 \text{ product}^n &= \frac{2.0}{5} \times 10^{-4} \times 60 \\ &= \underline{2.4 \times 10^{-3}} \text{ gms/hr.} \end{aligned}$$

A2.2 Overall Conversion to Hydrazine (wt.%)

$$\text{overall conversion } (X_{N_2H_4}) = \frac{\text{gms hydrazine formed}}{\text{gms ammonia passed}} \times 100$$

For Run 1

$$\text{Ammonia passed in 5 mins.} = 50 \times 5 \times 0.000716$$

$$= 0.179 \text{ gms}$$

$$\begin{aligned} \therefore X_{N_2H_4} &= \frac{2.0 \times 10^{-4}}{0.179} \times 10^2 \\ &= \underline{0.112\%} \end{aligned}$$

### A2.3. Energy Yield of Hydrazine

#### (a) Continuous DC case (Run 1)

$$\text{Running voltage} = 630 \text{ volts}$$

$$\text{current} = 10 \text{ mA}$$

$$\text{kWh in 5 mins} = \frac{630 \times 10 \times 10^{-3}}{10^3} \times \frac{5}{60}$$

$$= 5.25 \times 10^{-4}$$

$$\therefore \text{Energy yield (Y)} = \frac{2.0 \times 10^{-4}}{5.25 \times 10^{-4}}$$

$$= 0.381 \text{ gms /kWh}$$

#### (b) Pulsed DC case (Run 51)

$$t = 7.5 \text{ mins}$$

$$m = 0.24 \text{ p.p.m.}$$

$$\frac{20 + \pi}{\pi} = 21$$

$$f_c = 1.085$$

$$\text{Pulse OFF-time} = 0.1 \text{ msec.}$$

$$\text{Energy/Pulse} = 35 \times 10^{-12} \text{ kWh/Pulse}$$

$$\text{No. Pulses in 7.5 mins.} = \frac{7.5 \times 60}{0.1 \times 10^{-3}}$$

$$= 4.5 \times 10^6$$

$$\text{Overall energy} = 35 \times 10^{-12} \times 4.5 \times 10^6$$

$$= 1.575 \times 10^{-4} \text{ kWh}$$

$$\text{gms } \text{H}_2\text{N}_2 \text{ produced} = 1.085 \times 0.24 \times 10^{-6} \times 21 \times 100$$

$$= 5.46 \times 10^{-4} \text{ gms}$$

$$\therefore \text{Energy yield (Y)} = \frac{5.46 \times 10^{-4}}{1.575 \times 10^{-4}}$$

$$= 3.46 \text{ gms /kWh}$$

#### A2.4. Overall Ammonia Conversion and Molar Conversion to Hydrazine

From Section 4.6.2, the overall stoichiometric equations for ammonia decomposition were given as:



Assume the percentage molar composition of the gaseous mixture leaving the reactor is x% hydrazine; y% nitrogen; s% hydrogen. y and s are given by the gas chromatograph whilst x is calculated from y and s together with the observed overall conversion to hydrazine ( $X_{\text{N}_2\text{H}_4}$ ). If we consider 100 moles of gaseous mixture then,

| <u>component</u>       | <u>λ molar</u>      | <u>wt. in 100 moles of mixture</u> |
|------------------------|---------------------|------------------------------------|
| $\text{N}_2\text{H}_4$ | x                   | 32x                                |
| $\text{N}_2$           | y                   | 28y                                |
| $\text{H}_2$           | s                   | 2s                                 |
| $\text{NH}_3$          | $100 - (x + y + s)$ | $17(100 - (x + y + s))$            |

$$\begin{aligned} \text{total wt. of mixture} &= 1700 + 15x + 11y - 15s \\ &= \text{wt. of ammonia before decomposition} \end{aligned}$$

$$\begin{aligned} \therefore X_{\text{N}_2\text{H}_4} &= \frac{32x}{1700 + 15x + 11y - 15s} \times 100 \\ \text{or } x &= X_{\text{N}_2\text{H}_4} (17 - 0.15s + 0.11y) / (32 - 0.15 X_{\text{N}_2\text{H}_4}) \\ &\dots\dots\dots(\text{A28}) \end{aligned}$$

$$\begin{aligned} \text{Also, moles of ammonia to produce 100 moles of mixture} &= \frac{1700 + 15x + 11y - 15s}{17} \\ &= 100 + 0.882x + 0.647y - 0.882s \end{aligned}$$

∴ overall ammonia conversion,  $X_{\text{NH}_3}$

$$= \frac{2(x+y)}{100 + 0.882x + 0.647y - 0.882z} \times 100 \quad \dots(A19)$$

and molar conversion to hydrazine,  $\bar{X}_{\text{N}_2\text{H}_4}$

$$= \frac{x}{x+y} \times 100 \quad \dots\dots\dots(A210)$$

Typical case (Run 1)

$$X_{\text{N}_2\text{H}_4} = 0.112\% \quad (\text{wt.})$$

$$y = 1.115\% \quad (\text{molar})$$

$$z = 3.40\% \quad (\text{molar})$$

$$\therefore x = 0.0582\% \quad (\text{molar})$$

$$\text{and } X_{\text{NH}_3} = 2.35\% \quad (\text{molar})$$

$$\bar{X}_{\text{N}_2\text{H}_4} = 4.96\% \quad (\text{molar})$$

A2.5. Energy Efficiency of the Discharge

Taking the dissociation energy of the (NH<sub>2</sub> - H) bond to be 4.5 e.v. or 104 kcal/mole, then the maximum theoretical yield of hydrazine will be 133 gms/kWh according to the following equation,



Similarly, the maximum theoretical amount of ammonia decomposed per kWh will be 141 gms. If  $Y_{\text{N}_2\text{H}_4}$  and  $Y_{\text{NH}_3}$  are the energy yield of hydrazine and the amount of ammonia decomposed/kWh, then the efficiency of the discharge will be,

$$\eta_{\text{N}_2\text{H}_4} = \frac{Y_{\text{N}_2\text{H}_4}}{133} \times 100 \%$$

$$\text{and } \eta_{\text{NH}_3} = \frac{Y_{\text{NH}_3}}{141} \times 100 \%$$

$$\text{But, } Y_{\text{NH}_3} = \frac{\text{gas decomposed/hr}}{\text{Power}}$$

$$= \frac{X_{\text{NH}_3} F}{W} \times \frac{1}{100}$$

$$\text{Then, } \eta_{\text{NH}_3} = \frac{X_{\text{NH}_3} F}{141 W}$$

Where,

$X_{\text{NH}_3}$  = overall conversion of ammonia %

$F$  = mass flowrate, gms/hr

$W$  = discharge power, kW

Since in practice the ammonia is found to by-pass the negative glow, the energy efficiency is based on the power dissipated in the positive column.

### Typical Examples

#### (a) Continuous DC Discharge (Run 1)

$$X_{\text{NH}_3} = 2.35\%$$

$$F = 50 \times 0.000716 \times 60$$

$$= 2.148 \text{ gms/hr}$$

$$\text{kW} = 1.55 \times 10^{-3} \text{ (power in the positive column)}$$

$$Y_{\text{N}_2\text{H}_4} = 1.56 \text{ gms/kWh (based on power in the positive column)}$$

$$\therefore \text{N}_2\text{H}_4 = \frac{1.56}{133} \times 100$$

$$= 1.17\%$$

$$\text{NH}_3 = \frac{2.35 \times 2.148}{1.41 \times 1.55 \times 10^{-3}}$$

$$= 23\%$$

(b) Pulsed DC Discharge (Run 48)

$$\text{Pulse OFF-time} = 2 \text{ msec}$$

$$\text{Energy/Pulse} = 24.4 \times 10^{-12} \text{ kWh (total)}$$

$$\text{Energy/Pulse} = 18.6 \times 10^{-12} \text{ kWh (positive column only)}$$

$$x_{\text{NH}_3} = 0.054\%$$

$$F = 2.148 \text{ gms/hr}$$

$$Y_{\text{N}_2\text{H}_4} = 15.7 \text{ gms/kWh (based on power in the positive column)}$$

$$\begin{aligned} \eta_{\text{N}_2\text{H}_4} &= 15.7 \times 100/133 \\ &= \underline{11.8\%} \end{aligned}$$

$$\begin{aligned} \eta_{\text{NH}_3} &= \frac{x_{\text{NH}_3} F/\text{Pulse}}{\text{Energy/Pulse}} \times \frac{1}{141} \\ &= \frac{6.45 \times 10^{-8}}{18.6 \times 10^{-12} \times 141} \\ &= \underline{24.6\%} \end{aligned}$$

A2.6 Fraction of Electrons with Energies in Excess of a Certain Value

In a gas discharge the energy distribution of the electrons is usually taken to be Maxwellian and the number of electrons having energies between  $\epsilon$  and  $\epsilon + d\epsilon$  is given by,

$$N(\epsilon) d\epsilon = \frac{2N_e}{\sqrt{\pi}} \left[ \left( \frac{\epsilon}{\epsilon_m} \right)^{\frac{1}{2}} e^{-\epsilon/\epsilon_m} d\left( \frac{\epsilon}{\epsilon_m} \right) \right] \dots\dots\dots(\text{A2.14})$$

where,

$N(\epsilon)$  = number of electron in the energy band  $d\epsilon$

$N_e$  = total number of electrons

$\epsilon_m$  = mean electron energy =  $kT_e$

$k$  = Boltzmann constant

$T_e$  = electronic temperature.

