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Synthesis of Hydrazine.

Synthesis Of Hydrazine
By The Fixation Process

by

Terence John Jermyn

A thesis submitted to The University
of Aston in Birmingham for the
degree of Doctor of Philosophy

Department of Chemical Engineering

November, 1969

TO MY PARENTS

SUMMARY

A critical review of the literature concerning organic derivatives of hydrazine, the ammonia-chlorine reaction and the electrolytic formation of hydrazine has been carried out. Apparatus was constructed to study the electrolysis of liquid ammonia, the formation of chloramine and the fixation of chloramine with a ketone to form an isohydrazone. In the latter case the reaction was carried out in a 3" diameter stirred tank and also in a 1" diameter, 2' high column reactor where the liquid phase was continuously recirculated.

Two methods of analysis of azines and isohydrazones in a ketone solution have been developed. One is a colorimetric technique using p-dimethylaminobenzaldehyde and the other involves the hydrolysis of the organic derivative to hydrazine sulphate.

Hydrazine was detected in low concentration in some of the electrolytic experiments carried out but it was concluded that this method did not show sufficient promise to warrant further investigation. The gas phase formation of chloramine and acetone isohydrazone has also been studied but in this system difficulties were encountered with the chlorine jet blocking with ammonium chloride.

The formation of isohydrazones in a stirred tank reactor has been investigated in some detail and the effect of several parameters was determined. The yield was found to be extremely sensitive to chlorine concentration and in order to obtain yields of more than 90 per cent. the molar concentration of chlorine in the gas phase had to be of the order of 5 per cent. An optimum temperature in the region of 0°C was also detected. These results disagree with those quoted in previous studies but extensive experimental work has confirmed the information presented in this thesis. It has also been shown that at high yields the chloramine formation reaction took place in the gas phase.

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NOMENCLATURE

A	optical density	-
C	concentration of equivalent hydrazine hydrate	parts/10^5
CB	concentration of sodium hydroxide	gm.moles/litre
CK	concentration of ketone	gm.moles/litre
Cw	concentration of water	gm.moles/litre
d_B	bubble diameter	cm
d_s	agitator diameter	cm
D	diffusevity	cm^2/sec
E_D	Reversible decomposition potential	volts
ΔF	free energy of formation	Kcal/gm.mole
k_g^o	gas phase mass transfer coefficient due to physical absorption	cm/sec
k_L^o	liquid phase mass transfer coefficient due to physical absorption	cm/sec
K	molar extinction coefficient	litres/gm.mole, cm.
l	optical path	cm
N	speed of rotation of agitator	revs/min
Q	gas flow rate at S.T.P.	ml/min
R_A	ammonia to chlorine ratio	-
R_c	ratio of ammonium chloride carried out of reactor to total amount formed	-
R_D	nitrogen to chlorine ratio	-
R_p	ratio of ammonium chloride removed from gas phase to amount initially present in the gas phase	-
t_D	contact time	secs
V_A	ammonia flow rate at S.T.P.	ml/min

V_c	chlorine flow rate at S.T.P.	ml/min
V_D	diluent gas flow rate at S.T.P.	ml/min
W	weight of ammonium chloride	gms
X_c	mole fraction of chlorine	-
X_K	mole fraction of ketone	-
Y_c	yield of chloramine	per cent
Y_s	yield obtained by colorimetric method	per cent
Y_T	**yield obtained by titration** method	per cent

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CHAPTER ONE

INTRODUCTION

1. INTRODUCTION

Although hydrazine has been known for many years it remained a laboratory speciality until World War II. At that time its value as a rocket propellant was discovered in Germany and since then a considerable amount of research has been carried out to develop new methods of manufacture. Furthermore many new uses have been discovered so that today hydrazine is an important commercial chemical.

Anhydrous hydrazine is a colourless, highly polar, hygroscopic liquid completely miscible with water. It boils at 113.5°C. (1 atm.) and melts at 2.0°C. Hydrazine and water form an azeotropic mixture which boils at 120.3°C (1 atm.) and which contains 55 mole per cent. hydrazine (68.5 weight per cent.). It is doubtful if hydrazine hydrate ($N_2H_4.H_2O$) exists as a pure component; nevertheless it is a convenient means of reference for specifying the strength of solutions containing hydrazine less than 50 mole per cent.

Hydrazine is used increasingly in boiler water treatment for scavenging oxygen. Hydrazine hydrate and some other hydrazine compounds are used instead of materials such as sodium sulphite for this purpose /1/. Thus organic derivatives of hydrazine have found wide use in medical and biological applications. Isonicotinic acid hydrazide is manufactured in vast quantities for the treatment of tuberculosis. Maleic hydrazide is used as a growth suppressant for a wide range of plant species /2/.

During World War II it was discovered in Germany that hydrazine hydrate containing 15 per cent. methanol could be used as a rocket fuel. Since then derivatives of hydrazine such as unsymmetrical dimethyl hydrazine have been used for this purpose /3/. If its cost could be reduced, an important potential use of hydrazine would be as a fuel in a low temperature fuel cell. Hydrazine is one of the best liquid fuels satisfying the two basic requirements for such a cell /4/.

1. The free energy of oxidation should be as large as possible.
2. The rate of oxidation must be as high as possible.

Other advantages of hydrazine are that its products of oxidation are harmless and that it can deliver power at appreciable current densities, at temperatures below 0°C. Also the hydrazine fuel cell does not require noble metals as electrodes and the fuel can easily be stored in a concentrated form as hydrazine hydrate [5]. However hydrazine costs 7s.6d. per pound [5] and this is a serious disadvantage. Therefore research into new and less costly methods of manufacture are necessary if this versatile chemical is to find increased use in such applications.

Hydrazine derivatives are also employed in such applications as soldering fluxes, reducing agents for the production of metallic films, insecticides and photographic materials. An increasingly large outlet for some organic hydrazine derivatives is in the manufacture of blowing agents for the production of expanded plastics and rubber. Hydrazine derivatives are also used for the production of dyes, textile treating agents and as antioxidants for fats, oils and rubber.

Raschig [6-10], following a suggestion by Thiele [11], showed that hydrazine could be produced by the oxidation of aqueous ammonia by sodium hypochlorite. Initially chloramine is formed by a rapid reaction, which then reacts with excess ammonia to form hydrazine by a much slower reaction.

$$\mathrm{Na\,O\,Cl} + \mathrm{NH_3} \longrightarrow \mathrm{NH_2Cl} + \mathrm{Na\,OH} \quad \ldots\ldots\ldots\ldots 1.1$$

$$\mathrm{NH_2Cl} + \mathrm{NH_3} + \mathrm{Na\,OH} \longrightarrow \mathrm{N_2H_4} + \mathrm{Na\,Cl} + \mathrm{H_2O} \quad \ldots\ldots\ldots\ldots 1.2$$

Although the demand for hydrazine has increased and research into new methods of manufacture have been intensified the main methods of production are still based on the original Raschig process. However the overall yield in this process, based on the sodium hypochlorite, is of the order of 60 per cent. In addition the recovery costs are high as the hydrazine must be produced in low concentrations of the order of 2 per cent in order to minimise decomposition of the product. Consequently if hydrazine is to find increased use then a better method of manufacture must be found.

The low cost of ammonia makes it the logical starting material for the manufacture of hydrazine but at the present time the only oxidising agents of practical importance are sodium hypochlorite and chlorine [12-15]. Theoretically it should be possible to oxidise ammonia to hydrazine by a low voltage electrolysis process in liquid ammonia. If a ketone is present in the cell to fix the products of electrolysis, then a ketazine or an isohydrazone should be formed. A study of the possibility of this synthesis is the subject of the first part of this investigation.

During the last decade the reaction between chlorine, ammonia and ketone has been investigated by several workers [16-22]. The ketone reacts with the hydrazine or chloramine to form either a ketazine or an isohydrazone which can then be converted to hydrazine hydrate or hydrazine sulphate. In this way it is possible to increase the yield of hydrazine, by preventing decomposition reactions, and also to increase its concentration in the reaction liquor. Thus if such a process was found to be practical on an industrial scale then the cost of hydrazine could be reduced considerably. However, very little information has been published on the effects of the various parameters on the yield of ketone intermediate obtained, and a study of these effects is the subject of the second part of this investigation.

CHAPTER TWO

LITERATURE SURVEY

2. LITERATURE SURVEY

Before hydrazine itself was isolated, many of its derivatives such as the hydrazo-compounds and the simple aryl hydrazines were known. Hydrazine was first prepared by Curtuis in 1887 [23, 24] by the action of caustic potash on diazoacetic ester. It was not until 1894 that Lobry de Bruyn [25] first prepared anhydrous hydrazine and determined its properties.

Since that time many papers have been published on the chemistry and uses of hydrazine [26-33]. The main method of manufacture, the Raschig process, has been studied by several workers and the results of their investigations have been fairly well documented [34-40]. Therefore this survey will be mainly concerned with literature of interest to the ketone intermediates obtained during the synthesis of hydrazine, the electrochemical synthesis of hydrazine and the chlorine-ammonia reaction.

2.1. Organic intermediates used in the synthesis of hydrazine.

In the Raschig synthesis of hydrazine there is a yield reducing side reaction between hydrazine and chloramine.

$$2NH_2Cl + N_2H_4 \longrightarrow N_2 + 2NH_4Cl \quad \text{........................} \quad 2.1$$

Also chloramine is decomposed in alkaline solutions [36].

The probable mechanism is

$$3NH_2Cl + 3\ NaOH \longrightarrow 3\ NaCl + NH_3 + N_2 + 3H_2O \quad \text{........} \quad 2.2$$

Although reaction 2.1 can be suppressed by the use of inhibitors such as glue, it still constitutes a serious loss in yield at high concentrations of chloramine and hydrazine. Consequently the effluent from the reactor must contain a low concentration of hydrazine. This dilution increases the cost of hydrazine produced by the Raschig process because of the energy required to separate it from the large amounts of water. However if the reaction is carried out in the presence of a carbonyl compound, the hydrazine or chloramine will be fixed in the form of an organic intermediate which could later be converted to hydrazine hydrate or hydrazine sulphate. In this manner the side reactions would be eliminated and the overall yield of hydrazine increased. Furthermore it would be possible to allow a higher concentration of hydrazine (in the form of the intermediate) to be present in the reactor liquor and thus reduce the recovery costs. The type of organic intermediate formed depends on the conditions prevailing in the reactor and a brief review of these intermediates will now be given.

Aldehydes and ketones can react with one or both amino groups of hydrazine to form either a hydrazone or an azine with evolution of heat.

$$R_1CHO + N_2H_4 \longrightarrow \underset{\text{Aldehyde Hydrazone}}{R_1CHNNH_2} + H_2O \ \ldots\ldots\ldots\ldots\ldots\ldots \ 2.3$$

$$R_1CHO + R_1CHNNH_2 \longrightarrow \underset{\text{Aldazine}}{R_1CHNNHCR_1} + H_2O \ \ldots\ldots\ldots\ldots\ldots\ldots \ 2.4$$

$$R_1COR_2 + N_2H_4 \longrightarrow \underset{\text{Ketone Hydrazone.}}{R_1R_2CNNH_2} + H_2O \ \ldots\ldots\ldots\ldots\ldots\ldots \ 2.5$$

$$R_1COR_2 + R_1R_2CNNH_2 \longrightarrow \underset{\text{Ketazine}}{R_1R_2CNNCR_2R_1} + H_2O \ \ldots\ldots\ldots\ldots\ldots\ldots \ 2.6$$

Aldehydes are more reactive than ketones, and normally the aldehyde hydrazone reacts with a further molecule of aldehyde to form the aldazine. An example of this is the reaction between benzaldehyde and hydrazine, a precipitate of benzalazine being immediately obtained. The formation of ketazines however requires excess ketone and in some cases a catalyst as well.

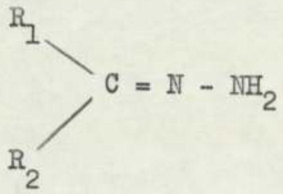
During the synthesis of hydrazine ketones are best used as the carbonyl compound because of increased yields [16, 18, 20, 21, 41].

Usually if the organic intermediate is of the type shown above, then a mixture of both the hydrazone and the ketazine is formed [42]. Because the ketone is present in excess the ketazine is formed in the greater quantity.

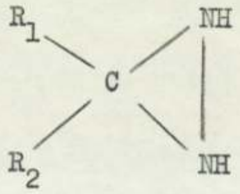
Another type of organic intermediate which can be formed are the C,C disubstituted diaziridines [16-22, 43]. These compounds are also known as C,C disubstituted diazacyclopropanes or isohydrazones. Henceforth in this investigation they will normally be referred to as isohydrazones. They are formed in accordance with the following reaction.

$$4NH_3 + Cl_2 + R_1COR_2 \longrightarrow R_1R_2CN_2H_2 + H_2O + 2NH_4Cl \quad ....2.7$$

Hydrazones and isohydrazones have the same chemical composition although their structure is totally different as shown below.



Hydrazone



Isohydrazone

A list of some of the common properties of the organic intermediates derived from acetone is shown in Table 2.1

TABLE 2.1

Property	Hydrazone	Ketazine	Isohydrazone
Boiling Point (760 mm)	124°C	131°C	105°C
Melting Point	- 30°C	Less than - 80°C	40°C

2.2. Electrochemical Investigation.

Most of the work on the formation of hydrazine by electrolysis has been carried out in liquid ammonia solutions. Therefore some of the more important electrolytic properties of this solvent will now be discussed.

2.2.1. Liquid ammonia as a solvent.

On electrolysis of solutions in liquid ammonia an evolution of nitrogen often occurs at the anode. This phenomenon is analagous to the evolution of oxygen during the electrolysis of aqueous solutions. However, although water and liquid ammonia have enough similarities in their properties to make comparisons useful, there are several important differences in the behaviour of the two solvents. One of these is the unusually low value of the free energy of formation of ammonia. Jolly [44] gives a value of -2.7 K cal mole^{-1} for $\triangle F_{(298^\circ K)}$. The corresponding value for water is -54.65 K cal mole^{-1}. When the value for ammonia is corrected to -50°C, which is the temperature at which many electrochemical investigations have been carried out, it is found that $\triangle F_{(223^\circ K)}$ is -6 K cal mole^{-1}. Thus the reversible decomposition potential of an ammonia solution in which the products of electrolysis are nitrogen and hydrogen is very low. The decomposition of one mole of ammonia requires the passage of three faradays. Therefore:

$$E_D = \frac{-6000 \times 4.18}{3 \times 96500} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2.8$$

$$= -\frac{6.00}{3 \times 23.1} = -0.0865 \text{ volts.}$$

In comparison the reversible decomposition potential for water is 1.18 volts. If the actual decomposition potential of ammonia was near to the theoretical value then the products of electrolysis would be almost certainly nitrogen and hydrogen. However there is a large anode over-potential, which was measured by Gessler and Pleskov [45], and consequently even at low current densities, the decomposition voltage is more than one volt.

The primary electrode processes taking place in liquid ammonia for acid and alkaline solutions can be represented by the following equations [46].

Cathode Reaction.

Acidic Solution. $NH_4^+ + e \longrightarrow NH_3 + \frac{1}{2} H_2$ 2.9

Alkaline Solution. $xNH_3 + e \longrightarrow e\,(NH_3)_x$ 2.10

These solvated electrons $e\,(NH_3)_x$ give the solution a characteristic blue colour which fades as reaction 2.11 takes place.

$e\,(NH_3)_x \longrightarrow NH_2^- + (x-1)\,NH_3 + \frac{1}{2} H_2$ 2.11

Anode Reactions.

These reactions have not been studied to any great extent. However the following reactions represent the overall stoichiometry for the electrolysis of inert electrolytes at inert electrodes.

Acidic Solution. $4NH_3 \longrightarrow \frac{1}{2} N_2 + 3NH_4^+ + 3e$ 2.12

Basic Solution. $3NH_2^- \longrightarrow \frac{1}{2} N_2 + 2NH_3 + 3e$ 2.13

These processes are complex and take place in several stages and contribute considerably to the overpotential in the electrolysis of liquid ammonia solutions. Although nitrogen appears to be the main anode product, it is quite feasible that under the appropriate experimental conditions hydrazine would be formed in either of the following ways.

$NH_2^- \longrightarrow NH_2 + e$ 2.14

$2NH_2 \longrightarrow N_2H_4$ 2.15

or

$NH_2 + NH_3 \longrightarrow N_2H_4 + \frac{1}{2} H_2$ 2.16

If a ketone is present in the cell it is possible that a hydrazone or a ketazine might be formed. Another possibility leading to the formation of an isohydrazone will be discussed in chapter 2.2.2.

2.2.2. Formation of hydrazine by electrolysis.

For many years the possibility of synthesising hydrazine by the electrochemical oxidation of ammonia has been postulated. Turentine and Olin [47] claimed to have obtained detectable traces of hydrazine by electrolysis at 100°C of a 25 per cent. aqueous ammonia solution to which sodium chloride was slowly added. Howard and Browne [48] state that traces of a reducing compound, presumably hydrazine, are formed when a solution of ammonium chloride in liquid ammonia is electrolysed between graphite or platinum electrodes. In 1945 Pleskov [49] suggested that hydrazine might be formed by the electrolysis of alkaline solutions in liquid ammonia. Gessler and Pleskov [45] reported the formation of hydrazine in yields of 5-10 per cent. (calculated on the current consumption). The means of detection was stated to be "Raschigs method", but no further details of the procedure were given.

In 1952 Ogg [50] unsuccessfully attempted to synthesise hydrazine by the electrolysis of liquid ammonia solutions of alkali metal amides, ammonium halides and alkali metal bromides. Ogg did not state that in the case of alkali metal bromides a possible product at the anode would be bromamine which under suitable conditions is an intermediate in the formation of hydrazine [51, 52, 53]. In none of his experiments did Ogg detect hydrazine by the salicylaldehyde method and concluded that the synthesis of hydrazine by an electrochemical method was unlikely. Hammer [46] also attempted to synthesise hydrazine by electrolysis of liquid ammonia under various conditions. However, using the salicylaldehyde method he was unable to detect hydrazine in any of his experiments. The electrolytes he used were ammonium chloride, potassium amide, and sodium chloride. The anode was made of either graphite or bright platinum. Hammer also investigated the stability of hydrazine under the conditions of the electrolysis and he concluded that if hydrazine was formed during the electrolysis of either acid or alkaline liquid ammonia solutions it would be sufficiently stable to be detected by the test procedure employed.

Stuart [54] obtained hydrazine by the electrolysis of solutions of alkaline earth metal amides in formamide. Hydrazine was formed at the anode and the metal at the cathode. The solution was at 130°C during the electrolysis and hydrazine was withdrawn from the anode in the gaseous state. Stuart gave no details of his analytical procedure or of the yield of hydrazine. Haller [55] found that hydrazine was produced by electrolysis when the liquid ammonia solution was allowed to continuously flow through a specially designed cell. The cell is shown in figure 2.1. In the examples given Haller used sodium amide, water or sodium hydroxide as the electrolyte. Again no details of the yield or of the concentration of hydrazine in the cell effluent were given. In one of the examples the flow rate through the cell was 100 ml in 43 minutes. The means of detection were the acidified potassium iodate and the para-dimethylaminobenzaldehyde methods.

Pursley [51] reacted potassium amide with bromamine in liquid ammonia and obtained hydrazine in accordance with the following reaction.

$$ZNH_2 + XNH_2 \longrightarrow N_2H_4 + ZX \quad \ldots\ldots\ldots\ldots \quad 2.17$$

where Z represents a metal selected from Group IA or IIA of the Periodic Classification of elements, and X represents a halogen atom. Later Pursley [52] electrolysed solutions of alkali metal halides in liquid ammonia to obtain the following products.

<u>At the Cathode.</u>

$$M^+ + e \longrightarrow M \quad \ldots\ldots\ldots\ldots \quad 2.18$$

$$M + NH_3 \longrightarrow MNH_2 + \tfrac{1}{2} H_2 \quad \ldots\ldots\ldots\ldots \quad 2.19$$

where M is an alkali metal.

CELL USED BY HALLER (55)

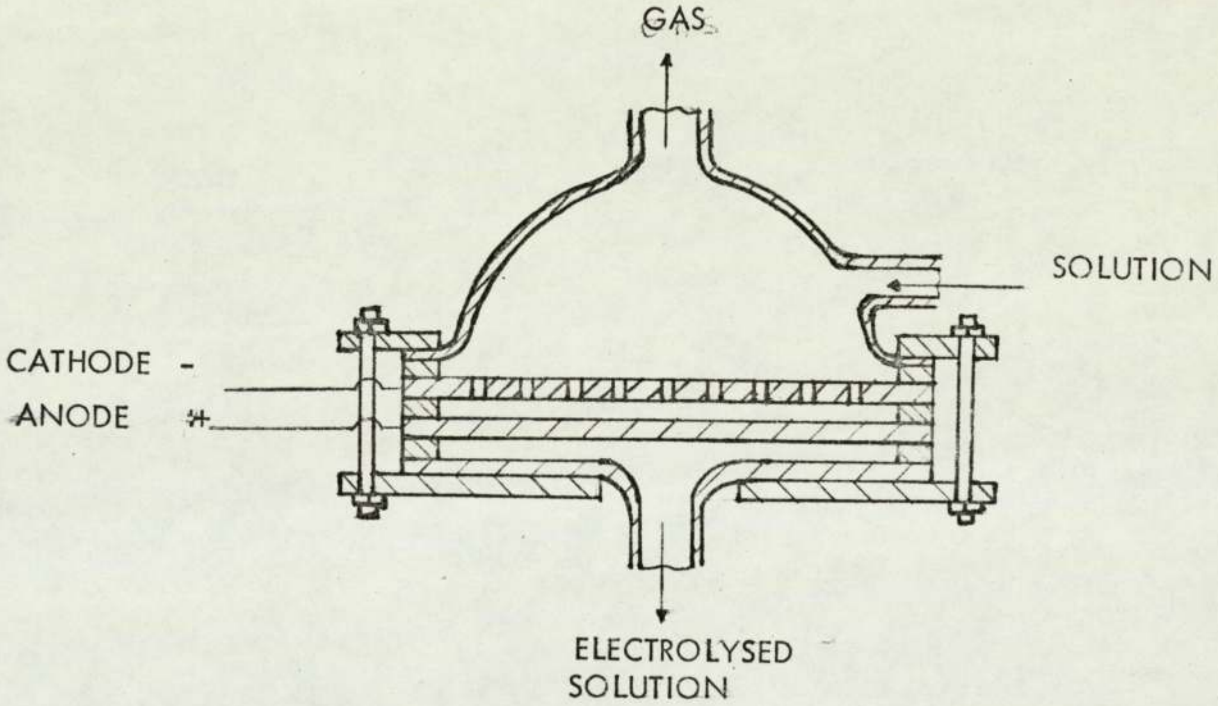


FIGURE 2.1

At the Anode.

$X^- \longrightarrow X + e$ 2.20

$X_2 + 2NH_3 \longrightarrow XNH_2 + NH_4X$ 2.21

where X is a halogen.

The products are removed from the cell and reacted to form hydrazine as in equation 2.17. Lacey [124] also obtained hydrazine by electrolysis of liquid ammonia solutions of sodium chloride or potassium chloride. Omietanski et al [56] found that the reaction of chloramine with potassium amide in liquid ammonia produced only a small yield of hydrazine and in most cases none at all. Pursley had quoted yields of up to 66 per cent. based on potassium amide. Jander [53] investigated the reaction of bromamine with potassium amide in liquid ammonia and discovered that hydrazine was formed in substantial quantities. However if the molar ratio of bromamine to potassium amide exceeded unity then the yield fell to zero because of the decomposition reaction between bromamine and hydrazine. This does not explain Omietanski's results as the molar ratio of potassium amide to bromamine he used was greater than 2 in most cases.

Mayland [57] synthesised hydrazine by electrodialysis of aqueous solutions of sodium chloride, ammonia and ammonium chloride. The concentration of hydrazine in the cell was up to .5 per cent. and the yield was 1 grain of hydrazine per 10,000 coulombs. Injection of hypochlorite into the anode chamber improved yields. Hydrazine has also been obtained by the electrolytic reduction of nitrous oxide at a mercury cathode [58].

From the above review it would appear that electrolysis of alkali metal halides would be the best prospect of forming hydrazine or one of its derivatives. If a ketone is present in the cell there is the possibility of an isohydrazone being formed in accordance with the following reaction

$NH_2Br + 2NH_3 + R_1COR_2 \longrightarrow R_2R_1CN_2H_2 + NH_4Br + H_2O$ 2.22

Because of the presence of a ketone there are various other products of electrolysis which could be formed depending on the conditions of the electrolysis. The formation of these products will now be discussed briefly.

2.2.3. Effect of a ketone during electrolysis.

Electrolytic reduction of carbonyl compounds can result in three different products depending on the conditions of the electrolysis and the electrodes used [59]. If acetone is used the products can be isopropyl alcohol, propane or acetone pinacol. With methyl ethyl ketone secondary butyl alcohol, butane or methyl ethyl pinacol or a mixture of all three can be formed. Often condensation products are also obtained.

If alkali metal halides are employed, e.g. potassium bromide, then there are several possible side reactions that can take place. If bromine is formed in accordance with reaction 2.20 it is possible that this will react with the enol form of the ketone. With acetone the following reaction can take place [60].

$CH_2C(OH)CH_3 + Br_2 \xrightarrow{\text{rapid}} CH_2Br\,COCH_3 + HBr$ 2.23

In some cases a mixture of dibromo products is also formed. The bromination of methyl ethyl ketone yields a mixture of $CH_3CH_2COCH_2Br$ and $CH_3CHBrCOCH_3$.

If potassium amide is formed in accordance with reaction 2.19 then it also can react with the enol form of acetone as follows [61].

$CH_2C(OH)CH_3 + KNH_2 \longrightarrow CH_2C(OK)CH_3 + NH_3$ 2.24

In addition if there is any isohydrazone formed then it also can be reduced under special conditions to an amine or an imine [62].

There are therefore several possible electrode reactions that can take place leading to a variety of different products. However if it is possible to fix the products of electrolysis with a ketone then it is feasible that a ketazine or an isohydrazone would be formed in sufficient amounts to form the basis of a reaction process.

2.3. The reaction of chlorine with ammonia.

The study of the reaction between chlorine and ammonia has been carried on by numerous investigators since 1813. The complete equation for the oxidation of ammonia is

$$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2 \quad \ldots\ldots \quad 2.25$$

Mattair and Sisler [63] prepared chloramine by reacting chlorine, diluted with nitrogen, with a large excess of ammonia in the gas phase and the chloramine so formed was subsequently reacted with liquid ammonia to produce hydrazine.

The factors influencing each stage of this reaction will now be considered.

2.3.1. The synthesis of chloramine.

Early experiments on the reaction of chlorine with ammonia indicated that when ammonia is in excess ammonium chloride and nitrogen are formed and when chlorine is in excess nitrogen trichloride is formed. Under some conditions explosions occurred. Bray and Dowell [64] postulated a mechanism for the reaction in aqueous solution based on chloramine as an intermediate. The final equation is

$$3NH_3 + 6\,Cl_2 \longrightarrow N_2 + NCl_3 + 9\,HCl \quad \ldots\ldots \quad 2.26$$

Dowell and Bray [65] reported the following reaction between aqueous ammonia and nitrogen trichloride

$$4NH_3 + NCl_3 \longrightarrow N_2 + 3NH_4Cl \quad \ldots\ldots \quad 2.27$$

Noyes and Lyon [66] obtained a similar equation to Bray and Dowell

$$12\ NH_3 + 6\ Cl_2 \longrightarrow N_2 + NCl_3 + 9NH_4Cl \quad \text{.................} \quad 2.28$$

Combining equations 2.27 and 2.28 yields equation 2.25 which is the complete equation for the oxidation of ammonia.

Markwald and Wille [67] reported the preparation of chloramine. It solidified at -66°C to a crystalline form and exploded at -50°C to form nitrogen, chlorine and ammonium chloride. Mattair and Sisler [15, 63] prepared chloramine by the gas phase reaction of chlorine with ammonia.

$$2\ NH_3 + Cl_2 \longrightarrow NH_4Cl + NH_2Cl \quad \text{..........................} \quad 2.29$$

The chlorine was diluted with nitrogen and ammonia was present in considerable excess. The study of this reaction was continued by Sisler et al [68] and by Neth [69] who reported good yields of chloramine at lower ammonia to chlorine mole ratios.

One of the difficulties encountered in carrying out this reaction in the gas phase is the blocking of the chlorine jet with ammonium chloride. Initially Neth used a ramrod technique in which the ammonium chloride was repeatedly forced off the tube. This was not entirely satisfactory and later he used a device which involved electrostatic precipitation. He found that diluting the chlorine stream with nitrogen improved yields and that in some cases reasonable yields of chloramine of the order of 60 per cent. could be obtained at ammonia to chlorine molar ratios of only 4 to 1. Cooling the walls of the reactor decreased the yield of chloramine.

It was found that it was essential to avoid any local excess of chlorine because this resulted in a lowering of the yield of chloramine by the reaction of chlorine with either chloramine or with ammonium chloride. For the latter case Noyes [70] showed the reaction to be

$$3\ Cl_2 + NH_4Cl \longrightarrow NCl_3 + 4\ HCl \quad \text{..........................} \quad 2.30$$

Nitrogen trichloride subsequently reacts with ammonia to form ammonium chloride in accordance with reaction 2.27.

Drago [71] attempted to eliminate the problem of the chlorine jet blocking by altering the design of the reactor. Narrow high velocity jets were used for introducing chlorine into the reactor in such a way as to favour rapid mixing of the chlorine with an excess of ammonia. A diagram of his reactor is shown in figure 2.2. Drago stated that he obtained yields of chloramine of the order of 80 per cent. without using nitrogen dilution of the chlorine stream. In some cases a yellow flame was observed at the chlorine jet and this coincided with a decrease in yield of chloramine. The reaction reducing the yield was considered to be

$$6\ NH_3 + NH_2Cl + 2\ Cl_2 \longrightarrow N_2 + 5NH_4Cl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ 2.31$$

It was also found that the yield of chloramine was proportional to the total flow of gas along the reactor. Drago recalculated the flow of gas taking into account the loss in volume due to reactions 2.29 and 2.25 and plotted it against the yield of chloramine as shown in figure 2.3.

Haller [72] produced chloramine by reacting chlorine with an excess of ammonia in an inert solvent such as carbon tetrachloride. In order to obtain yields in the region of 60 per cent. it was found to be essential to remove the ammonium chloride as soon as possible, otherwise the yield of chloramine fell to about 10 per cent. Dexter [73] attempted to overcome the problem of the chlorine jet blocking with ammonium chloride by designing a mushroom shaped reactor. However a ramrod was still needed to keep the jet free.

Dexter and Haller [74] used a reactor of this type to produce chloramine which was then reacted with excess liquid ammonia to form hydrazine. The overall yield of hydrazine based on chlorine was in the region of 50 per cent. Braude and Cogliano [75] discovered that if the temperature of the reaction of ammonia with chlorine rose above 220-240°C

Reactor used by Drago (71)

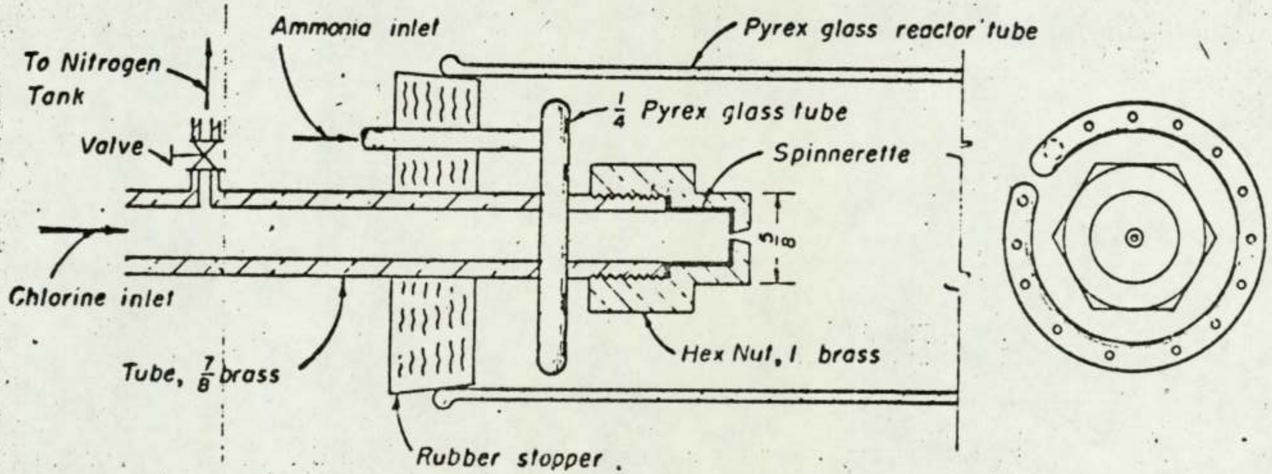


Figure 2.2

Results obtained by Drago (71)

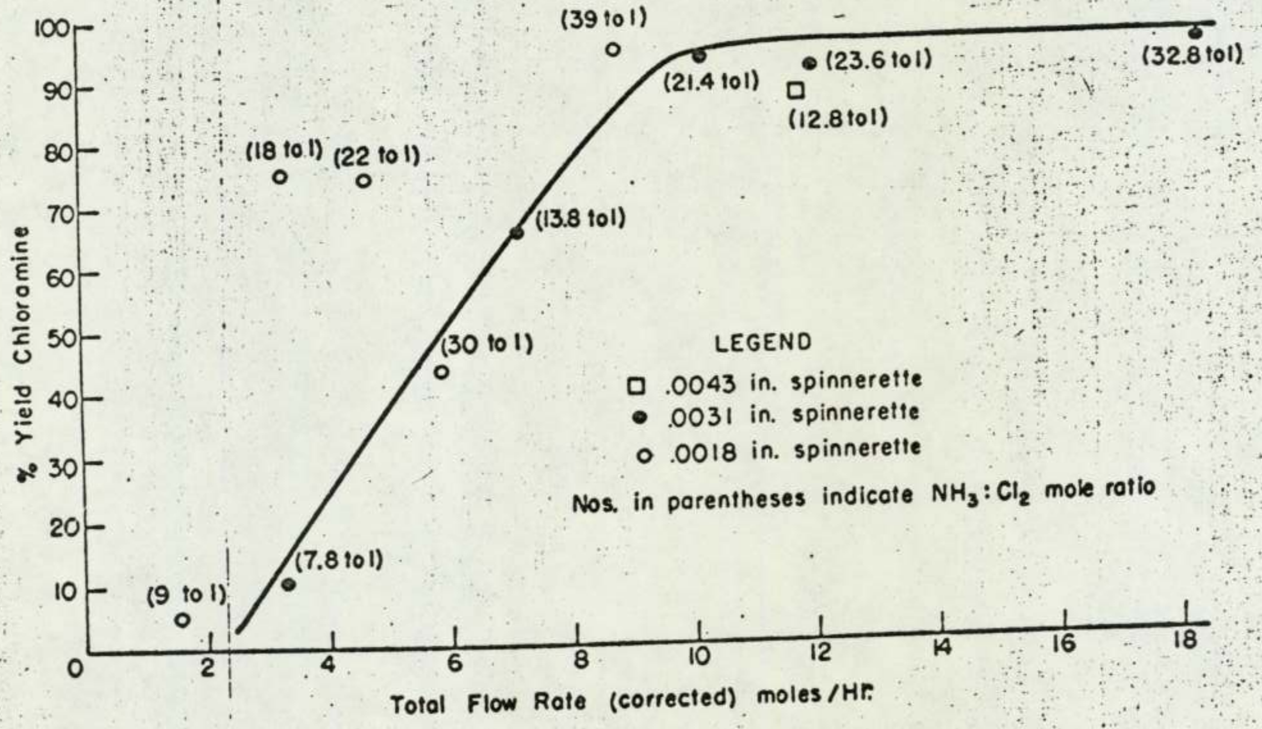


Fig. 2.3

the yield of chloramine fell to zero. A reactor was developed in which the heat of reaction was used to evaporate liquid ammonia. Thus chlorine, gaseous ammonia and liquid ammonia were injected into the reactor through specially designed nozzles. Unfortunately, however, no details of the yield of chloramine obtained were given.

2.3.2. The synthesis of hydrazine.

Mattair and Sisler [63] described a process in which hydrazine is synthesised by the reaction of chloramine with liquid ammonia.

$$NH_2Cl + 2\,NH_3 \longrightarrow N_2H_4 + NH_4Cl \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 2.32$$

The yield of hydrazine however is reduced by the undesirable side reaction of chloramine with hydrazine.

$$2NH_2Cl + N_2H_4 \longrightarrow N_2 + 2NH_4Cl \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 2.1$$

Additional studies on the reaction of chloramine with liquid ammonia were reported by Sisler et al [76] and Neth [69]. It was found that the yield of hydrazine increased as the reaction temperature was raised. Some results obtained by Neth are shown in figure 2.4. However even at 100°C a molar ratio of ammonia to chlorine of 400 to 1 was required to give a yield of hydrazine of 80 per cent. The large excess of ammonia increases the rate of reaction 2.32, and decreases the rate of reaction 2.1 by lowering the concentration of chloramine and hydrazine. Haller [13, 14] formed hydrazine by the gas phase reaction of either chloramine with ammonia or chlorine with ammonia. Each gas was passed separately over activated alumina and the hydrazine was later recovered by washing the alumina with water.

There have been several mechanisms suggested for the reaction of chloramine with ammonia. Wiberg and Schmidt [77] maintained that the presence of water was essential for the formation of hydrazine. However the fact that hydrazine can be synthesised in anhydrous ammonia and other

Results obtained by Neth (69)

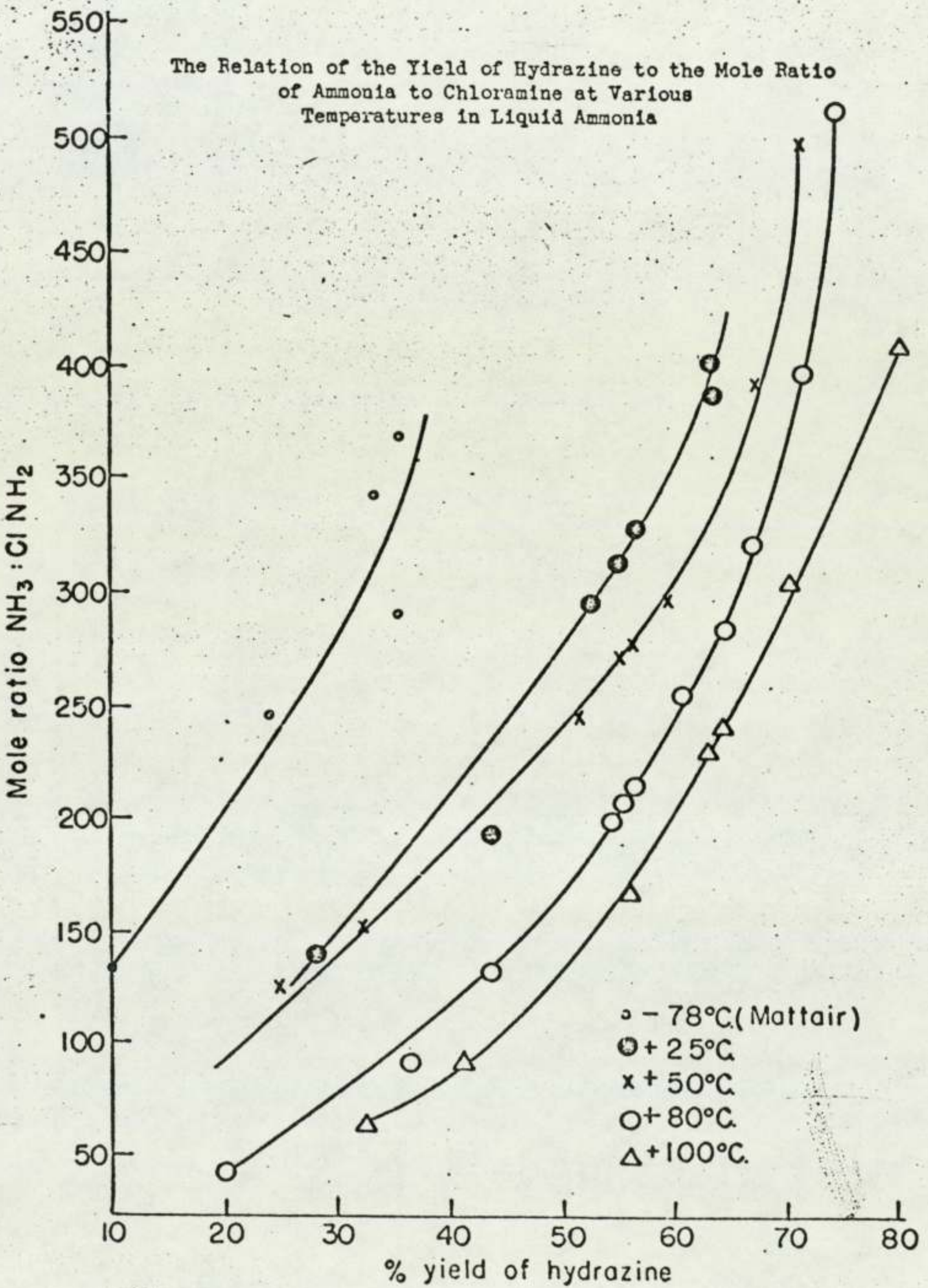


Figure 2.4

non-aqueous solvents disproves this theory. Cahn and Powell [78] suggested the following mechanism for hydrazine formation in aqueous solution.

$$NH_2Cl + NH_3 \xrightarrow{slow} (N_2H_5Cl) \xrightarrow{OH^-} N_2H_4 + H_2O + Cl^- \quad \ldots\ldots\ 2.33$$

Audrieth et al [79] proposed a mechanism involving the formation of the chloramide ion which is the conjugate base of chloramine. Jander [80] supported this theory and stated that chloramine decomposes in the presence of a substance with proton affinity to $NHCl^-$. In support of this theory is the increase in yield of hydrazine when potassium amide is added to liquid ammonia that has been observed by Jander [53, 81] and Pursley [51, 52]. The sequence of reactions would be as follows.

$$NH_2Cl + B \longrightarrow NHCl^- + BH^+ \quad \ldots\ldots\ 2.34$$

B is a base such as NH_2^-, NH_3 or OH^-. The chloramide ion can react directly with ammonia or alternatively can lose the chlorine ion to form the imine radical.

$$NH\,Cl^- + NH_3 \longrightarrow N_2H_4 + Cl^- \quad \ldots\ldots\ 2.35$$

or

$$NH\,Cl^- \longrightarrow NH + Cl^- \quad \ldots\ldots\ 2.36$$

$$NH + NH_3 \longrightarrow N_2H_4 \quad \ldots\ldots\ 2.37$$

The reaction between chloramine and ammonia was studied in water and other solvents by Sisler et al [82]. Hydrazine was formed in all the solvents tested except ethyl ether. The kinetics of the reaction between chloramine and liquid ammonia were studied by Collier et al [83]. They found that the reaction was first order in chloramine and a bimolecular displacement reaction similar to the mechanism of Cahn and Powell was proposed.

$$NH_3 + NH_2Cl \longrightarrow NH_2NH_3^+ + Cl^- \quad \text{.......................} \quad 2.38$$

$$NH_2\ NH_3^+ + NH_3 \longrightarrow NH_4^+ + N_2H_4 \quad \text{................} \quad 2.39$$

Omietanski et al [56] prefer the Cahn and Powell mechanism because, unlike Jander, in most of their experiments they did not detect any hydrazine in liquid ammonia when potassium amide was present.