From (A2.14), the number of electrons having energies in excess of  $\epsilon$  will be given by,

$$N(\epsilon) = \frac{2N_e}{\sqrt{\pi}} \int_{\epsilon/\epsilon_m}^{\infty} \left(\frac{\epsilon}{\epsilon_m}\right)^{\frac{1}{2}} e^{-\epsilon/\epsilon_m} d\left(\frac{\epsilon}{\epsilon_m}\right) \dots\dots(A2.15)$$

Equation (A2.15) was used to evaluate the fraction of electrons having energies in excess of  $\epsilon$  as a function of  $\frac{\epsilon}{\epsilon_m}$ . The result of this computation is shown in Figure A2.1.

#### A2.7. Calculation of the Optimum Scanning Frequency, $N^*$

From Section 5.3.2(a) the fraction of reactor cross-section scanned by the discharge at a frequency of  $N \text{ min}^{-1}$  is given as:

$$\begin{aligned} F_s &= N(t_1 + t_2) \\ &= Nt_1 + Nt_2 \end{aligned}$$

But  $t_2 = \frac{W}{2\pi RN}$

$$\therefore F_s = Nt_1 + \frac{W}{2\pi R}$$

The optimum scanning frequency will correspond to  $F_s$  being unity

$$\therefore N^* = \frac{1 - \frac{W}{2\pi R}}{t_1} \dots\dots\dots(A2.16)$$

##### (a) Continuous DC Case

The values of  $t_1$  corresponding to the three flowrates investigated, namely 50, 100, and 200 cc/min (STP), are 0.266, 0.133,

and 0.0665 sec. respectively. Also,  $(\frac{W}{2\pi R})$  was estimated to be 0.1275, on the assumption that only the visible zone was responsible for chemical activation.

$$\begin{aligned} \therefore N^A &= \frac{1 - 0.1275}{0.266} \times 60 = 197 \text{ min}^{-1} \text{ (at 50 cc/min)} \\ &= \frac{1 - 0.1275}{0.133} \times 60 = 384 \text{ min}^{-1} \text{ (at 100 cc/min)} \\ &= \frac{1 - 0.1275}{0.0665} \times 60 = 787 \text{ min}^{-1} \text{ (at 200 cc/min)} \end{aligned}$$

(b) Pulsed DC Case

Here, scanning was investigated at a flowrate of 50 cc/min only. Due to a slightly greater cross-sectional area available for gas flow (Section 4.1),  $t_1$  was calculated to be 0.298 sec. The value of  $\frac{W}{2\pi R}$  was estimated to be 0.032.

$$\therefore N^B = \frac{1 - 0.032}{0.298} \times 60 = 195 \text{ min}^{-1}$$

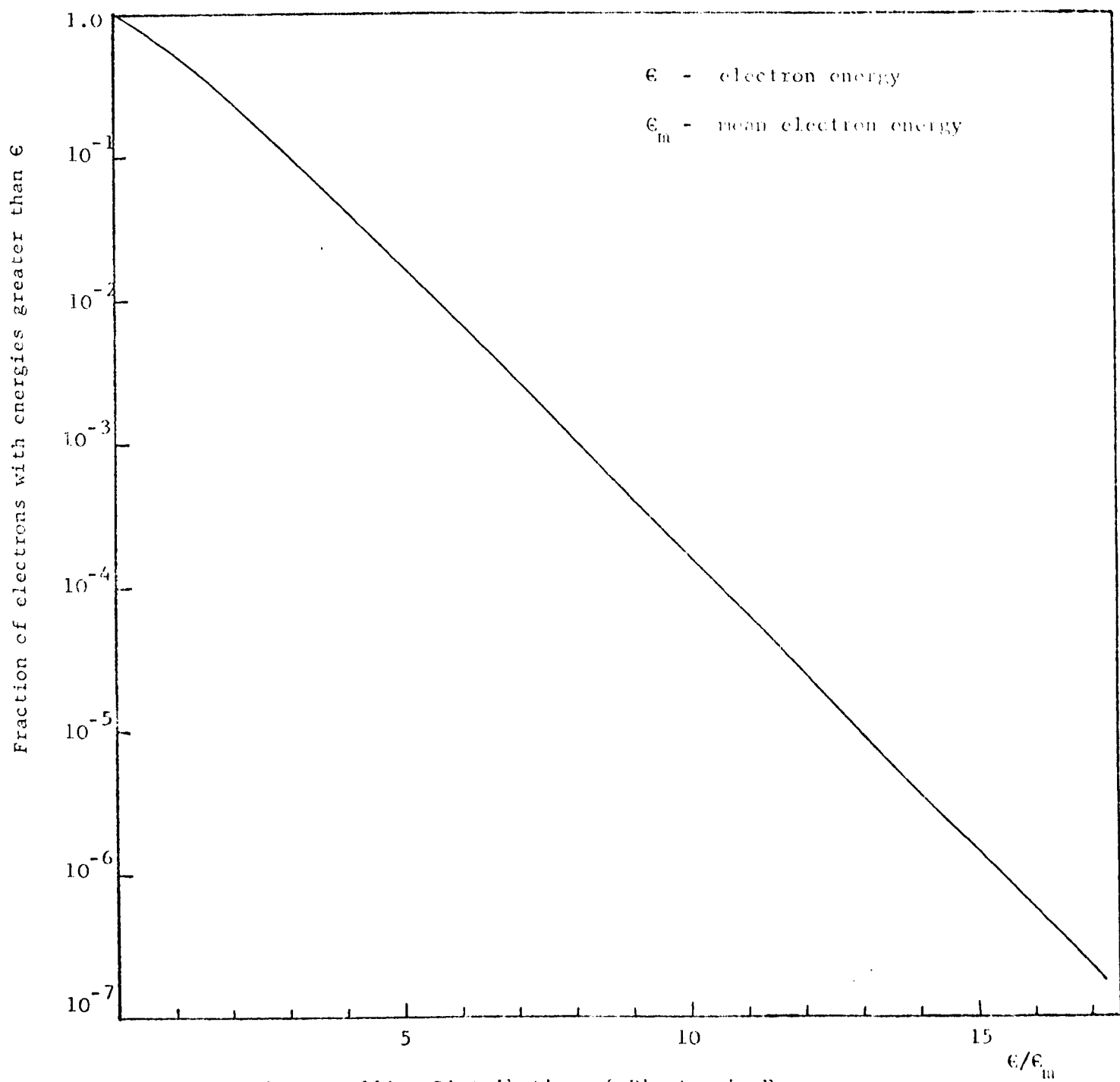


Figure A2.1 Maxwellian Distribution of Electronic Energy

APPENDIX 3.