In an attempt to distinguish between the mechanisms Yagil and Anbar [84] investigated the reaction of chloramine with ammonia over a range of pH values. They concluded that in the pH range 10-14 the reaction proceeds by the substitution mechanism of Cahn and Powell, but at higher alkalinities chloramide ions are involved in the reaction. They could not however confirm the participation of the imine radical.

2.4. Hydrazine fixation processes.

It was stated in Chapter 2.1. that the yield of hydrazine in the Raschig process is only of the order of 60 per cent. In order to improve the yield a carbonyl compound can be added to the reaction liquor to form an organic intermediate. The conditions prevailing inside the reactor determine which intermediate is produced. In this chapter the process where hydrazine is formed and subsequently reacts with the carbonyl compound to give either an azine or a hydrazone will be considered.

Grosskinsky et al [41] described a process for the manufacture of ketazines. A gas stream consisting of nitrogen and chlorine was mixed with a stream of ammonia saturated with acetone in a reaction tube at 40°C. The gaseous mixture remained in the tube for 2 seconds and was then passed into a solution containing sodium hydroxide, ammonia and glue. This solution was kept boiling so that the acetone ketazine formed in it was distilled off at once. With acetone a yield of 71 per cent. of hydrazine was obtained. However it is not clear if this figure is based on the ketazine produced or on the chlorine originally supplied to the reactor. Similar results were obtained with other carbonyl compounds.

It was found by Paulsen and Huck [43] that when chlorine and ammonia were reacted with acetophenone the azine was formed even in the absence of sodium hydroxide. However in the case of other ketones such as acetone and methyl ethyl ketone the isohydrazone was formed under these conditions. Abendroth and Henrich [85, 86] improved the yields of hydrazine obtained in the Raschig process by reacting sodium hypochlorite and ammonia in the presence of acetone. The hydrazine which is formed reacts with the acetone to produce the hydrazone and the azine. Under similar conditions it was found that the yield of hydrazine was 43 per cent. when acetone was not present and 77 per cent. when it was. In the latter case the yield is based on the quantity of organic intermediate formed. Mundil [87, 88] also conducted the Raschig process in the presence of a ketone. Under similar conditions the presence of acetone improved the yield from 24 per cent. to 95 per cent. Mundil and Abendroth state that if the carbonyl compound is of the general formula R_1COR_2, the sum of the carbon atoms represented by R_1 and R_2 should not exceed 5. Needham and Smith [125] carried out the reaction in two stages, the first stage comprising the formation of chloramine, and the second stage comprising the reaction of chloramine with ammonia in the presence of a carbonyl compound. A yield of acetone ketazine of 97 per cent. was claimed.

It is most probable that the organic intermediate formed is a mixture of the hydrazone and the azine. In all the examples outlined above, except in the case of acetophenone, alkali has been present in the reactor and normally this is an essential condition for the formation of hydrazones and azines by the fixation process. The sequence of reactions is

$$\mathrm{Na\,O\,Cl + NH_3 \longrightarrow Na\,OH + NH_2\,Cl} \quad \ldots\ldots \quad 2.40$$

$$\mathrm{NH_2Cl + Na\,OH + NH_3 \longrightarrow N_2H_4 + H_2O + Na\,Cl} \quad \ldots\ldots \quad 2.41$$

$$\mathrm{R_1COR_2 + N_2H_4 \longrightarrow R_1R_2CNNH_2 + H_2O} \quad \ldots\ldots \quad 2.5$$

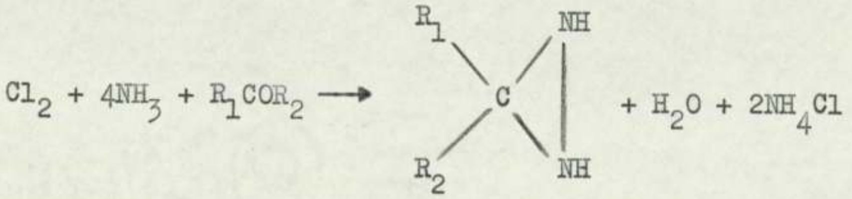
$$\mathrm{R_1R_2CNNH_2 + R_1COR_2 \longrightarrow R_1R_2CNNCR_2R_1 + H_2O} \quad \ldots\ldots \quad 2.6$$

Thus the effect of the side reaction 2.1 is eliminated. The hydrazones and azines can subsequently be hydrolysed to give hydrazine hydrate and the ketone [89-96].

2.5. Isohydrazones and the fixation of chloramine.

2.5.1. The synthesis of isohydrazones.

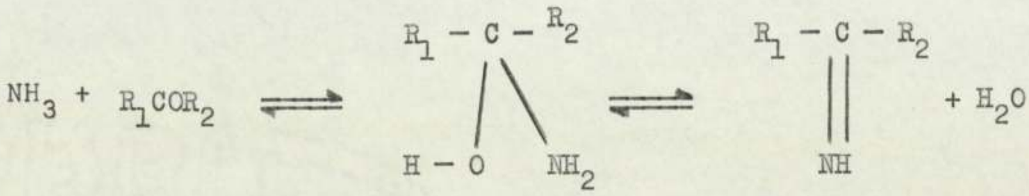
In 1958 Abendroth and Henrich [16, 20, 97] reacted ammonia, chlorine and acetone in the gas phase and obtained a new type of compound which was an isomer of acetone hydrazone. This new isohydrazone had a melting point of 40°C and its heat of combustion was 3.5 K cals per mole higher than acetone hydrazone. In this process Abendroth and Henrich obtained hydrazine salts in yields of 80 per cent., based on the original chlorine used, when acetone and cyclohexanone were employed as the carbonyl compound. However the yield fell to 11 per cent. when acetaldehyde was used. It was found advantageous to carry out the reaction under reduced pressure at a temperature of 60-100°C. As the reaction was strongly exothermic this temperature could be maintained without any heat being supplied to the system. An advantage of this process over the hydrazine fixation process discussed in chapter 2.4. is that the chlorine is recovered in the form of ammonium chloride which is a more valuable by-product than sodium chloride. The overall reaction takes place according to the following equation.



.... 2.7

At the same time, and independently of Abendroth and Henrich, several isohydrazones were synthesised and isolated by Paulsen and Huck [18, 22, 43]. They reacted gaseous chlorine and ammonia with liquid ketones. The chlorine was diluted with nitrogen in order to improve the yield, and the addition of alcohol in amounts of 1-10 per cent. also improved the yield [18]. This probably applied to those ketones, such as methyl isobutyl ketone, in which ammonia has a low solubility. Paulsen and Huck proposed the following sequence of reactions for the formation of isohydrazones.

$$2\ NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl$$ 2.29



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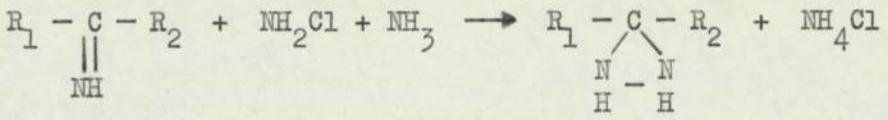


..... 2.43

Combining equations 2.29, 2.42 and 2.43 gives equation 2.7. Thus it can be seen that the formation of isohydrazones results from the fixation of chloramine. It is probable that the chloramine initially forms the chloramide ion in accordance with the mechanism proposed by Jander [81] and discussed in chapter 2.3. Equation 2.43 therefore takes place in several stages.

There are other possible products of the reaction apart from isohydrazones. These include chlorimines, hydrazones, azines and undesirable products caused by the condensation of ammonia with the carbonyl compound. Paulsen and Huck claim that the formation of azines is enhanced by the presence of water and by the elevation of reaction temperature. However reasonably good yields of the isohydrazone were obtained in a water emulsion at temperatures of 0-20°C.

In the case of acetophenone it would seem that temperature plays an important part in determining which product is formed. It is claimed [43] that at 10°C using this carbonyl compound the main product is the azine, with the isohydrazone present only in trace quantities. It is evident that in order to achieve this temperature, at normal conditions, some other compound such as methyl alcohol would be required in the reactor as acetophenone freezes at 20.2°C. However Paulsen [21] states that at 0°C when a mixture of 1200 parts of acetophenone and 480 parts of methanol is reacted with chlorine and ammonia the isohydrazone is obtained in a yield of 71 per cent.

Paulsen and Huck [18, 43] claimed that better yields were obtained when both the ammonia and chlorine were diluted with nitrogen and allowed to remain in the reactor for a longer period. The same authors also claimed that superatmospheric pressure caused an acceleration of the reaction. However in the examples quoted there is no instance of both gas streams being diluted and only one example of superatmospheric pressure being used. Furthermore these conditions of higher pressure combined with both gas streams being diluted would appear to be contradictory as in one case the partial pressure of the gases is being raised and at the same time it is being lowered through dilution with nitrogen. It is possible however that diluting the chlorine stream only and operating the reactor at an elevated pressure would increase the yield. In this manner local excess of chlorine would be avoided and since the overall reaction proceeds with a decrease in volume it is possible that excess pressure would assist the reaction. However Paulsen and Huck claimed good yields at atmospheric pressure and it would therefore appear that higher pressures are not necessary.

The ammonia to chlorine molar ratio was also varied and an optimum value of 20 to 1 was suggested. Benzaldehyde was also employed as the carbonyl compound, giving a 41 per cent. yield of isohydrazone [18]. No mention was made of the very stable complex which ammonia forms with benzaldehyde.

Paulsen and Huck [43] suggested a method of analysis of isohydrazones involving the hydrolysis to hydrazine sulphate by boiling with a considerable amount of excess of 50 per cent. [W/W] sulphuric acid. However, because isohydrazones are unstable, it is likely that under the conditions quoted the conversion to hydrazine sulphate would not be quantitative. This process of first fixing the chloramine as an isohydrazone and subsequently converting it to hydrazine hydrate or hydrazine sulphate has been suggested as an improved means of manufacture of hydrazine [98-102].

The fixation process has also been carried out in liquid ammonia. Yields of the order of 20 per cent. were obtained when the ketone was added to the reaction mixture after the introduction of chlorine [18]. However when the ketone was added to the liquid ammonia prior to the introduction of chlorine, yields of isohydrazone of 93.5 per cent. were claimed [17, 19]. In each experiment it appears that the chlorine was not diluted with nitrogen; this seems unusual as the reaction would be difficult to control because the chlorine jet would almost certainly block with ammonium chloride. The advantages of using the liquid ammonia system were quoted as:-

(1) Higher yields were obtained.
(2) A higher concentration of isohydrazone in the ketone is obtained.
(3) The condensation of carbonyl compounds with ammonia is avoided.

Similar yields were however quoted when gaseous ammonia was employed.

Rudner [103-105] prepared the hydrazone and the azine of cyclohexanone by a process which involved the formation of cyclohexanechlorimine as an intermediate. If a base stronger than ammonia such as triethylamine is present the hydrazone is the major product, but if the base is sodium hydroxide the azine is formed. The mechanism proposed by Rudner is:

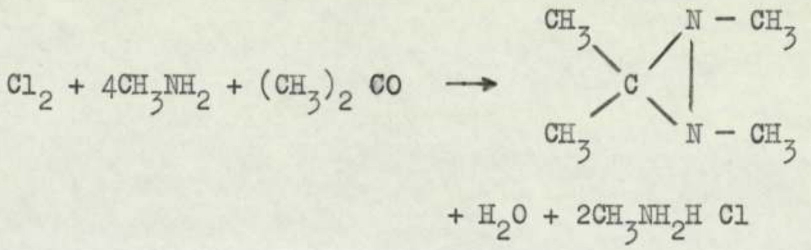
$C_6H_{10}\,O + NH_2\,Cl \longrightarrow C_6H_{10}\,N\,Cl + H_2O$ 2.44

$C_6H_{10}\,N\,Cl + NH_3 \longrightarrow C_6H_{10}\,NNH_2 + H\,Cl$ 2.45

$C_6H_{10}\,NNH_2 + C_6H_{10}O \longrightarrow C_6H_{10}NNC_6H_{10} + H_2O$ 2.46

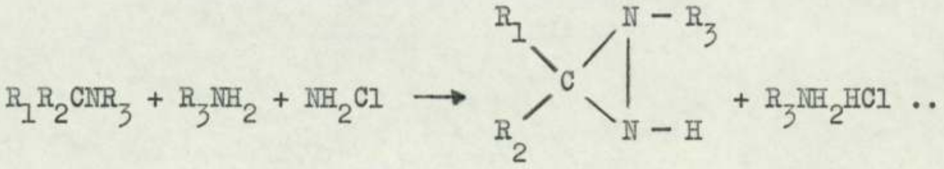
Fuchs [106] carried out the same reaction and formed the isohydrazone, but in this case there was no other base present apart from ammonia.

If amines are used in place of ammonia N- substituted isohydrazones are obtained. Abendroth [107-109] obtained tetramethyl diaziridine in a yield of 49 per cent. by the gas phase reaction of a mixture of chlorine in nitrogen with acetone and methylamine. The reaction proceeds according to the following equation:-



.... 2.47

When ethylamine was employed a 60 per cent. yield of the corresponding diaziridine was obtained. In order to obtain diaziridines with one free NH group the carbonyl compound must be replaced by a ketimine and chloramine must be used with the amine from which the imine is derived [110],



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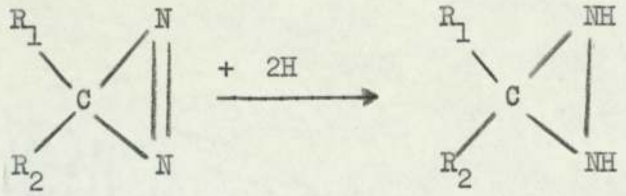
Other methods of manufacture of isohydrazones include the hydrogenation of diazirines and the reaction of ammonia and carbonyl compounds with hydroxylamine - 0 - sulphonic acid. Schmitz and Ohme [111] prepared isohydrazones by the reduction of diazirines with sodium amalgam in aqueous methanol.



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They also prepared monosubstituted isohydrazones by the action of Grignard reagents in ether solution on the diazirine [112].

Abendroth [113] prepared acetone isohydrazone by the action of excess ammonia and acetone on hydroxylamine - O - sulphonic acid.

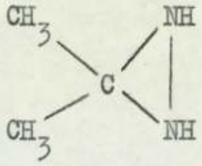
$$NH_2 - O - SO_3H + 3NH_3 + (CH_3)_2CO \longrightarrow (NH_4)_2 SO_4 + H_2O + R_1R_2CN_2H_2 \quad \text{..................} \quad 2.50$$

Schmitz and Ohme [114] prepared cyclohexanone isohydrazone in a similar manner.

From the above discussion it can be seen that although research has been carried out on the fixation of chloramine there has been no precise information about the effects of the various parameters on the yield of isohydrazone. Also, most of the information published has been in the form of patents and is consequently not very informative and in some cases appears to be contradictory. Thus a study of the various factors affecting the yield are presented in some detail, and an attempt is made to determine the rate controlling step in the reaction.

2.5.2. Properties and reactions of isohydrazones.

Abendroth and Henrich [16, 20, 97], who first isolated acetone isohydrazone, found that it was chemically very distinct from acetone hydrazone. It liberated a mole of iodine from an acidified iodide solution; also the new compound contained no - N - NH_2 group and its infra-red spectrum showed the presence of an NH group. From their results Abendroth and Henrich concluded that the new compound must have the following structure:-

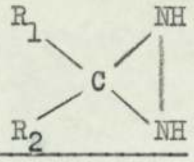


In 1962 Evans [115] reviewed the organic chemistry of hydrazine but only briefly mentioned the isohydrazones. Since that time Reed [110] has reviewed some of the earlier work on isohydrazones and diazirines, and discussed some of the complex reactions in which these compounds can participate.

Paulsen and Huck [43] isolated and determined the properties of some isohydrazones. Their results are shown in Table 2.2.

Table 2.2.

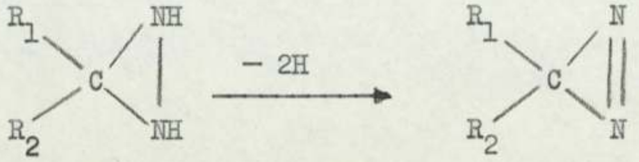
Isolated isohydrazones.



R_1	R_2	b.p. °C/mm. Hg.	m.p. °C
methyl	ethyl	32°/17	22°
ethyl	ethyl	58°/24	56°
methyl	n- propyl	48°/15	ca. -10°
methyl	i- propyl	67°/50	55 - 56°

The boiling points of these compounds are substantially higher than those of the corresponding ketones. Abendroth and Henrich [97] found that the reaction of acetone isohydrazone with benzoylchloride yielded symmetrical dibenzoyl hydrazine and acetone. However unlike acetone hydrazone the isohydrazone did not react with mercuric oxide, benzaldehyde or acetone. For a more detailed review of the properties of isohydrazones reference should be made to Paulsen and Huck [43] and Reed [110].

An interesting reaction of isohydrazones is their dehydrogenation to diazirines. Paulsen [116, 117] discovered that suitable dehydrogenating agents are yellow mercuric oxide, chromium trioxide, osmium tetroxide, potassium dichromate and potassium permanganate. The reactions can be represented as:-



.... 2.51

Good yields were obtained using freshly prepared yellow mercuric oxide. Schmitz and Ohme [111] used silver oxide to dehydrogenate the isohydrazones.

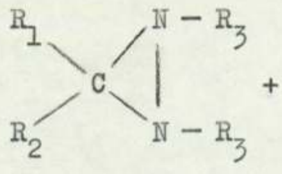
Jankowski and Paulsen [118] discovered that the dehydrogenation took place, simply by heating to 125°C. The addition of cuprous or cupric salts was also found to effect the dehydrogenation yielding as products the diazirine, ammonia and the ketone. The diazirine has been prepared by the direct action of excess chloramine on the ketone [119]. The isohydrazone which is formed initially is oxidised by the excess chloramine to the diazirine. In this reaction the ketone is considerably diluted with a solvent such as methanol.

2.5.3. Recovery of hydrazine from isohydrazones.

It was stated in chapter 2.5.1. that isohydrazones can be hydrolysed to hydrazine sulphate by the reaction:-

$$R_1R_2CN_2H_2 + H_2SO_4 + H_2O \longrightarrow N_2H_4H_2SO_4 + R_1COR_2 \quad \ldots\ldots\ldots\ldots \; 2.52$$

They can also be hydrolysed to dihydrazine sulphate [16, 20]. In a similar manner to equation 2.52, the substituted isohydrazones can be converted to the symmetrical dialkyl hydrazinium sulphates [107, 108, 109].



$+ H_2SO_4 + H_2O \longrightarrow R_3NH.NHR_3H_2SO_4 + R_1COR_2$ ... 2.53

Paulsen and Huck [43] proposed the hydrolysis of the isohydrazone to hydrazine sulphate, followed by titration with standard potassium iodate solution, as a means of analysis for isohydrazones. This hydrolysis to the sulphate has been suggested as a possible means of recovery of hydrazine for an industrial scale process [98, 99, 101].

From an industrial point of view hydrazine hydrate is a more useful product than hydrazine sulphate and consequently it would be advantageous to convert the isohydrazone to the hydrate without first forming the sulphate. Jankowski [120] stated that isohydrazones could not be hydrolysed in neutral or alkaline media and this does to some extent limit their application in the synthesis of hydrazine. They can however be catalytically converted to the azine in the presence of a carbonyl compound and with the medium kept acidic.

$$R_1R_2CN_2H_2 \ + \ R_1COR_2 \xrightarrow{H^+} R_1R_2CNNCR_2R_1 + H_2O \ \ldots\ldots\ 2.54$$

Jankowski stated that the reaction is strongly temperature dependant and that at 50°C methyl ethyl isohydrazone is completely transformed to the azine after 30 minutes whereas at 25°C the conversion takes 9 hours. The optimum pH for the reaction is 2.5. Below this temperature the azine is partially converted to a hydrazine salt and above it a side reaction occurs which forms nitrogen and ammonia. When the azine is formed it can easily be hydrolysed to hydrazine hydrate. This method of first forming the isohydrazone and then converting it to the azine which is in turn hydrolysed to hydrazine hydrate has been proposed as an industrial process for the manufacture of hydrazine [98, 99, 101].

Needham and Smith [121] hydrolysed azines, hydrazones and isohydrazones to hydrazine and the corresponding carbonyl compound in quantitative amounts using a cation exchange column operating at a temperature higher than 40°C. The cation exchange column is preferably one containing strongly acidic groups such as sulphonic or phosphoric groups. Abendroth [122, 123] discovered a means of so concentrating aqueous solutions of acetone isohydrazone that it can be obtained in the pure state by distillation, even at atmospheric pressure. The isohydrazone solution is shaken with a warm solution of caustic soda and the temperature is kept below 50°C by cooling. Two liquid phases result with the top phase being rich in isohydrazone.

2.6. Alternative Syntheses of hydrazine.

Besides the Raschig process the only other synthesis that has been used commercially is the oxidation of urea by sodium hypochlorite [32]. In this process the hydrazine formation reaction is also accompanied by a side reaction.

$$CO(NH_2)_2 + NaOCl + 2\,NaOH \longrightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O \quad \ldots\ldots\ 2.55$$

$$CO(NH_2)_2 + 3\,NaOCl \longrightarrow 3\,NaCl + N_2 + CO_2 + 2H_2O \quad \ldots\ldots\ 2.56$$

This process is similar to the Raschig synthesis but the latter has the advantage of a lower raw materials cost. Colton et al [140] modified the above method by using t-butyl hypochlorite in place of sodium hypochlorite. There have been many other methods of manufacture investigated and some of these have been reviewed by Powell [141].

Deutschman and Bull [142, 143] prepared hydrazine by the reaction of excess ammonia on either semicarbazide or aminoguanidine. The vapour phase reaction of nitrous oxide with either ammonia or hydrogen in the presence of a photochemical agent has also yielded hydrazine [144].

$$N_2O + 3H_2 \longrightarrow N_2H_4 + H_2O \quad \ldots\ldots\ 2.57$$

$$N_2O + 2NH_3 \longrightarrow N_2H_4 + H_2O + N_2 \quad \ldots\ldots\ 2.58$$

Robell [145, 146] synthesised hydrazine by the combustion of hydrogen or methane followed by quenching with a high velocity stream of ammonia. Kennedy [147] discovered a novel method of manufacture of anhydrous hydrazine by heating a mixture of toluene and ammonia to temperatures of 600-800°C and maintaining the pressure at 200-500 p.s.i.g. The process proceeds through a series of reactions initiated by the free radical dissociation of the methyl substituent of toluene. Ammonolysis of hydroxylamine - O - sulphonic acid [148] and hydrazine sulphate [149-152] has also been used to synthesise anhydrous hydrazine.

Numerous methods such as the photolysis, radiolysis or glow discharge of gaseous ammonia have been employed to prepare hydrazine. In addition Hickling and Newns [153, 154] reported that the glow discharge electrolysis of liquid ammonia yielded 2.5 moles of hydrazine per faraday. Nuclear radiation of liquid ammonia, urea and melamine has also been used to synthesise hydrazine [155, 156]. A process of this nature based on liquid ammonia could possibly be less costly than the Raschig synthesis but at this stage in its development it is difficult to predict its future.

CHAPTER THREE

APPARATUS AND EXPERIMENTAL PROCEDURE

3. APPARATUS AND EXPERIMENTAL PROCEDURE

3.1. Electrochemical Apparatus.

In this series of experiments solutions of liquid ammonia containing a ketone and an electrolyte were electrolysed in an attempt to form an organic derivative of hydrazine. Initially a cell similar to that used by Haller [55] was employed but as the investigation progressed the type of cell used was modified to include such features as a stirred anode and a means of altering the polarity of the electrodes. In this manner it was hoped to bring the products of electrolysis into more intimate contact and also prevent any possible decomposition of the products at the electrodes.

3.1.1. Description of Apparatus.

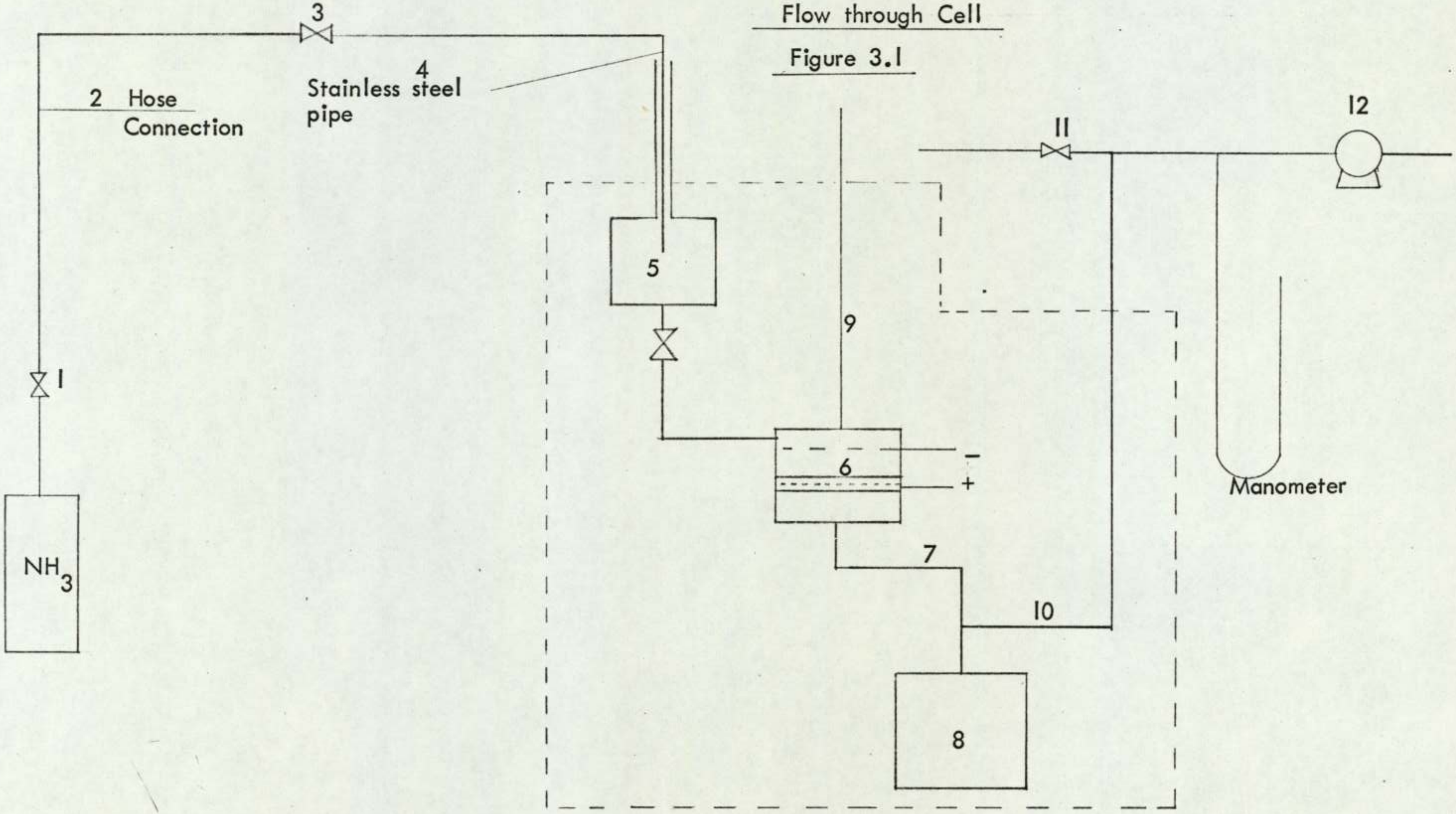
3.1.1.1. Continuous Electrolysis.

In the early part of this investigation it was decided to employ a system similar to that used by Haller [55] in which the solution flowed through a cell consisting of a porous anode and a perforated cathode. The system is shown in figure 3.1. and is itemised in Table 3.1. The voltage was supplied by two Brandenburg 'Stabpak' Type ST.1. power packs, so arranged that they can be connected in series or parallel to give an output voltage of between 6 and 50 volts at a current of 250 mA. The simple circuit diagram is shown in figure 3.2.

In figure 3.1., the equipment surrounded by the dotted line was enclosed in a low temperature cooling bath. This equipment was mounted on an aluminium alloy framework which could easily be lifted in and out of the bath. The bath consisted of a QVF glass pipe section 30" long, 18" diameter flanged at its base to a brass plate $\frac{3}{8}$" thick. The top of the bath was open to atmosphere and it could be drained through a valve screwed into the brass plate. An acetone - dry ice mixture was used as

Flow through Cell

Figure 3.1



Electrolysis Circuit

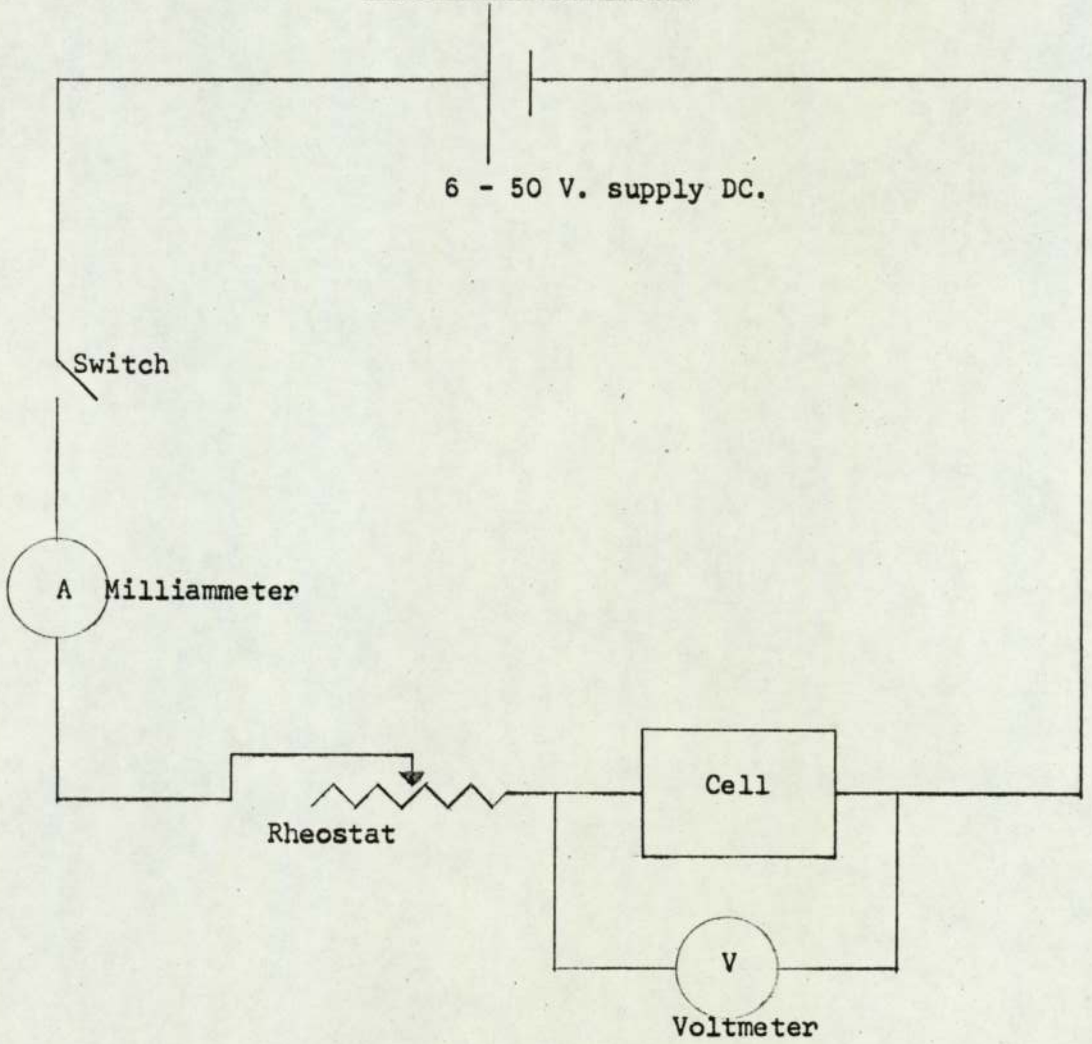


Figure 3.2

the coolant and the temperature was measured by a red spirit thermometer, calibrated at total immersion, having a maximum error of ± 1°C.

TABLE 3.1.

Items in figure 3.1.

Code	Item	Specification
1	Ammonia supply valve.	Mild steel cylinder valve.
2	Flexible connection.	Double braid butyl hose.
3	Control valve.	Ermeto $\frac{1}{4}$" cadmium plated mild steel needle valve.
4	Ammonia supply pipe.	2' length of $\frac{1}{4}$" OD stainless steel pipe.
5	Solution reservoir.	Fisons. 100 ml funnel (Ref. SFSC/10/11) A glass tube was inserted into the ground glass socket at the top in order to prevent the coolant entering.
6	Cell.	Two QVF PRI/B24S pipe reducers flanged together. The gaskets used were asbestos with PTFE inserts. A glass spacer was inserted to separate the electrodes. A sidearm was put on the top pipe reducer.
7	Connecting line.	Fisons glassware. Recovery bend (RB33) and vacuum receiving adaptor (RAVC 33).
8	Recovery flask.	Fisons flask (FSRB/10/3).
9	Gas take-off tube.	2' long glass tube terminating in a B24 cone at the bottom.
10	Vacuum line.	$\frac{3}{8}$" ID pressure tubing.
11	Vacuum control valve.	Ermeto $\frac{1}{4}$" cadmium plated mild steel needle valve.
12	Vacuum pump.	Edwards "Speedivac" stainless steel water jet pump.

It was necessary that the top of all the equipment immersed in the bath was not only above the level of the liquid but also about 6" above the top of the QVF pipe section. This insured that carbon dioxide could not enter the immersed apparatus and react with the ammonia to form ammonium carbamate.

$$CO_2 + 2NH_3 \longrightarrow NH_2CO_2NH_4 \quad \ldots\ldots\ldots 3.1$$

The equipment including the control panel, which was mounted on the framework supporting the cooling bath, is shown in Plate 1.

When a porous anode was used a layer of araldite was placed around its edge in order to prevent any of the cooling solution seeping into the cell. The porosity of these anodes was 6.5 μ and they were constructed of either nickel or stainless steel. A platinized titanium disc in which a small pin hole was made was also employed as anode. This hole allowed the solution to flow through the cell. The rate of flow through the cell was controlled by the valve (11) which regulated the vacuum applied to the system. In practice it was found that this system was not entirely satisfactory but it did give some measure of control of the liquid flow rate through the cell. In this apparatus the distance between the two electrode was normally $\frac{1}{8}$ - $\frac{3}{8}$".

3.1.1.2. Batch Electrolysis.

3.1.1.2.1. Fixed electrode cells.

This apparatus, shown in Plate 2, was in many ways similar to that described above. The major difference was that the vacuum system, the receiver (8) and the line (7) were replaced by a glass stopper inserted into the lower QVF glass reducer (PR1/B24S). In addition the anode was non-porous and formed the base of the cell. Several types of material were used for the anode including platinized titanium, platinum and stainless steel.

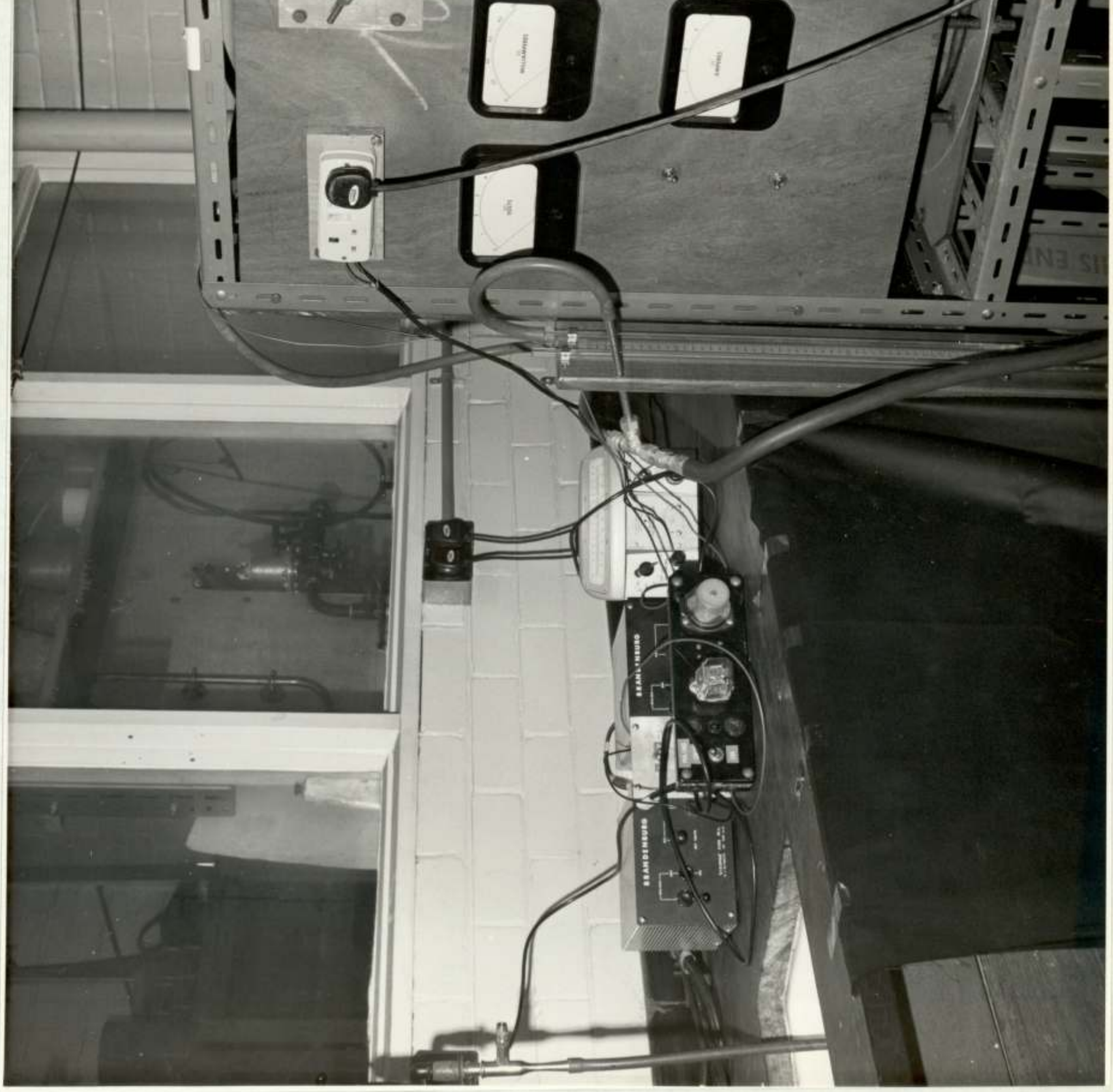
When the experiment was completed, the electrical circuit was disconnected and the apparatus was raised out of the bath. The glassware was dismantled and the contents of the cell emptied into a beaker from which the liquid ammonia was allowed to evaporate.