**CALIBRATION CURVES**

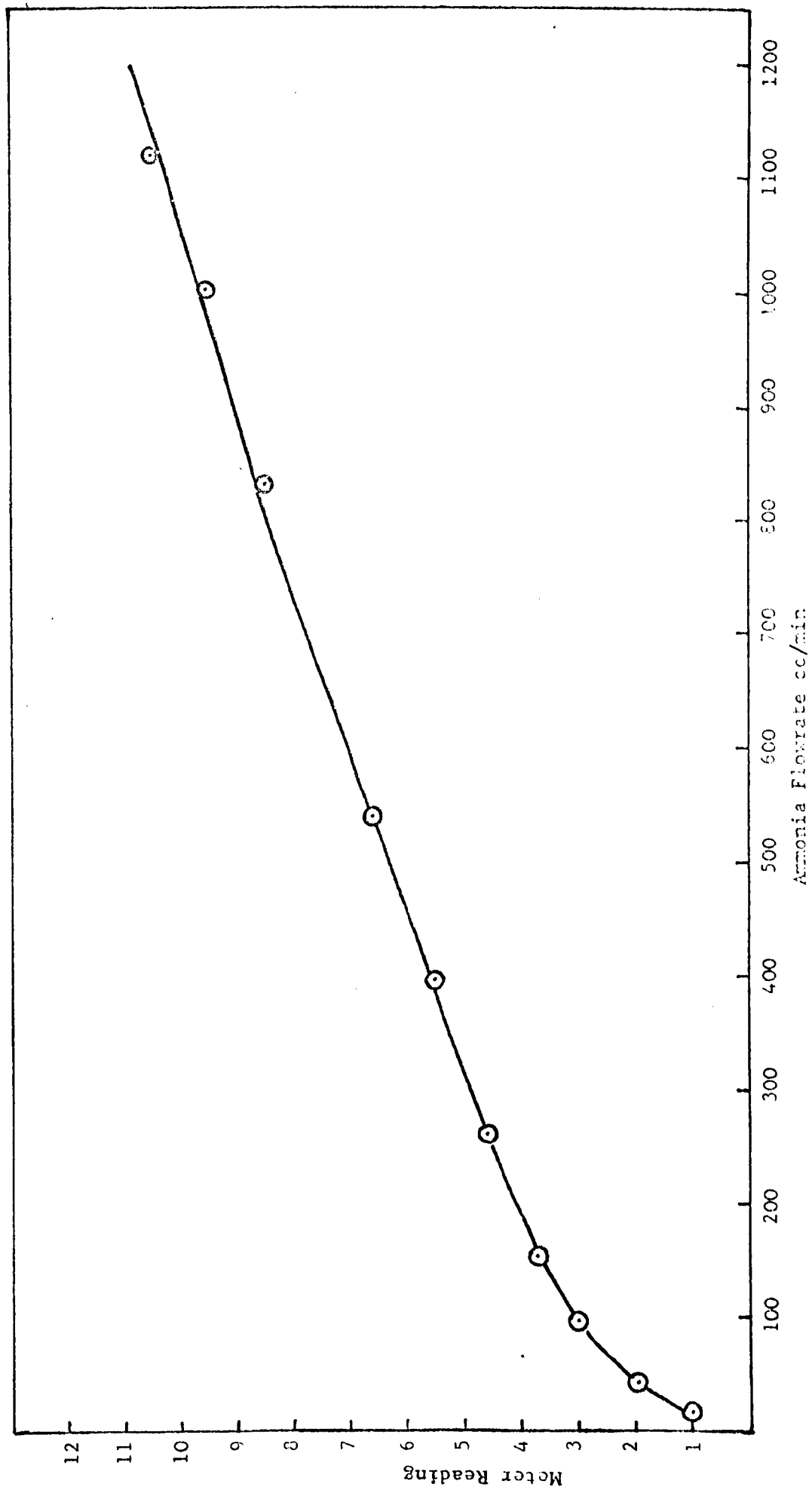


Figure A2.1 Calibration curve for a Tri-Flat Rotameter FP 4-12-G-3 at 20°C and 760 mm Hg

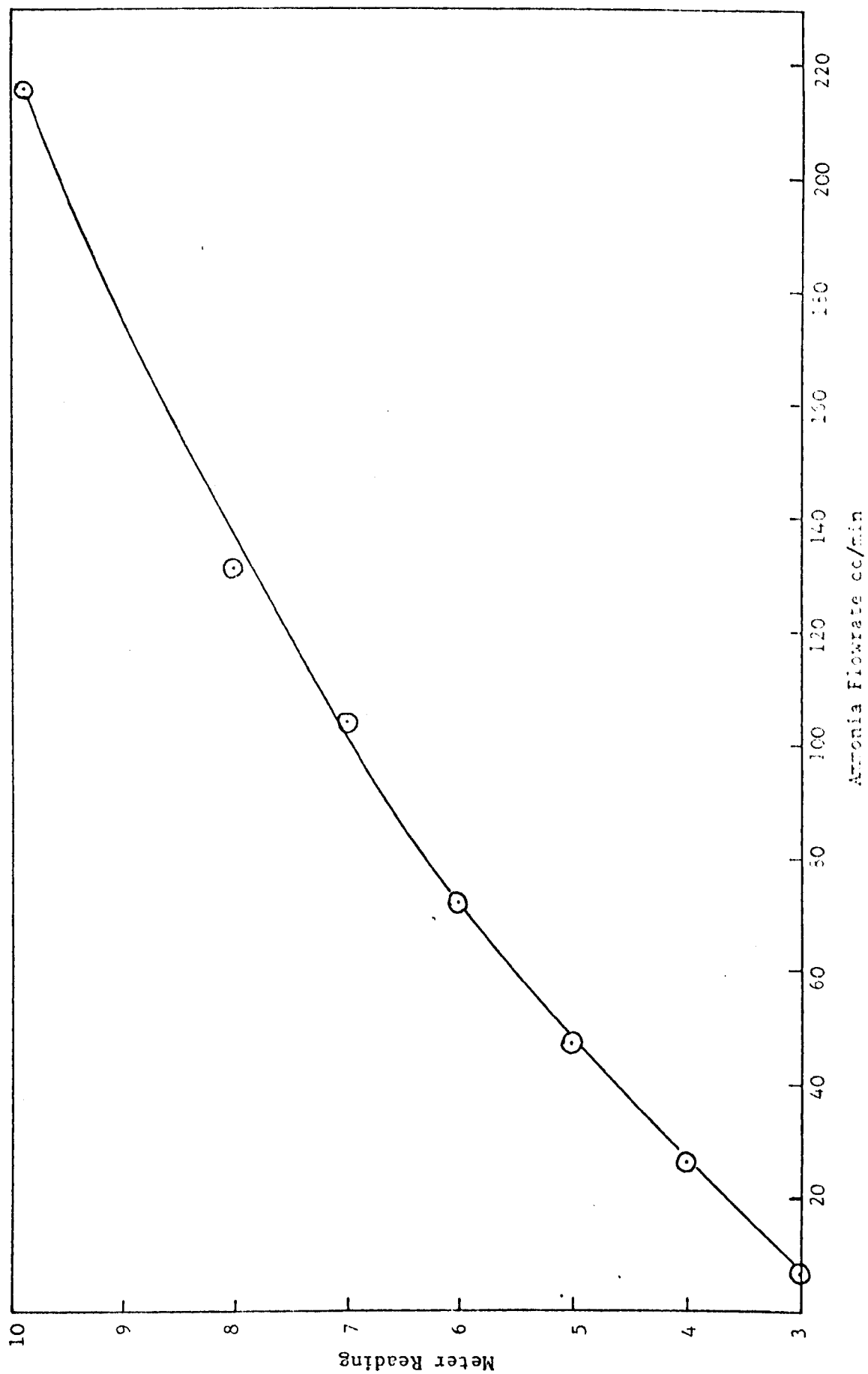


Figure A3.2 Calibration Curve for a Tri-Flat Potometer Of  $r^2/10 - 10^{-4}/35$  at  $20^\circ\text{C}$  and  $760\text{ mm Hg}$ .

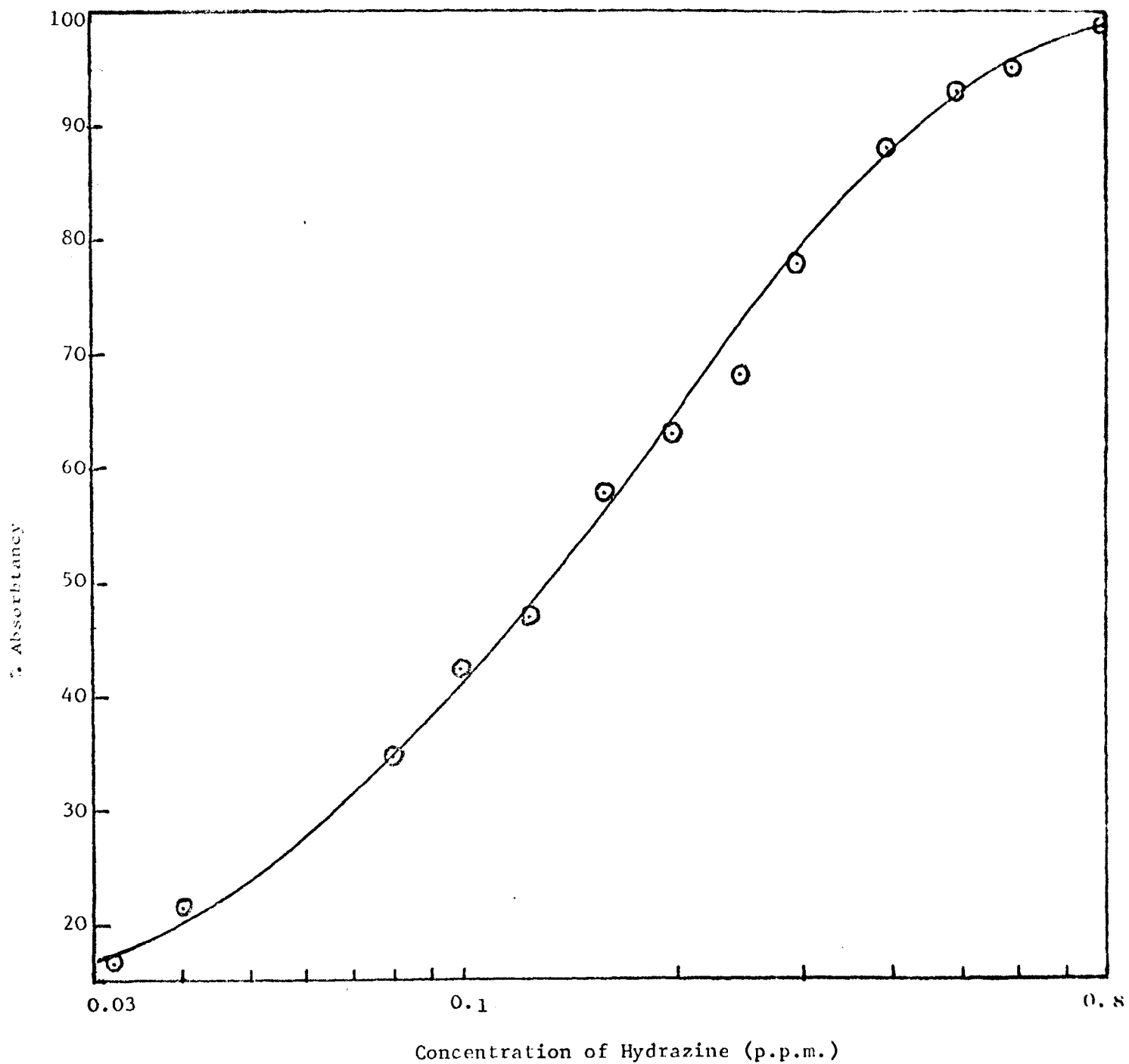


Figure A3.3 Calibration Curve for Hydrazine Determination

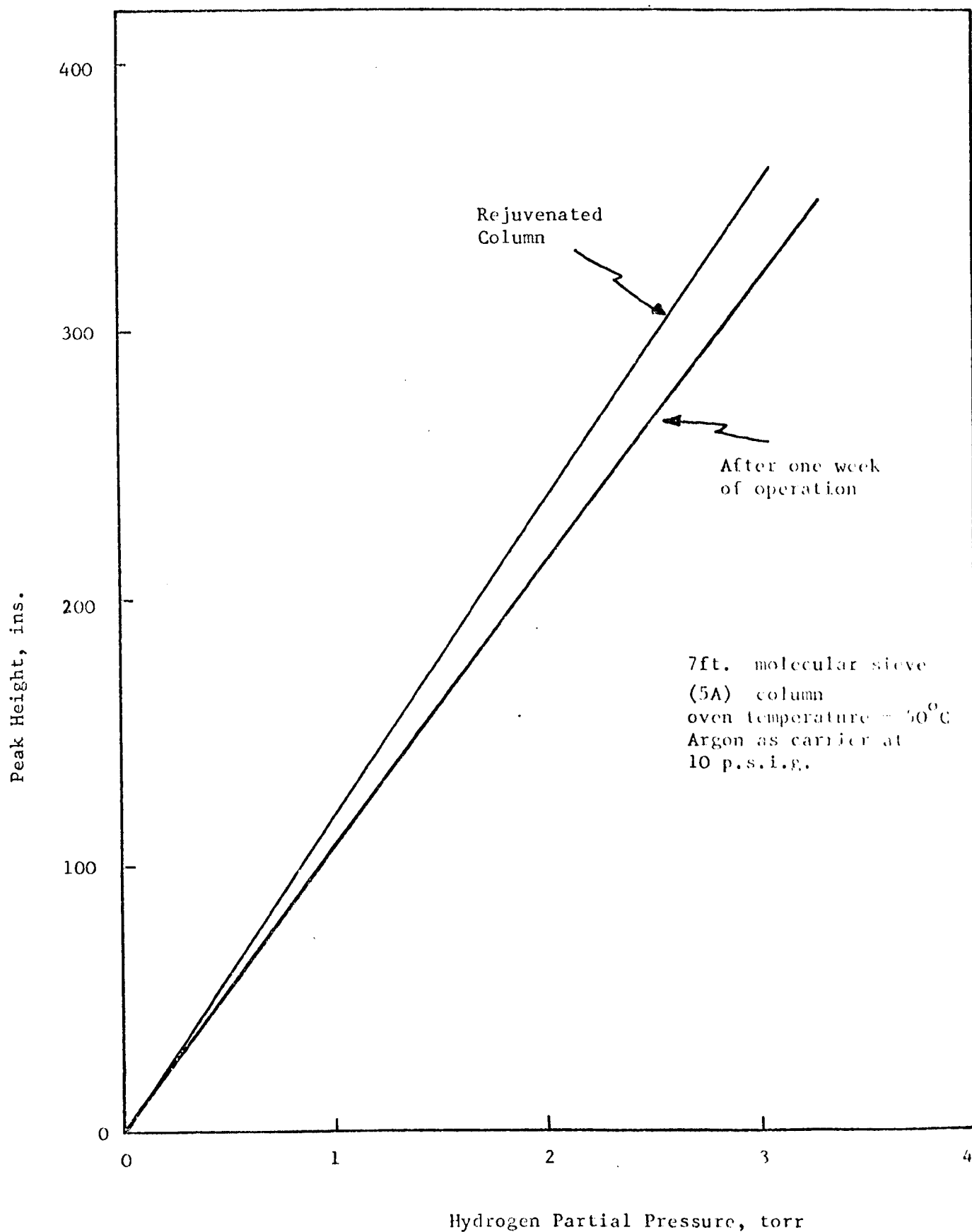


Figure A3.4 Chromatograph Response for Hydrogen

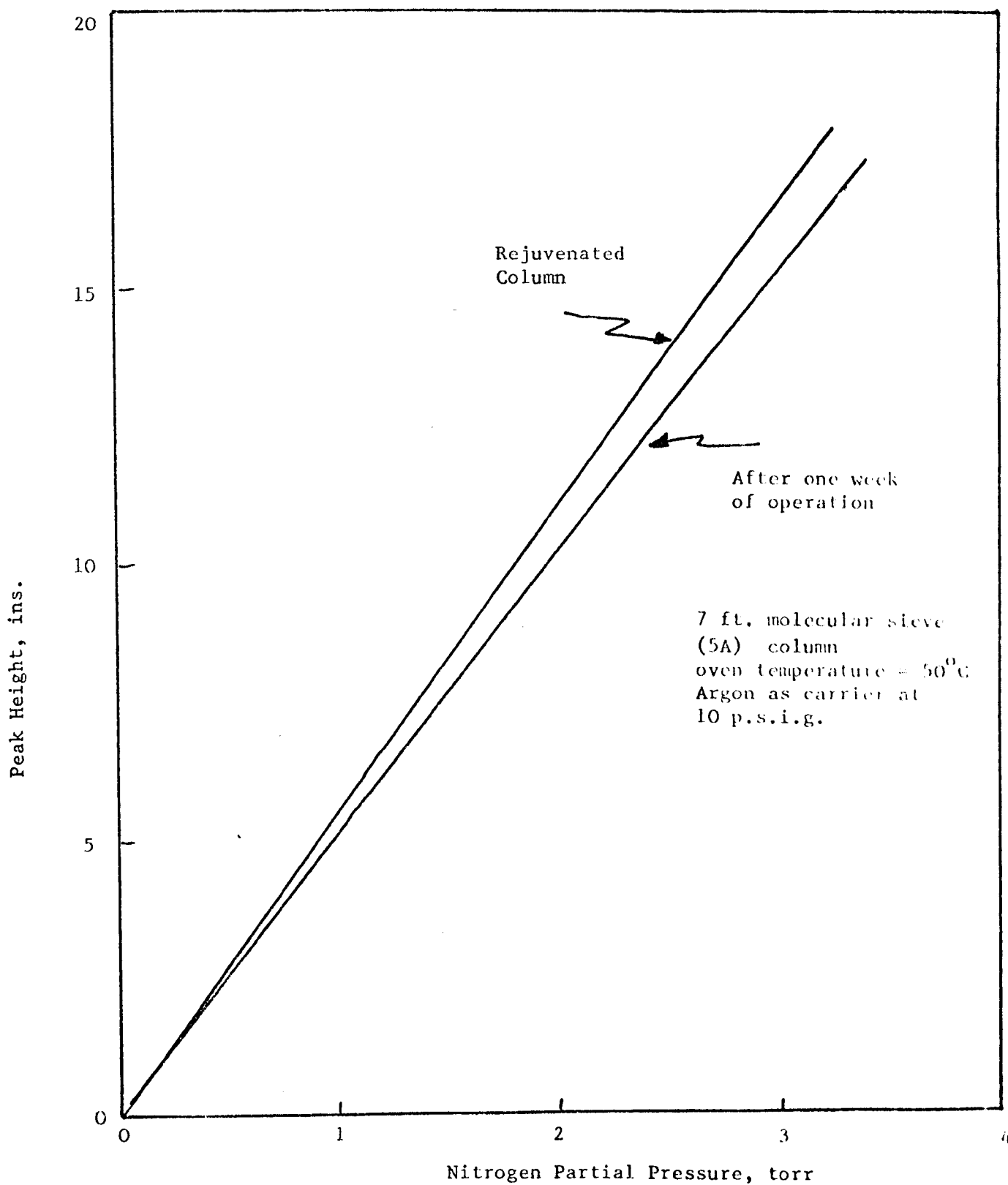


Figure A3.5 Chromatograph Response for Nitrogen

APPENDIX 4.

**TABULATED RESULTS**

Continuous DC Discharge without Beam Scanning

Discharge current = 10 mA

Discharge voltage = 630 volts

Pressure = 10 torr

| Run<br>number | NH <sub>3</sub><br>flowrate<br>cc/min(STP) | Run<br>duration<br>mins | Dilution<br>ratio | P.p.m. * | % H <sub>2</sub><br>molar | % H <sub>2</sub><br>molar | Overall NH <sub>3</sub><br>conversion<br>% | Overall<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>wt.-% | Molar<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>% | Energy yield<br>of N <sub>2</sub> H <sub>4</sub><br>gms/kWh |
|---------------|--------------------------------------------|-------------------------|-------------------|----------|---------------------------|---------------------------|--------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------|
| 1             | 50                                         | 5                       | 21                | 0.084    | 3.4                       | 1.115                     | 2.35                                       | 0.112                                                              | 4.96                                                         | 0.382                                                       |
| 2             | 75                                         | 5                       | 11                | 0.268    | 2.39                      | 0.775                     | 1.68                                       | 0.12                                                               | 7.6                                                          | 0.61                                                        |
| 3             | 100                                        | 5                       | 41                | 0.102    | 1.875                     | 0.605                     | 1.34                                       | 0.134                                                              | 9.85                                                         | 0.845                                                       |
| 4             | 150                                        | 2.5                     | 21                | 0.139    | 1.365                     | 0.435                     | 0.986                                      | 0.11                                                               | 11.2                                                         | 1.12                                                        |
| 5             | 200                                        | 2.5                     | 11                | 0.274    | 1.105                     | 0.352                     | 0.8                                        | 0.089                                                              | 12.0                                                         | 1.22                                                        |

\* - concentration of hydrazine in gas/10<sup>6</sup> ml of colored solution.

TABLE 2.

Continuous DC Discharge without Beam Scanning

Discharge current = 5 mA

Discharge voltage = 680 volts

Pressure = 10 torr

| Run<br>number | NH <sub>3</sub><br>flowrate<br>cc/min(STP) | Run<br>duration<br>mins | Dilution<br>ratio | P.P.M. | % N <sub>2</sub><br>molar | % N <sub>2</sub><br>molar | Overall NH <sub>3</sub><br>conversion | Overall<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>wt. % | Molar<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>% | Energy yield<br>of N <sub>2</sub> H <sub>4</sub><br>gms/kwh |
|---------------|--------------------------------------------|-------------------------|-------------------|--------|---------------------------|---------------------------|---------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------|
| 6             | 50                                         | 5                       | 11                | 0.1454 | 2.2                       | 0.708                     | 1.556                                 | 0.132                                                              | 9.0                                                          | 1.03                                                        |