ELECTROLYSIS APPARATUS

POWER PACK

REVERSE POLARITY
SWITCH

PLATE I

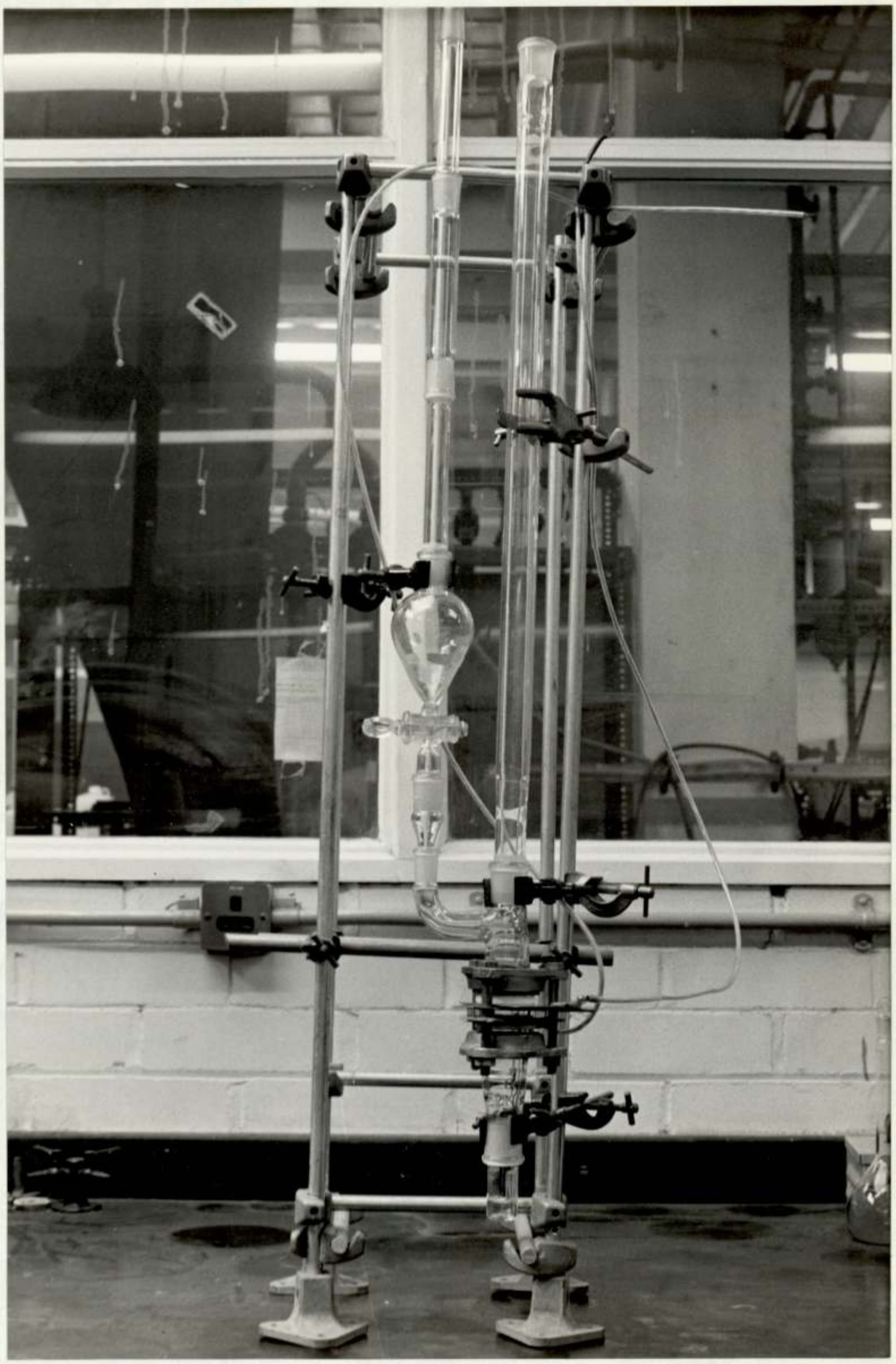

BRANDENBURG
BRANDENBURG

BATCH ELECTROLYSIS CELL

FUNNEL

CELL

PLATE 2



Following this it was decided to study the electrolysis in a H-type cell and the apparatus employed is shown in figure 3.3. When the solution was actually in the cell the apparatus was lifted out of the bath and the section containing items (1) and (2) was replaced by the long glass tube (3). These tubes (3) and (4) served the same purpose as those in the previous apparatus, that is to allow the gaseous products of electrolysis to escape and to prevent any carbon dioxide entering the system. In this apparatus both the electrodes were of platinized titanium or carbon.

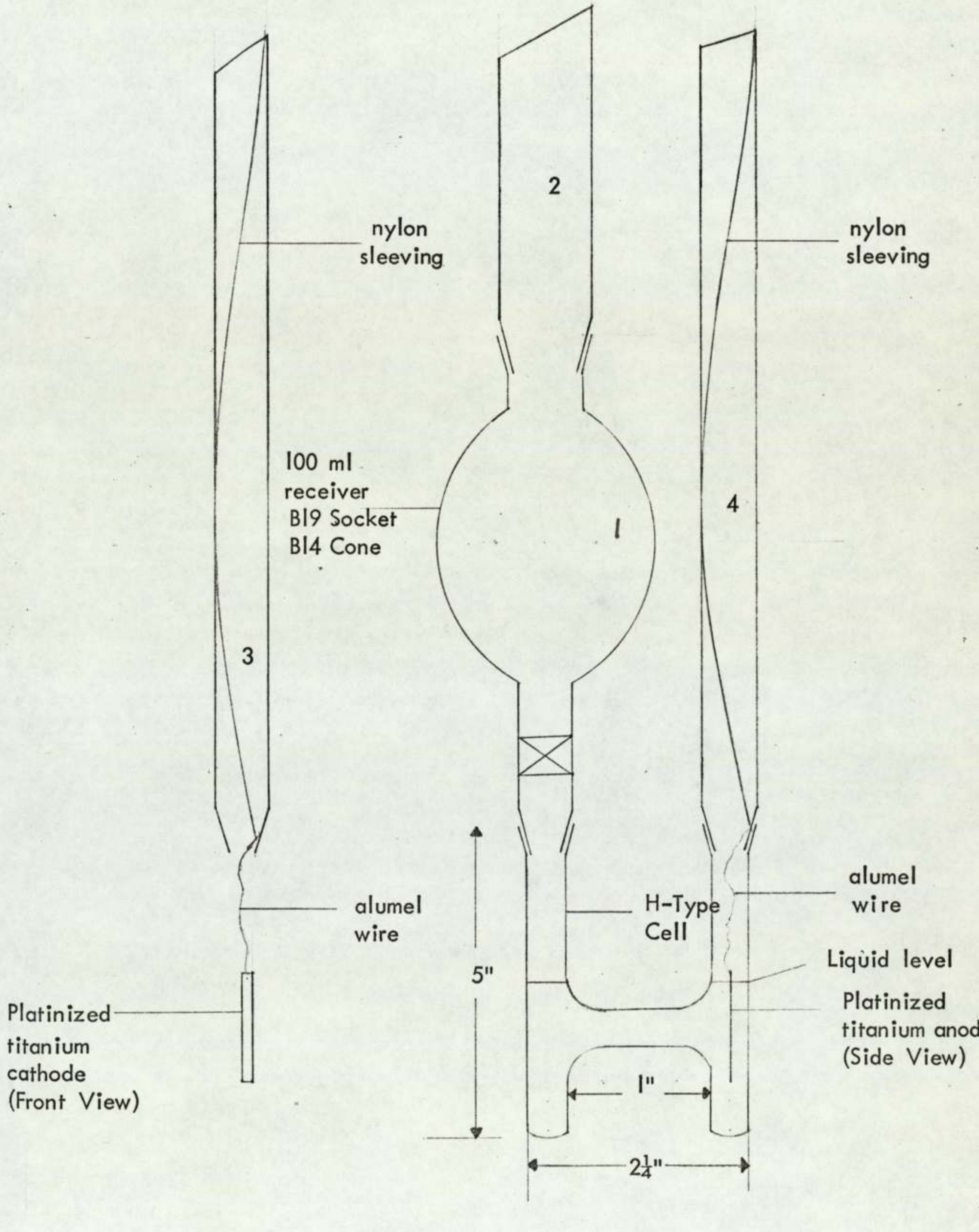
Several modifications of the above two systems were investigated and apparatus was developed to incorporate features of both types of cell such as an anode as shown in figure 3.3. in a cell similar to that shown in Plate 2. In this type of apparatus the cathode formed the base of the cell. In addition experiments were carried out using a carbon anode in a cell similar to that shown in Plate 2. The carbon formed a disc with a central hole, to allow the solution to flow through to the cathode, and rested on a glass spacer flanged between the two sections of the cell. The cathode again formed the base of the cell.

3.1.1.2.2. Stirred electrode cells.

This type of equipment is shown in Plate 3 and illustrated in figure 3.4. All the equipment including the stirrer was mounted on an aluminium alloy framework to facilitate entry and removal from the bath. Two stirrer guides were employed, the top one of brass and the lower one of stainless steel. Both contained PTFE bushes. This apparatus differed from those previously described in that the cell was constructed from 1½" QVF glassware because extra room was required by the stirrer and the PTFE sleeve.

The electrical connection from the anode to the stirrer consisted of platinum wire, and the connection to the external circuit consisted of a

H-Type Cell Figure 3.3



STIRRED ELECTRODE CELL

STIRRER
GUIDES

CELL

PLATE 3

clamp on to the top of the aluminium framework. The distance between the two electrodes was approximately $\frac{3}{8}$". In order to prevent the formation of ammonium carbamate inside the apparatus the stirrer motor and the top of tube (1), were sited about 6" above the top of the bath.

3.1.1.2.3. Reverse Polarity Switch.

This switch enabled the polarity of the electrodes to be reversed at given time intervals. The switch is shown in Plate 1 and the electrical circuit is shown in figure 3.5. Essentially the apparatus consisted of a motor, which rotated at a fixed speed of 1 RPM to which a mild steel cam was attached. Every half revolution the cam operated the microswitch which actuated the relay and reversed the direction of the D.C. output voltage. Thus the polarity of the electrodes was changed every 30 seconds.

3.1.1.3. Summary.

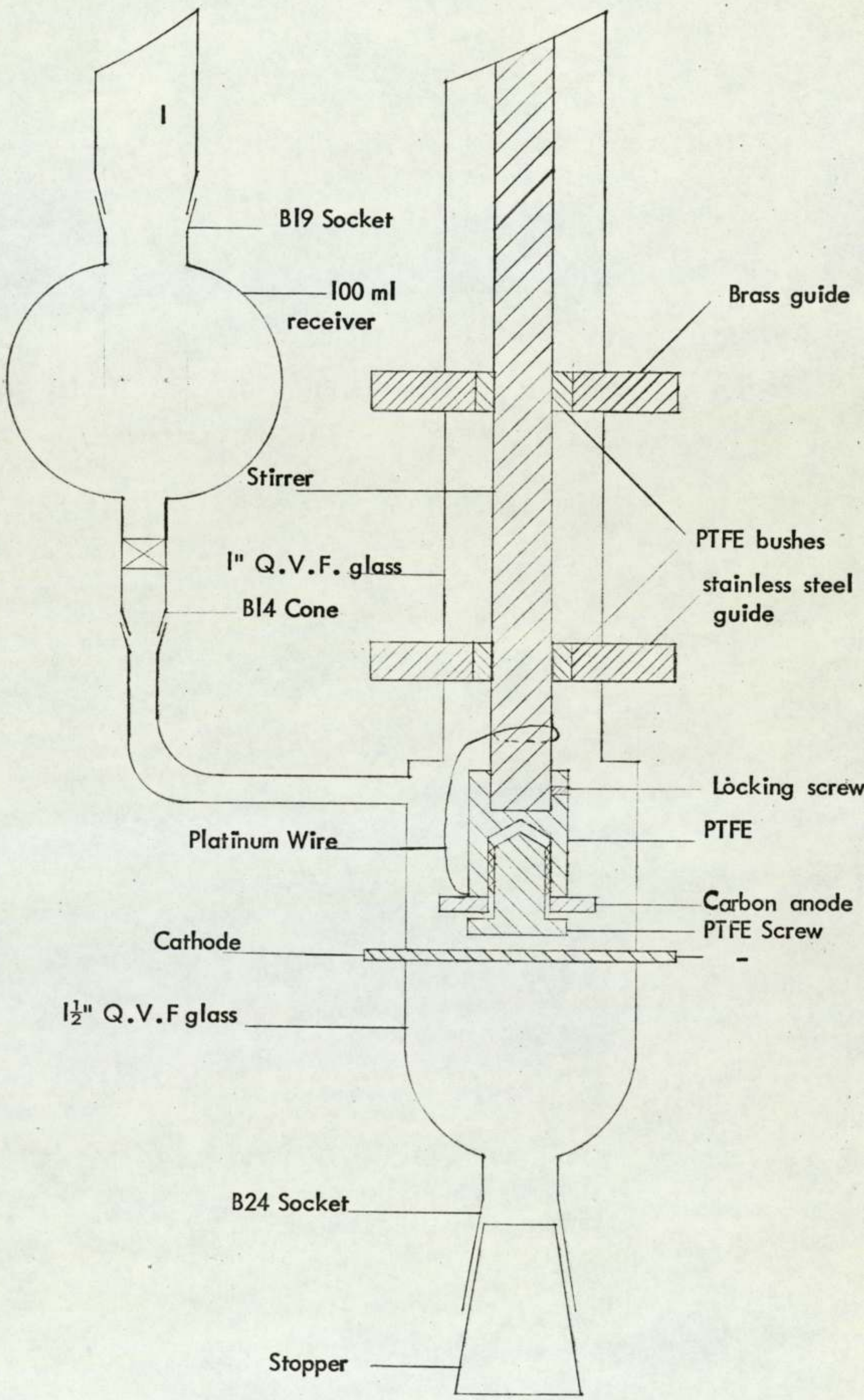
Several types of apparatus have been described in the preceding sections. However, as has been stated, various modifications to the equipment were made for some experiments and most of these have been discussed. It is not possible or important to describe these cells in detail as they only differ slightly from those already shown. In addition most of the experimental work in this investigation was performed on the type of cell shown in Plate 2. The means of supplying ammonia to the different cells was exactly the same as that shown for continuous operation in figure 3.1.

3.1.2. Experimental Procedure.

The basic procedure was the same for all the types of apparatus employed. Referring to figure 3.1., the bath was first of all brought down to the required temperature by mixing approximately 20 gallons of acetone with the appropriate quantity of dry ice. In order to control the considerable frothing which took place with this system, the acetone

Stirred Anode Cell

Figure 3.4



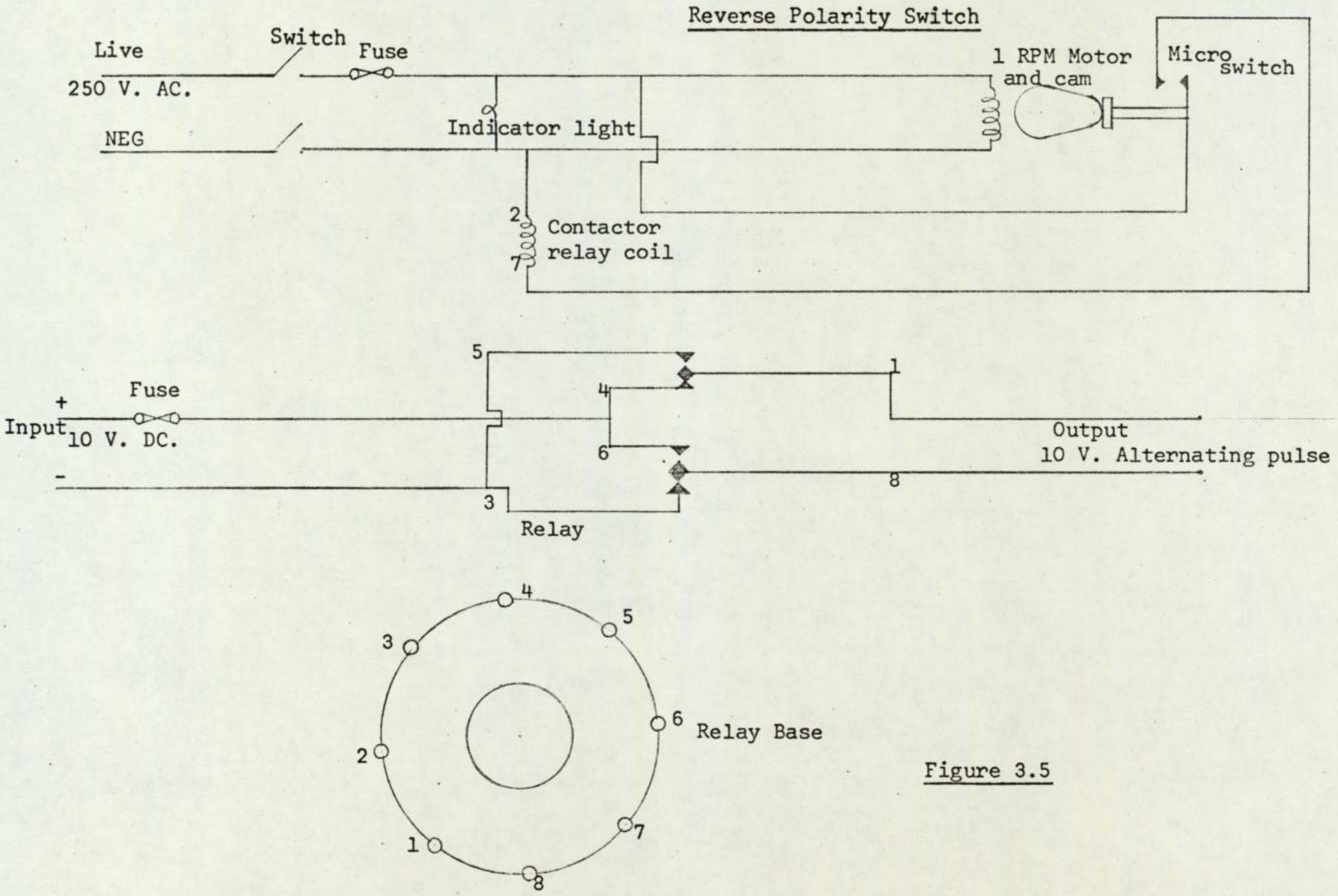

Reverse Polarity Switch
Live
250 V. AC.
NEG
Switch
Fuse
Indicator light
2
7
Contactor
relay coil
1 RPM Motor
and cam
Micro switch
+
Input 10 V. DC.
-
Fuse
5
4
6
3
Relay
1
8
Output
10 V. Alternating pulse
4
5
3
6
Relay Base
2
7
1
8

Figure 3.5

and the dry ice were added alternately. During the course of an experiment the temperature was kept at the desired value by the addition of extra dry ice. Because the apparatus was at atmospheric pressure the temperature of the bath had to be less than -33.35°C [Boiling point of ammonia at 1 atm]. In most experiments the temperature was kept at approximately -40°C but it was not possible to maintain this value exactly and in practice there was a fluctuation of ± 1°C.

When the bath was at the required temperature the apparatus which was mounted on the aluminium alloy framework, was placed inside. The desired quantity of ketone and electrolyte had previously been placed inside the funnel (5). Ammonia was then supplied to the funnel by opening the needle valve (3) and the cylinder valve (1). The ammonia condensed in the funnel and when the required quantity of ammonia had been collected, which was indicated by a mark on the flask, the supply (valve 1) was shut off. By this time the liquid ammonia, ketone and the electrolyte had formed a well mixed solution.

In a batch electrolysis experiment the apparatus was temporarily lifted out of the bath and the glass stopcock on the funnel was opened to allow the solution to flow into the cell. The apparatus was then replaced, the electrical connections were made and the run was then started by applying a given voltage to the cell. The duration of the run, the current, the voltage, the temperature and any other experimental effects were noted.

In a continuous electrolysis experiment the electrical connections to the external circuit were first made and a given voltage was then applied to the cell. Only then was the solution allowed to enter the cell. The stopcock was turned with the apparatus remaining in the bath, using a rubber glove to protect the operator's hand from the acetone-dry ice solution. By adjustment of the vacuum the desired flow rate was obtained.

When the run was completed the voltage supply was switched off and the apparatus was disconnected electrically and removed from the bath. The solution was recovered in the cell or in the flask (8) depending on the type of experiment carried out. This solution was poured into a beaker and the liquid ammonia was allowed to evaporate leaving behind a sediment and most of the ketone. This mixture was filtered and the ketone was analysed for hydrazine by the method described in Chapter 4.1.2.

3.2. Apparatus for Gas Phase Reaction.

Two different reactors were employed for this investigation. The first was designed to study the formation of chloramine by reacting chlorine diluted with nitrogen with ammonia, and the second was used to study the formation of acetone isohydrazone by carrying out the above reaction in the presence of acetone.

3.2.1. Description of Apparatus.

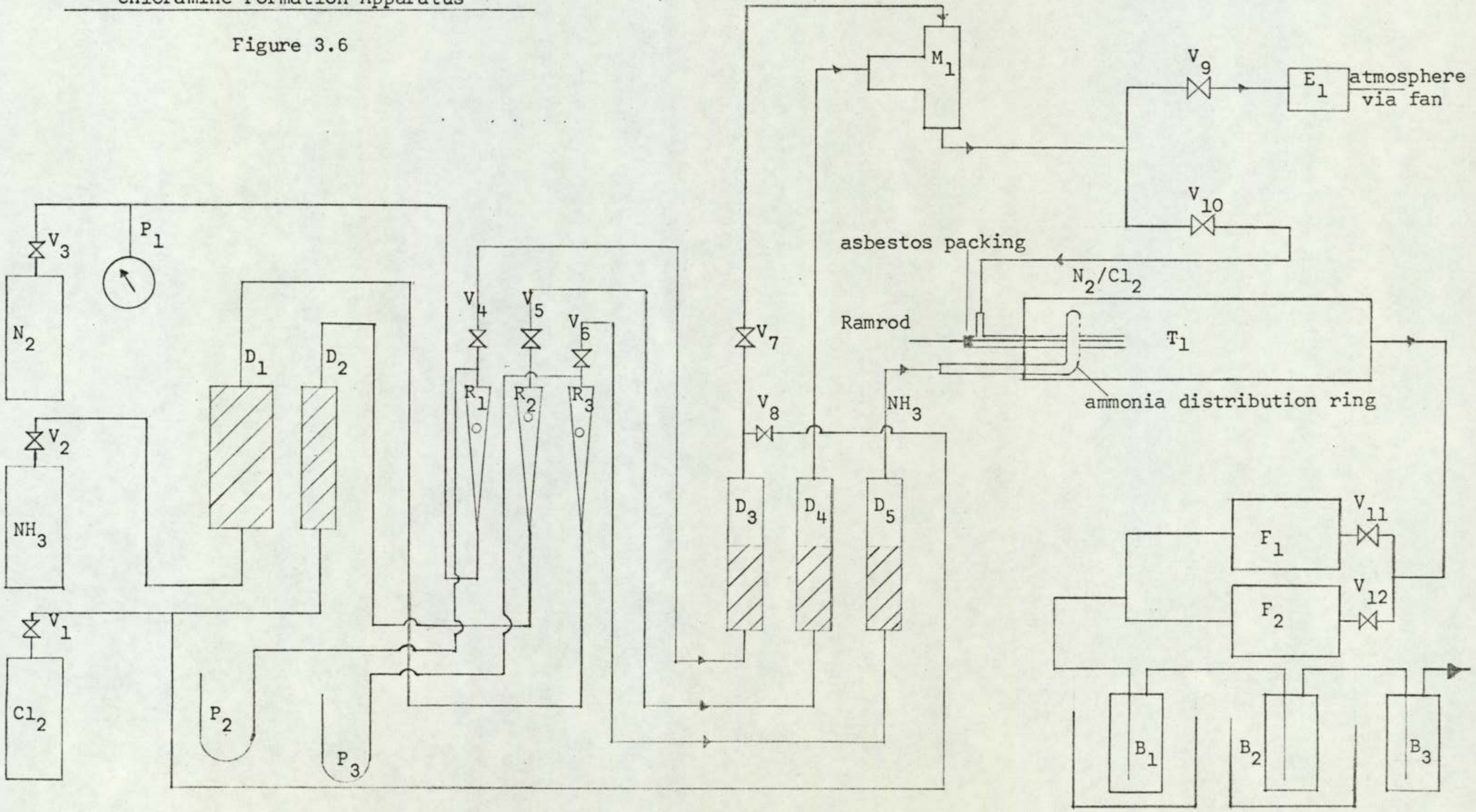
3.2.1.1. Chloramine formation system.

The apparatus constructed was similar to that used by Drago [72] to investigate the formation of chloramine. However in this investigation rotameters instead of capillary tubes were used to measure the gas flow rates. In some experiments a vertical reactor was used whereas Drago always worked with a horizontal reactor. The apparatus is shown in figure 3.6. and the items are listed in Table 3.2.

Ammonia, chlorine and nitrogen were supplied from their respective cylinders by opening valves V_2, V_1 and V_3; ammonia and chlorine were stored in liquid form in an 18 lb. and a $3\frac{1}{2}$ lb. cylinder respectively. The gases were dried prior to entering the reactor, and, in the case of ammonia and chlorine, they were also dried before entering the rotameters. Silica gel was used as a drying agent for nitrogen and alumina for the ammonia and chlorine. These driers were not essential as the gases were

Chloramine Formation Apparatus

Figure 3.6



supplied in anhydrous form, but to insure against the possibility of moisture being present, the dryers were installed in the system as only traces of moisture caused corrosion of the chlorine rotameter.

The rotameters used were Fischer and Porter tri-flat instruments. These were calibrated for nitrogen against a Parkinson Cowan liquid sealed gas meter and reasonable agreement was obtained; the results and calibrations are shown in Appendix 1. Two meters were used for measuring the flow of nitrogen in order that the different ranges could be covered. There was considerable oscillation of the sapphire float in the chlorine rotameter. Therefore this instrument could only be regarded as giving an indication of the flow. As will be seen later, an exact determination of the amount of chlorine consumed was made by determining the quantity of ammonium chloride formed. The rotameters were initially calibrated using the method outlined in the handbook of Tri-flat variable area flow meters [158]. This method is given in Appendix 1.

TABLE 3.2.

Items in figure 3.6.

Code	Item	Specification
B_1, B_2	Chloramine recovery vessels.	Two dreschel bottles.
B_3	Flow indicator.	Dreschel bottle.
D_1	First ammonia drier.	QVF pipe section PS3/12 filled with alumina. End plates were mild steel.
D_2	First chlorine drier.	QVF pipe section PS1/12 filled with alumina. End plates were mild steel.
D_3	Nitrogen drier.	QVF pipe section PS1/12 half filled with silica gel. End plates were mild steel.
D_4	Second chlorine drier.	QVF pipe section PS1/12 half filled with alumina. End plates were mild steel.

TABLE 3.2. (continued).

Code	Item	Specification.
D_5	Second ammonia drier.	QVF pipe section PS1/12 half filled with alumina. End plates were mild steel.
E_1	Extraction fan.	Vent-Axier.
F_1, F_2	Filters.	QVF pipe section PS2/12. This was flanged at both ends to QVF PR2/B24S reducers. Asbestos was packed into one end.
M_1	Nitrogen - chlorine mixer.	QVF tee-piece PT/1. End plates were mild steel.
P_1	Nitrogen pressure gauge.	Part of cylinder regulator.
P_2	Nitrogen manometer.	Mercury manometer.
P_3	Ammonia manometer.	Mercury manometer.
R_1	Nitrogen rotameter.	Fischer and Porter $\frac{1}{8}$" tube. Scale = 8. Range = 0-550 ml per min. Sapphire float. or $\frac{1}{8}$" tube. Scale = 20 Range = 0-3000 ml per min. Stainless steel float.
R_2	Chlorine rotameter.	Fischer and Porter, 1/16" tube. Scale = 10. Range = 0-75 ml per min. Sapphire float. or 1/16" tube. Scale = 20. Range = 0-220 ml per min. Sapphire float.
R_3	Ammonia rotameter.	Fischer & Porter. $\frac{1}{8}$" tube. Scale = 20. Range = 0-4000 ml per min. Stainless steel float.
T_1	Reactor.	QVF pipe section PS2/12. At one end was flanged a mild steel end plate to which the entry jets were connected. At the other end was flanged a QVF pipe reducer PR2/B24S.

TABLE 3.2. (continued)

Code	Item	Specification.
V_1	Chlorine supply valve.	Mild steel cylinder valve.
V_2	Ammonia supply valve.	Mild steel cylinder valve.
V_3	Nitrogen supply valve.	Cylinder regulator.
V_4	Nitrogen control valve.	Ermeto ¼" cadmium plated mild steel needle valve.
V_5	Chlorine control valve.	"
V_6	Ammonia control valve.	"
V_7	Nitrogen supply valve.	"
V_8	Nitrogen purge valve.	"
V_9	Atmosphere purge valve.	Negretti and Zambra ¼" OD brass needle valve.
V_{10}	Reactor supply valve.	"
V_{11}, V_{12}	Filter change-over valves.	Two Hoffman Clips.

Nitrogen and chlorine were mixed in the QVF tee-piece (M_1) and the gas mixture could either be passed to the reactor or purged to the atmosphere. In the latter case valve (V_{10}) was closed, valve (V_9) was opened and the extraction fan (E_1) was switched on. This operation was carried out before and after each run, as a safety measure, in order to purge the system of chlorine. The fan was situated at the window of the laboratory and the gases were harmlessly discharged to the atmosphere. If it was required to remove any piece of equipment in the chlorine line, it was first purged with nitrogen by opening valves (V_8), (V_7) and (V_9) and closing valve (V_{10}). All the pipework in the system was made of either stainless steel or copper; the pipe fittings were made of cadmium plated mild steel. The backing flanges for the driers and for the reactor were made of mild steel.

The reactor was constructed of QVF glass pipe section of 2" diameter and the jets were made of stainless steel. In some experiments a stainless steel cap, with a 1/32" hole drilled into the centre, was screwed over the chlorine jet in order to assist the mixing of the chlorine with ammonia. However this hole blocked very rapidly with ammonium chloride. The reactor was arranged in a vertical or in a horizontal position, and in some experiments a glass tee-piece was inserted into the reactor so that the ammonia could be introduced through the side.

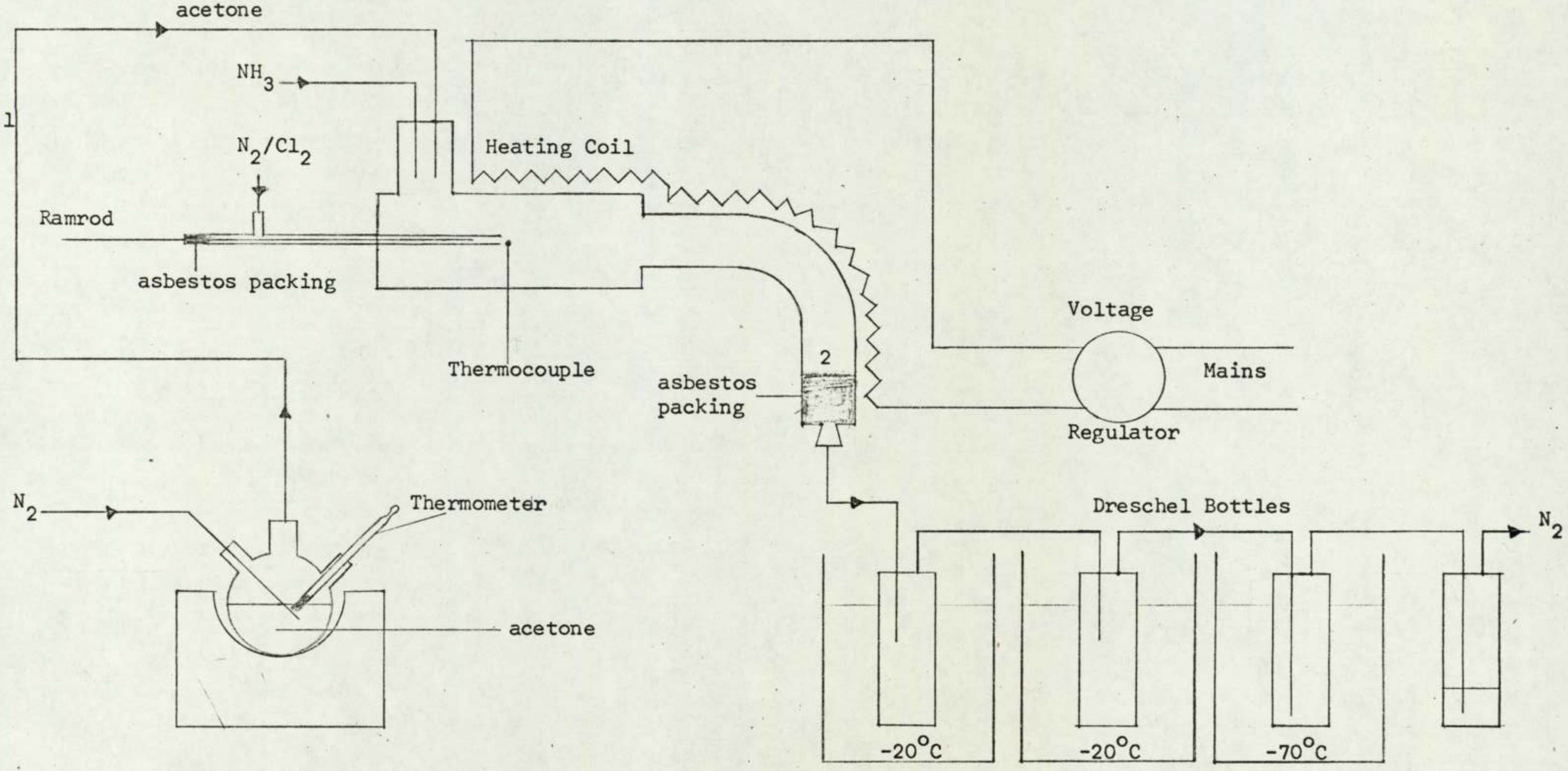
The filters were constructed of QVF 2" glass pipe section with one end packed with asbestos. They were very effective in removing ammonium chloride from the gas stream. The effluent gases from the filter passed into three dreschel bottles - (B_1), (B_2) and (B_3). The first two contained liquid ammonia and were maintained at -70°C by the coolant baths and the third bottle contained distilled water and was at room temperature. The first two traps, in addition to capturing the chloramine in the gas phase, also condensed liquid ammonia out of the gas stream. The third trap served to remove any chloramine remaining in the gas phase, and also gave a visual indication that the reactor was operating normally; that is the chlorine jet had not blocked with ammonium chloride.

3.2.1.2. Isohydrazone formation system.

The reactor and recovery system is shown in figure 3.7. The means of supplying the gases to the reactor was exactly the same as in figure 3.6. However this system was provided with a means for passing acetone vapour into the reactor. This simply consisted of a litre flask containing the acetone which was heated by an isomantle. Sidearms in the flask enabled a thermometer to be inserted and a stream of nitrogen to be bubbled into the acetone. The acetone was carried in this gas stream

Gas Phase Isohydrazone reactor

Figure 3.7



into the reactor through PTFE tubing (1). In some experiments the acetone vapour was supplied to the reactor by only boiling the liquid; in these cases the nitrogen sidearm was closed with a stopper.

The reactor was made of 2" diameter QVF glass pipe section with a $1\frac{1}{2}$" reducer attached at the exit end. Asbestos was packed into the glass section (2) and this filtered ammonium chloride from the gas stream. The reactor was heated by electrical heating tape controlled through a voltage regulator and the temperature inside the reactor was measured by a chromel-alumel thermocouple connected to a George Kent multipoint recorder.

The effluent gases from the filter were passed into four dreschel bottles maintained at various temperatures. The first two, which had been specially cleaned and dried, were used to separate acetone and isohydrazone from the gas stream and were maintained at -20°C. Initial experiments had shown that two bottles were necessary for this operation. The glass delivery tubes of these bottles were arranged to extend to only 2" from the bottom of the bottles so that the gas stream did not bubble into the liquid condensed. In this way it was hoped to reduce the amount of ammonia in the product solution. All the connections between the filter and these bottles were made with glass and PTFE tubing.

The third dreschel bottle was maintained at -70°C to remove ammonia from the gas stream. As in the chloramine formation system, the final dreschel bottle contained distilled water and was at room temperature. It also served as a visual indication that the reactor was operating normally. The coolant baths consisted of acetone and dry ice in appropriate quantities.

3.2.2. Experimental Procedure.

3.2.2.1. Chloramine formation system.

In every experiment carried out involving chlorine, the first operation was to switch on the fan E_1. The temperature of the coolant baths for the two dreschel bottles was reduced to -70°C by the addition of dry ice. Ammonia from a separate cylinder, not shown in figure 3.6., was then passed into the dreschel bottles until 50 cc of liquid ammonia had been collected in each. In the meantime by keeping valves (V_8) and (V_{10}) closed and opening valves (V_3), (V_4), (V_7) and (V_9) the apparatus from the mixer onwards was purged of any residual chlorine by blowing nitrogen through the apparatus.

When the apparatus had been purged, the dreschel bottles were connected as shown in figure 3.6. and valve (V_9) was closed and valve (V_{10}) opened. The ammonia supply was switched on by opening valves (V_2) and (V_6) and its flow rate was controlled by valve (V_2). Following this the chlorine supply was turned on by opening valve (V_1). This valve was found to be adequate for controlling the flow and thus valve (V_5) was normally left open all the time. The stopclock was started to time the run.

White fumes of ammonium chloride appeared in the reactor and these were removed in the filters (F_1) and (F_2). If the chlorine jet blocked the bubbling in dreschel bottle (B_3) stopped. Therefore the jet was then unblocked by means of the ramrod. Whilst this operation was being carried out the chlorine and nitrogen mixture was diverted to atmosphere via valve (V_9) and the stopclock was stopped. When the jet was unblocked the experiment was resumed as before.

At the end of the run the chlorine flow was stopped by closing valve (V_1) but the flow of nitrogen and ammonia was continued for a few minutes longer in order to purge any chlorine remaining in the approach tubes to the reactor. The ammonia flow was then stopped and the nitrogen stream was diverted to atmosphere by closing valve (V_{10}) and opening valve (V_9). After a few more minutes the nitrogen flow was also turned off.

The dreschel bottles containing liquid ammonia were removed from their coolant baths and ground glass stoppers with PTFE sleeves were inserted. The bottles were then stored, at approximately -60°C for 18 hours, in a box containing dry ice. They were then removed and placed in a fume cupboard and the ammonia was allowed to evaporate. The residue that was left in these two dreschel bottles was combined with the distilled water from the third trap and the solution was analysed for chloride content by the Volhard procedure. The total amount of ammonium chloride deposited in the reactor, the tubes and in the filters was also determined by washing each component with water and then analysing this solution for chloride content by the Volhard procedure. These results were then used to determine the yield of chloramine as described in chapter 4.3.

In practice this reactor was very difficult to control because the chlorine jet persistently blocked with ammonium chloride. This trouble was encountered even when the chlorine was diluted with large amounts of nitrogen. It was however observed that the reactor operated for a longer period without blocking when it was arranged vertically. The ramrod proved to be very effective for removing ammonium chloride but great care had to be taken that chlorine did not leak past the asbestos packing.