| 7             | 75                                         | 5                       | 11                | 0.235  | 1.47                      | 0.477                     | 1.09                                  | 0.127                                                              | 12.4                                                         | 1.21                                                        |
| 8             | 100                                        | 5                       | 21                | 0.194  | 1.0                       | 0.311                     | 0.75                                  | 0.1205                                                             | 17.0                                                         | 1.45                                                        |
| 9             | 150                                        | 2.5                     | 11                | 0.242  | 0.8                       | 0.248                     | 0.61                                  | 0.108                                                              | 18.8                                                         | 1.8                                                         |
| 10            | 200                                        | 2.5                     | 11                | 0.252  | 0.619                     | 0.192                     | 0.472                                 | 0.0825                                                             | 18.6                                                         | 1.9                                                         |

**TABLE 3.**

**Continuous DC Discharge without Beam Scanning**

Discharge current = 2.6 mA

Discharge voltage = 730 volts

Pressure = 10 torr

| Run number | NH <sub>3</sub> flowrate cc/min(STP) | Run duration min | Dilution ratio | P-P-S. | % N <sub>2</sub> molar | % N <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to N <sub>2</sub> H <sub>4</sub> wt.-% | Molar conversion to N <sub>2</sub> H <sub>4</sub> % | Energy yield of N <sub>2</sub> H <sub>4</sub> gms/kWh |
|------------|--------------------------------------|------------------|----------------|--------|------------------------|------------------------|--------------------------------------|-----------------------------------------------------------|-----------------------------------------------------|-------------------------------------------------------|
| 11         | 50                                   | 5                | 11             | 0.1175 | 1.42                   | 0.45                   | 0.978                                | 0.116                                                     | 12.0                                                | 1.43                                                  |
| 12         | 75                                   | 5                | 11             | 0.224  | 0.916                  | 0.285                  | 0.692                                | 0.114                                                     | 17.5                                                | 1.93                                                  |
| 13         | 100                                  | 5                | 21             | 0.183  | 0.725                  | 0.221                  | 0.563                                | 0.114                                                     | 21.4                                                | 2.57                                                  |
| 14         | 150                                  | 5                | 21             | 0.222  | 0.42                   | 0.124                  | 0.344                                | 0.09                                                      | 27.8                                                | 3.14                                                  |
| 15         | 200                                  | 2.5              | 11             | 0.25   | 0.336                  | 0.096                  | 0.28                                 | 0.0818                                                    | 30.7                                                | 3.62                                                  |

TABLE 4.