3.2.2.2. Isohydrazone formation system.

The chlorine line from the mixer onwards was purged of chlorine in a manner similar to that described in the previous section. The heater was then switched on, and the reactor was heated until the temperature inside was approximately 80°C. At this point the isomantle which heated the flask of acetone was also switched on. By means of a voltage regulator the temperature inside the reactor could be controlled manually. If it was going to be employed during the experiment the nitrogen stream to the reactor was now turned on.

When the acetone was passing through the system and condensing in the dreschel bottle at a reasonable rate, the nitrogen purge valve (V_9) was closed and the reactor line valve (V_{10}) was opened. The ammonia supply was turned on by opening valve (V_2) and finally chlorine was passed into the system by opening valve (V_1).

As described in the previous apparatus, white fumes of ammonium chloride appeared in the reactor and these were removed from the gas stream by the filter~~s~~. It was also necessary to release any blockage of the chlorine jet periodically by means of the ramrod. Temperatures of the order of 130°C were encountered in the reaction zone and this, combined with the heat supplied by the heater, ensured that the acetone isohydrazone remained in the gas phase in the reactor and did not condense until it passed to the two dreschel bottles from which it was recovered.

When the run was completed the isomantle was switched off and the shut-down procedure described in the previous section was followed. Again all the ammonium chloride deposited in the reactor, the tubes and the filter was recovered and analysed for chloride content by the Volhard procedure. The contents of the first two dreschel bottles could be analysed separately or combined and the resultant solution analysed for isohydrazone content by the methods described in chapter 4.1.3.

3.3. Apparatus for Gas-Liquid reaction.

In this series of experiments the formation of azines and isohydrazones was investigated using either a stirred tank reactor or a column reactor. Both reactors were in some cases modified to suit individual experiments but the basic design remained essentially the same.

3.3.1. Description of Apparatus.

3.3.1.1. Stirred tank reactor.

A diagram of the top section of this reactor is shown in figure 3.8. and a line diagram of the whole reactor is shown in figure 3.9. In table 3.3. the apparatus is itemised. The means of supplying the gases to the reactor and treatment of the effluent gas is similar to that described in chapter 3.2. and is shown in Plate 4. The nitrogen-chlorine mixture entered the reactor through the dip pipe and bubbled into the ketone through four holes drilled into the side of the tube near its end. The end of the tube was itself blocked with a PTFE plug. Several types of chlorine inlet nozzles were employed by varying the number and size of the holes. The ammonia, upon entering the reactor, was evenly distributed by means of the stainless steel distribution ring which consisted of four equally spaced 1/16" holes.

These gases were bubbled into the ketone, previously placed in the reactor, and there they reacted to form the desired product. Some of the ammonium chloride formed as a by-product was removed from the reactor in the effluent gas stream which consisted mainly of nitrogen with small percentages of ketone vapour and ammonia. The gas outlet pipe was made of $\frac{3}{8}$" I.D. stainless steel. A smaller bore pipe was used initially but this caused considerable trouble, blocking with ammonium chloride.

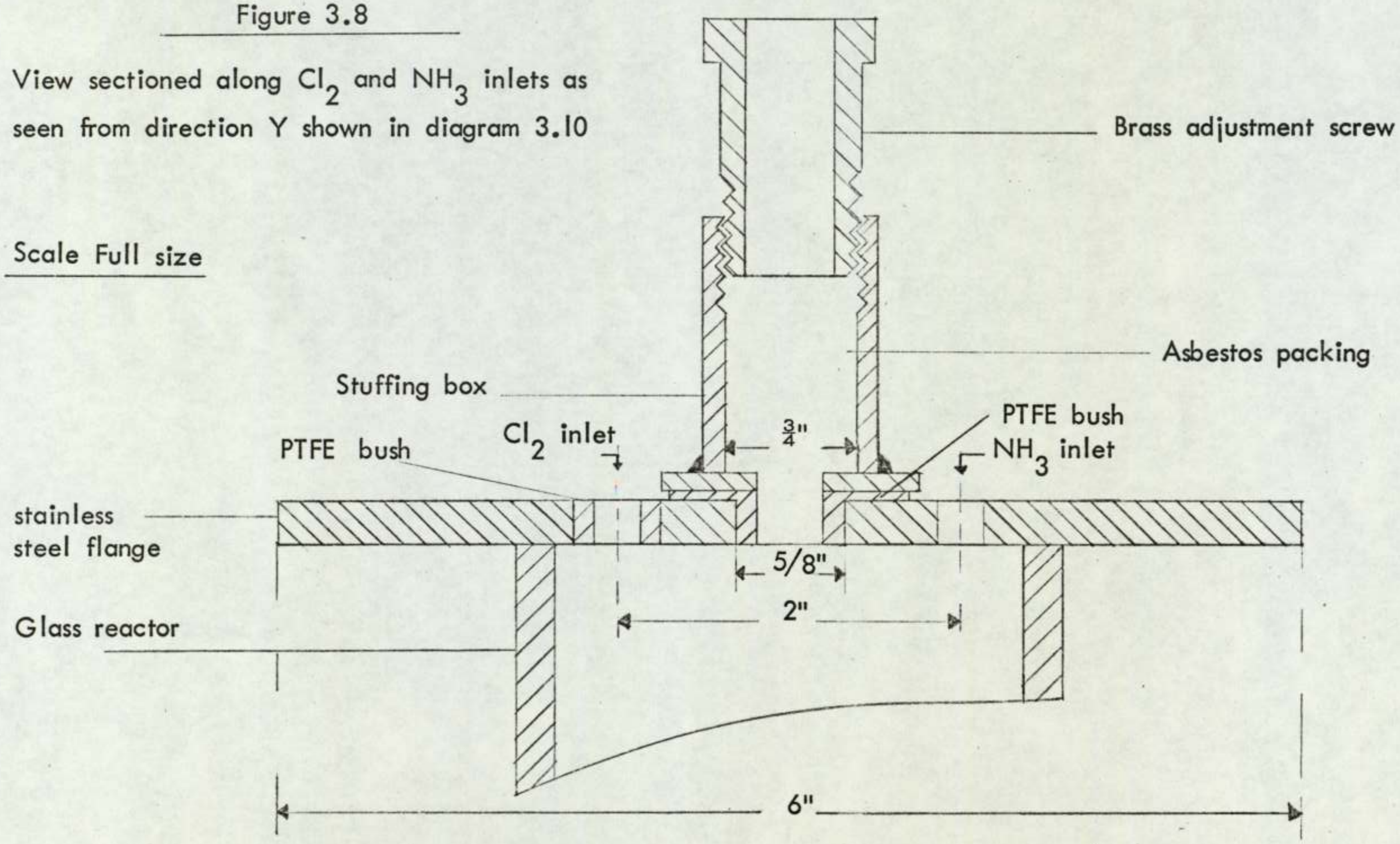
The reactor was constructed of QVF glass flanged to a stainless steel cover. The dimensions of the glassware employed is given in figure 3.9. The reason for the small bore section at the base of the reactor is that there can be intense mixing in the reaction zone, but a quiescent layer can exist below this section, so that any ammonium

Reactor cover and stuffing box

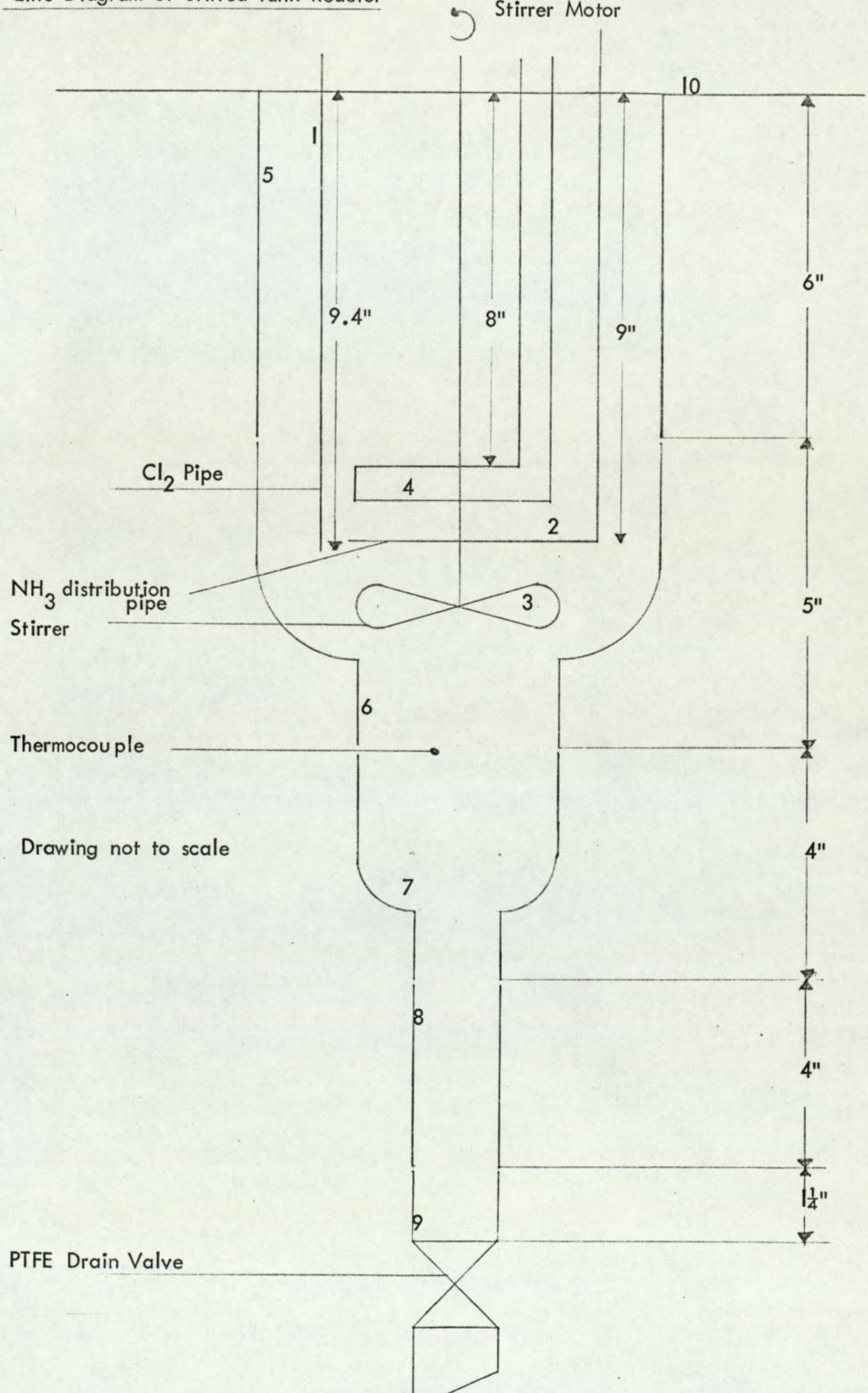
Figure 3.8

View sectioned along Cl_2 and NH_3 inlets as seen from direction Y shown in diagram 3.10

Scale Full size



Line Diagram of Stirred tank Reactor



Drawing not to scale

Figure 3.9

chloride formed in the liquid phase was partially separated from the reaction mixture by sedimentation.

TABLE 3.3.

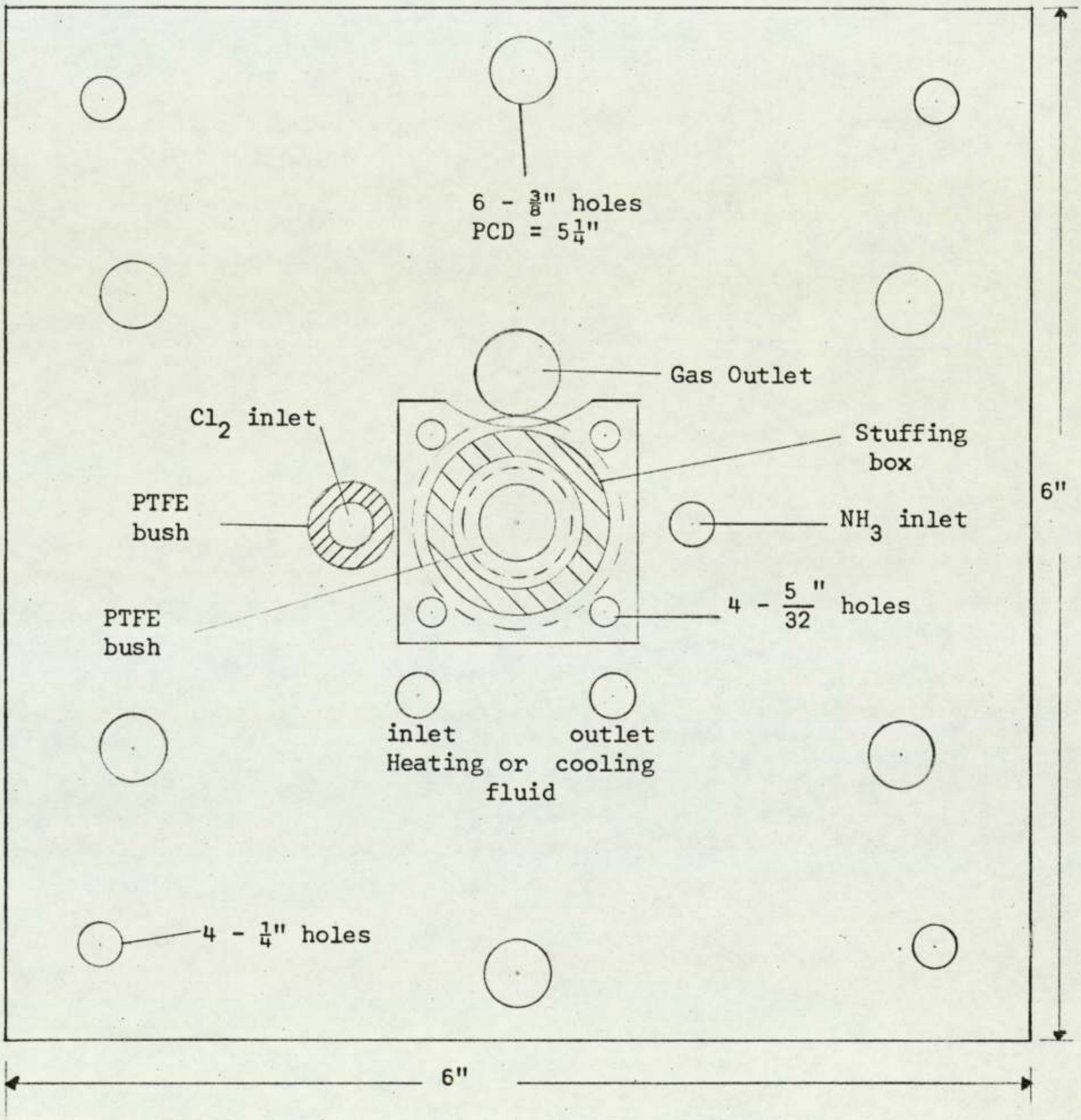
Items listed in figure 3.9.

Code	Item	Specification.
1	Chlorine inlet.	¼" O.D. stainless steel pipe.
2	Ammonia inlet.	¼" O.D. stainless steel pipe. The end of this pipe formed a ring of 2" diameter with 4 equally spaced 1/16" holes.
3	Stirrer	Three bladed marine impeller.
4	Coolant coil.	¼" O.D. stainless steel pipe.
5	Section of reactor.	QVF pipe section PS3/6.
6	"	QVF pipe reducer PR3/1½.
7	"	QVF pipe reducer PR1½/58.
8	"	QVF pipe section PS58/4.
9	Drain valve.	QVF valve VAA58.
10	Reactor Cover.	¼" thick stainless steel cover.

The reactor contents were agitated by using a 1/25 HP, 2200 r.p.m. Kestner stirrer. The stirrer shaft formed a gas tight seal with the reactor by means of a brass stuffing box assembly using asbestos packing as shown in figure 3.8. A plan view of the stainless steel cover, showing the stuffing box but not the adjustment screw, is seen in figure 3.10.

The reactor coil is shown in figure 3.9. It consists of two turns of ¼" O.D. stainless steel forming a helix of mean diameter 2". This coil was used for heating or cooling depending on the nature of the experiment. If heating was required a Townson and Mercer thermostatically controlled circulating unit was employed but if cooling was

Reactor Cover
Plan View
Full Scale
Figure 3.10



Pipes not shown
Adjustment screw of stuffing box not shown

Direction Y
↑

CHLORINE/AMMONIA SUPPLY SYSTEM

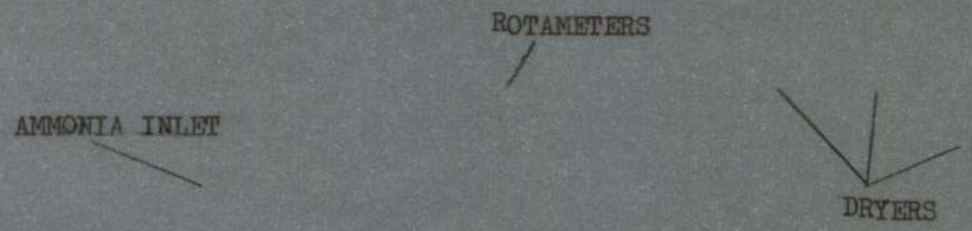
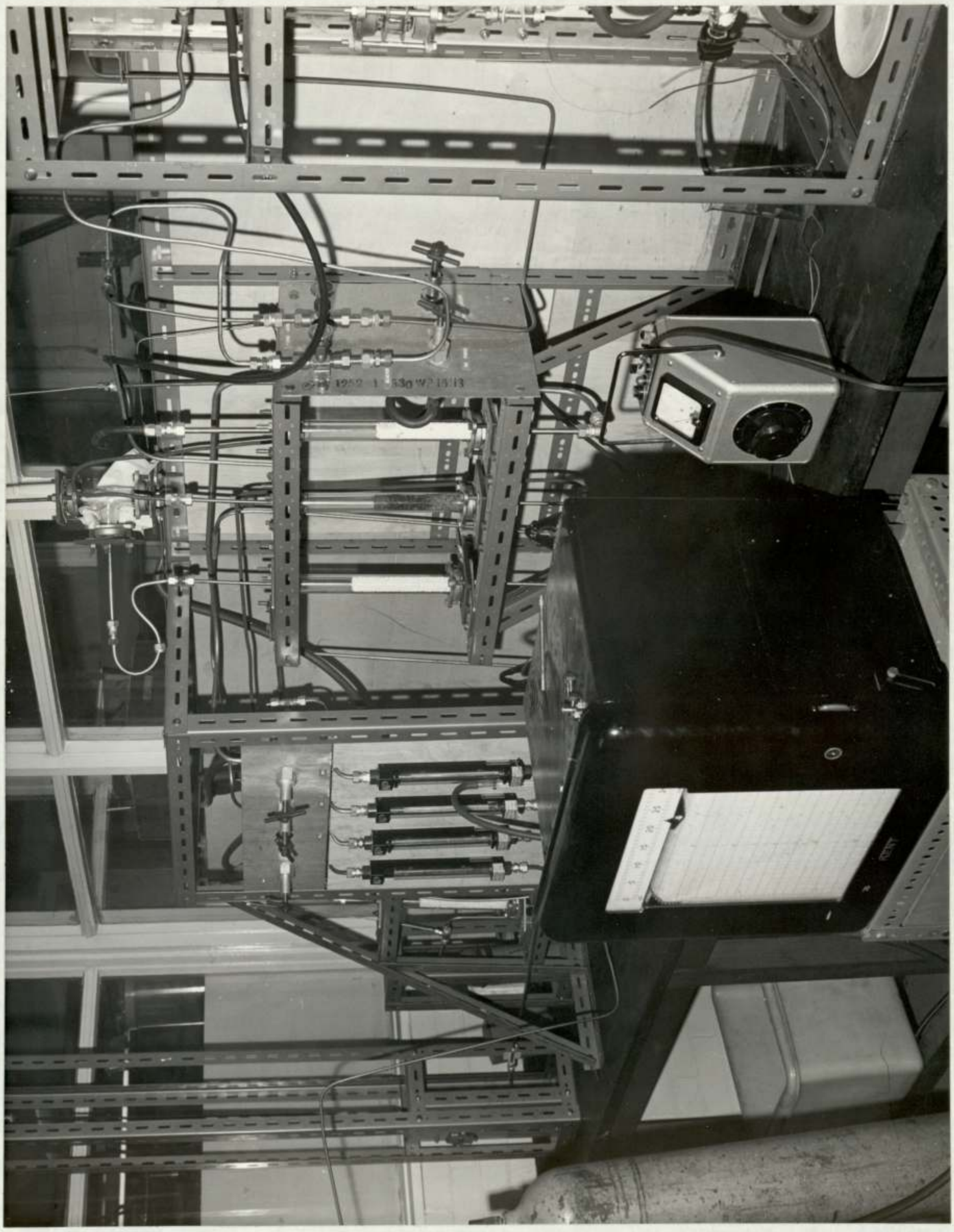


PLATE 4



required, a dry ice - acetone coolant solution was used. The stirred tank reactor is shown on plate 5 and the coolant reservoir can be seen on the right hand side.

The coolant solution was circulated through the coil, by gravity, and was collected in a beaker on the floor of the laboratory. It was then returned to the reservoir with make-up dry ice. The temperature of the reactor was measured by an alumel-chromel thermocouple connected to a George Kent multipoint recorder.

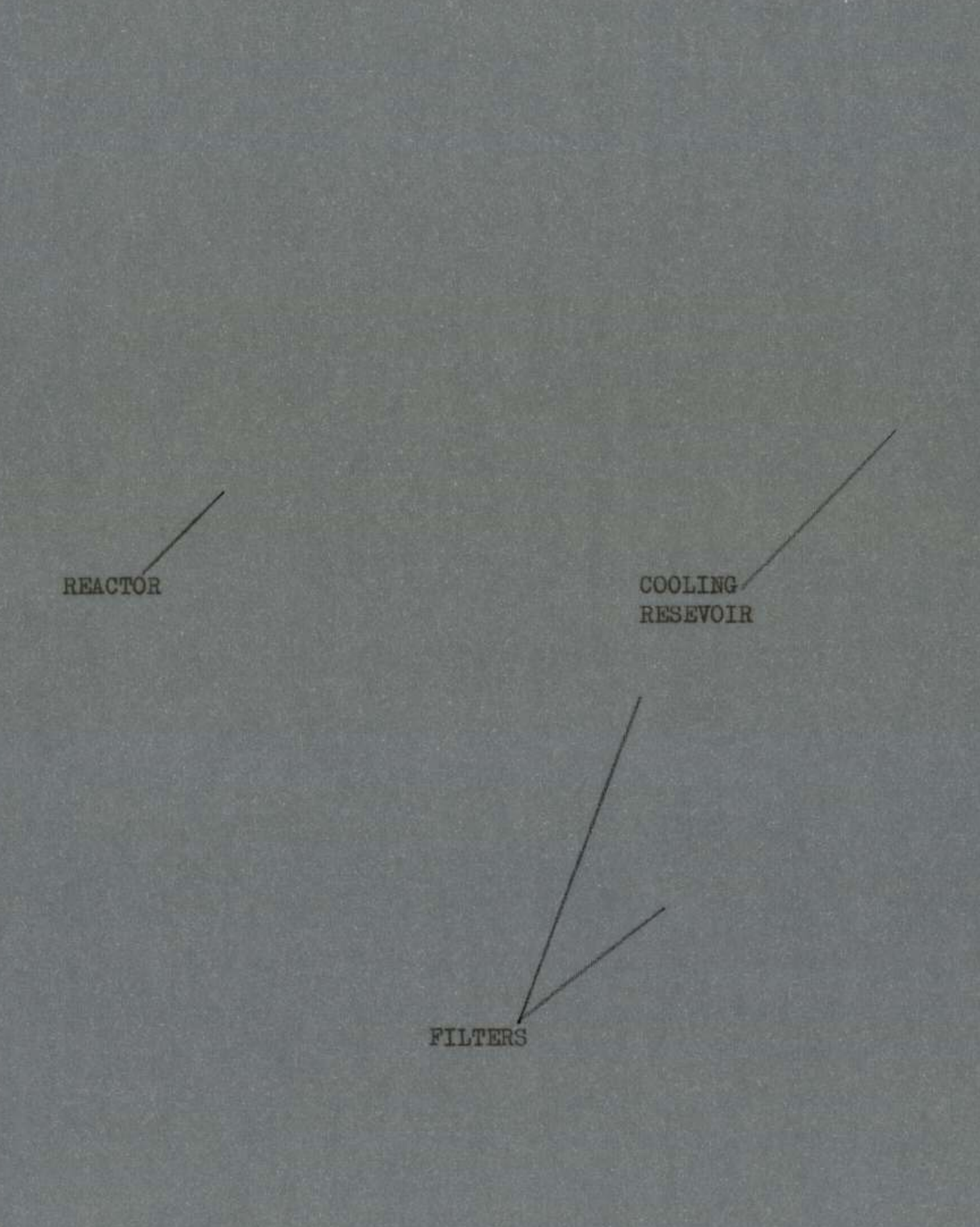
The stirrer shaft was $16\frac{1}{2}$" long and was made of $\frac{3}{8}$" stainless steel. It was coupled to the stirrer motor by means of a length of pressure tubing which formed a flexible connection. The impeller used was a three bladed marine type of diameter 1.3". By means of a portable tachometer the stirrer speed could be measured.

In most experiments the quantity of ketone put in the reactor was of the order of 600 cc and therefore the distance to which the chlorine inlet pipe dipped beneath the level of liquid was usually about 6.5 cm. The design of the base of the reactor was frequently altered to suit individual experiments but essentially the reactor was the same as that previously described. The drain valve at the base of the reactor was in each case a QVF screw down type with a PTFE bellows and plug.

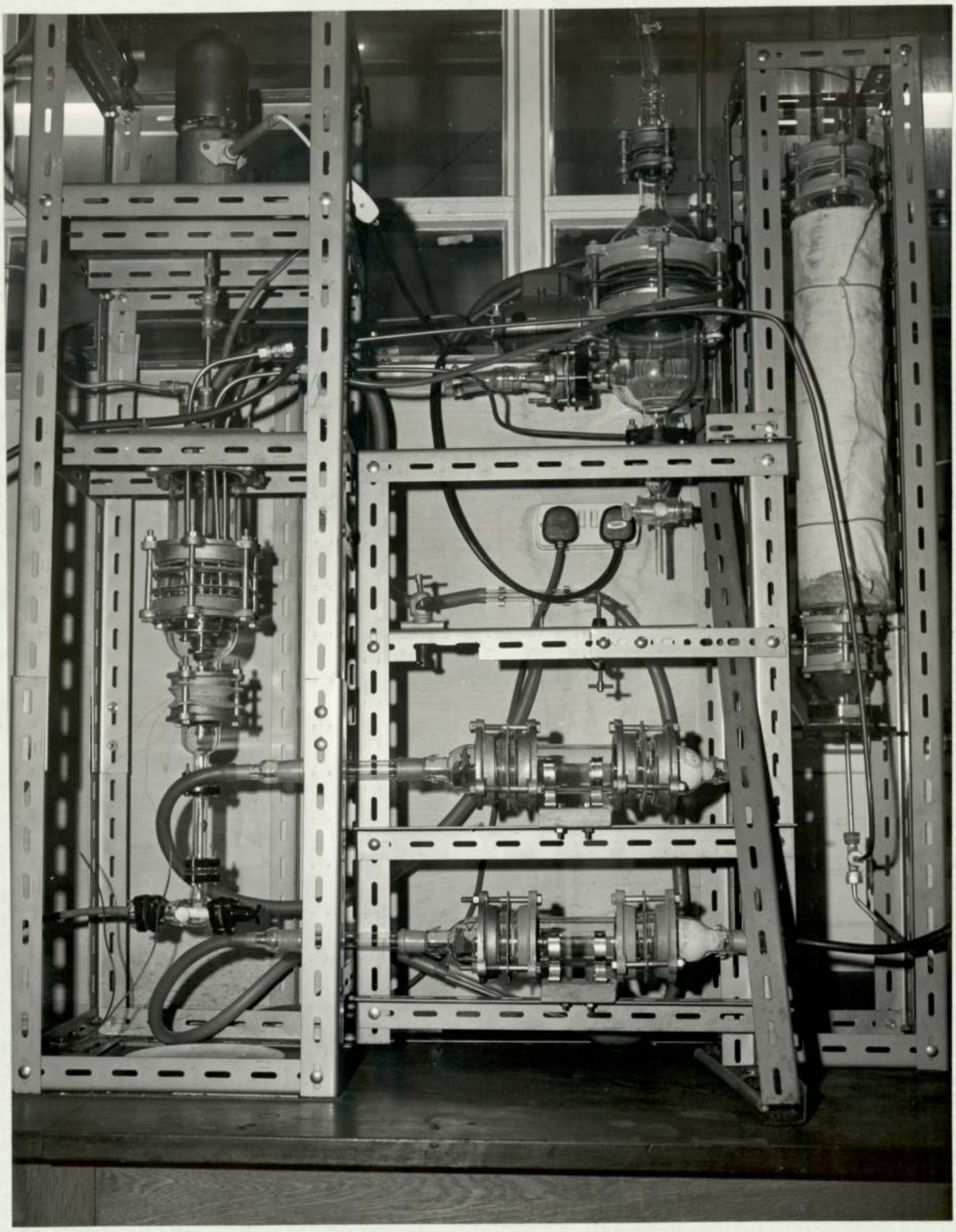
3.3.1.2. Column reactor.

A line diagram of the reactor showing the supply and recovery systems is shown in figure 3.11. The gases entered the reactor and bubbled into the ketone through the annular jet system, ammonia passing through the annulus and the nitrogen-chlorine mixture passing through the central pipe. The effluent gas stream left the reactor through the exit (8) and consisted of nitrogen, ammonium chloride and small percentages of ketone vapour and ammonia. The reactor was constructed of QVF glassware and was 1" diameter for most of its length. It is

STIRRED TANK REACTOR



PLATES 5



shown in Plate 6 and is itemised in Table 3.4. The enlarged top section was to prevent any slugs of liquid being carried out of the reactor.

The ketone was recirculated by a No. 10 Stewart and Turner stainless steel centrifugal pump. The rate of recirculation was approximately 1.5 litres per minute and was controlled by means of a voltage regulator. Most of the experiments in this investigation were of short duration and therefore this type of system worked satisfactorily. However for experiments lasting longer than 30 minutes, the recirculation pipe (1) tended to block with ammonium chloride. Consequently to run the reactor for longer periods a filter would have had to be inserted in the liquid line. However it was not necessary to carry out such lengthy experiments. The gas dryers (D_3), (D_4) and (D_5) were only half filled with the drying agent so that they also functioned as pulse removers, to cushion the effect of any sudden changes in gas flow rates. As in the previous apparatus the temperature was measured by a chromel-alumel thermocouple.

TABLE 3.4.

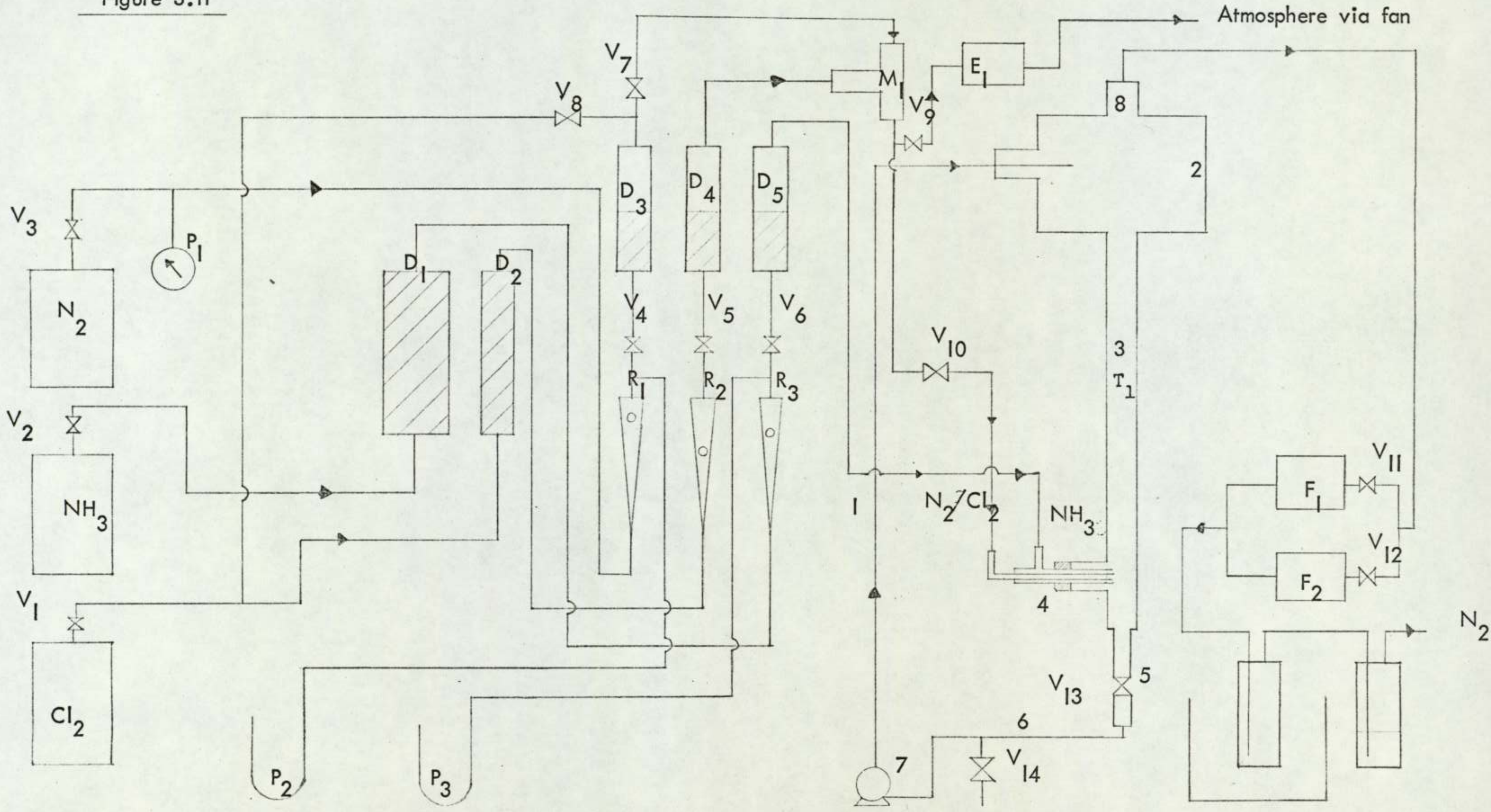
Items in figure 3.11.

Code	Item	Specification
1	Ketone recirculation line.	3/16" O.D. stainless steel.
2	Top section of reactor.	QVF column adaptor CA4/1/1 and pipe reducer PR4/1.
3	Main section of reactor.	QVF glassware. 2 Pipe sections PS1/12. 1 Tee Piece PT/1. 1 Pipe reducer PR1/58.
4	Gas inlet system.	Modified Fisons reflux condenser CRD/1
5	Column valve.	QVF valve VAA58.
6	Pump supply line.	$\frac{3}{8}$" I.D. PTFE tubing.
7	Pump.	No. 10 Stewart and Turner stainless steel centrifugal pump.
8	Gas outlet.	$\frac{1}{2}$" I.D. PVC tubing.

The remainder of the items shown in figure 3.11. are listed in Table 3.2.

Column Reactor Apparatus

Figure 3.11

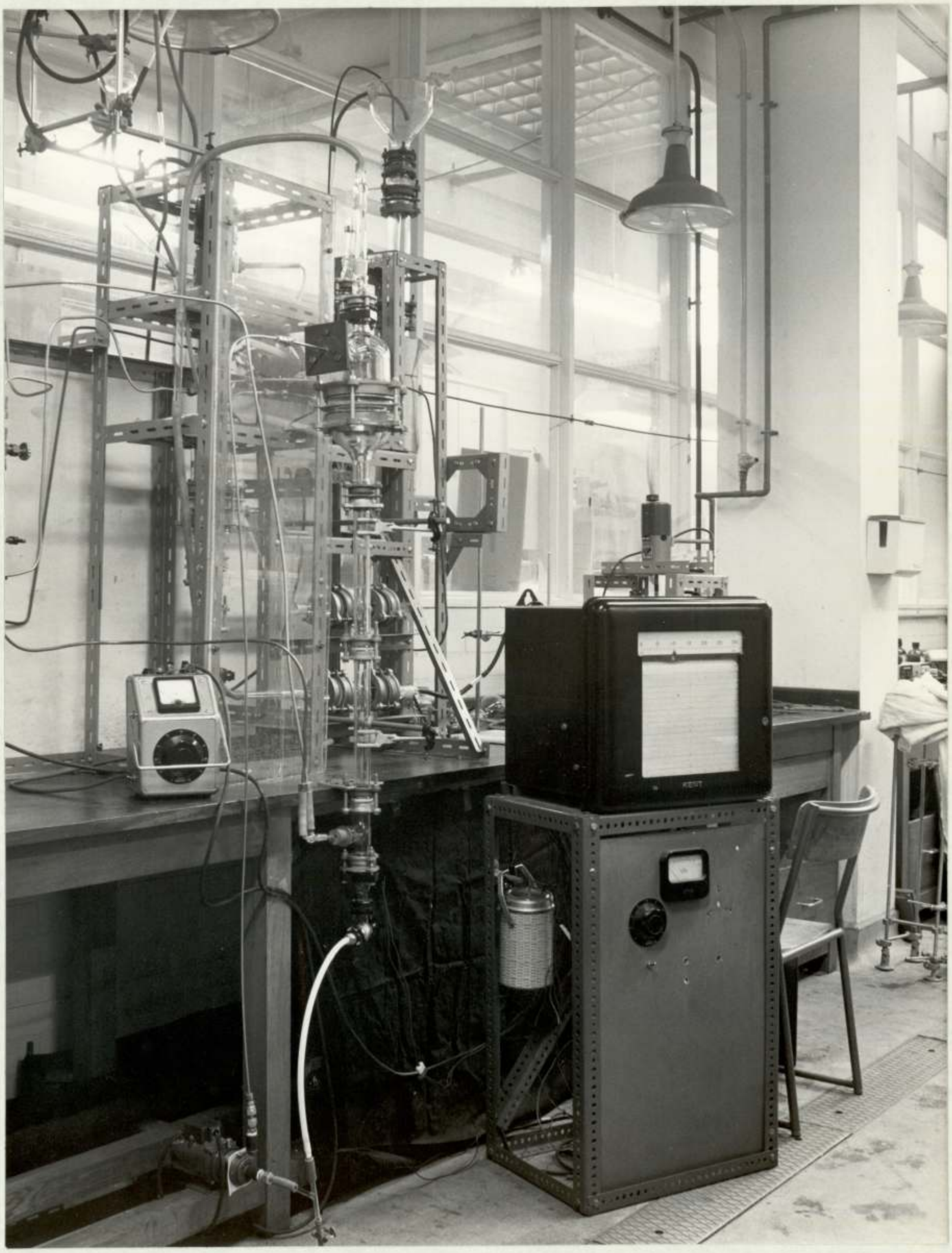


RECIRCULATING COLUMN REACTOR

—COLUMN

PUMP

PLATE 6



KENT

Several types of gas inlet were used, varying from a sintered glass disc on the end of the chlorine jet, to a system in which the ammonia and chlorine jets were several inches apart. The sintered glass inlet was found to be unsuitable as it blocked very easily with ammonium chloride. Another system was also tested in which the nitrogen-chlorine mixture was bubbled through fine pin holes in a PTFE cap placed over the jet. Some experiments were carried out in which there was no recirculation of the ketone, and in some cases a packed column was also employed. A system such as this is shown in Plate 7. The materials used as packing were either carbon chips or glass ballotini.