Continuous DC Discharge with Beam Scanning

Ammonia flowrate = 200 cc/min (STP)

Discharge current = 10 mA

Pressure = 10 torr

| Run number | Scanning frequency min. <sup>-1</sup> | Discharge voltage volts | Run duration min | Dilution ratio | P.p.m. | % H <sub>2</sub> molar | % H <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to N <sub>2</sub> H <sub>4</sub> % | Molar conversion of N <sub>2</sub> H <sub>4</sub> to N <sub>2</sub> H <sub>4</sub> % | Energy yield gas/torr |
|------------|---------------------------------------|-------------------------|------------------|----------------|--------|------------------------|------------------------|--------------------------------------|-------------------------------------------------------|--------------------------------------------------------------------------------------|-----------------------|
| 1          | 0                                     | 630                     | 2.5              | 1:1            | 0.274  | 1.166                  | 0.352                  | 0.6                                  | 0.069                                                 | 12.0                                                                                 | 1.22                  |
| 16         | 140                                   | 640                     | 2.5              | 2:1            | 0.21   | 1.25                   | 0.394                  | 0.927                                | 0.131                                                 | 15.0                                                                                 | 1.76                  |
| 17         | 320                                   | 650                     | 2.5              | 2:1            | 0.237  | 1.285                  | 0.403                  | 0.96                                 | 0.1475                                                | 16.35                                                                                | 1.95                  |
| 18         | 500                                   | 660                     | 2.5              | 2:1            | 0.257  | 1.25                   | 0.398                  | 0.95                                 | 0.16                                                  | 18.2                                                                                 | 2.09                  |
| 19         | 760                                   | 700                     | 2.5              | 2:1            | 0.295  | 1.285                  | 0.3957                 | 0.986                                | 0.183                                                 | 19.9                                                                                 | 2.25                  |

TABLE 3.

Continuous DC Discharge with Beam Scanning

Ammonia flowrate = 100 cc/min (STP)

Discharge current = 10 mA

Pressure = 10 torr

| Run<br>number | Scanning<br>frequency<br>min <sup>-1</sup> | Discharge<br>voltage<br>volts | Run<br>duration<br>mins | Milston<br>ratio | P-P.M. | $\% \text{H}_2$<br>molar | $\% \text{H}_2$<br>molar | Overall $\text{NH}_3$<br>conversion<br>$\%$ | Overall<br>conversion<br>to $\text{H}_2\text{H}_4$<br>wt.-% | Molar<br>conversion<br>to $\text{H}_2\text{H}_4$<br>$\%$ | Energy yield<br>of $\text{H}_2\text{H}_4$<br>gms/kWh |
|---------------|--------------------------------------------|-------------------------------|-------------------------|------------------|--------|--------------------------|--------------------------|---------------------------------------------|-------------------------------------------------------------|----------------------------------------------------------|------------------------------------------------------|
| 3             | 0                                          | 630                           | 5.0                     | 41               | 0.162  | 1.875                    | 0.605                    | 1.34                                        | 0.124                                                       | 9.85                                                     | 0.845                                                |
| 20            | 75                                         | 640                           | 5.0                     | 41               | 0.13   | 1.910                    | 0.607                    | 1.383                                       | 0.1585                                                      | 12.2                                                     | 1.06                                                 |
| 21            | 300                                        | 640                           | 5.0                     | 41               | 0.159  | 2.07                     | 0.655                    | 1.52                                        | 0.1935                                                      | 13.6                                                     | 1.26                                                 |
| 22            | 620                                        | 700                           | 5.0                     | 41               | 0.177  | 2.22                     | 0.701                    | 1.63                                        | 0.214                                                       | 14.0                                                     | 1.32                                                 |
| 23            | 825                                        | 720                           | 5.0                     | 41               | 0.196  | 2.23                     | 0.7                      | 1.655                                       | 0.239                                                       | 15.4                                                     | 1.42                                                 |

TABLE 6.

Continuous DC Discharge with Beam Scanning

Ammonia flowrate = 50 cc/min (STP)

Discharge current = 10 mA

Pressure = 10 torr

| Run Number | Scanning frequency min <sup>-1</sup> | Discharge voltage volts | Run duration mins | Dilution ratio | P.P.M. | % N <sub>2</sub> molar | % N <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to N <sub>2</sub> H <sub>4</sub> to N <sub>2</sub> H <sub>4</sub> % | Molar conversion of N <sub>2</sub> H <sub>4</sub> to N <sub>2</sub> H <sub>4</sub> % | Energy yield gms/kwh |
|------------|--------------------------------------|-------------------------|-------------------|----------------|--------|------------------------|------------------------|--------------------------------------|----------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------|
| 1          | 0                                    | 630                     | 5                 | 21             | 0.084  | 3.4                    | 1.115                  | 2.35                                 | 0.112                                                                                  | 4.96                                                                                 | 0.382                |
| 24         | 60                                   | 630                     | 5                 | 21             | 0.118  | 3.75                   | 1.22                   | 2.61                                 | 0.157                                                                                  | 6.4                                                                                  | 0.538                |
| 25         | 130                                  | 630                     | 5                 | 21             | 0.1555 | 3.81                   | 1.23                   | 2.68                                 | 0.207                                                                                  | 8.25                                                                                 | 0.705                |
| 26         | 200                                  | 645                     | 5                 | 21             | 0.168  | 3.8                    | 1.23                   | 2.725                                | 0.223                                                                                  | 8.8                                                                                  | 0.745                |
| 27         | 270                                  | 660                     | 5                 | 21             | 0.179  | 3.788                  | 1.22                   | 2.765                                | 0.233                                                                                  | 9.25                                                                                 | 0.755                |
| 28         | 370                                  | 665                     | 5                 | 21             | 0.1925 | 3.95                   | 1.27                   | 2.84                                 | 0.257                                                                                  | 9.7                                                                                  | 0.83                 |
| 29         | 470                                  | 675                     | 5                 | 21             | 0.21   | 4.0                    | 1.3                    | 2.90                                 | 0.28                                                                                   | 10.3                                                                                 | 0.89                 |

TABLE 7.

Continuous DC Discharge with Beam Scanning

Ammonia flowrate = 200 cc/min (STP)

Discharge current = 5 mA

Pressure = 10 torr

| Run number | Scanning frequency min <sup>-1</sup> | Discharge voltage volts | Run duration min | Dilation ratio | P-P-M. | % H <sub>2</sub> molar | % H <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to H <sub>2</sub> N <sub>2</sub> Vt-% | Molar conversion to H <sub>2</sub> N <sub>2</sub> % | Energy yield of H <sub>2</sub> N <sub>2</sub> gms/ctmh |
|------------|--------------------------------------|-------------------------|------------------|----------------|--------|------------------------|------------------------|--------------------------------------|----------------------------------------------------------|-----------------------------------------------------|--------------------------------------------------------|
| 10         | 0                                    | 680                     | 2.5              | 11             | 0.252  | 0.619                  | 0.192                  | 0.472                                | 0.0825                                                   | 18.6                                                | 1.9                                                    |
| 30         | 30                                   | 680                     | 2.5              | 21             | 0.1615 | 0.64                   | 0.196                  | 0.49                                 | 0.088                                                    | 19.0                                                | 2.05                                                   |
| 31         | 100                                  | 685                     | 2.5              | 21             | 0.153  | 0.724                  | 0.22                   | 0.545                                | 0.0948                                                   | 19.7                                                | 2.38                                                   |
| 32         | 300                                  | 710                     | 2.5              | 21             | 0.171  | 0.709                  | 0.218                  | 0.535                                | 0.1065                                                   | 20.4                                                | 2.57                                                   |
| 33         | 550                                  | 745                     | 2.5              | 21             | 0.206  | 0.763                  | 0.212                  | 0.561                                | 0.1285                                                   | 24.4                                                | 2.97                                                   |
| 34         | 800                                  | 775                     | 2.5              | 21             | 0.2255 | 0.728                  | 0.218                  | 0.585                                | 0.1395                                                   | 25.3                                                | 3.12                                                   |

TABLE 8.

Continuous DC Discharge with Beam Scanning

Ammonia flowrate = 100 cc/min (STP)

Discharge current = 5 mA

Pressure = 10 torr

| Run number | Scanning frequency min. <sup>-1</sup> | Discharge voltage volts | Run duration min | Dilution ratio | P-P-M. | % H <sub>2</sub> molar | % H <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to H <sub>2</sub> NH <sub>2</sub> wt.-% | Molar conversion to H <sub>2</sub> NH <sub>2</sub> % | Energy yield of H <sub>2</sub> NH <sub>2</sub> gms/kwh |
|------------|---------------------------------------|-------------------------|------------------|----------------|--------|------------------------|------------------------|--------------------------------------|------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------|
| 8          | 0                                     | 680                     | 3                | 21             | 0.194  | 1.0                    | 0.311                  | 0.73                                 | 0.1205                                                     | 17.0                                                 | 1.43                                                   |
| 35         | 100                                   | 680                     | 3                | 21             | 0.244  | 1.034                  | 0.314                  | 0.79                                 | 0.132                                                      | 20.4                                                 | 1.91                                                   |
| 36         | 400                                   | 720                     | 3                | 21             | 0.29   | 1.097                  | 0.333                  | 0.86                                 | 0.1805                                                     | 22.4                                                 | 2.155                                                  |
| 37         | 600                                   | 750                     | 3                | 41             | 0.155  | 1.12                   | 0.338                  | 0.88                                 | 0.192                                                      | 23.2                                                 | 2.21                                                   |
| 38         | 800                                   | 770                     | 3                | 41             | 0.161  | 1.135                  | 0.343                  | 0.9                                  | 0.20                                                       | 23.7                                                 | 2.24                                                   |

**TABLE 2.**

**Continuous DC Discharge with Beam Scanning**

Ammonia flowrate = 200 cc/min (STP)

Discharge current = 2.6 mA

Pressure = 10 torr

| Run number | Scanning frequency min <sup>-1</sup> | Discharge voltage volts | Run duration min | Dilution ratio | P.P.M. | % H <sub>2</sub> molar | % H <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to N <sub>2</sub> H <sub>4</sub> wt.-% | Molar conversion to N <sub>2</sub> H <sub>4</sub> | Energy yield of N <sub>2</sub> H <sub>4</sub> gms/min |
|------------|--------------------------------------|-------------------------|------------------|----------------|--------|------------------------|------------------------|--------------------------------------|-----------------------------------------------------------|---------------------------------------------------|-------------------------------------------------------|
| 13         | 0                                    | 730                     | 2.5              | 11             | 0.25   | 0.138                  | 0.098                  | 0.28                                 | 0.0818                                                    | 30.7                                              | 3.63                                                  |
| 39         | 100                                  | 730                     | 2.5              | 21             | 0.135  | 0.158                  | 0.101                  | 0.391                                | 0.084                                                     | 30.7                                              | 3.81                                                  |
| 40         | 200                                  | 730                     | 2.5              | 21             | 0.152  | 0.264                  | 0.1045                 | 0.31                                 | 0.0945                                                    | 32.3                                              | 4.15                                                  |
| 41         | 300                                  | 760                     | 2.5              | 21             | 0.163  | 0.284                  | 0.1095                 | 0.327                                | 0.1015                                                    | 33.0                                              | 4.43                                                  |
| 42         | 700                                  | 770                     | 2.5              | 21             | 0.17   | 0.377                  | 0.107                  | 0.326                                | 0.1035                                                    | 34.4                                              | 4.53                                                  |

**TABLE 10.**

**Continuous DC Discharge with Beam Scanning**

**Ammonia flowrate = 100 cc/min (STP)**

**Discharge current = 2.6 mA**

**Pressure = 10 torr**

| Run number | Scanning frequency min <sup>-1</sup> | Discharge voltage volts | Run duration mins | Dilution ratio | P-p.m. | % N <sub>2</sub> molar | % N <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to N <sub>2</sub> H <sub>4</sub> wt.-% | Molar conversion to N <sub>2</sub> H <sub>4</sub> % | Energy yield of N <sub>2</sub> H <sub>4</sub> gae/kwh |
|------------|--------------------------------------|-------------------------|-------------------|----------------|--------|------------------------|------------------------|--------------------------------------|-----------------------------------------------------------|-----------------------------------------------------|-------------------------------------------------------|
| 13         | 0                                    | 739                     | 5                 | 21             | 0.183  | 0.725                  | 0.221                  | 0.563                                | 0.114                                                     | 21.4                                                | 2.57                                                  |
| 43         | 170                                  | 740                     | 5                 | 21             | 0.227  | 0.735                  | 0.219                  | 0.588                                | 0.141                                                     | 25.5                                                | 3.15                                                  |
| 44         | 375                                  | 750                     | 5                 | 21             | 0.247  | 0.732                  | 0.217                  | 0.597                                | 0.1535                                                    | 27.3                                                | 3.4                                                   |
| 45         | 500                                  | 770                     | 5                 | 21             | 0.265  | 0.745                  | 0.219                  | 0.613                                | 0.165                                                     | 28.5                                                | 3.53                                                  |
| 46         | 800                                  | 780                     | 5                 | 21             | 0.290  | 0.786                  | 0.231                  | 0.65                                 | 0.18                                                      | 29.4                                                | 3.81                                                  |

TABLE 11.

Pulsed DC Discharge without Beam Scanning

Pulse OFF-time = 2 msec  
Pulse ON-time = 4.5  $\mu$ sec  
Peak current = 150 mA  
Energy/pulse =  $24.4 \times 10^{-12}$  kWh  
Pressure = 10 torr

| Run number | NH <sub>3</sub> flowrate cc/min(577) | Run duration mins | Mission ratio | P-P.M. | % N <sub>2</sub> molar | % N <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to H <sub>2</sub> N <sub>2</sub> wt. % | Molar conversion of H <sub>2</sub> N <sub>2</sub> to H <sub>2</sub> N <sub>2</sub> | Energy yield of H <sub>2</sub> N <sub>2</sub> gm/kwh |
|------------|--------------------------------------|-------------------|---------------|--------|------------------------|------------------------|--------------------------------------|-----------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------|
| 47         | 15                                   | 30                | 5             | 0.287  | 0.167                  | 0.0485                 | 0.1436                               | 0.0455                                                    | 33.8                                                                               | 6.8                                                  |
| 48         | 50                                   | 15                | 11            | 0.115  | 0.055                  | 0.014                  | 0.054                                | 0.0246                                                    | 49.0                                                                               | 12.0                                                 |
| 49         | 100                                  | 10                | 11            | 0.1083 | 0.0251                 | 0.0049                 | 0.0309                               | 0.0172                                                    | 59.2                                                                               | 16.8                                                 |
| 50         | 200                                  | 5                 | 5             | 0.207  | 0.0104                 | 0.0009                 | 0.0172                               | 0.0168                                                    | 91.5                                                                               | 29.0                                                 |

**TABLE 12.****Pulsed DC Discharge without Beam Scanning**

Ammonia flowrate = 50 cc/min (STP)

Peak current = 150 mA

Pressure = 10 torr

| <u>Run<br/>number</u>                              | <u>OFF-time<br/>msec</u>                                                  | <u>ON-time<br/>μsec</u>                                             | <u>Peak voltage<br/>kV</u>                                        | <u>Energy/pulse<br/>mJ × 10<sup>12</sup></u> |
|----------------------------------------------------|---------------------------------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------------------|----------------------------------------------|
| 51                                                 | 0.1                                                                       | 6.0                                                                 | 1.433                                                             | 35                                           |
| 52                                                 | 0.2                                                                       | 5.5                                                                 | 1.80                                                              | 30                                           |
| 53                                                 | 0.5                                                                       | 5.0                                                                 | 1.86                                                              | 28.4                                         |
| 48                                                 | 2.0                                                                       | 4.5                                                                 | 2.0                                                               | 24.4                                         |
| 54                                                 | 10.0                                                                      | 3.0                                                                 | 2.1                                                               | 18.6                                         |
| <u>Run<br/>duration<br/>min</u>                    | <u>Dilution<br/>ratio</u>                                                 | <u>p.p.m.</u>                                                       | <u>% N<sub>2</sub><br/>molar</u>                                  | <u>% N<sub>2</sub><br/>molar</u>             |
| 7.5                                                | 21                                                                        | 0.24                                                                | 1.7                                                               | 0.535                                        |
| 15                                                 | 21                                                                        | 0.292                                                               | 0.76                                                              | 0.233                                        |
| 15                                                 | 11                                                                        | 0.282                                                               | 0.267                                                             | 0.079                                        |
| 15                                                 | 11                                                                        | 0.115                                                               | 0.055                                                             | 0.014                                        |
| 15                                                 | 5                                                                         | 0.0925                                                              | 0.0064                                                            | 0.0006                                       |
| <u>Overall NH<sub>3</sub><br/>conversion<br/>%</u> | <u>Overall<br/>conversion<br/>to N<sub>2</sub>H<sub>4</sub><br/>wt. %</u> | <u>Molar<br/>conversion<br/>to N<sub>2</sub>H<sub>4</sub><br/>%</u> | <u>Energy yield<br/>of N<sub>2</sub>H<sub>4</sub><br/>gmo/100</u> |                                              |
| 1.268                                              | 0.203                                                                     | 17.1                                                                | 3.46                                                              |                                              |
| 0.586                                              | 0.1185                                                                    | 21.5                                                                | 4.72                                                              |                                              |
| 0.22                                               | 0.0602                                                                    | 29.0                                                                | 6.35                                                              |                                              |
| 0.054                                              | 0.0246                                                                    | 49.0                                                                | 12.0                                                              |                                              |
| 0.0104                                             | 0.009                                                                     | 92.0                                                                | 28.8                                                              |                                              |

TABLE 13.