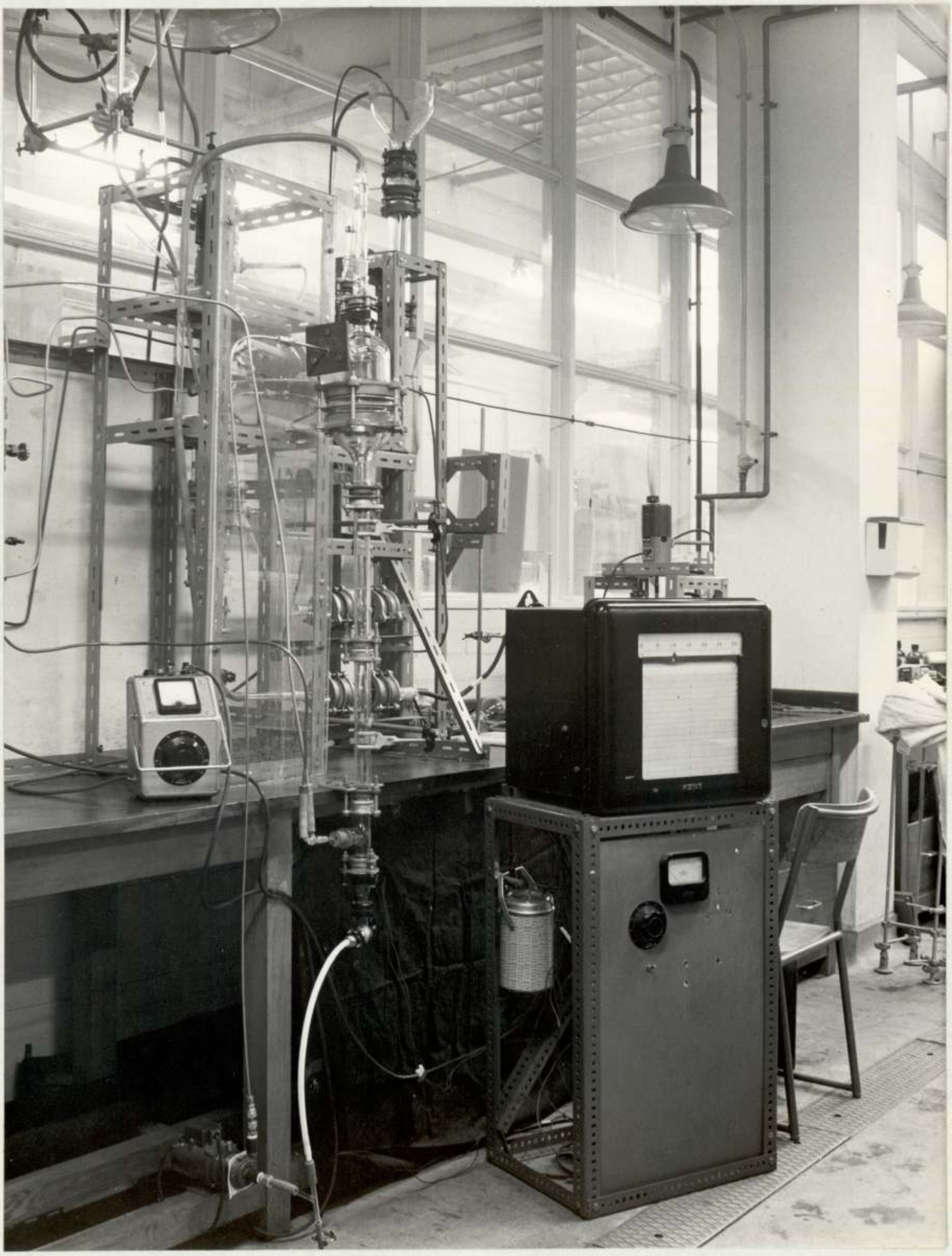
3.3.2. Experimental Procedure.

3.3.2.1. Stirred tank reactor.

The chlorine line from the mixer onwards was first purged to atmosphere with nitrogen by opening valve (V_9), closing valve (V_{10}) and switching on the fan E_1. The ketone was introduced into the reactor through the ammonia inlet pipe by means of a filter funnel, first making certain that the PTFE drain valve was closed. When this operation was completed the ammonia inlet pipe was reconnected to its supply.

The nitrogen flow was then diverted to the reactor by opening valve (V_{10}) and closing valve (V_9), and immediately after this operation ammonia was supplied to the reactor by opening valve (V_2). When these gases were bubbling into the reactor in the desired quantity the stirrer was switched on, chlorine was admitted to the reactor by opening valve (V_1) and the stopclock which timed the run was started.

As described previously white fumes of ammonium chloride immediately appeared, some of which left the reactor in the effluent gas stream and was removed in the filters. During the course of an experiment a careful check had to be maintained on the gas flow rates, especially the



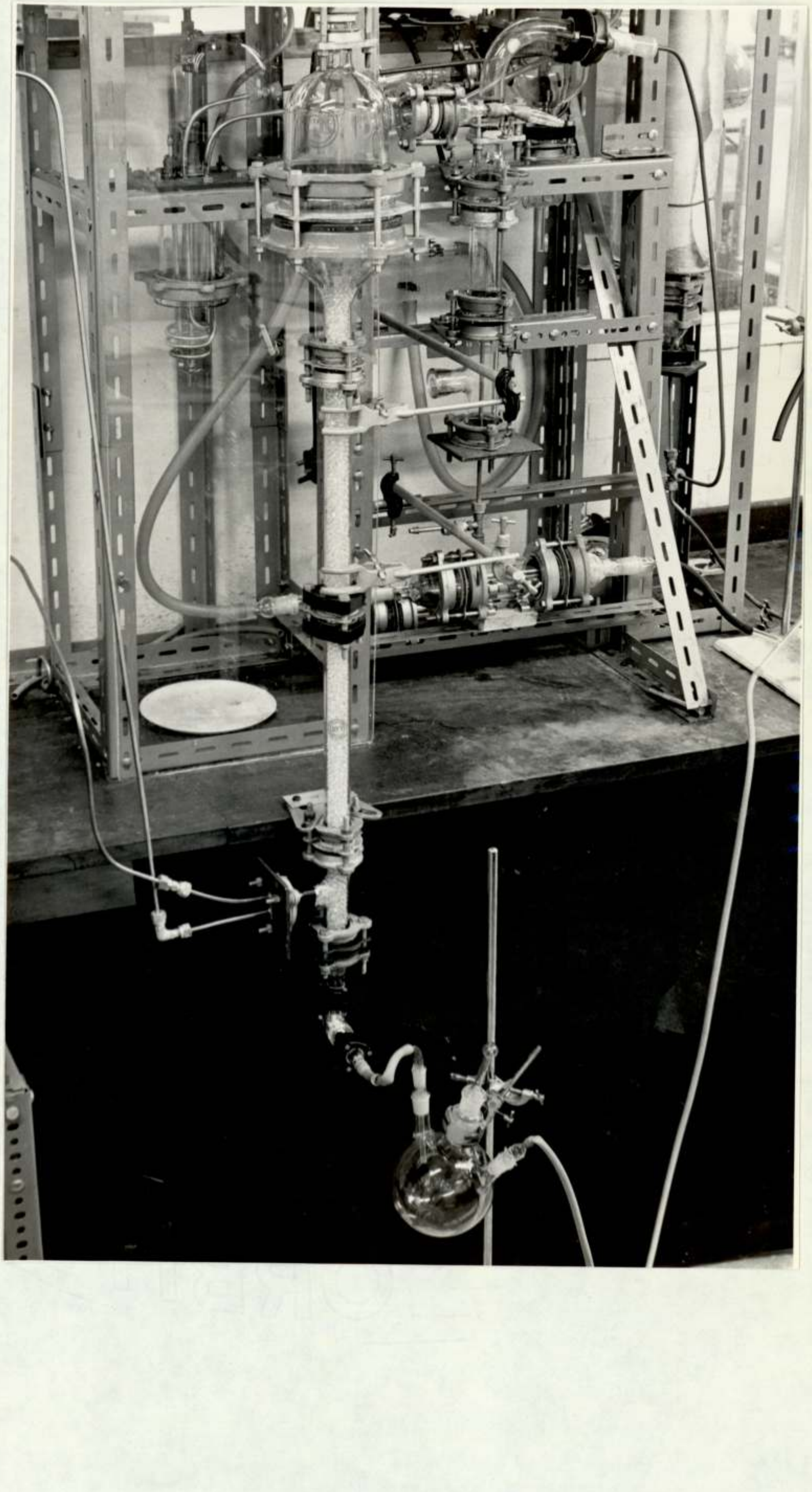
KENT

PACKED COLUMN REACTOR

—COLUMN

GAS
INLETS

PLATE 7



ammonia and nitrogen flows, in order to ensure that they were kept at constant values. The filters F_1 and F_2 were operated alternately by means of the two valves V_{11} and V_{12}. Tn some experiments, using high chlorine flow rates, the outlet pipe from the reactor to the filter blocked with ammonium chloride, and in these cases the run was stopped, while the line was released, and then the experiment was restarted. A note was also made of the temperature inside the reactor at frequent intervals.

The shut-down procedure for the reactor was the same as that described for the gas phase reactors. In this case an extra operation was switching off the stirrer after the chlorine supply was turned off. The outlet tube from the reactor was disconnected and the reactor effluent consisting of approximately 600 ml of ketone containing ammonia, isohydrazone and ammonium chloride was drained into a measuring cylinder by opening the drain valve. This mixture was completely filtered and the filtrate was analysed for hydrazine content by both of the methods described in chapter 4.1.3. It was important that the volume of the reactor effluent be known reasonably accurately as the yield is based on this quantity. Thus a sample of the effluent was taken for analysis immediately after filtration. Care was taken to minimise ketone evaporation losses. For this reason methyl ethyl ketone was used instead of acetone in most experiments because of its lower volatility.

All the ammonium chloride precipitated in the reactor, filters and connecting pipes was collected as described above and its quantity determined by the Volhard procedure. This involved completely dismantling the reactor in order that all the precipitate could be collected. When this operation was completed the reactor etc. were washed dried and reassembled for the next experiment. In some experiments the quantities of ammonium chloride left in the reactor and carried out in the gas stream were analysed separately.

The procedure was essentially the same when water or aqueous alkali were present in the reactor; the major difference was that most of the chloride was in solution in the reactor liquor. Therefore a sample of this solution was diluted several times with water to analyse for the presence of chloride ion [see chapter 4.2.].

3.3.2.2. Column reactor.

The procedure for this reactor was almost identical to that described above for the stirred tank reactor. The only difference in start up was that the pump was switched on instead of the stirrer. It was not possible to run this reactor for as long as the stirred tank reactor because the ketone recirculation pipe tended to block with ammonium chloride and therefore the duration of most experiments was between 15 and 30 minutes. In addition, because of the height of liquid in the reactor, problems were encountered in controlling the flow of the gases to the reactor. However by paying careful attention to the rotameter readings it was possible to maintain the nitrogen flow rate reasonably constant, and the ammonia flow rate between certain limits.

It was found that when packed columns were employed the column itself frequently blocked because ammonium chloride accumulated between packings, and therefore only a small number of experiments were performed

3.4. Miscellaneous.

The reactor temperatures in the equipment described in chapters 3.2. and 3.3. were measured by means of a chromel-alumel thermocouple. These were calibrated below zero by immersion in an acetone-dry ice bath and checked against an E-mil gold line mercury thermometer and a red spirit thermometer. Above zero they were calibrated by immersion in steam and in an ice solution. The calibration graphs for both ranges were almost identical.

All the chemicals used in the analysis were of analytical standard. The methyl ethyl ketone used in electrochemical experiments was of M.F.C. standard but in experiments on the stirred tank and column reactors it was of G.P.R. grade. The same applied to other ketones apart from acetone which was always of analytical standard. Chlorine and ammonia were supplied in liquid form from Imperial Chemical Industries, and "White Spot" nitrogen was supplied by the British Oxygen Company.

Normally the pipettes, burettes and flasks used were British Standard Class A. The Ermeto compression fittings used in the pipework were in most cases either brass or cadmium plated mild steel of $\frac{1}{4}$" or $\frac{3}{8}$" O.D. Because of the reaction of copper with ammonia, brass was never used for any connection involving this gas.

CHAPTER FOUR

CHEMICAL ANALYSIS

4. CHEMICAL ANALYSIS.

In this chapter the various techniques employed to analyse chloramine, chlorine and hydrazine in the form of its organic derivatives will be discussed.

4.1. Hydrazine and its organic derivatives.

Procedures for the quantitative determination of hydrazine normally depend on its behaviour as a weak base, a reducing agent, or its reactions with certain aldehydes to form the aldazine. However not all the methods are specific for hydrazine as other compounds such as hydroxylamine will effect the same changes. Consequently great care must be taken when developing an analytical method. The following review of the methods of analysis of hydrazine will not be complete and for a more exhaustive treatment of this topic reference should be made to Audrieth and Ogg [27] or Mellor [127].

4.1.1. Review of methods of analysis of hydrazine.

By far the most widely used method of analysis of hydrazine is that involving oxidation. In this method ammonia which is one of the decomposition products of hydrazine does not interfere, but other compounds such as reducing agents frequently do interfere. Because at high pH air oxidation takes place to an appreciable extent, analytical methods involving the oxidation of hydrazine should be carried out in acid solution. Penneman and Audrieth [128] used potassium iodate in acid solution with carbon tetrachloride present as a solvent layer. The end point is reached when this solvent layer is decolorized. The reactions taking place can be represented as:-

$$N_2H_4 \longrightarrow N_2 + 4H^+ + 4e \quad \ldots\ldots \quad 4.1$$

$$5e + IO_3^- + 6H^+ \longrightarrow 3H_2O + \tfrac{1}{2} I_2 \quad \ldots\ldots \quad 4.2$$

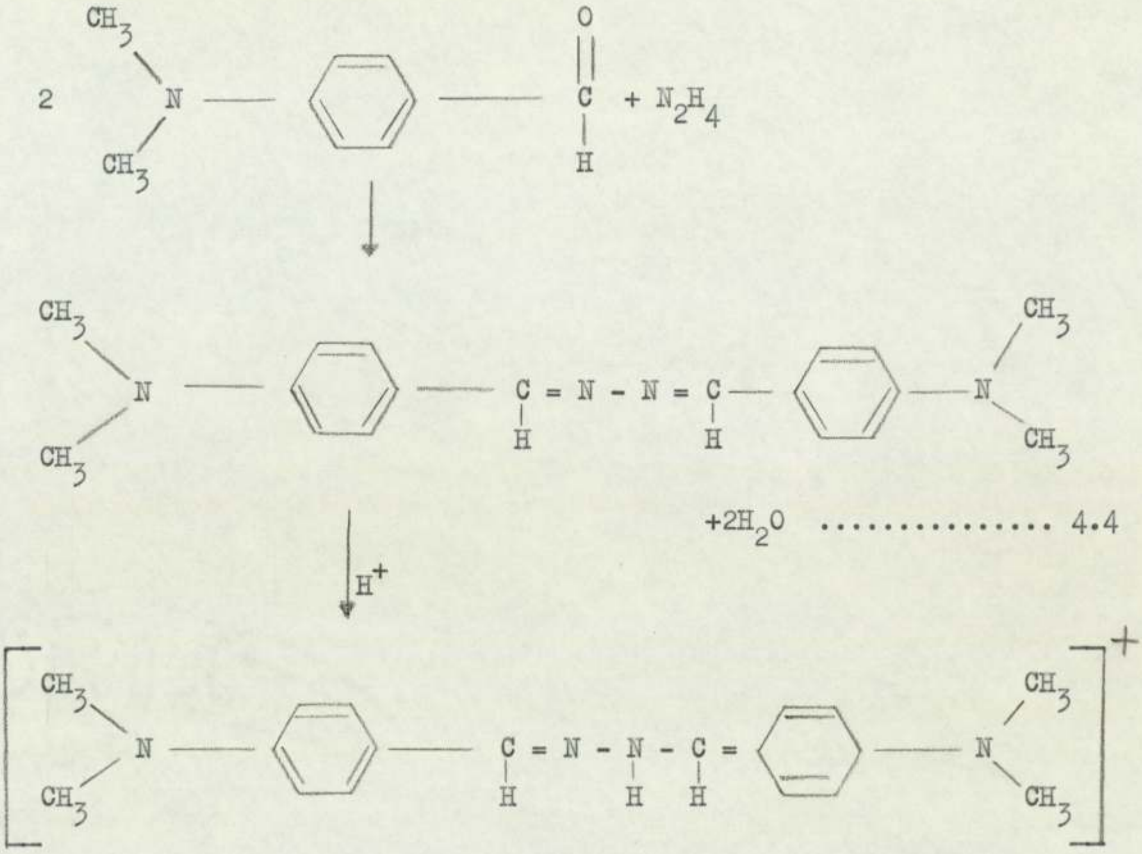
$$\frac{1}{2}\ I_2 + Cl^- \longrightarrow ICl + e \quad \ldots\ldots \quad 4.3$$

It is necessary that the final normality of the hydrochloric acid be kept within certain limits, preferably 3 and 5.

This method was also used by Feinsilver et al [129] who compared it favourably with two other methods, one of which was the potentionmetric titration with potassium bromate and the other a colour reaction based upon the reduction of phosphomolybdic acid to molybdenum blue. Singh et al [130] employed potassium periodate as a volumetric agent for the determination of hydrazine and several of its organic derivatives including benzalazine. A method which utilised the reducing power of hydrazine was developed by Ashworth [131]. This was a turbidimetric method in which selenium oxide was reduced to yield a suspension of selenium.

There have been numerous methods proposed based upon the reaction of hydrazine with aldehydes. Early investigators used either benzaldehyde or salicylaldehyde. In the latter case it is claimed that hydrazine can be detected at a concentration of 2 p.p.m. Hydroxylamine does not interfere since the oxime is soluble. Momose et al [132] developed a fluorometric method using 2 - hydroxy - 1 - napthaldehyde in the presence of dilute sulphuric acid. The aldazine which is formed shows a strong yellow-green fluoresence which has a maximum intensity at 534 m µ. Vanag and Matskanova [133] found that 2 - nitro - 1 - 3 - indandione formed an orange-red azine and developed a method of analysis based on this reaction. The solution must however be gently boiled to form the azine. A method in which hydrazine reacts with trinitrobenzene sulphonic acid or picryl chloride to form violet hexanitrohydrazobenzene has also been used for the analysis of hydrazine [134].

However the most widely used colorimetric tebhnique is that in which hydrazine reacts with p - dimethylaminobenzaldehyde to form the azine which subsequently rearranges itself in the presence of strong acid to form a quinoid structure possessing an intense orange-red colour.



.... 4.4

.... 4.5

Watt and Crisp /135/ found that the peak absorbence was at 458 m µ. In their method a solution of p - dimethylaminobenzaldehyde in ethanol and concentrated hydrochloric were used. Ammonium chloride did not interfere with the method and even high concentrations of semicarbazide and urea could be tolerated. A modified technique was developed by Dambrauskas and Cornish /136/ in which a solution of p-dimethylaminobenzaldehyde in methanol, and glacial acetic acid were employed. This method is sensitive to hydrazine concentrations down to 1 part per 10^8. Several other authors /137-139/ have also adopted this colour reaction for the analysis of hydrazine.

4.1.2. Methods of analysis attempted for electrochemical experiments.

It was not possible to develop a quantitative method of analysis for this series of experiments because the concentration of hydrazine formed was extremely low and therefore very difficult to detect. In addition the hydrazine was in the form of an organic derivative and in an organic solution with a ketone and ammonia. These factors caused an interference to some degree in all the methods attempted. In addition water was normally present as an impurity and this also interfered in some methods.

In chapter 2.2.3 it was shown that there are numerous possible products of electrolysis and it is quite feasible that these will cause inaccuracies in the analysis. At the end of each experiment the liquid ammonia was allowed to evaporate, leaving behind the ketone and the electrolyte. This mixture was then filtered and the ketone was then analysed for hydrazine. Because the concentration was so low techniques like the potassium iodate method could not be employed and therefore more sensitive methods were considered.

A solution of picryl chloride was tested on solutions of hydrazine in acetone. However the test was not sensitive in the range required. Because it was necessary to heat the solution it was decided not to use 2 - nitro - 1 - 3 - indandione as a means of analysis. Benzaldehyde and salicylaldehyde were tested under similar conditions but proved to be unsatisfactory. In the latter instance instead of the usual white precipitate being formed, the solution turned a green colour. 2-hydroxy - 1 - napthaldehyde was also found to be unsuitable in the range required and therefore it was decided to use p - dimethylaminobenzaldehyde. This method was found to be very sensitive for low concentrations of hydrazine in acetone, but some of the compounds in solution caused severe interference when present in sufficient quantity. The effect of ammonia and water is shown in figures 4.7, 4.8, 4.9 and 4.11.

In addition is was found that the electrolyte used could also interfere with this method of analysis. In the case of ammonium nitrate this affect was considerable. However most experiments were carried out with potassium or rubidium bromide and in these instances the only affect was to give the solution a yellow colour and not the intense orange-red colour obtained with hydrazine. As well as the methods outlined above, attempts were also made at employing gas chromatography and nuclear magnetic resonance techniques but without success. It must be stressed however that in the experiments carried out on the electrolysis of liquid ammonia the results can only be regarded as qualitative.

4.1.3. Analysis of azines, hydrazones and isohydrazones.

In the series of experiments in which chlorine and ammonia were reacted with a ketone, the organic intermediates were formed in much greater quantities than in the electrolysis experiments and consequently quantitative methods of analysis could be developed.

4.1.3.1. Direct iodate method.

In this method the organic derivative of hydrazine was hydrolysed to hydrazine sulphate which was recovered and made up to an approximately 0.05M solution. A sample of this solution was then titrated against 0.05M potassium iodate solution using the method of Penneman and Audrieth /128/. Paulsen and Huck /43/ suggested this means of analysis, but it seems unlikely that stoichiometric conversion of the organic intermediate to hydrazine sulphate takes place under the specified conditions. They mixed the isohydrazone with excess 50 per cent. (W/W) sulphuric acid and allowed it to stand for three hours. The solution was then distilled until only water was received at a boiling point of

100°C and hydrazine sulphate was then crystallised from the undistilled residue. Several attempts were made to use this means of analysis, including distillation under vacuum, but in each case the conversion to hydrazine sulphate was normally only in the region of 20 per cent.

A method was therefore developed in which the solution was not heated in order to increase the conversion of the isohydrazone to hydrazine sulphate. A sample of the reactor effluent, normally 50 or 100 ml, was placed on a watch glass. A small quantity, between 3 and 10 ml, of 50 per cent sulphuric acid was added to the watch glass and the solution was mixed and allowed to evaporate in a dust free uncontaminating atmosphere. After 24 hours there remained on the watch glass hydrazine sulphate, sulphuric acid and possibly a small quantity of ketone. There were also condensation compounds present and these imparted a yellowish colour to the solution. It was found that under these conditions the conversion to hydrazine sulphate was almost quantitative.

The method developed here was also tested with organic solutions of azines and similar conversions to hydrazine sulphate were obtained. It was found however that a large excess of acid did tend to reduce the yield of hydrazine sulphate. Results of some of the tests performed are presented in table 4.1.

The hydrazine sulphate was recovered from a liquor in which, it was likely that, ketone was present and therefore the effect of ketone on the subsequent titration with potassium iodate was investigated. The following procedure for the titration which was developed by Penneman and Audrieth [128] was used. To a 10 ml sample of the hydrazine sulphate solution was added 12 mls of concentrated hydrochloric acid and 5 mls of carbon tetrachloride. This mixture was titrated with 0.05M potassium iodate solution. When the aqueous layer turned from a dark brown to a light yellow colour, the iodate was added dropwise and the solution was shaken vigorously after each drop. The end point was reached when the

TABLE 4.1.

Conversion of organic intermediates to hydrazine sulphate.

Type of organic intermediate.	Quantity of organic intermediate. gms	Volume of ketone. mls	Volume of 50 per cent sulphuric acid. mls	Yield of hydrazine sulphate.
acetone ketazine *	2.31	50 acetone	10.0	98.7
acetone ketazine *	2.31	50 acetone	20.0	97.0
diethyl isohydrazone	0.224	20 diethyl ketone	10.0	99.1
methyl isopropyl isohydrazone	0.12	20 methyl isopropyl ketone	5.0	97.5

* These solutions were formed by adding 1 ml of hydrazine hydrate to 50 ml of acetone and therefore the intermediate is most probably a mixture of hydrazone and ketazine. However this was unimportant as both could be hydrolysed to hydrazine sulphate.

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iodine colour was completely discharged from the solvent layer. A series of tests was carried out in which varying quantities of methyl ethyl ketone were added to pure solutions of 0.05M hydrazine sulphate. The solutions were then titrated with 0.05M potassium iodate in the usual manner. Methyl ethyl ketone was chosen because it was used in most experiments in the reactor research programme. The results of the tests are shown in Table 4.2.

TABLE 4.2.

Effect of ketone on iodate titration.

Test	Quantity of methyl ethyl ketone. ml	Quantity of $\frac{N}{20}$ hydrazine sulphate. ml	Quantity of $\frac{N}{20}$ potassium iodate to titrate ml
1 *	5.0	5.0	-
2	0.5	5.0	4.7
3	1.2	5.0	3.0
4	0.1	5.0	4.9

* In test 1 no colour whatsoever was obtained in the solvent layer.

The above results show that the presence of ketone did interfere in in the titration, but at low concentration the effect was quite small. In fact since the hydrazine sulphate obtained on the watch glass was made up to an approximately 0.05M solution and only a sample of this was taken for the titration the effect of ketone could be completely ignored in this analytical method.

4.1.3.2. Colorimetric method.

This method is based on the reaction of hydrazine with p - dimethylaminobenzaldehyde to produce an orange-red colour. In the past this method has been used for the analysis of aqueous solutions of hydrazine but not for organic solutions of carbonyl derivatives of hydrazine. A procedure was developed which was similar for azines and isohydrazones. However, as will be shown later the calibration graph for these two classes of compounds was different. The method employed for the calibration of azines will be considered.

1 ml of hydrazine hydrate was placed into a 100 ml flask and made up to the mark with acetone. The solution was well shaken and then 1 ml was taken and placed in a second 100 ml flask and again acetone was used to make up to 100 ml. This solution is referred to as solution B and consists of 0.01 ml. of hydrazine hydrate made up to 100 ml with acetone. The hydrazine was in the form of the azine or azine-hydrazone mixture, but for convenience in this and in other calibrations the concentration will be referred to the equivalent quantity of hydrazine hydrate present. Thus the concentration of solution B is 10 parts per 10^5; the concentration on a volumetric basis. The solutions as shown in table 4.3. were then made up in 100 ml flasks.

TABLE 4.3.

Colour Samples.

Sample	Quantity of Solution B ml	Quantity of acetone ml
Blank	0.0	10.0
1	1.0	9.0
2	2.0	8.0
3	3.0	7.0
4	4.0	6.0
5	5.0	5.0
6	6.0	4.0
7	7.0	3.0
8	8.0	2.0
9	9.0	1.0
10	10.0	0.0

To each flask was added 10 ml of a 2.5 per cent by weight solution of p - dimethylaminobenzaldehyde in methanol, and each sample was made up to the mark by adding 80 ml of glacial acetic acid. Thus all the hydrazine was contained in a 10 ml solution of acetone and all concentrations were referred to this solution. Therefore the concentration of hydrazine hydrate in sample 1 was 1 part per 10^5, and in sample 10 was 10 parts per 10^5 on a volumetric basis. Unless otherwise stated this procedure was always followed.

After half an hour had elapsed the bottled samples developed a green colour and after about 2 hours they were yellow. After 5 hours the more concentrated samples developed a strong orange colour. The optical density of the samples relative to a blank was measured after various time intervals and it was found that after about 100 hours the colour development was complete. The results obtained for calibration 2 are shown in Table 4.4. The final oolour in the higher concentration range was a very strong orange-red. The optical densities were measured on a Hilger and Watts Spekker absorptiometer [Type H760].

TABLE 4.4.

Colour development of azines.

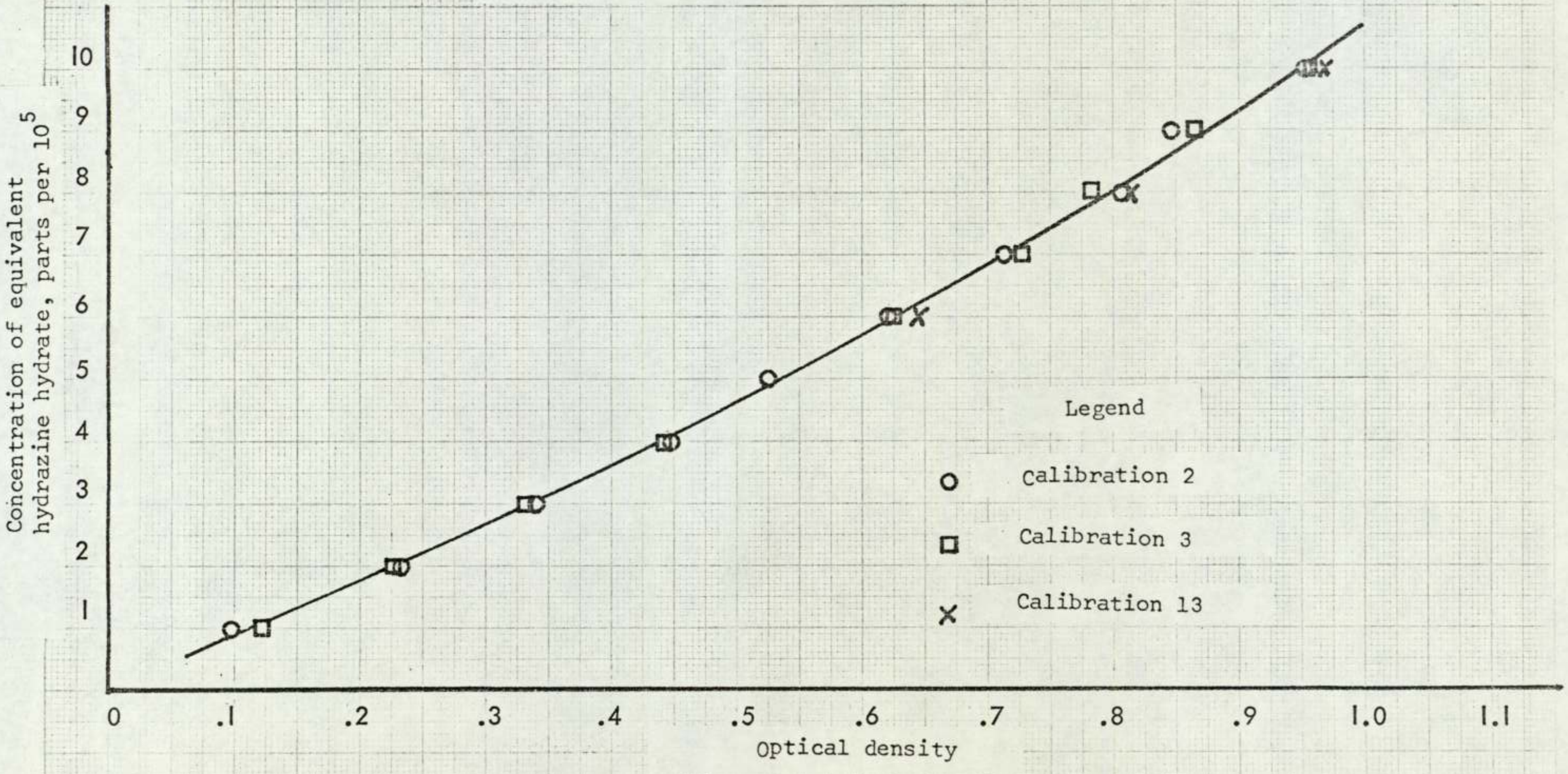
Calibration 2.

Time (Hrs.)	15	44	96	145	197
Sample	Optical density				
1	0.09	0.095	0.098	0.102	0.09
2			0.232	0.222	0.215
3			0.340	0.331	0.322
4		0.41	0.448	0.442	0.412
5	0.37		0.525	0.523	0.502
6			0.620	0.624	0.593
7	0.525		0.712	0.703	0.685
8		0.752	0.806	0.798	0.773
9			0.846	0.832	0.814
10	0.71	0.895	0.952	0.942	0.910

Filter 2 was used, giving a peak transmission in the range 460-470 m μ, which is very near to the value recommended by Watt and Crisp [135]. The cells were 0.5 cm fused glass.

Figure 4.1.

Calibration of azines



Several such calibrations were carried out and the results are shown in Table 4.5. The optical density quoted is the value, at the time, at which the samples were at their maximum. As can be seen from Table 4.4. the change in optical density over the period 100-150 hours is very small and so, providing the optical density was measured immediately after 100 hours, any error will be infinitesimal. The temperature of the solutions in the laboratory was maintained at 20°C and since Watt and Crisp [135] found the effect of temperature to be only 0.14 per cent per 1°C absolute transmittance in the range 20-40°C the very small variation in temperature possible, would have a negligible affect on the accuracy.

Using a standard autocode program for an Elliot 803 computer, the best plot for the results of table 4.5 was obtained by the method of orthogonal polynomials and is shown in figure 4.1. The equation best fitting the data is:-

TABLE 4.5.

Calibration of Azines.

Sample	1	2	3	4	5	6	7	8	9	10
Calibration No.	Optical density									
2	0.098	0.232	0.34	0.448	0.525	0.62	0.712	0.806	0.846	0.952
3	0.122	0.225	0.332	0.445	0.525	0.622	0.728	0.782	0.865	0.956
13		0.23		0.445		0.645		0.812		0.968

$$A = -0.001555 + 0.1196C - 0.002452\ C^2 \quad \ldots\ldots\ldots\ldots \quad 4.6$$

where A is the optical density and

C is the concentration of an equivalent volume of hydrazine hydrate in parts per 10^5.

TABLE 4.6.

Use of different filters

Filter No.	Average wavelength m µ	Optical density
1	430	0.482
2	470	0.484
3	490	0.400
4	515	0.260
5	545	0.055
6	570	0.013
7	600	0.002
1	430	0.995
2	470	1.030
3	490	0.945
4	515	0.620
5	545	0.115
6	570	0.025
7	600	0.005

The optical density of two given samples were measured using different filters on the Spekker. The results are shown in Table 4.6 and plotted on figure 4.2. They show that peak absorbence is obtained with filter 2.

A similar procedure was carried out for isohydrazones. The isohydrazone had to be isolated and purified. Thus the gas-liquid reactor described in chapter 3.3.1.1. was used to make a solution of diethyl isohydrazone in diethyl ketone. The solution, which was approximately 500 ml in volume, was placed on an evaporating dish and the ketone was allowed to evaporate. After 18 hours the ketone had evaporated and there was left on the dish diethyl isohydrazone with impurities such as ammonium chloride and condensation products. The diethyl isohydrazone was dissolved in acetone and the solution was filtered. The isohydra-

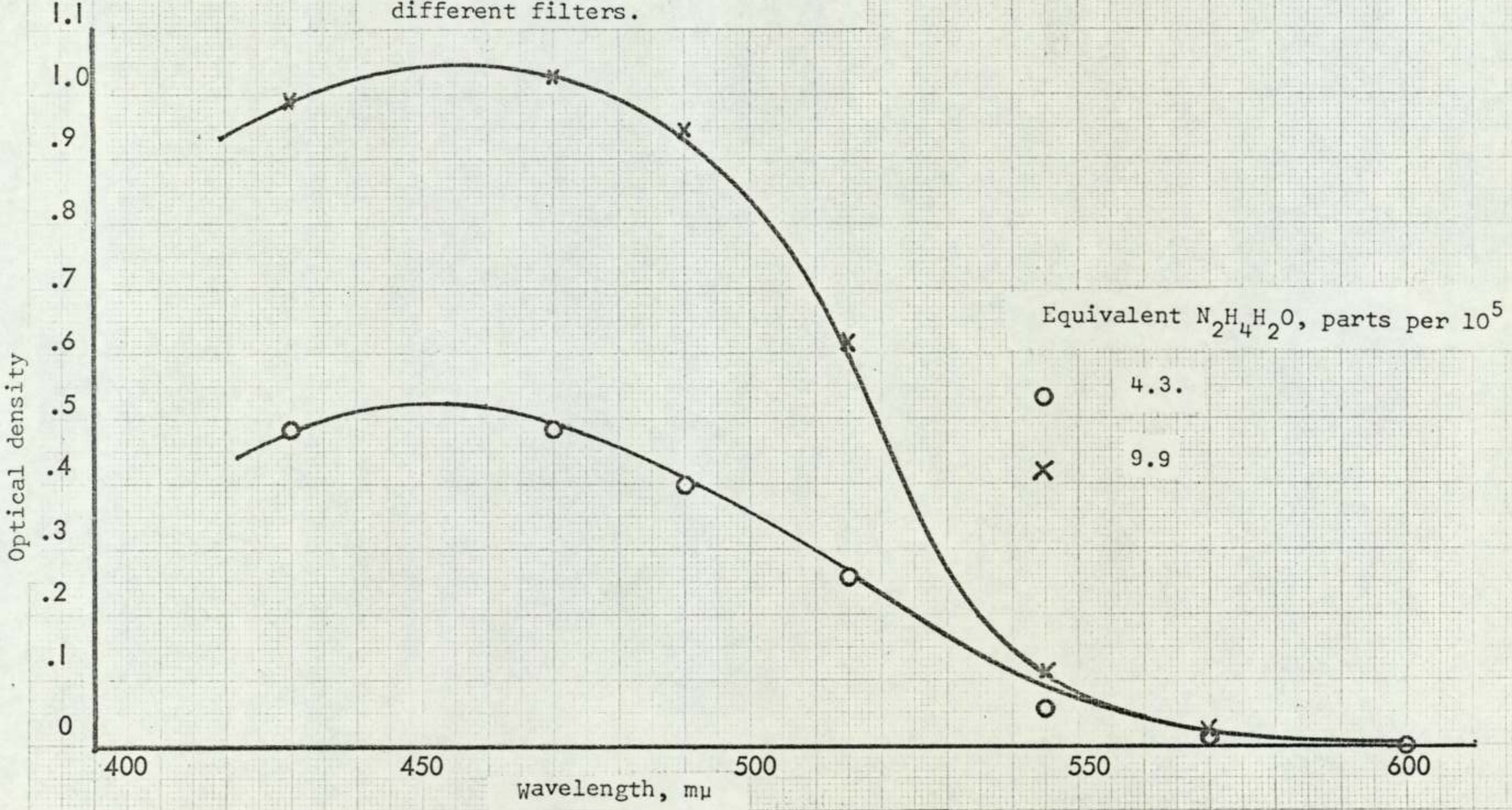


Figure 4.2.

Variation of optical density with different filters.

zone was recovered and recrystallised several times from acetone. In a similar manner methyl isopropyl isohydrazone was obtained in the pure state.

Appropriate dilutions of the isohydrazone in acetone were made until a sample was obtained in which the concentration was approximately 0.01 ml in 100 ml of acetone when referred to hydrazine hydrate. The example of calibration 4 is shown below.

wt. of diethyl hydrazone = 0.2484 gms.

Equivalent weight of hydrazine hydrate = 0.1242 gms.

Density of hydrazine hydrate = 1.03 $\frac{\text{gms}}{\text{ml.}}$

Equivalent volume of hydrazine hydrate = 0.1205 ml.

This quantity was made up to 100 ml with acetone. 8 ml of this solution were taken and again diluted to make 100 ml in acetone.

Concentration equivalent of hydrazine hydrate in the final solution $= \frac{0.1205}{10^2 x 12.5} = \frac{9.65}{10^5}$

This concentration is again on a volumetric basis. This solution will be referred to as C.

Details of samples 1 to 6 in 100 ml flasks are presented in table 4.7.

TABLE 4.7.

Colour samples. Calibration 4.

Sample	Concentration of equivalent hydrazine hydrate parts per 10^5	Volume of solution C ml	Volume of acetone ml
Blank	0.0	0.0	10.0
1	0.4825	0.5	9.5
2	0.9650	1.0	9.0
3	1.9300	2.0	8.0
4	2.8950	3.0	7.0
5	3.8600	4.0	6.0
6	4.8250	5.0	5.0

These samples were made up to 100 ml with a 2.5 per cent solution of p - dimethylaminobenzaldehyde in methanol and glacial acetic acid in the manner described above, i.e. 10 ml of the former solution and 80 ml of acid were added to each sample. The colour development of these solutions relative to a blank is shown in table 4.8; as above the optical density was measured on a Spekker absorptiometer using filter No. 2 and cells of 0.5 cm optical path.

TABLE 4.8.

Colour development of isohydrazones

Calibration 4.

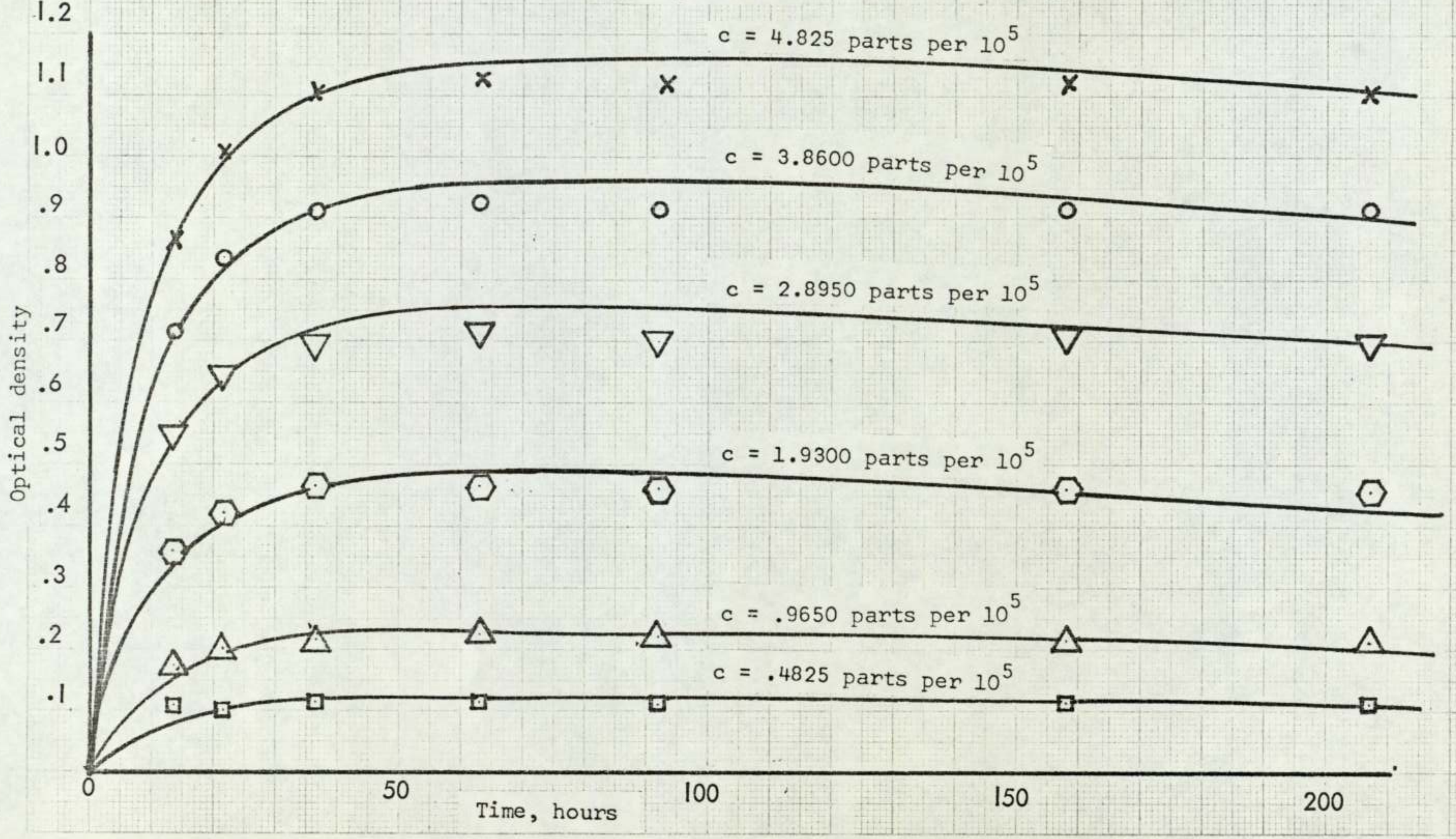
Time (hrs.)	13½	21½	36½	63	92	158	207
Sample	Optical density						
1	0.11	0.102	0.115	0.115	0.112	0.114	0.112
2	0.173	0.202	0.218	0.225	0.222	0.216	0.213
3	0.360	0.422	0.464	0.466	0.462	0.461	0.458
4	0.545	0.645	0.695	0.712	0.70	0.705	0.695
5	0.715	0.838	0.912	0.925	0.918	0.918	0.912
6	0.865	1.012	1.105	1.128	1.130	1.122	1.103

These results are plotted on figure 4.3. As can be seen the maximum colour development is obtained after about 60 hours.

Two similar calibrations were carried out, one for diethyl isohydrazone and the other for methyl isopropyl isohydrazone. The results for all three calibrations are shown in Table 4.9. The values of optical density are those at the time at which the samples were at their maximum. The following equation was obtained in a similar manner to that employed to construct figure 4.1., using the method of orthogonal polynomials.

$$A = -0.00927 + 0.2582\,C - 0.004444\,C^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 4.7.$$

This curve is plotted with the results of table 4.9 on figure 4.4. It can be seen that the colour development is independent of the alkyl groups



Colour development of isohydrazones.

Figure 4.3.

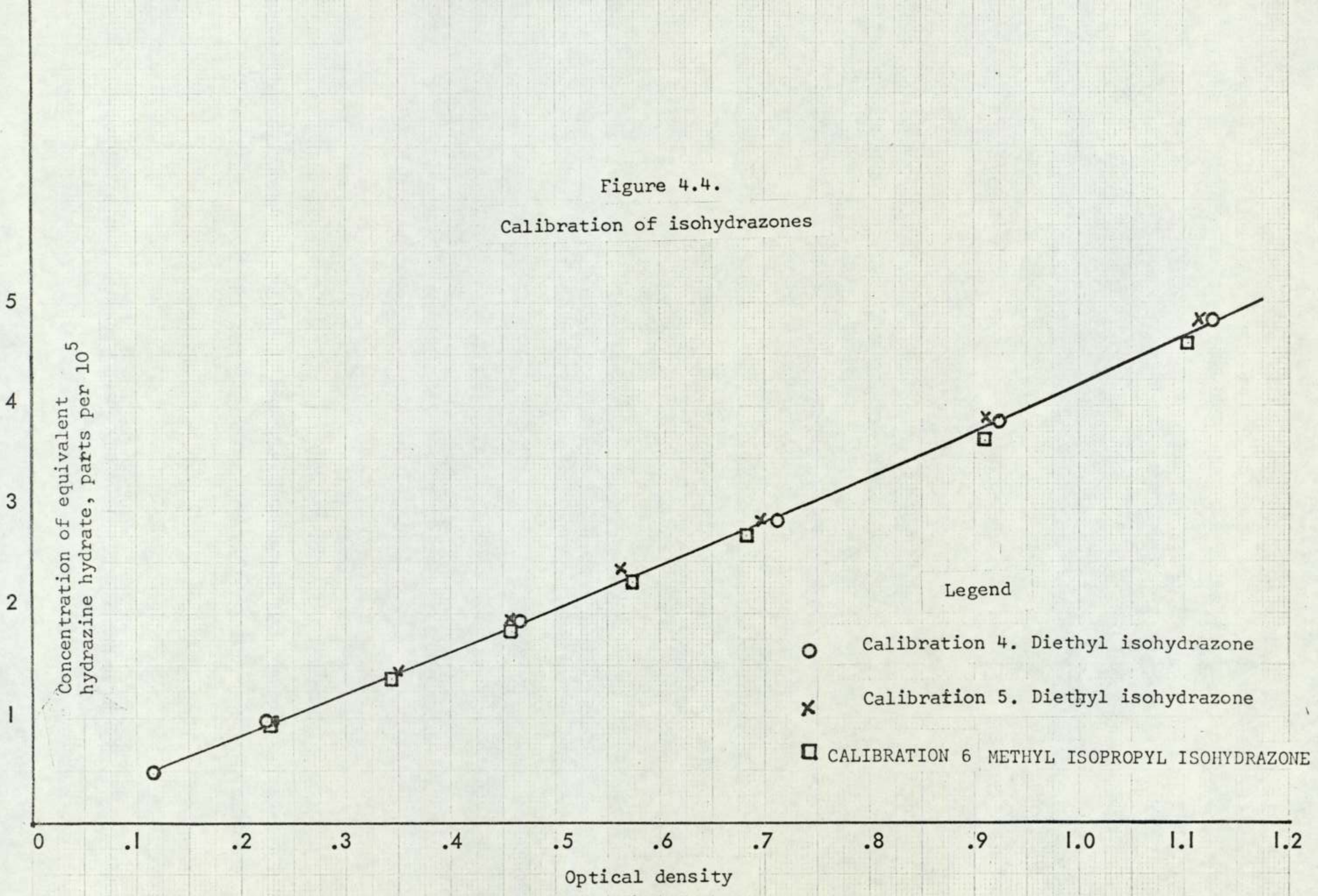


Figure 4.4.

Calibration of isohydrazones

as similar results were obtained for diethyl isohydrazone and methyl isopropyl isohydrazone. Hence the calibration is suitable for the isohydrazones of acetone and methyl ethyl ketone. The isohydrazones of diethyl ketone and methyl isopropyl ketone were chosen for the calibrations because they are the easiest to isolate and purify. The colours in the azine and isohydrazone systems develop along different paths. It has been stated that in the azine system the samples turn green, then yellow and finally orange. This was not observed for the isohydrazones; the colours, at all concentrations, initially turn a very faint orange which gradually increase in intensity. Therefore, this difference provides a means of distinguishing between the two classes of compounds, simply by visual inspection of their colour development.

Calibrations were carried out for the azines of benzaldehyde and acetophenone in a similar manner to that employed for isohydrazones. In the latter case two calibrations were obtained. One was on a sample of the azine prepared by reacting hydrazine hydrate with acetophenone and the other on a sample of the azine recovered from an experiment on the stirred tank reactor. These results are shown in figure 4.5 and the data is recorded in Appendix 2. The equation best fitting the data was found by the method of orthogonal polynomials to be

$$A = 0.01688 + 0.1125c - 0.001191\ c^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4.8$$

This calibration is similar to the one obtained for acetone ketazine, except that at higher concentrations it gives a higher value of optical density. An interesting point in this set of calibrations is that although the final value of optical density for a given concentration is the same, the rate of approach to this maximum is totally different for the azines of acetophenone and benzaldehyde. This is shown quite clearly in figure 4.6.

Calibrations 2, 3 and 13 were repeated using different ketones to replace acetone at all stages. The results obtained for these

Figure 4.5.

Calibration of azines

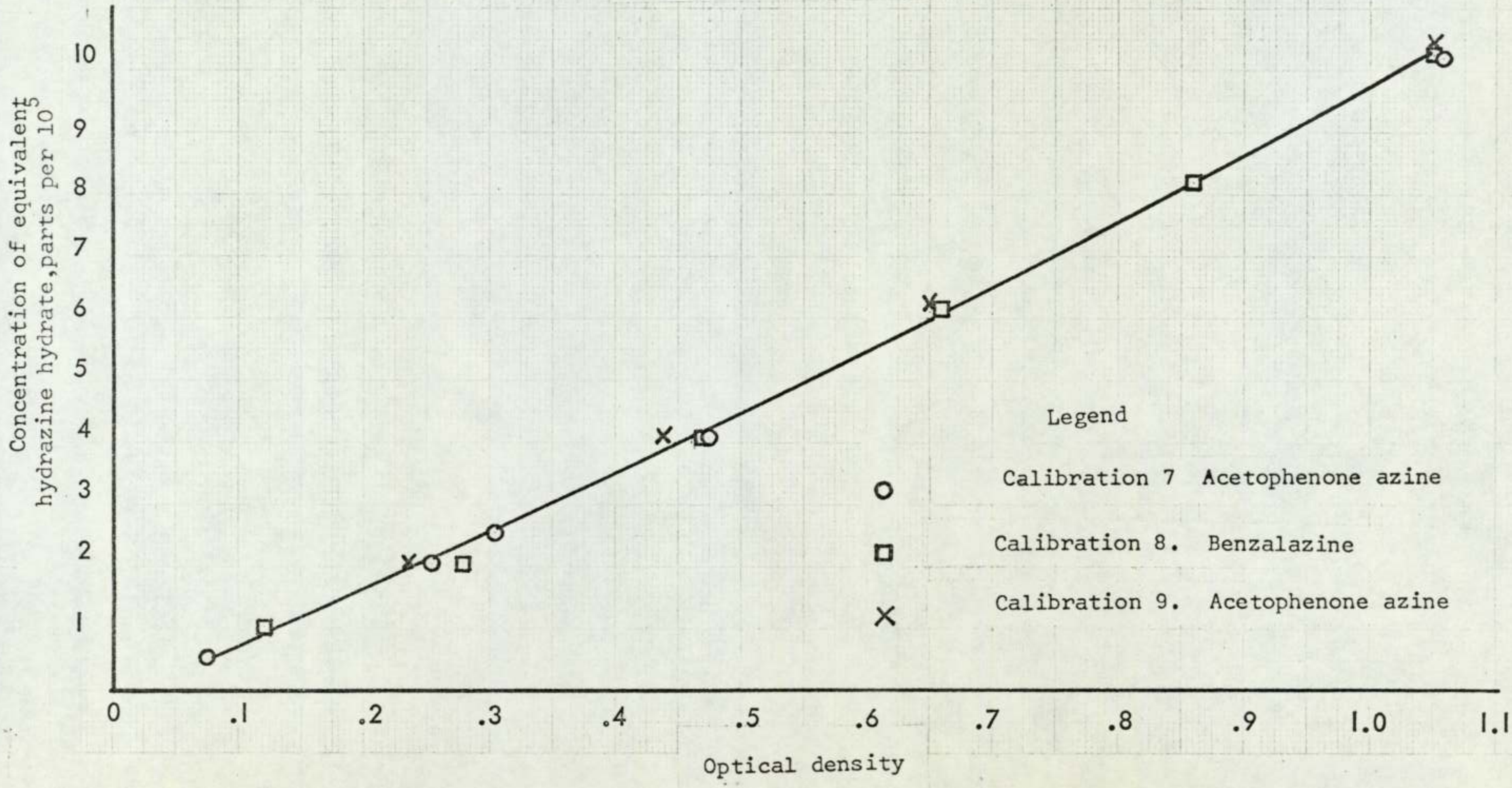


Figure 4.6.

Colour development of azines

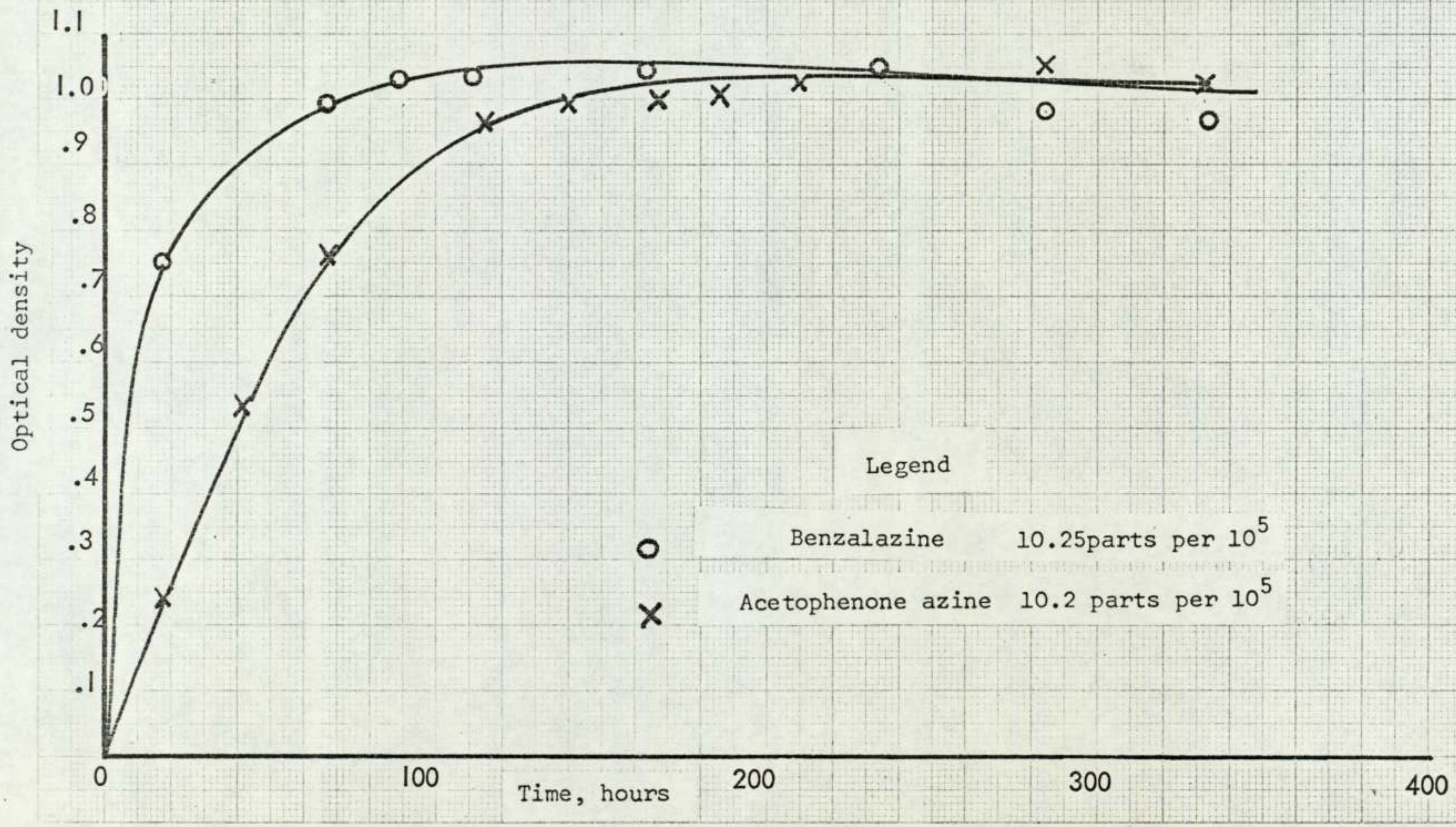


TABLE 4.9.

Calibration of isohydrazones.

Calibration No.	Concentration of equivalent hydrazine hydrate parts per 10^5.	Optical density	Nature of isohydrazone.
4	0.4825	0.115	diethyl
	0.9650	0.225	isohydrazone
	1.9300	0.466	
	2.8950	0.712	
	3.8600	0.925	
	4.8250	1.128	
5	0.485	0.117	diethyl
	0.970	0.225	isohydrazone
	1.455	0.349	
	1.940	0.461	
	2.425	0.563	
	2.910	0.695	
	3.880	0.912	
	4.850	1.115	
6	0.4590	0.113	methyl
	0.9180	0.228	isopropyl
	1.3770	0.344	isohydrazone
	1.8360	0.458	
	2.2950	0.574	
	2.7540	0.683	
	3.6720	0.910	
	4.5900	1.103	

calibrations (11, 16, 17, 22) are shown in Appendix 3. Because of the wide variation in these results it was decided to carry out further investigations. Calibrations were therefore obtained in which 1 ml of hydrazine hydrate was made up to 100 ml with a different ketone, but all subsequent dilutions were made with acetone. The results of these calibrations (18, 19, 21, 27) are shown in Appendix 3. As can be seen the optical densities obtained are similar to calibrations 2, 3 and 13.

The diverging results in calibrations 11, 16, 17 and 22 must be due to differences in the following equilibrium with the different ketones employed.

$$\text{hydrazine} \rightleftharpoons \text{hydrazone} \rightleftharpoons \text{ketazine}$$

The more the equilibrium lies to the left the greater will be the optical density for a given equivalent concentration of hydrazine. In calibrations 18, 19, 21 and 27 the dilution with acetone was such that the above equilibrium for different ketones was similar to that given by acetone alone and therefore they gave almost the same results. It was likely that in these calibrations mixed ketazines were formed and consequently, providing the correct procedure was adhered to, the colorimetric method was applicable to ketazines of any of the ketones quoted in Appendix 3. An exception to the above rule was methyl isobutyl ketone and the data obtained for this carbonyl compound is shown in Appendix 4. No explanation is offered for its behaviour.

The colour development of the blank solution was also followed over a period of time and the results are shown in Appendix 5. In this instance the optical densities are absolute values and are not relative to any other blank. The effect of small quantities of other ketones on the blank colour development is also shown in Appendix 5. As can be seen at low concentrations the effect was negligible. Thus when ketones other than acetone were used in the experiments a blank based on acetone could still be employed.

4.1.3.3. Comparison of methods.

Both of the above two methods of analysis are applicable to ketone solutions of azines and isohydrazones. When simple solutions such as those normally encountered were employed the agreement between the methods was excellent. In Appendix 6 the Student's t method is used to test the significance of any difference in the results given by the two methods.

Difficulties were encountered when the solutions became more complex, such as in the synthesis of azines where considerable quantities of water and alkali were present. In the iodate method of analysis it was found that the time required for the liquor to evaporate was much greater and also that there were several other compounds formed apart from hydrazine sulphate. These probably included sodium sulphate, ammonium sulphate and condensation products.

It was found that the time of evaporation could be decreased by placing the watch glass at the entrance to a fume cupboard and allowing a stream of air to continuously pass over its surface. Some of the products formed caused considerable interference in the subsequent titration with potassium iodate and in fact prevented any colour whatsoever being formed in the organic layer. This effect was eliminated by washing several times with acetone, filtering and collecting the sediments. Hydrazine sulphate is insoluble in acetone but the condensation products, which interfered with the titration, dissolved and were removed.

In some of the complex systems encountered there was also interference in the colorimetric method and therefore tests were carried out to investigate the effects of various impurities on the colour formation. Water and ammonia were found to affect the final value of optical density of both azine and isohydrazone solutions. The effect of water on isohydrazones is shown in table 4.10. Each sample was based on 5 ml of a solution of methyl ethyl isohydrazone in acetone to which varying quantities of water and acetone were added to make up to the standard 10 ml. A comparison run was performed with no water present. The maximum effect is seen to be when 1 ml of water is present in the sample. The results are plotted on figures 4.7 and 4.8.

In table 4.11 is shown in a similar manner the effect of ammonia on the isohydrazone calibration. In this case ammonia was bubbled into acetone for a time and the samples were made up to 10 ml with varying quantities of this solution and pure acetone. The results were therefore only qualitative as the quantity of ammonia in each sample was unknown. However the quantity of ammonia in each sample varied by an amount proportional to the quantity of acetone - ammonia solution added. The results are plotted on figure 4.9.

TABLE 4.10.

Effect of water on the isohydrazone calibration.

Calibration No.	Sample	Volume of isohydrazone solution ml	Volume of acetone ml	Volume of water ml	Optical density
28	1	5.0	0.0	5.0	0.392
	2	5.0	4.0	1.0	0.310
	3	5.0	4.9	0.1	0.378
	4	5.0	5.0	0.01	0.396
	5	5.0	5.0	0.0	0.405
29	1	5.0	0.0	5.0	0.607
	2	5.0	4.0	1.0	0.500
	3	5.0	4.9	0.1	0.622
	4	5.0	5.0	0.01	0.660
	5	5.0	5.0	0.001	0.670
	6	5.0	5.0	0.0	0.683

TABLE 4.11.

Effect of ammonia on the isohydrazone calibration.

Calibration No.	Sample	Volume of isohydrazone solution ml	Volume of acetone ml	Volume of acetone containing ammonia. ml	Optical Density
31	1	5.0	0.0	5.0	0.232
	2	5.0	4.0	1.0	0.263
	3	5.0	4.9	0.1	0.352
	4	5.0	5.0	0.01	0.398
	5	5.0	5.0	0.0	0.400

TABLE 4.12.

* Effect of concentration of p-dimethylaminobenzaldehyde on the isohydrazone calibration.

Calibration No.	Sample	Concentration of p-dimethylaminobenzaldehyde % wt.	Optical density
36	1	0.5	0.19
	2	1.0	0.33
	3	2.5	0.58
	4	5.0	0.763
	5	10.0	0.875

* These values of optical density are not relative to a blank.

TABLE 4.13.

Effect of water on the azine calibration.

Calibration No.	Sample	Volume of azine solution ml	Volume of acetone ml	Volume of water ml	Optical density
30	1	5.0	0.0	5.0	1.036
	2	5.0	4.0	1.0	0.630
	3	5.0	4.9	0.1	0.538
	4	5.0	5.0	0.01	0.520
	5	5.0	5.0	0.001	0.515
	6	5.0	5.0	0.0	0.517

TABLE 4.14.

Effect of ammonia on the azine calibration. (Samples are similar to those of table 4.3. except that acetone containing dissolved ammonia was used.

Calibration No.	Sample	Optical density	Optical density given by equation 4.6.
32	1	0.225	0.116
	2	0.250	0.228
	4	0.342	0.438
	6	0.428	0.628
	8	0.54	0.798
	9	0.575	0.876
	10	0.675	0.949

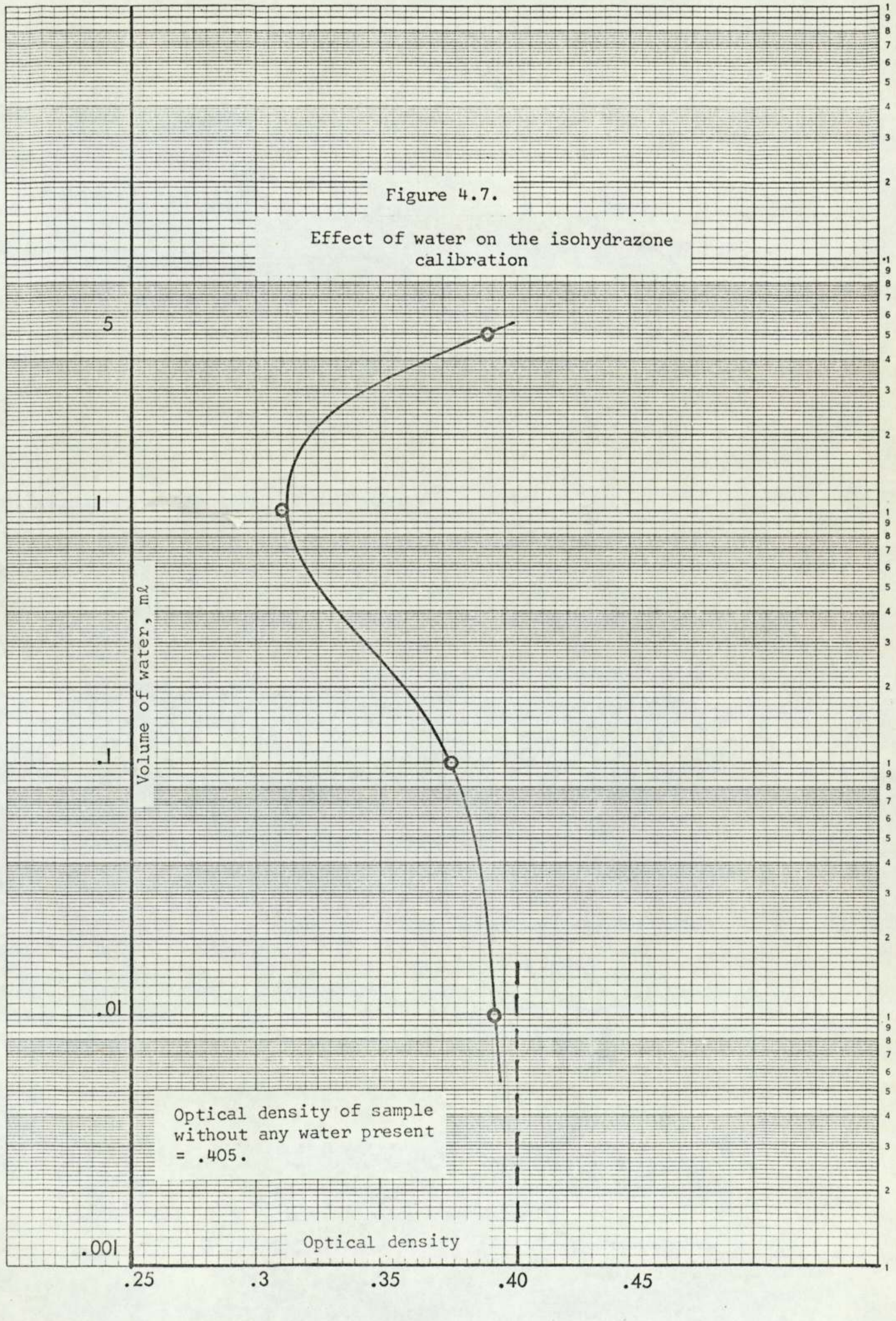


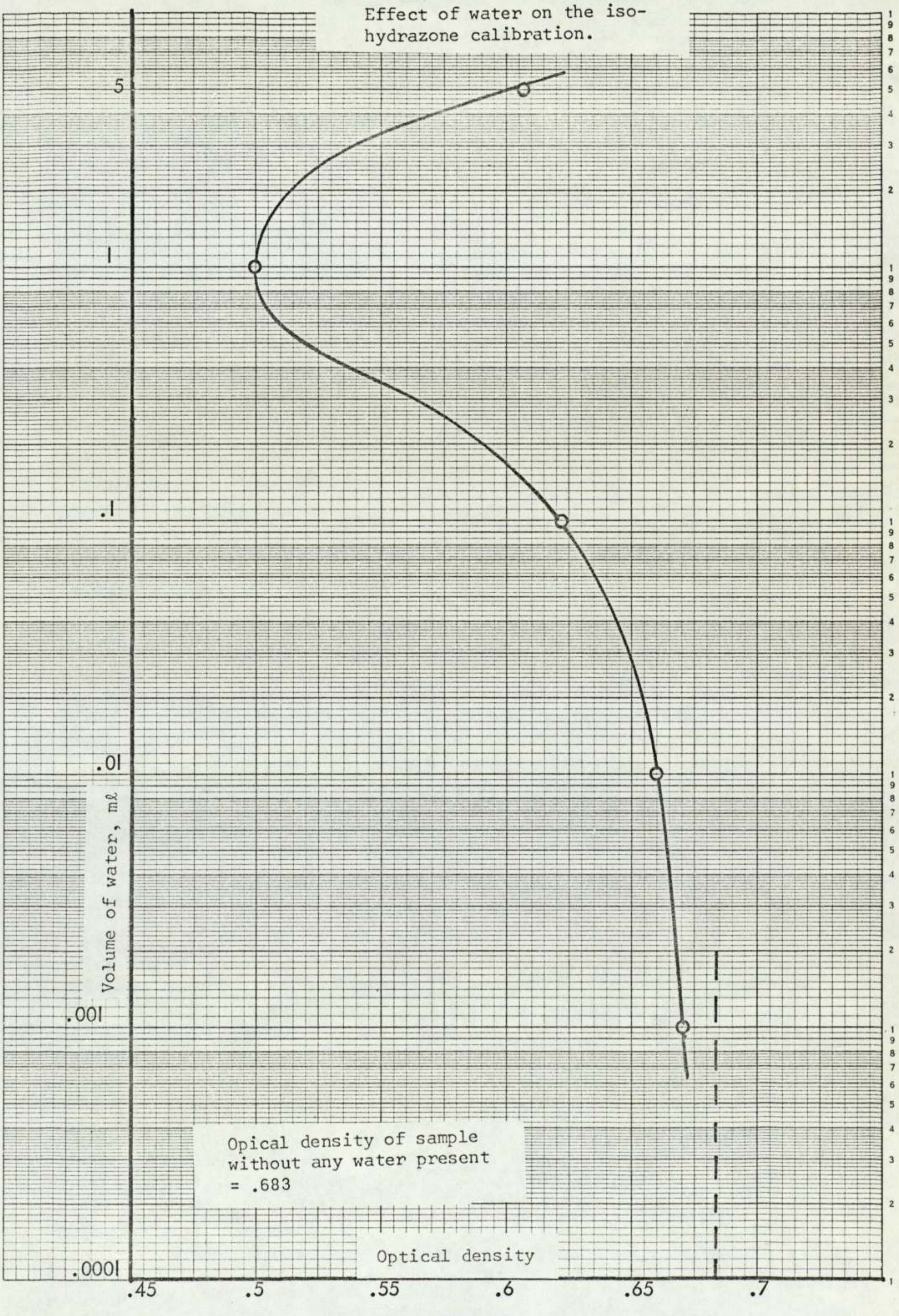
Figure 4.7.

Effect of water on the isohydrazone calibration

Optical density of sample without any water present = .405.

Figure 4.8.

Effect of water on the iso-hydrazone calibration.



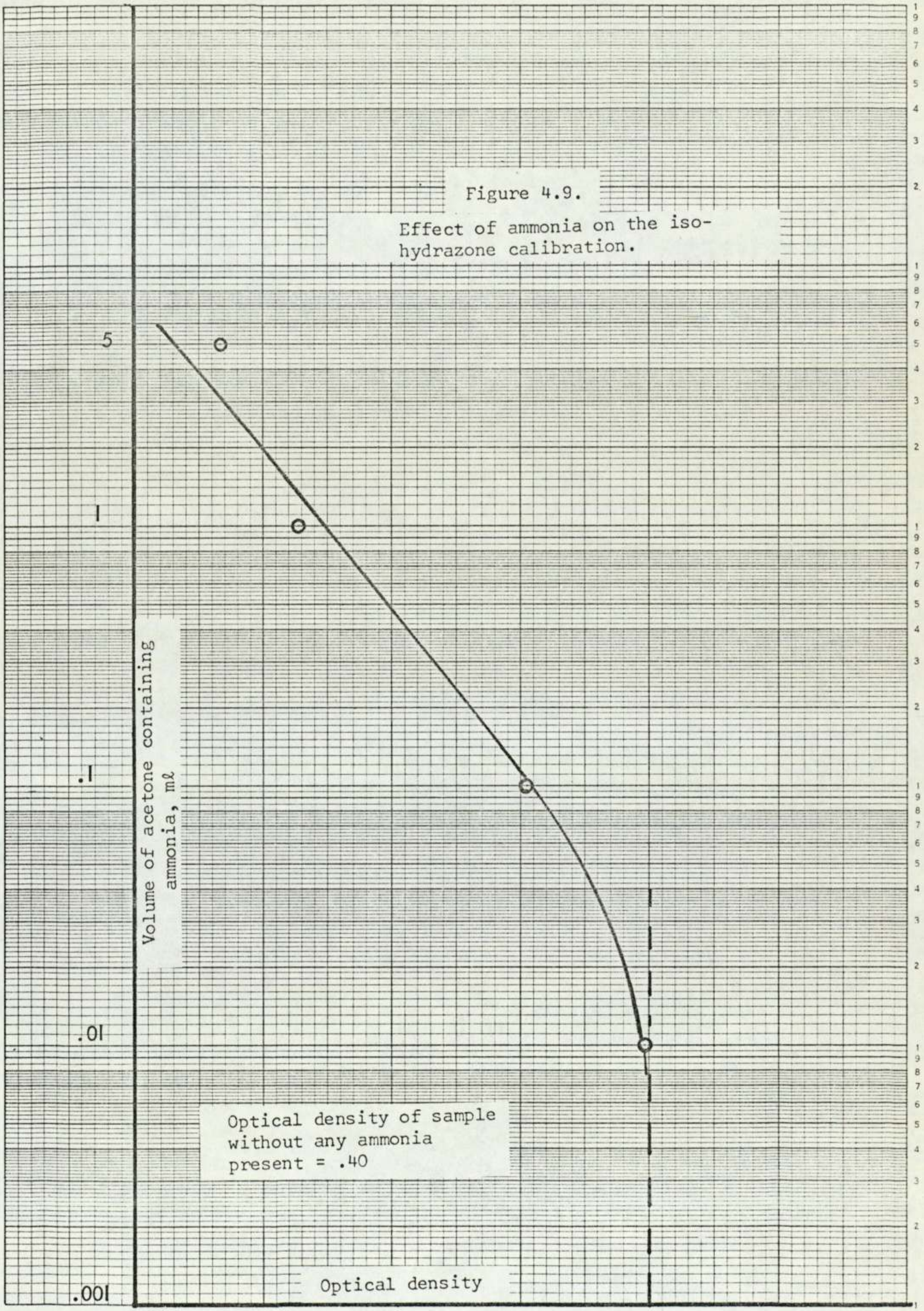


Figure 4.9.

Effect of ammonia on the iso-hydrazone calibration.

It is seen that increased quantities of ammonia reduce the optical density. This was thought to be due to ammonia reacting with p - dimethylaminobenzaldehyde and therefore reducing the concentration of this compound in the samples. A test was therefore carried out in which samples were made up using the same concentration of isohydrazone but different concentrations of p - dimethylaminobenzaldehyde in methanol. The results are shown in table 4.12 and plotted on figure 4.10. where it is seen that it is important to keep this concentration constant, and in all the calibrations and experiments in this investigation a 2.5 per cent. by weight solution was employed. The effect of ammonia and water on optical density is seen to be considerably reduced by dilution and under most experimental conditions encountered in this work their effect could be ignored.

An investigation was also carried out into the effect of water and ammonia on the colour development of azines. The results are shown in tables 4.13 and 4.14. The interference caused by water does not reach a maximum value as in the case of isohydrazones. Instead, for a given concentration of azine, water increases the value of optical density obtained as shown in figure 4.11. Ammonia has a similar effect in this case as in the isohydrazone system except at low concentrations of azine where it appears to increase the value of optical density obtained. However as in the case of isohydrazones the effect is considerably reduced by dilution.

It was observed that during the analysis of experiments in which water was present in the reactor, a precipitate of ammonium chloride was obtained when a sample of the reactor effluent was diluted with acetone. This "salting out" of the ammonium chloride was found to have no effect on the analysis.

Under most experimental conditions both the analytical methods were applicable and gave excellent agreement with each other. However with the following experiments the results given by the two methods did show some variation.

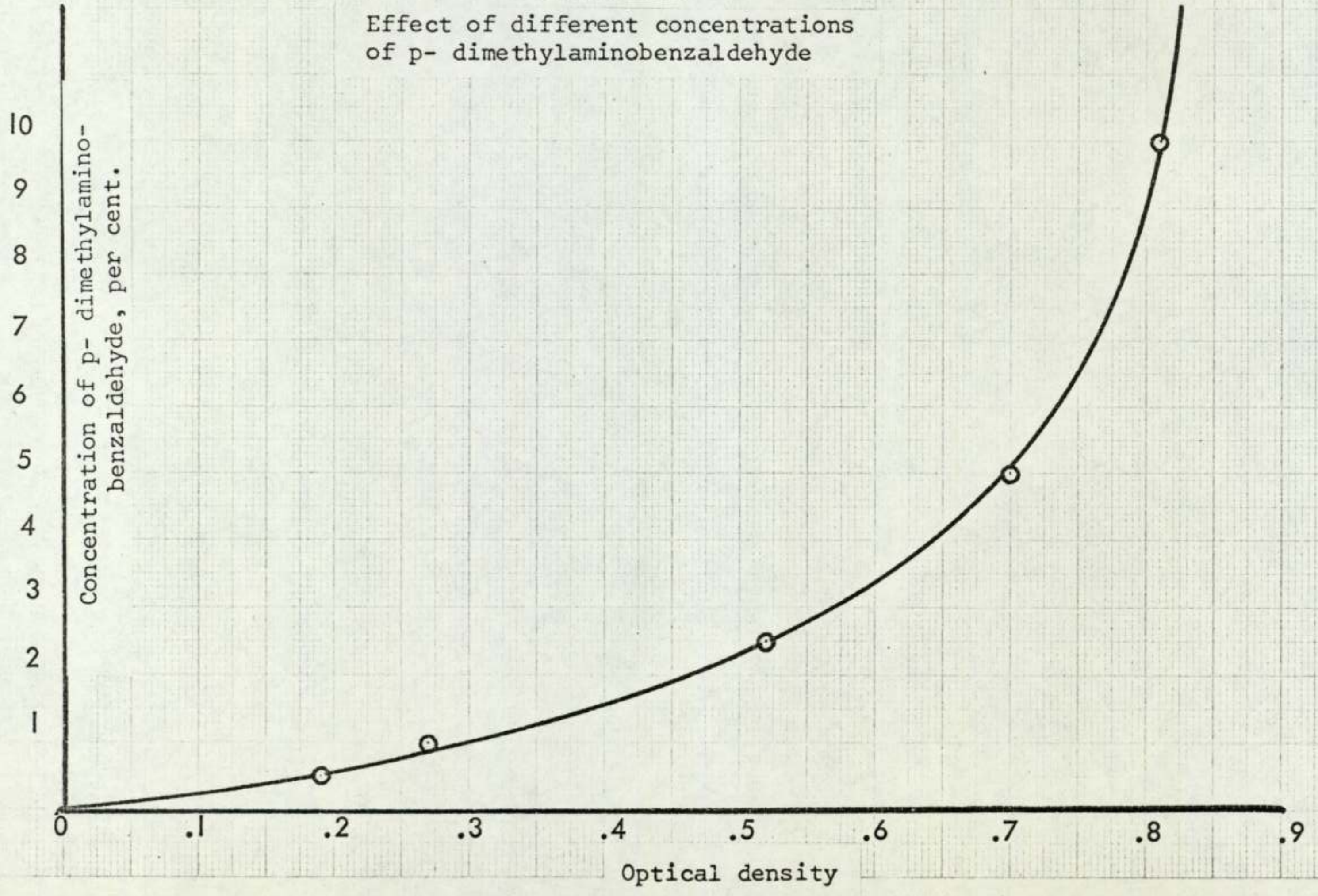


Figure 4.10

Effect of different concentrations of p- dimethylaminobenzaldehyde

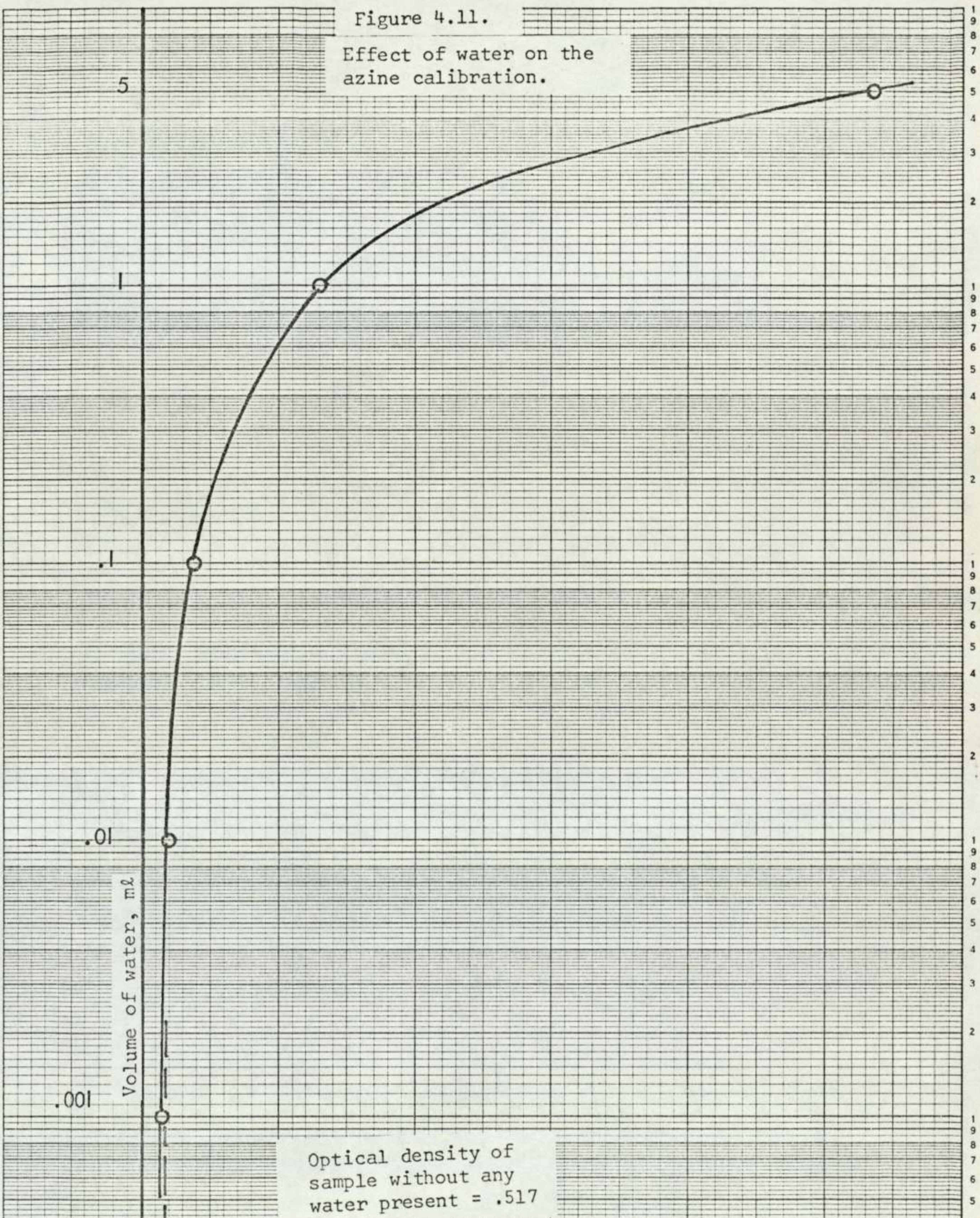


Figure 4.11.