Pulsed DC Discharge with Beam Scanning

Ammonia flowrate = 50 cc/min (STP)  
Pulse OFF-time = 2 msec  
Pulse ON-time = 4.5  $\mu$ sec  
Peak current = 150 mA  
Energy/pulse =  $24.4 \times 10^{-12}$  kWh  
Pressure = 10 torr

| Run No. | Scanning frequency<br>min <sup>-1</sup> | Run duration<br>mins | Dilution ratio | p.p.m. | % H <sub>2</sub><br>molar | % N <sub>2</sub><br>molar | Overall NH <sub>3</sub><br>conversion<br>% | Overall conversion<br>to N <sub>2</sub> H <sub>4</sub><br>wt.-% | Molar conversion<br>to N <sub>2</sub> H <sub>4</sub><br>% | Energy yield<br>of N <sub>2</sub> H <sub>4</sub><br>gms/kWh |
|---------|-----------------------------------------|----------------------|----------------|--------|---------------------------|---------------------------|--------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|
| 48      | 0                                       | 15                   | 11             | 0.115  | 0.055                     | 0.014                     | 0.054                                      | 0.0246                                                          | 49                                                        | 12.0                                                        |
| 55      | 30                                      | 15                   | 11             | 0.126  | 0.056                     | 0.0139                    | 0.0565                                     | 0.027                                                           | 50.5                                                      | 13.2                                                        |
| 56      | 60                                      | 15                   | 11             | 0.133  | 0.058                     | 0.0143                    | 0.059                                      | 0.0285                                                          | 51.5                                                      | 13.9                                                        |
| 57      | 100                                     | 15                   | 11             | 0.135  | 0.058                     | 0.0142                    | 0.06                                       | 0.0289                                                          | 52                                                        | 14.1                                                        |
| 58      | 200                                     | 15                   | 11             | 0.134  | 0.057                     | 0.0139                    | 0.057                                      | 0.0287                                                          | 54                                                        | 14.0                                                        |

TABLE 14.

Pulsed DC Discharge with Beam Scanning

Ammonia flowrate = 50 cc/min (STP)  
Pulse OFF-time = 0.5 msec  
Pulse ON-time = 5  $\mu$ sec  
Peak current = 150 mA  
Energy/pulse =  $28.4 \times 10^{-12}$  kWh  
Pressure = 10 torr

| Run No. | Scanning frequency<br>min <sup>-1</sup> | Run duration<br>mins | Dilution ratio | p.p.m. | % H <sub>2</sub><br>molar | % N <sub>2</sub><br>molar | Overall NH <sub>3</sub><br>conversion<br>% | Overall<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>wt. % | Molar<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>% | Energy yield<br>of N <sub>2</sub> H <sub>4</sub><br>gas/kwh |
|---------|-----------------------------------------|----------------------|----------------|--------|---------------------------|---------------------------|--------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------|
| 53      | 0                                       | 15                   | 11             | 0.282  | 0.267                     | 0.079                     | 0.22                                       | 0.0602                                                             | 29                                                           | 6.35                                                        |
| 59      | 20                                      | 15                   | 11             | 0.312  | 0.270                     | 0.0788                    | 0.226                                      | 0.0665                                                             | 30.2                                                         | 7.0                                                         |
| 60      | 60                                      | 15                   | 11             | 0.352  | 0.284                     | 0.0814                    | 0.241                                      | 0.0751                                                             | 32.0                                                         | 7.87                                                        |
| 61      | 105                                     | 15                   | 11             | 0.356  | 0.280                     | 0.080                     | 0.24                                       | 0.076                                                              | 32.8                                                         | 8.0                                                         |
| 62      | 170                                     | 15                   | 11             | 0.361  | 0.281                     | 0.0805                    | 0.24                                       | 0.0768                                                             | 32.8                                                         | 8.1                                                         |
| 63      | 210                                     | 15                   | 11             | 0.355  | 0.278                     | 0.079                     | 0.236                                      | 0.0759                                                             | 33.0                                                         | 7.98                                                        |

TABLE 15.

Pulsed DC Discharge with Beam Scanning

Ammonia flowrate = 50 cc/min (STP)  
 Pulse OFF-time = 0.2 msec  
 Pulse ON-time = 5.5  $\mu$ sec  
 Energy/pulse =  $30 \times 10^{-12}$  kWh  
 Pressure = 10 torr

| Run No. | Scanning frequency<br>min <sup>-1</sup> | Run duration<br>mins | Dilution ratio | p.p.m. | % H <sub>2</sub><br>molar | % N <sub>2</sub><br>molar | Overall NH <sub>3</sub><br>conversion<br>% | Overall<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>wt.-% | Molar<br>conversion<br>to N <sub>2</sub> H <sub>4</sub><br>% | Energy yield<br>of N <sub>2</sub> H <sub>4</sub><br>gms/kwh |
|---------|-----------------------------------------|----------------------|----------------|--------|---------------------------|---------------------------|--------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------|
| 52      | 0                                       | 15                   | 21             | 0.292  | 0.76                      | 0.233                     | 0.586                                      | 0.1185                                                             | 21.5                                                         | 4.72                                                        |
| 64      | 45                                      | 9                    | 41             | 0.106  | 0.875                     | 0.260                     | 0.67                                       | 0.1395                                                             | 22.2                                                         | 5.53                                                        |
| 65      | 110                                     | 10                   | 41             | 0.124  | 0.845                     | 0.256                     | 0.67                                       | 0.148                                                              | 23.5                                                         | 5.90                                                        |
| 66      | 150                                     | 15                   | 41             | 0.1945 | 0.79                      | 0.236                     | 0.64                                       | 0.1545                                                             | 25.6                                                         | 6.13                                                        |
| 67      | 210                                     | 10                   | 41             | 0.13   | 0.85                      | 0.256                     | 0.68                                       | 0.155                                                              | 24.4                                                         | 6.14                                                        |

TABLE 16.

Pulsed DC Discharge with Beam Scanning

Ammonia flowrate = 50 cc/min (STP)  
Pulse OFF-time = 0.1 msec  
Pulse ON-time = 6  $\mu$ sec  
Energy/pulse =  $35 \times 10^{-12}$  kWh  
Pressure = 10 torr

| Run No. | Scanning frequency min <sup>-1</sup> | Run duration mins | Dilution ratio | p.p.m. | % H <sub>2</sub> molar | % N <sub>2</sub> molar | Overall NH <sub>3</sub> conversion % | Overall conversion to N <sub>2</sub> H <sub>4</sub> wt. % | Molar conversion to N <sub>2</sub> H <sub>4</sub> % | Energy yield of N <sub>2</sub> H <sub>4</sub> gms/kWh |
|---------|--------------------------------------|-------------------|----------------|--------|------------------------|------------------------|--------------------------------------|-----------------------------------------------------------|-----------------------------------------------------|-------------------------------------------------------|
| 51      | 0                                    | 7.5               | 21             | 0.24   | 1.7                    | 0.535                  | 1.268                                | 0.203                                                     | 17.1                                                | 3.46                                                  |
| 68      | 30                                   | 7.5               | 21             | 0.284  | 1.735                  | 0.535                  | 1.325                                | 0.24                                                      | 19.3                                                | 4.10                                                  |
| 69      | 60                                   | 10                | 41             | 0.2145 | 1.75                   | 0.535                  | 1.36                                 | 0.265                                                     | 20.8                                                | 4.52                                                  |
| 70      | 120                                  | 10                | 41             | 0.212  | 1.72                   | 0.528                  | 1.34                                 | 0.262                                                     | 20.5                                                | 4.47                                                  |
| 71      | 210                                  | 10                | 41             | 0.2135 | 1.725                  | 0.528                  | 1.34                                 | 0.264                                                     | 21.0                                                | 4.50                                                  |