Effect of water on the azine calibration.

Optical density of sample without any water present = .517

1. Experiments on the synthesis of azines using aqueous alkali.
2. Experiments on the synthesis of isohydrazones using a water-ketone mixture.
3. Experiments using acetophenone.

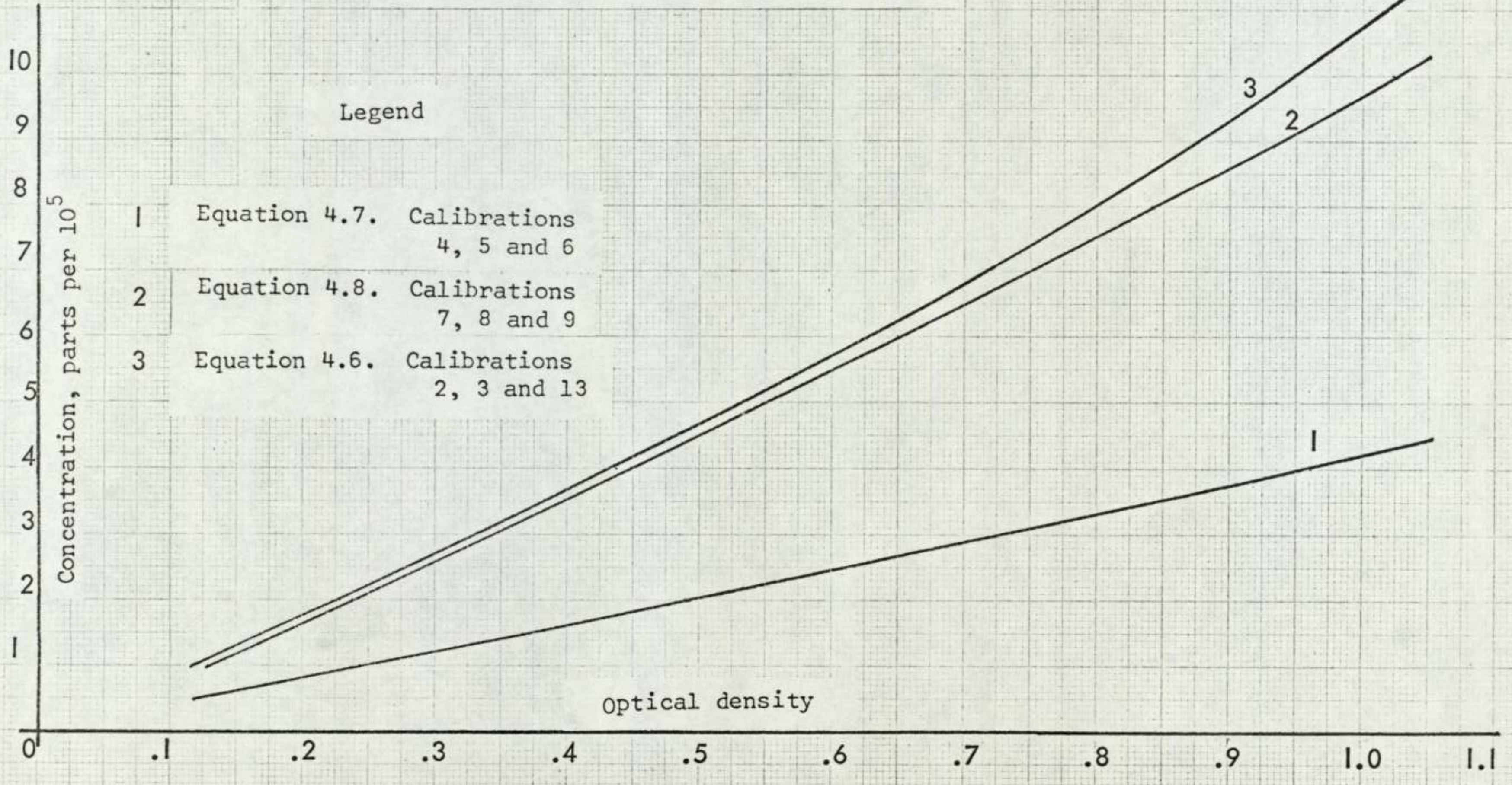
Although in these runs the results were not so accurate as those obtained from experiments using a pure ketone as the liquid phase, they could be regarded as an approximate measure of the yield. In most of these cases an average of the two results obtained was taken. In addition the experiments mentioned above constituted only a small proportion (about 10 per cent.) of the total number of runs performed in the investigation. Thus for 90 per cent. of the runs carried out both methods were applicable. It is quite possible that the methods could be adapted to overcome the adverse conditions in the above list of experiments as indeed the iodate method was, by washing the precipitate with acetone. A possible means of modifying the colorimetric method would be to employ Spekker cells of greater optical path and stronger solutions of p - dimethylaminobenzaldehyde in methanol.

4.1.4. Discussion.

In the preceding sections an attempt has been made to review most of the available methods of analysis of hydrazine and also to describe in some detail methods developed in the present investigation. It has been seen that because the hydrazine is synthesised in the form of an organic intermediate the existing methods of analysis had to be modified. However the experiments carried out in the electrochemical investigation could not be analysed accurately. Two methods were developed for the series of experiments involving the chlorination of ammonia in the presence of a ketone which gave excellent agreement with each other under most experimental conditions.

FIGURE 4.12

Comparison of calibrations of isohydrazones and azines



Both methods were applicable for the analysis of azines and isohydrazones although in the case of the colorimetric method, the calibrations were different. In figure 4.12. the three kinds of calibrations obtained are shown. The following average values of molar extinction coefficient (K) were determined.

1. For isohydrazones. $K = 2290 \frac{\text{litres}}{\text{gm mole. cm}}$
   Calibrations, 4.5.6.
   Figure 4.4.
2. For ketazines. $K = 923 \frac{\text{litres}}{\text{gm mole. cm.}}$
   Calibrations, 2.3.13.
   Figure 4.1.

The calculations are shown in Appendix 7.

The isohydrazones were only first synthesised by Abendroth [16] in 1958. Therefore there is not a great deal of information in the literature concerning them. Paulsen and Huck [43] obtained the infra-red spectrum of several of these compounds which helped them to determine their structure. The infra-red spectrum for diethyl isohydrazone was obtained in this investigation and is similar to that shown by Paulsen and Huck. It is displayed in figure 4.13. In figures 4.14 and 4.15 are shown the infra-red spectrums for:-

1. A sample of acetophenone azine synthesised in run 3.39.
2. A sample of acetophenone azine prepared by reacting hydrazine and acetophenone.

Experiments were also carried out to investigate the stability of solutions of isohydrazones in acetone. The results are shown in Appendix 8 and prove that over a period of several months there was decomposition of the isohydrazone.

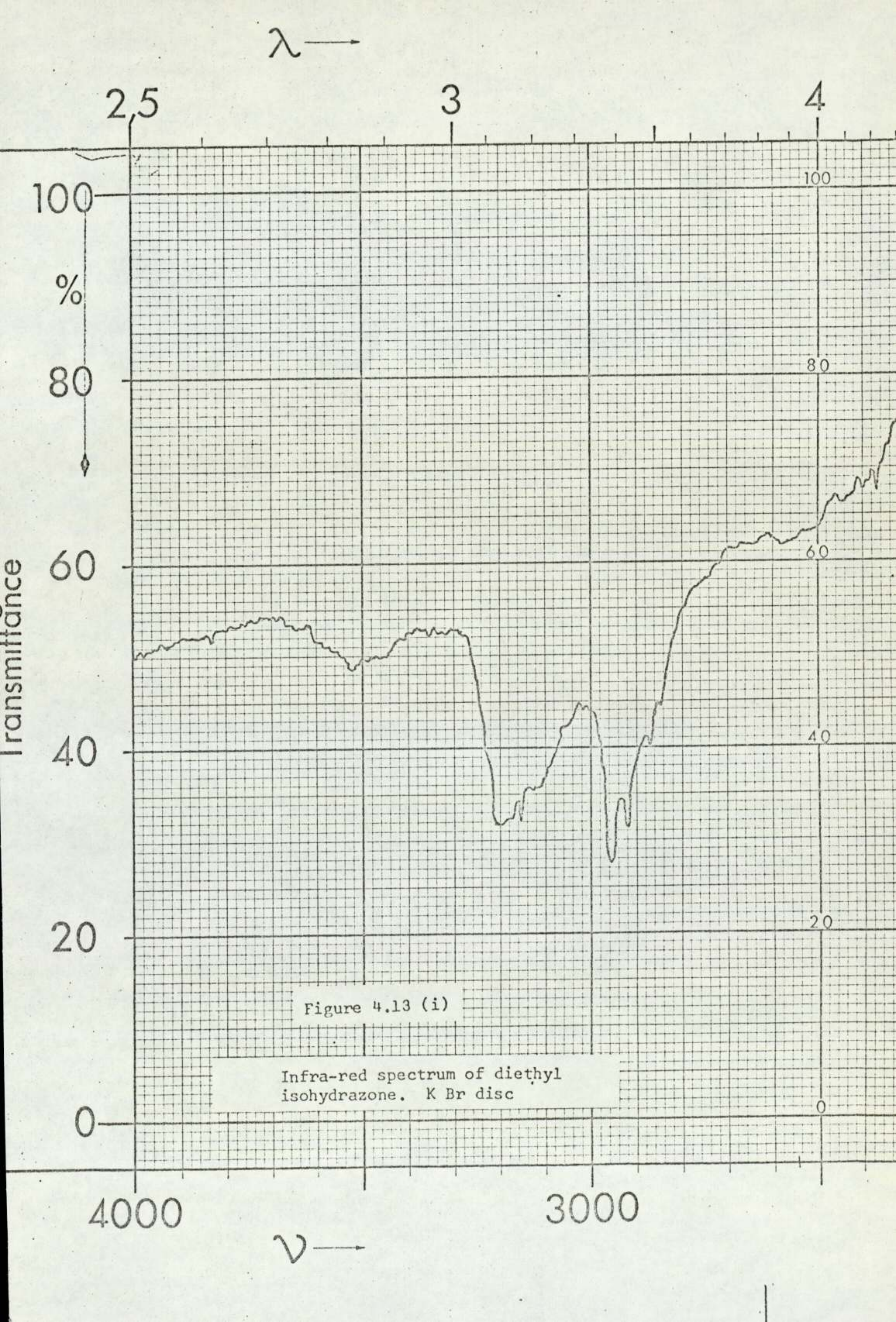


Figure 4.13 (i)

Infra-red spectrum of diethyl isohydrazone. K Br disc

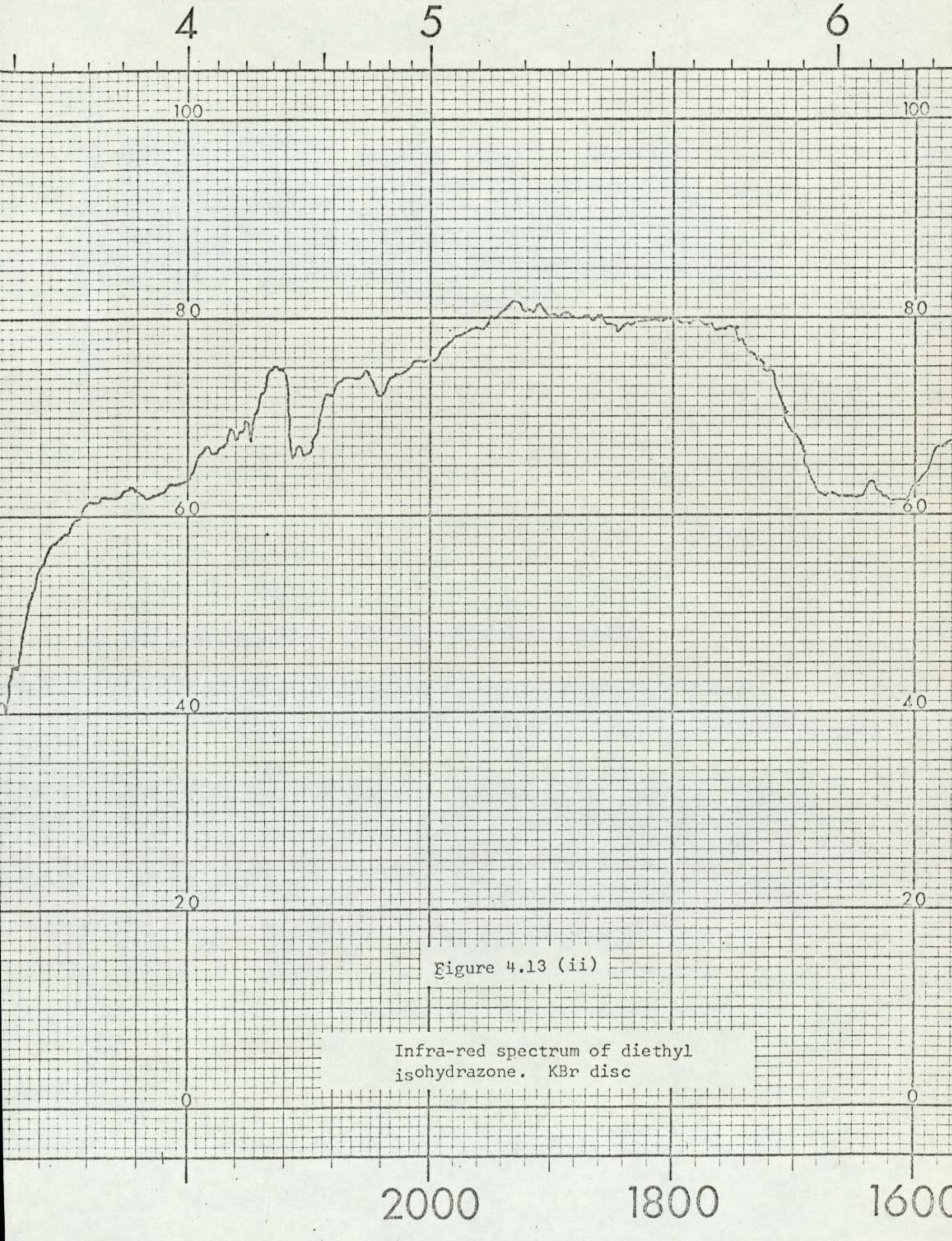


Figure 4.13 (ii)

Infra-red spectrum of diethyl isohydrazone. KBr disc

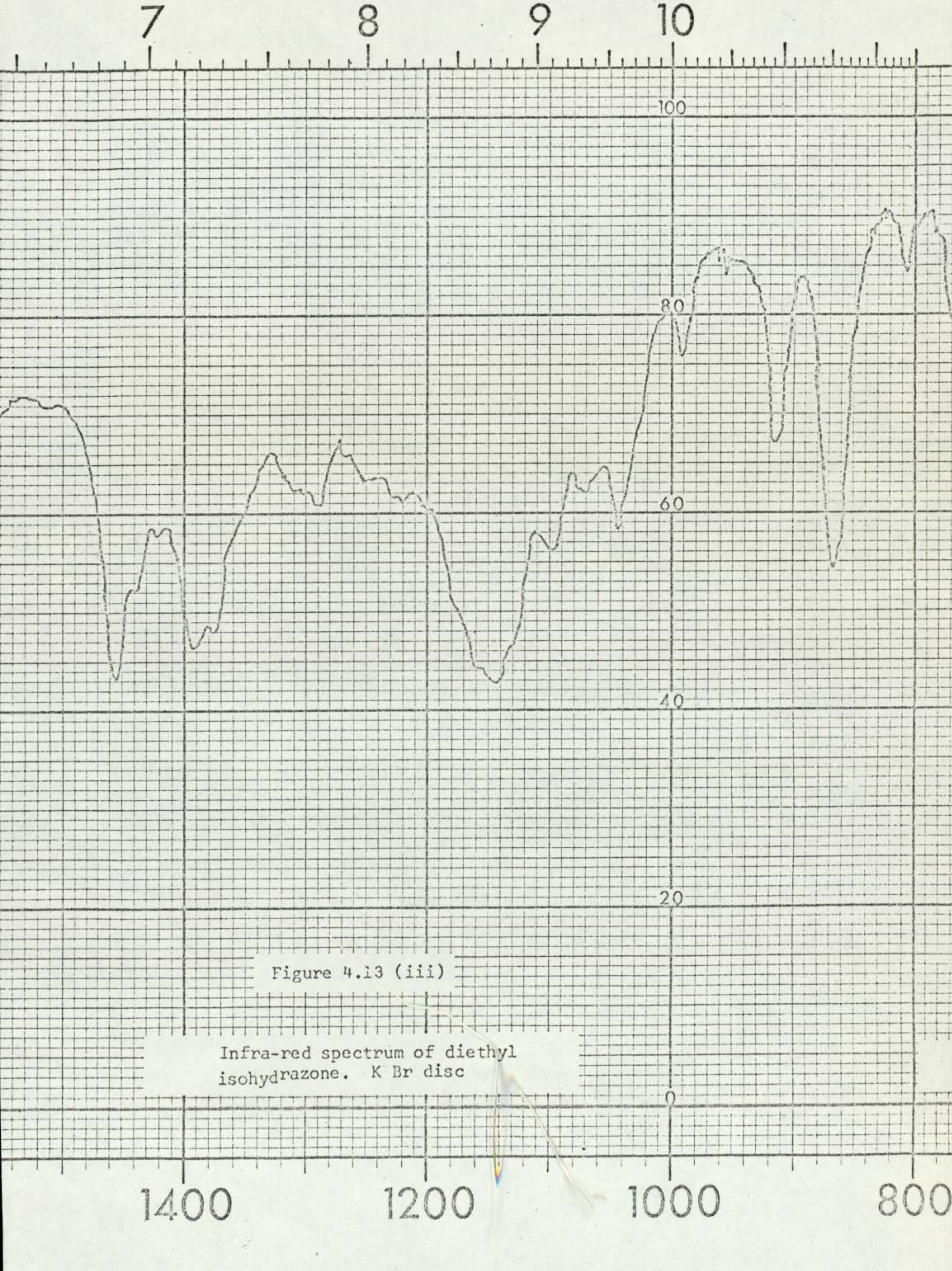


Figure 4.13 (iii)

Infra-red spectrum of diethyl isohydrazone. K Br disc

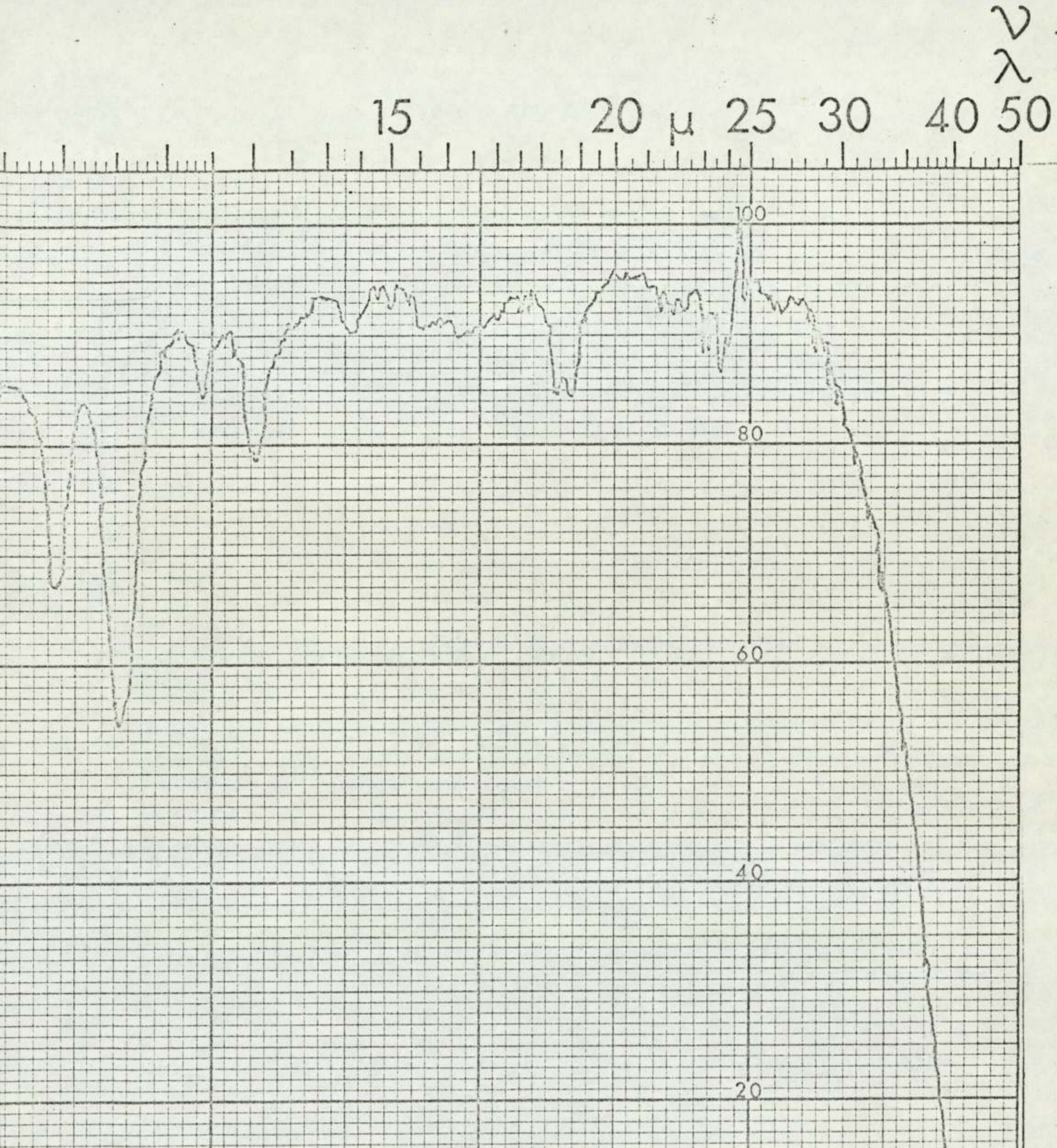
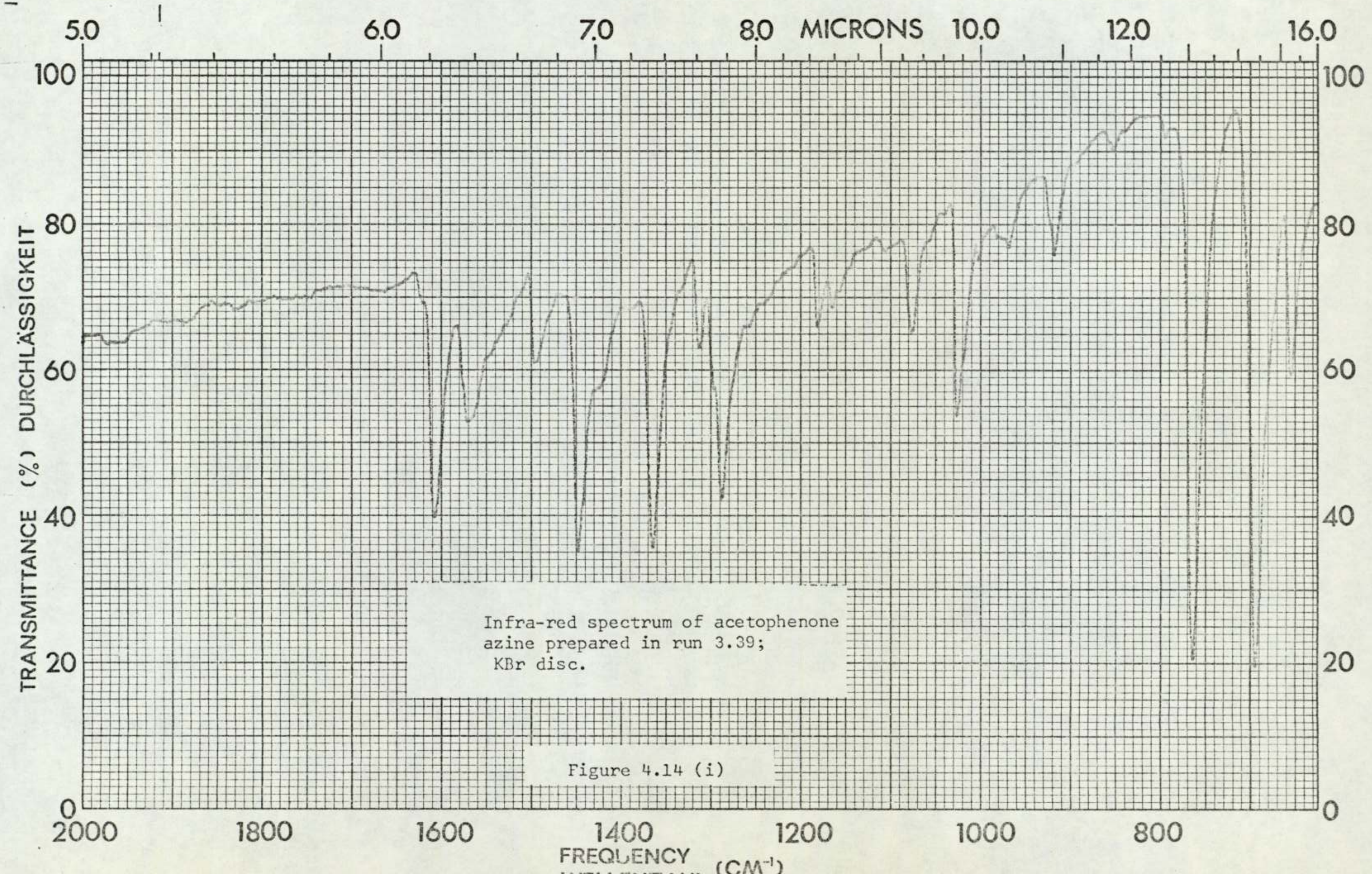


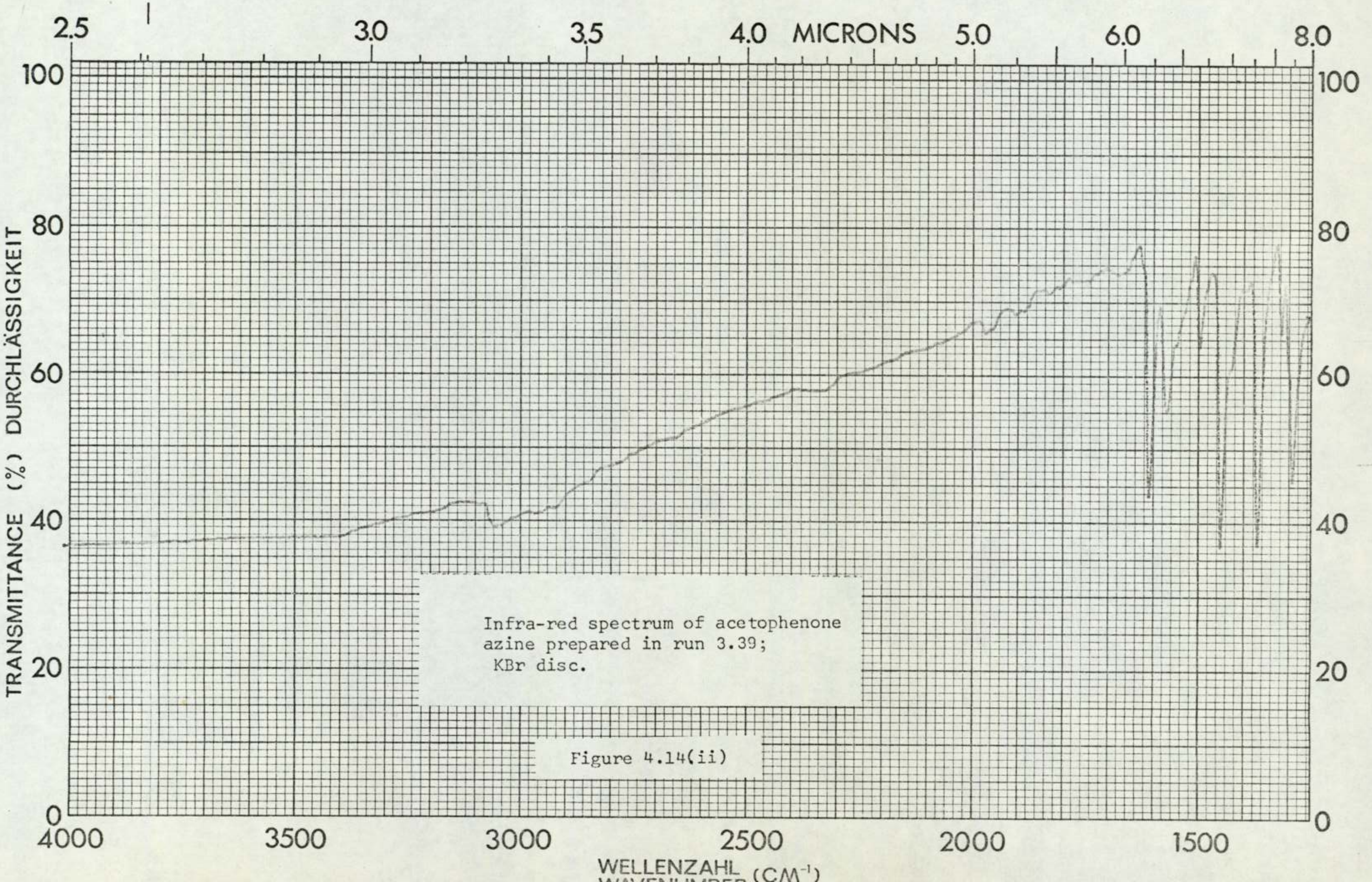
Figure 4.13 (iv)

Infra-red spectrum of diethyl isohydrazone. K Br disc



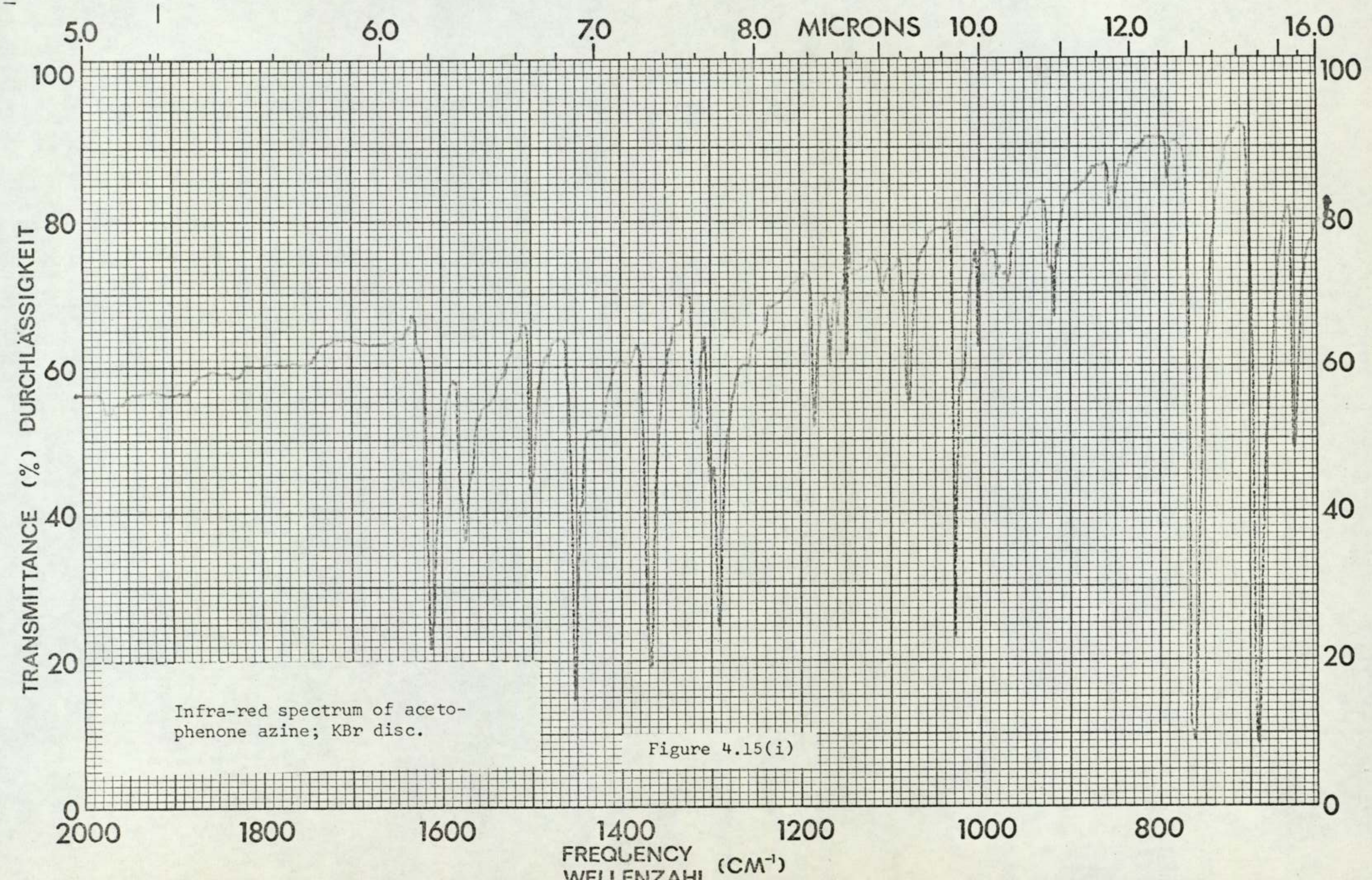
Infra-red spectrum of acetophenone azine prepared in run 3.39; KBr disc.

Figure 4.14 (i)



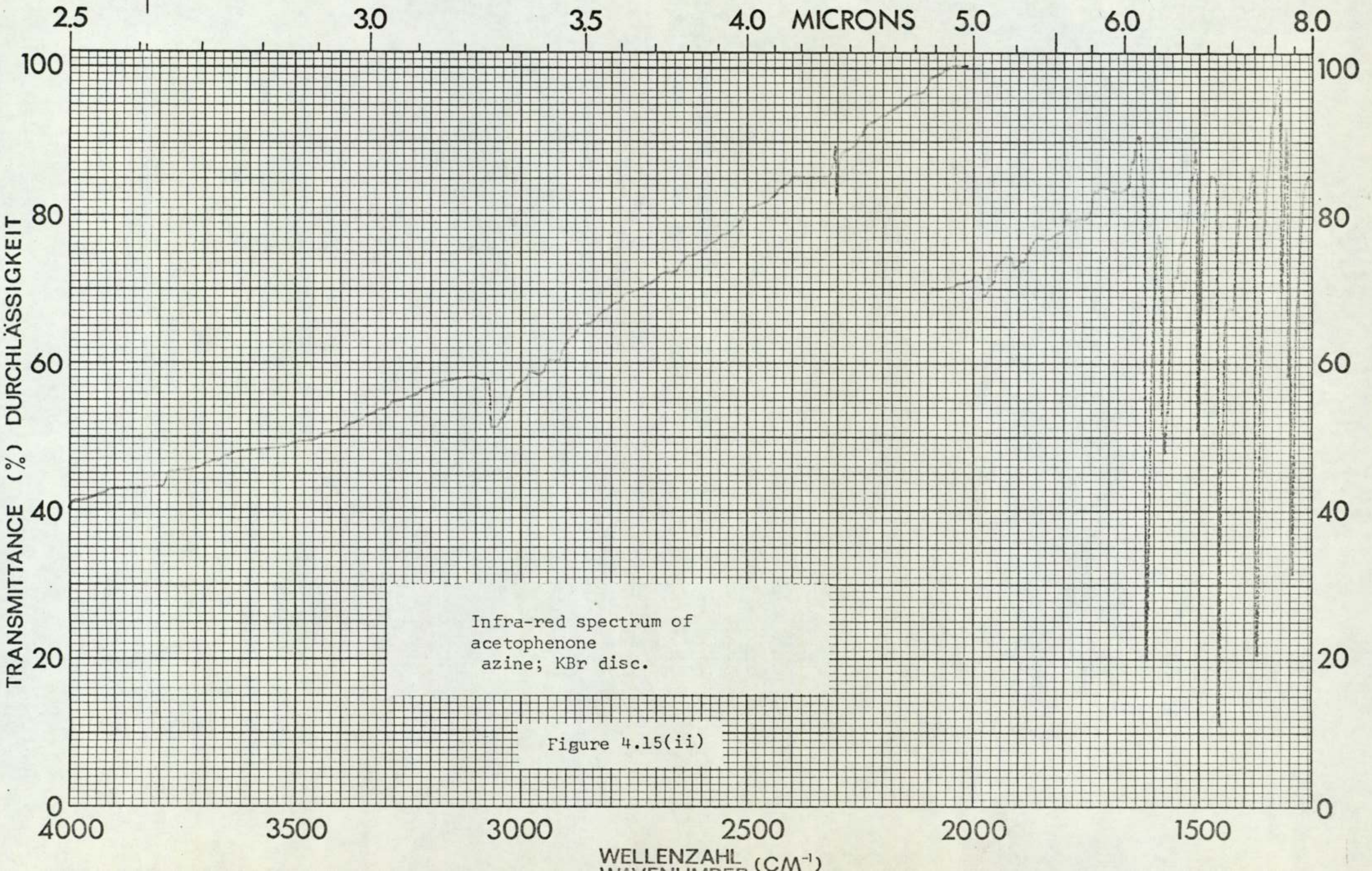
Infra-red spectrum of acetophenone
azine prepared in run 3.39;
KBr disc.

Figure 4.14(ii)



Infra-red spectrum of aceto-
phenone azine; KBr disc.

Figure 4.15(i)



Infra-red spectrum of
acetophenone
azine; KBr disc.

Figure 4.15(ii)

4.2. Chlorine.

The yield of organic intermediate formed was based on the quantity of chlorine used in the experiment and hence this quantity had to be determined with reasonable accuracy. The chlorine was metered by a rotameter before entering the reactor but there was considerable oscillation of the sapphire float and therefore this instrument only served as an indication of the quantity of chlorine being used. However under most experimental conditions all the chlorine was converted to ammonium chloride and consequently it was decided to determine the quantity of chlorine by recovering all the ammonium chloride deposited and analysing for chloride by the Volhard procedure.

This procedure is discussed in detail in the various text books on volumetric analysis /157/ and therefore only a brief outline of the method will be described here. A sample of the chloride solution was treated with an excess of standard silver nitrate. The mixture was boiled for a few minutes and then filtered. The filter paper was washed through several times with distilled water and the filtrate was acidified and then back titrated with standard potassium thiocyanate. A few drops of a 40 per cent. aqueous solution of ammonium ferric sulphate served as indicator and the end point was reached when a pale red-orange colour was obtained.

This method was found to be ideal for most experimental conditions as normally the ammonium chloride, being insoluble in ketone, was precipitated and it could then be collected. Although this process was laborious it proved to be both reproducible and accurate. In those experiments where water was present in the reactor the chloride was in solution in the reactor effluent. Therefore the sample of chloride solution taken contained an appreciable quantity of ammonia which interfered in the analysis. This effect was overcome by diluting the sample several times with distilled water and removing the ammonia dissolved in this solution by boiling for 5 minutes.

4.3. Chloramine.

Several experiments were carried out on the gas phase reaction of chlorine with ammonia, in the absence of a ketone, in order to determine the yield of chloramine. It was decided to employ the method of analysis developed by Drago [71].

Chloramine was formed in accordance with the following reaction:-

$$2NH_3 + Cl_2 \longrightarrow NH_2Cl + NH_4Cl \quad \ldots\ldots 4.9$$

The ammonium chloride was filtered out of the emergent gas stream which then consisted of ammonia, nitrogen and chloramine. These gases were first bubbled into two dreschel bottles containing liquid ammonia, immersed in dry ice - acetone baths, and then into a dreschel bottle containing distilled water. All but a very small quantity of the chloramine was trapped in this way.

The dreschel bottles, containing the liquid ammonia, were then stoppered and maintained at -60°C for 18 hours. They were then opened and the ammonia was allowed to evaporate off. By this time all the chloramine had been converted to ammonium chloride or hydrazine hydrochloride in accordance with the following reactions:-

$$NH_2Cl + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl \quad \ldots\ldots 4.10$$

$$N_2H_4 + NH_4Cl \longrightarrow N_2H_5Cl + NH_3 \quad \ldots\ldots 4.11$$

$$3NH_2Cl + 2NH_3 \longrightarrow 3NH_4Cl + N_2 \quad \ldots\ldots 4.12$$

All the dreschel bottle washings were then combined and analysed for chloride by the Volhard procedure. In a similar manner all the ammonium chloride deposited in the reactor and the filters was analysed. The yield of chloramine was then calculated from the following equation.

$$\%\ \text{yield}\ NH_2Cl = \frac{2\ W_B}{(W_B + W_R)} \times 100 \quad \ldots\ldots 4.13$$

where

W_B is the weight of ammonium chloride deposited in the dreschel bottles and

W_R is the weight of ammonium chloride retained in the reactor and filters.

This equation arises from the fact that if the reaction proceeds according to equation 4.9. the yield of chloramine will be 100 per cent. and 50 per cent.of the chlorine will be obtained in the dreschel bottles as chloride. However the following yield reducing reaction can occur.

$$3\,Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl \quad \text{.........................} \quad 4.14$$

If the reaction proceeds completely according to this equation then the yield of chloramine will be zero and all the chlorine will be retained in the reactor as ammonium chloride.

CHAPTER FIVE

EXPERIMENTAL RESULTS

5. EXPERIMENTAL RESULTS

The results obtained are presented in tabular form in this section. They are discussed and in some cases plotted in chapter 6 which has the same headings as the present chapter.

5.1. Electrochemical Investigation.

5.1.1. Continuous System.

The apparatus shown in figure 3.1. was used to obtain this set of results.

TABLE 5.1.

Experiments giving a positive indication of hydrazine formation.

Electrolyte; KBr. Ketone; acetone. Anode; Platinized titanium /Type 1/

Run	Quantities of reagents			Cathode material
	KBr gms	Acetone ml	liquid ammonia. ml	
1.3	0.1	6	34	Platinized titanium /Type I/
1.15	0.15	5	35	Stainless steel.
1.19	0.2	5	35	Stainless steel

	Voltage volts	Current m amps	Time of run mins	Temperature °C
1.3	18	150	8.5	- 49
1.15	10	100	14	- 38
1.19	10.5	122	5	- 40

TABLE 5.2.

Experiments giving negative indication of hydrazine formation.

Electrolyte : KBr
Ketone : Acetone
Anode : Platinized titanium [Type I]

Run	Quantities of reagents			Cathode material
	KBr gms	Acetone ml	Liquid ammonia. ml	
1.1	0.1	5	20	Stainless steel.
1.2	0.1	6	34	Platinized titanium [Type I]
1.4	0.1	5	30	Stainless steel.
1.7	0.1	5	25	Platinized titanium [Type I]
1.10	0.075	10	40	" "
1.20	0.2	5	35	Stainless steel
1.26	0.24	6	44	"
1.27	0.15	5	35	"
1.28	0.15	5	35	"
1.29	0.15	5	35	"

	Voltage volts	Current m amps	Time of run mins	Temperature ^{o}C
1.1	9	20	2	- 49
1.2	7.8	50	6	- 44
1.4	12	7.5	2.5	- 40
1.7	11.5	100	7	- 40
1.10	20	87	8.5	- 40
1.20	16.5	210	2	- 40

TABLE 5.2. (continued).

Run	Voltage volts	Current m amps	Time of run mins	Temperature °C
1.26	10	95	2.5	- 43
1.27	10	88	7	- 40
1.28	10.5	100	15	- 40
1.29	10	100	3	- 41

TABLE 5.3.

Miscellaneous Experiments

Electrolyte : KBr.

Ketone : Methyl ethyl ketone /MEK/ except run 1.13 where no ketone was employed.

Anode : Platinized titanium /Type I/

Cathode : Stainless steel.

Run	Quantities of reagents used			Temperature
	KBr gms	MEK ml	liquid ammonia ml	°C
1.13	0.2	0	40	- 37
1.30	0.15	5	35	- 41
1.32	0.2	5	35	- 38

Run	Voltage volts	Current m amps	Time of run mins	Remarks
1.13	10	130	11	N_2H_4 was detected.
1.30	10	87	$4\frac{3}{4}$	N_2H_4 was not detected.
1.32	10	100	5	N_2H_4 was not detected.

5.1.2. Batch System.

In this series of experiments several types of cell were employed and a variety of electrode materials tested. The following abbreviations are used for the different electrode materials.

Carbon	C
Platinum	P
Stainless steel	S
Platinized titanium [Type 1]	T_1
Platinized titanium [Type 2]	T_2

The two different types of platinized titanium result from different methods of coating the platinum on to the surface of the titanium. In the case of type 1 this coating is deposited by painting an organic platinum compound on to the titanium, and then firing it in a furnace. For type 2 the coating operation is performed by electrolysing solutions of sodium hexahydroxyplatinate between titanium electrodes. In all experiments on electrolysis, including those already tabulated, the procedure employed for the detection of hydrazine was that involving p - dimethylaminobenzaldehyde. The apparatus shown in Plate 2 was used for the majority of the experiments.

TABLE 5.4.

Experiments using acetone.

Run	Cathode	Anode	Quantities of reagents			Temperature
			KBr	Acetone	Liquid ammonia	
			gms	ml	ml	°C
1.5	T_1	T_1	0.1	10	30	- 38
1.6	S	S	0.1	10	40	- 40
1.8	T_1	T_1	0.075	10	60	- 38
1.9	T_1	T_1	0.1	10	50	- 40
1.11	T_1	T_1	0.05	5	30	- 40
1.12	T_1	T_1	0.075	10	40	- 38
1.14	T_1	T_1	0.2	10	40	- 40

TABLE 5.4. (continued).

Run	Cathode	Anode	Quantities of reagents			Temperature
			KBr	Acetone	Liquid ammonia	
			gms	ml	ml	°C
1.16	T_1	T_1	0.05	10	40	- 41
1.17	T_1	T_1	0.2	10	40	- 42
1.18	T_1	T_1	0.2	10	40	- 42
1.21	T_1	T_1	0.2	10	40	- 40
1.22	T_1	T_1	0.15	10	40	- 38
1.23	S	T_1	0.3	5	35	- 40
1.24	T_1	T_1	0.15	10	40	- 42

	Voltage	Current	Time of run	Hydrazine detected	Remarks
	volts	m amps	mins	Yes/No	
1.5	16	115	51	Yes	
1.6	15	90	61	No	Cell effluent was very brown in colour.
1.8	16	76	60	No	
1.9	14	86	52	Yes	
1.11	18	120	35	No	
1.12	11	55	60	No	
1.14	11	100	65	Yes	
1.16	10	37	16	No	
1.17	11	105	60	Yes	
1.18	11	110	95	No	
1.21	11	110	31	No	
1.22	11.2	84	62.5	No	
1.23	8	245	13.5	Yes	
1.24	7	50	59	No	

TABLE 5.5.

Preliminary experiments using M.E.K.

Run	Cathode	Anode	Quantities of reagents			Temperature
			KBr gms	MEK ml	Liquid ammonia ml	°C
1.31	T_1	T_1	0.1	10	40	- 40
1.33	T_1	T_1	0.2	10	40	- 40
1.34	S	S	0.1	10	40	- 41
1.35	T_1	T_1	0.1	10	40	- 40
1.36	T_1	T_1	0.1	10	40	- 40
1.37	T_1	T_1	0.1	5	45	- 38
1.38	T_1	T_1	0.1	5	35	- 40
1.39	T_1	T_1	0.1	10	40	- 38
1.40	S	S	0.1	5	45	- 40
1.41	T_1	T_1	0.1	5	45	- 40
1.43	T_1	T_1	0.1	5	45	- 39
1.44	T_1	T_1	0.1	5	45	- 39
1.46	T_1	T_1	0.1	5	35	- 42
1.47	T_1	T_1	0.1	5	45	- 39
1.48	S	T_1	0.1	5	45	- 42

Run	Voltage volts	Current m amps	Time of run mins	Hydrazine detected YES/NO	Remarks
1.31	11	50	30	YES	
1.33	10	85	31	YES	
1.34	10	61	30	NO	Cell effluent was deep reddish brown.
1.35	11	52	30	NO	
1.36	11	57	30	NO	
1.37	11	75	30	NO	
1.38	10	66	30	YES	
1.39	11	54	30	NO	
1.40	10	67	30	NO	Effluent was deep reddish brown.
1.41	11	73	30	YES	
1.43	11	62	30	NO	
1.44	11	67	30	YES	
1.46	10	69	30	YES	
1.47	11	69	30	NO	
1.48	11	74	30	NO	

Investigation of anode condition.

In the following series of experiments, a note was made of the condition of the anode and the number of times that it had been used for previous experiments. Again the apparatus shown in Plate 2 was used in most experiments.

TABLE 5.6.

Electrolyte: 0.1 gm KBr. Ketone: 5 ml MEK

Time: 30 mins.

Run	Cathode	Anode	Liquid ammonia ml	Temperature °C	Anode condition.
1.51	T_1	T_1	45	- 38	Used before many times.
1.52	S	T_1	35	- 39	" " "
1.53	T_1	T_1	45	- 39	Used once before.
1.55	S	T_1	45	- 38	Used before many times.
1.56	T_1	T_1	45	- 38	Brand new.
1.57	S	T_1	45	- 36	" "
1.58	T_1	P	35	- 39	" "
1.59	T_1	T_1	45	- 40	Used once before.
1.60	T_1	T_1	45	- 42	" " "
1.68	T_1	T_1	35	- 39	Brand new.
1.69	T_1	P	45	- 39	Used once before.
1.70	T_1	C	45	- 38	-
1.76	T_1	C	45	- 39	Brand new.
1.78	S	C	45	- 37	-
1.79	S	C	45	- 40	-

TABLE 5.6. (continued)

Run	Voltage volts	Current m amps	Hydrazine detected YES/NO	Remarks about the effluent
1.51	11.6	72	NO	Yellowish brown.
1.52	11	75	NO	" "
1.53	11	78	YES	Faintly yellow.
1.55	11	69	NO	Yellowish brown.
1.56	11	69	YES	Faintly yellow.
1.57	12	40	YES	" "
1.58	13	29.5	YES	" "
1.59	11	63	YES	" "
1.60	11	69	YES	" "
1.68	14	39.5	YES	" "
1.69	11	66	YES	" "
1.70	12	42	YES	Greyish
1.76	11	81	YES	"
1.78	11	75	YES	Clear
1.79	11	81	NO	Greyish

TABLE 5.7.

Use of different quantities of KBr.

Electrolyte: 0.2 gms KBr in Run 1.54 and 1.62.

0.3 gms KBr in Run 1.65 and 0.06 gms. in Run 1.75.

M E K : 5 ml in all cases except run 1.75 where it was 3 ml.

In this run a H-type cell was used.

Time: 30 minutes.

Run	Cathode	Anode	Liquid ammonia ml	Temperature °C	Anode condition.
1.54	T_1	T_1	45	- 39	Used before many times.
1.62	T_1	T_1	45	- 42	Used twice before.
1.65	T_1	T_1	45	- 38	Used before many times.
1.75	T_1	T_1	27	- 46	Quite new.

	Voltage volts	Current m amps.	Hydrazine detected YES/NO	Remarks about the effluent
1.54	10	98	NO	Brown colour.
1.62	10	99	YES	Yellowish.
1.65	9	135	NO	Brown colour.
1.75	23	20	YES	Clear.

TABLE 5.8.

Use of rubidium bromide as electrolyte

Electrolyte: 1 gm. RbBr except in run 1.77 where 0.06 gms were used.

M E K : 5 ml except in run 1.77 where 3 ml were used. In this run a H-type cell was employed.

Time: 30 mins.

Run	Cathode	Anode	Liquid ammonia ml.	Temperature °C	Anode condition.
1.73	T_1	T_1	35	- 42	Brand new.
1.77	T_1	T_1	27	- 38	Used twice before.
1.81	T_1	T_2	35	- 39	Brand new.
1.84	T_1	T_2	40	- 39	Used once before.
1.86	T_1	T_2	25	- 37	Brand new.
1.88	T_1	T_2	35	- 40	" "

	Voltage volts.	Current m amps.	Hydrazine detected. YES/NO.	Remarks about the effluent.
1.73	11	58	YES	Clear.
1.77	30	23	YES	Clear.
1.81	12	63	NO	-
1.84	10	53	NO	Clear.
1.86	10	47	Possible	Clear.
1.88	11	60	"	Clear.

TABLE 5.9.

Use of different electrolytes.

Quantity of electrolyte = 0.1 gm. Quantity of M E K = 5 ml.

Cathode material: T_1. Time: 30 mins.

Run	Anode	Electrolyte	Liquid ammonia ml	Temperature °C	Anode condition.
1.61	T_1	Na Cl	35	- 40	Used twice before.
1.63	C	Na Cl	45	- 37	-
1.64	T_1	K I	45	- 42	Used thrice before.
1.80	T_1	CsBr	35	- 35	Used twice before.

	Voltage volts	Current m amps.	Hydrazine detected YES/NO	Remarks about the effluent.
1.61	10	81	NO	Slightly yellow.
1.63	11.2	70	NO	-
1.64	11	66.5	NO	Clear.
1.80	12	43.5	NO	Clear.

TABLE 5.10.

Use of reverse polarity switch.

H-type cell employed. Electrolyte: 0.06 gm **RbBr**.

Ketone: 3 ml M E K . Quantity of liquid ammonia = 27 ml.

Temperature = - 40°C.

Run	Cathode	Anode	Voltage volts.	Current m amps	Hydrazine detected YES/NO	Anode condition.
1.82	T_2	T_2	26	18	NO	Brand new.
1.87	C	C	30	21	NO	-

TABLE 5.11.

Rotating carbon anode.

Cell as in figure 3.4 employed. Cathode: Stainless steel.

Quantity of electrolyte = 0.1 gm. Quantity of liquid ammonia = 40 ml.

Ketone: 5 ml M E K. Temperature = - 38°C.

Run	Electrolyte	Voltage volts	Current m amps.	Hydrazine detected YES/NO	Remarks about the effluent.
1.83	KBr	14	40	YES	Yellowish.
1.85	RbBr	10	40	YES	-

5.2. Gas phase Investigation.

In this section of the investigation attempts were made to synthesise either chloramine or acetone isohydrazone in the gas phase. A comprehensive nomenclature is presented later, but in this section special reference is made to the following symbols.

$$R_A = \frac{\text{Ammonia flow rate (ml/min).}}{\text{Chlorine flow rate (ml/min).}}$$

$$R_D = \frac{\text{Air or Nitrogen flow rate (ml/min).}}{\text{Chlorine flow rate (ml/min).}}$$

5.2.1. Chloramine Synthesis.

This series of experiments was carried out in the apparatus shown in figure 3.6. The yield of chloramine was measured by the method outlined in chapter 4.3. The gas flow rates are referred to 70°F and 1 atmosphere.

TABLE 5.12.

Vertical Reactor.

Run No.	Time of run mins.	N_2 flow rate (V_D) ml/min.	NH_3 flow rate (V_A) ml/min.	NH_4Cl in reactor and filters gms	NH_4Cl in dreschel bottles. gms.
2.1.	3.5	420	1150	0.16	0.0223
2.2.	6	420	1150	0.351	0.055
2.3.	4	330	760	0.152	0.0199
2.4.	15	150	1150	1.642	0.0222
2.5.	11	420	760	0.698	0.066
2.6.	9	235	1350	0.704	0.1485
2.7.	5.5	420	1150	0.2254	0.0386

From the above results the following parameters were calculated.

TABLE 5.13.

Run	Cl_2 flow rate (V_c) ml/min	$R_D = \frac{V_D}{V_C}$	$R_A = \frac{V_A}{V_C}$		Yield of chloramine (Y_c) per cent.
2.1.	11.6	36.2	99.0	36.5	24.5
2.2.	15.1	27.8	76.2	36.5	27.1
2.3.	9.6	34.4	79.0	4.35	23.2
2.4.	24.8	6.05	46.4	134	2.67
2.5.	23.3	18.0	32.6	554	17.3
2.6.	21.1	11.1	64.0	172	34.8
2.7	10.7	39.4	107.5	366	29.2

TABLE 5.14.

Horizontal Reactor.

Run No.	Time of run mins.	N_2 flow rate (V_D) ml/min	NH_3 flow rate (V_A) ml/min	NH_4Cl in reactor and filters gms	NH_4Cl in dreschel bottles gms
2.8.	4	330	1150	0.2282	0.0538
2.9.	3.5	330	1350	0.402	0.0260
2.10.	8.5	420	1150	0.5900	0.0742
2.11.	7	330	1150	0.3895	0.0585
2.12.	9	235	1350	0.8825	0.0675

From the above results the following parameters were calculated.

TABLE 5.15.

Run No.	Cl_2 flow rate (V_c) ml/min.	$R_D = \frac{V_D}{V_C}$	$R_A = \frac{V_A}{V_C}$	Yield of chloramine (Y_C) per cent.
2.8.	15.7	21.0	73.2	38.2
2.9.	27.3	12.1	49.5	16.8
2.10.	17.4	24.2	66.0	22.4
2.11	14.3	23.0	80.5	26.1
2.12	23.5	10.0	57.4	14.2

Specimen calculation.

Example: Run 2.6.

Nitrogen flow rate = 235 ml/min.

Ammonia flow rate = 1350 ml/min.

Duration of run = 9 mins.

Determination of ammonium chloride.

Reactor and filter washings.

Volume of solution = 235 ml.

Volume taken for titration = 10 ml.

Volume of 0.1 M.$AgNO_3$ added = 10 ml.

Volume of O.M K C N S used = 4.4 ml.

in back-titration.

∴ Weight of ammonium chloride deposited in the reactor and filters (W_R)

$$= 0.235 \times \frac{(10 - 4.4)}{10} \times 5.35$$

$$= 0.235 \times 0.56 \times 5.35$$

$$= 0.704 \text{ gms.}$$

Dreschel bottle washings.

Volume of solution = 73 ml.

Volume taken for titration = 20 ml.

Volume of 0.1 M $AgNO_3$ added = 11 ml

Volume of 0.1 M KCNS used = 3.4 ml

in back-titration.

.˙. Weight of ammonium chloride $= 0.073 \times \frac{(11 - 3.4)}{20} \times 5.35$

deposited in the dreschel bottles (W_B)

$= 0.073 \times 0.38 \times 5.35$

$= 0.1485$ gms.

Total quantity of ammonium $= W_B + W_R$

chloride recovered

$= (0.1485 + 0.7040)$ gms

$= 0.8525$ gms

.˙. Chlorine consumed $= 0.8525 \times 0.664$ gms

$= 0.567$ gms

Chlorine flow rate $= \frac{0.567}{9} = 0.063$ gms/min.

Density of chlorine at = 0.00298 gms/ml

70°F, 1 atm.

Chlorine flow rate $= \frac{0.063}{0.00298}$ ml/min

$= 21.1$ ml/min.

$$R_D = \frac{235}{21.1} = 11.1$$

$$R_A = \frac{1350}{21.1} = 64.0$$

Yield of chloramine (Y_c) $= \frac{2\ W_B}{(W_B + W_R)}$

$= \frac{2 \times 0.1485}{0.8525} \times 100$

$= 34.8\%$

5.2.2. Isohydrazone Synthesis.

This series of experiments was carried out in the apparatus shown in figure 3.7. As in chapter 5.2.1. the gas flow rates are referred to 70°F and 1 atmosphere. The yield of isohydrazone was measured by both of the methods described in chapter 4.1.3. and as in previous experiments the quantity of chlorine consumed was determined by the Volhard procedure. Because of its lower volatility acetone was used in all the experiments. The pressure inside the reactor was approximately atmospheric and no experiment was carried out at reduced pressure.

TABLE 5.16.

Run	Duration of run mins	N_2 flow rate (V_D) ml/min	NH_3 flow rate (V_A) ml/min	Quantity of NH_4Cl recovered gms.	N_2 carrier gas flow rate. ml/min
2.13	5	420	2000	0.34	400
2.14	4	420	2000	0.389	400
2.15	6.5	420	1880	1.17	-
2.16	3.5	420	1770	0.512	-

From the above results and measurement of yields by the methods described in chapter 4.1.3. the following parameters were calculated.

TABLE 5.17.

Run	Chlorine flow rate (Vc) ml/min.	$R_D = \frac{V_D}{V_c}$	$R_A = \frac{V_A}{V_c}$		Yield of isohydrazone measured by KIO_3 method (Y_T).	Yield of isohydrazone measured by colorimetric method (Y_S).
2.13	15.1	27.8	132.0	21	49.0	46.8
2.14	21.6	19.45	92.5	21	46.8	47.8
2.15	40.1	10.45	46.8	223	84.0	82.1
2.16	32.6	12.9	54.3	238	49.0	44.5

Sample Calculation.

Example; Run 2.14.

Nitrogen flow rate = 420 ml per min

Ammonia flow rate = 2000 ml per min

Duration of run = 4 minutes

Volume of solution of ammonium chloride washings = 189 ml

Volume taken for titration = 20 ml

Volume of 0.1 M Ag NO_3 added = 15 ml

Volume of 0.1 M KCNS used in back - titration = 7.3 ml

∴ Weight of ammonium chloride deposited $= 0.189 \times \frac{(15 - 7.3)}{20} \times 5.35$

$= 0.189 \times 0.385 \times 5.35$

$= 0.389$ gms.

Quantity of chlorine consumed $= (0.389 \times 0.664)$ gms

$= 0.258$ gms.

Chlorine flow rate $= \frac{0.258}{4} = 0.0645$ gm/min

$= \frac{0.0645}{0.00298} = 21.6$ ml/min.

$$R_D = \frac{420}{21.6} = 19.45$$

$$R_A = \frac{2000}{21.6} = 92.5$$

The overall reaction taking place is

$$Cl_2 + 4NH_3 + R_1COR_2 \longrightarrow 2NH_4Cl + H_2O + R_1R_2CN_2H_2 \quad \ldots\ldots\ldots\ldots 5.1.$$

$\therefore$ 1 mole Cl_2 $\equiv$ 1 mole isohydrazone

$\equiv$ 1 mole $N_2H_4H_2O$.

$\equiv$ 1 mole $N_2H_4H_2SO_4$

$\therefore$ 70.92 gms Cl_2 $\equiv$ 50.064 gms $N_2H_4H_2O$

$\equiv \frac{50.064}{1.03}$ ml $N_2H_4H_2O$

$\equiv$ 48.6 ml $N_2H_4H_2O$

$\therefore$ 1 gm Cl_2 $\equiv \frac{48.6}{70.92} = 0.684$ ml $N_2H_4H_2O$

70.92 gms Cl_2 $\equiv$ 130.124 gms $N_2H_4H_2SO_4$

1 gm Cl_2 $\equiv \frac{130.124}{70.92} = 1.835$ gms $N_2H_4H_2SO_4$

Thus if in run 2.14 a yield of 100 per cent isohydrazone was obtained, then this would be equivalent to the following quantities of $N_2H_4H_2SO_4$ and $N_2H_4H_2O$.

$N_2H_4H_2SO_4$ = (1.835 x 0.258) gms

= 0.473 gms.

$N_2H_4H_2O$ = (0.684 x 0.258) ml

= 0.177 ml.

Potassium Iodate method of analysis.

Total volume of recovered solution = 130 ml.

50 ml of this solution was taken and placed on a watch glass. 10 ml of H_2SO_4 (50 per cent W/W) was added. The hydrazine sulphate formed was recovered and made up to a 27 ml solution.

Now if the yield of isohydrazone was 100 per cent, the quantity of hydrazine sulphate in the 50 ml sample would be $(\frac{50}{130} \times 0.473)$ gms.

= 0.182 gms.

If this were made up to a 0.05 M solution the volume would be

$$(0.182 \times \frac{20}{130.124} \times 1000) \text{ ml} = 27.7 \text{ ml.}$$

$\therefore$ Molarity of solution made up (assuming 100% yield). $= \frac{27.7}{27} \frac{M}{20}$

$$= 1.025 \frac{M}{20}$$

10 ml of this solution were taken and titrated with potassium iodate in the manner described in chapter 4.1.3.1.

Volume of 0.05 M KlO_3 required = 4.8 ml

$\therefore$ Yield based on KlO_3 method (Y_T) $= \frac{4.8}{10.25} \times 100$

$$= 46.8\%$$

Colorimetric method of analysis.

If the yield of isohydrazone was 100 per cent, the dilution of equivalent hydrazine hydrate in the condensed solution would be

$$\frac{0.177}{130} = \frac{136.0}{10^5}$$

Samples of different concentrations were made up as described in chapter 4.1.3.2. For the example where the reactor effluent was diluted one hundred times the optical density (A) was 0.16.

Referring to figure 4.4.

when

$A = 0.16$

$C = 0.652$

$\therefore$ Yield based on colorimetric method (Y_s) $= \frac{0.652}{1.36}$

$$= 47.8\%$$

5.3. Gas-Liquid Investigation.

The experiments carried out in this investigation were subdivided into two parts, depending on the type of reactor employed. Special reference is made in this chapter to the following symbols

$$R_A = \frac{\text{Ammonia flow rate}}{\text{Chlorine flow rate}}$$

X_c = Mole fraction of chlorine in the nitrogen stream entering the reactor.

$$= \frac{V_c}{V_c + V_D}$$

where

V_C = Chlorine flow rate.

V_D = Nitrogen flow rate.

X_K = Mole fraction of ketone in reactor liquid at the beginning of the experiment. In most experiments this value was equal to 1.

Y_S = Yield based on colorimetric method.

Y_T = Yield based on titration method.

As before the yields were based on the quantity of chlorine consumed.

In most experiments the carbonyl compound employed was methyl ethyl ketone. However other ketones were used in some runs and are indicated by the following abbreviations.

DEK	Diethyl ketone.
MNPK	Methyl n-propyl ketone.
MIPK	Methyl i-propyl ketone.
MIBK	Methyl i-butyl ketone.

5.3.1. Stirred Tank Reactor.

Several different systems were investigated in this reactor and the affects of parameters such as temperature, stirring and concentration of chlorine on the yield of organic intermediate were determined. In most of the experiments carried out the product was the isohydrazone, but the formation of azines was investigated in a few cases. The rate of stirring was normally about 1500 RPM.

5.3.1.1. Solution of chlorine in carbon tetrachloride.

These experiments were carried out in two different ways. In the first case the carbon tetrachloride inlet pipe terminated about 4" above the level of ketone and in the second case it dipped beneath the surface of the ketone. All experiments were at 20°C.

TABLE 5.18.

Quantity of MEK in reactor = 500 ml, except in run 3.14 where 400 ml were employed.

The chlorine was dissolved in 150 ml of $C\,Cl_4$ in runs 3.33 and 3.34, but was dissolved in 100 ml of $C\,Cl_4$ in the other experiments.

Run No.	Duration of run. mins	Ammonia flow rate ml/min	Equivalent chlorine flow rate. ml/min		Y_S per cent	Y_T per cent
Inlet pipe above level of ketone						
3.13	20	1150	53.4	21·4	23.5	14.7
3.14	105	1150	2.58	446	37.8	28.3
Inlet pipe beneath level of ketone.						
3.32	2	950	212.0	4·49	21.7	14.5
3.33	22	1050	10.5	100	50.1	-
3.34	39	1050	3.8	276	57.3	45.0
3.114	12	680	2.19	310	89.1	-

5.3.1.2. Effect of temperature and dilution of chlorine stream.

This series of experiments was carried out to investigate the effect of temperature and dilution of chlorine on the yield of isohydrazone. In all of these experiments the ketone employed was either acetone or MEK; normally the latter.

TABLE 5.19.

Temperature = 20°C.

Quantity of ketone in reactor = 600 mls.

The ketone was MEK except in run 3.74 where it was acetone.

Run No.	Duration of run mins.	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.12	60	24.8	46.4	0.0813	71.0	69.5
3.69	30	24.2	39.2	0.0546	80.0	77.8
3.72	30	35.1	27.1	0.0770	72.2	58.1
3.74	30	26.1	32.5	0.0585	72.3	75.0
3.91	45	14.1	60.0	0.0324	90.8	89.0
3.100	30	53.3	17.8	0.1125	66.2	65.2
3.101	20	43.8	26.2	0.0945	60.6	-
3.115	30	48.0	28.1	0.0327	80.5	-

TABLE 5.20.

Temperature = 20°C.

Quantity of ketone in reactor = 500 ml.

The ketone was MEK except in run 3.49 where it was acetone.

10 gms of activated carbon was placed in the reactor in runs 3.27 and 3.31.

Run No.	Duration of run. mins	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.27	60	38.1	19.7	0.1035	57.5	51.5
3.31	61	27.0	27.8	0.0756	66.0	65.7
3.42	41	15.3	49.0	0.0443	76.8	74.5
3.49	53	44.6	25.8	0.119	62.5	60.0
3.50	30	32.6	29.1	0.279	48.0	50.0
3.51	23	38.5	40.2	1.000	38.5	38.2
3.99	63	62.2	15.4	0.151	52.5	50.3

TABLE 5.21.

Temperature = 0°C.

Quantity of ketone = 600 ml except in runs 3.19 and 3.26 where it was 500 ml, and in run 3.9 where it was 400 ml.

The ketone was MEK in all experiments.

2 gms of activated carbon was placed in the reactor in run 3.19.

5 gms " " " " " " " " " run 3.26.

Run No.	Duration of run. mins.	Chlorine flow rate ml per min.	R_A	X_C	Y_S per cent	Y_T per cent
3.9	60	11.8	114	0.0404	91.0	-
3.10	165	24.5	55	0.0804	76.2	75.2
3.19	60	54.0	17.6	0.114	58.7	56.5
3.26	60	34.1	22.0	0.0935	70.0	66.7
3.66	31	70.8	17.7	0.141	60.2	57.5
3.71	30	46.7	20.3	0.10	65.0	60.8
3.82	31	29.5	32.2	0.0657	80.5	80.0
3.83	30	21.4	28.0	0.0484	85.1	87.8

TABLE 5.22.

Temperature = -10°C.

Quantity of ketone in reactor = 600 ml. except in runs 3.7 and 3.8. where it was 400 ml, and in runs 3.6 and 3.28 where it was 500 ml.

The ketone was MEK except in run 3.78 where it was acetone

10 gms of activated charcoal was placed in the reactor in run 3.28.

Run No.	Duration of run mins	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.6.	60	21.2	63.6	0.0826	56.5	-
3.7.	60	22.0	61.4	0.0728	75.0	-
3.8.	55	23.1	58.4	0.0762	67.2	-
3.11	65	36.4	37.1	0.1150	55.2	50.1
3.28	60	40.2	18.6	0.1085	61.5	63.5
3.78	30	28.5	36.8	0.0635	66.2	69.8
3.80	35	45.6	29,6	0.0980	58.5	57.2
3.84	30	21.5	28.0	0.0487	73.5	69.0

TABLE 5.23.

Temperature = -25°C.

Quantity of ketone in reactor = 600 ml.

The ketone was MEK except in run 3.81 where it was acetone.

Run No.	Duration of run. mins.	Chlorine flow rate ml per min.	R_A	X_C	Y_S per cent	Y_T per cent
3.76	30	47.2	22.3	0.101	51.5	50.6
3.77	31	12.6	75.4	0.0291	75.1	72.7
3.79	29.5	20.7	45.8	0.0469	72.5	71.8
3.81	30	28	26.8	0.0623	48.1	50.5
3.85	30	59.8	25.9	0.1245	48.3	39.0

TABLE 5.24.

Temperature = 58°C.

Quantity of ketone in reactor = 600 ml.

The ketone was MEK in all experiments.

Run No.	Duration of run. mins.	Chlorine flow rate ml per min.	R_A	X_C	Y_S per cent	Y_T per cent
3.87	30	26.7	28.1	0.0598	69.0	67.4
3.88	30	13.9	53.8	0.0321	89.0	91.6
3.89	27	20.1	32.4	0.0456	60.4	59.8

5.3.1.3. Unstirred reactor using either air or nitrogen as the chlorine diluent.

The following series of results were obtained without stirring the reactor during the run. Experiments were carried out at 0 and 20°C, and both air and nitrogen were used as the chlorine diluent.

TABLE 5.25.

Use of air as diluent.

Temperature = 20°C.

Quantity of MEK in reactor = 600 ml.

Air flow rate = 425 ml per min.

Ammonia flow rate = 950 ml per min for Runs 3.54 and 3.55.

" " " = 1150 ml per min for Runs 3.53 and 3.56.

Run No.	Duration of run mins.	Chlorine flow rate ml/min.	R_A	X_C	Y_S per cent	Y_T per cent
3.53	35	23.6	48.7	0.0526	68.2	69.0
3.54	60	22.5	42.1	0.0503	74.5	77.4
3.55	35	5.95	159	0.0138	99.4	95.0
3.56	30	56.3	20.8	0.1170	60.2	58.4

TABLE 5.26.

Use of air as diluent.

Temperature = 0°C.
Quantity of MEK = 600 ml.
Air flow rate = 425 ml per min.
Ammonia flow rate = 950 ml per min in Run 3.57.
" " " = 650 ml per min in Run 3.58.
" " " = 1150 ml per min in Run 3.59.

Run No.	Duration of run. mins.	Chlorine flow rate ml/min	R_A	X_C	Y_S per cent	Y_T per cent
3.57	36	51.6	18.4	0.108	64.0	62.2
3.58	40	16.55	39.2	0.0375	93.6	96.0
3.59	35	35.70	32.2	0.0775	76.5	75.4

TABLE 5.27.

USE OF NITROGEN AS DILUENT.

Temperature = 20°C.
Quantity of MEK = 600 ml.
Nitrogen flow rate = 420 ml per min.
Duration of run = 30 mins.

Run No.	Ammonia flow rate ml per min	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.60	1350	62.3	21.7	0.1280	52.5	44.2
3.61	950	16.9	56.2	0.0383	83.5	83.8
3.62	950	21.5	44.2	0.0482	76.2	74.8

TABLE 5.28.

Use of nitrogen as diluent.

Temperature = 0°C.

Quantity of MEK in reactor = 500 ml.

Quantity of MEK in second dreschel bottle = 70 ml.

Nitrogen flow rate = 330 ml per min.

Ammonia flow rate = 750 ml per min in Run 3.37.

" " " = 950 ml per min in Runs 3.22 and 3.38.

Run No.	Duration of run. mins.	Chlorine flow rate ml per min.	R_A	X_C	Y_S per cent	Y_T per cent
3.22	31	21.85	43.4	0.0622	78.0	76.5
3.37	44	9.3	80.6	0.0274	98.7	97.5
3.38	30	30.0	31.6	0.0834	75.8	73.8

5.3.1.4. Effect of high chlorine flow rates.

In these experiments the chlorine flow rate was much higher than that normally employed [70 ml per min.]. The effect on yield was noted and an attempt was made to determine the working limits of the reactor.

TABLE 5.29.

Ammonia flow rate = 3380 ml per min. except in run 3.52 where it was 1560 ml. per min.

Nitrogen flow rate = 2520 ml per min. except in run 3.52 where it was 420 ml per min.

Duration of runs = 20 mins. except in run 3.29 where it was 10 mins. and in run 3.52 where it was 9 mins.

Temperature = 20°C initially, except in run 3.35 where it was maintained at 0°C.

Quantity of MEK in reactor = 600 ml.

Run No.	Chlorine flow rate ml per min.	X_c	R_A	Y_S per cent	Y_T per cent	Quantity of activated carbon in the reaction zone. gms.
3.29	107	0.0408	31.6	82.1	76.4	20
3.30	270	0.0966	12.5	52.0	47.8	15
3.35	180	0.0667	18.8	53.8	51.1	5
3.36	161	0.060	21.00	64.1	-	5
3.52	406	0.492	3.84	17.0	17.1	0

5.3.1.5. Use of higher ketones.

In this series of experiments carbonyl compounds, other than acetone, MEK, acetophenone or any compound used in chapter 5.3.1.9, were employed.

TABLE 5.30.

Quantity of ketone = 500 ml.

90 ml methyl alcohol was added to the reactor in runs 3.17 and 3.20.

50 ml " " " " " " " " run 3.16.

Run No.	Ketone employed	Temperature °C	R_A	X_C	Y_S per cent	Y_T per cent
3.2	DEK	20	38.2	0.124	43.8	-
3.3	DEK	20	34.7	0.0912	65.2	-
3.4	DEK	0	25.8	0.124	58.2	-
3.5	MIPK	0	36.6	0.108	65.5	-
3.15	MIBK	-5	41.1	0.078	62.0	-
3.16	MIBK	-5	25.4	0.120	42.0	-
3.17	MIBK	-10	22.9	0.131	37.9	-
3.18	MNPK	20	22.4	0.124	47.5	43.5
3.20*	MIBK	-5	19.3	0.129	58.7	61.0
3.23	MIPK	-10	19.0	0.107	51.1	45.8
3.24	MIPK	0	20.1	0.102	57.0	-
3.25	DEK	0	17.5	0.0922	59.1	-

* Air was used as the chlorine diluent in this experiment.

5.3.1.6. Effect of ketone concentration.

The following results were carried out to investigate the effect of the concentration of ketone on the yield of isohydrazone. In these experiments the liquid feed to the reactor consisted of varying amounts of a homogeneous mixture of water and methyl ethyl ketone. Stirring was employed in these experiments.

TABLE 5.31.

Use of ketone-water mixtures.

Temperature = 20°C.
Nitrogen flow rate = 420 ml per min.
Ammonia flow rate = 1150 ml per min.
R_A = 21.1 for run 3.97.
" = 25.6 " " 3.112.
" = 26.7 " " 3.113.

Run No.	X_c	Volume of MEK ml	Volume of water ml	X_K	Y_S per cent	Y_T per cent
3.97	0.1145	50	450	0.0218	24.6	25.8
3.112	0.0965	150	500	0.0567	44.7	36.5
3.113	0.0930	750	50	0.75	62.0	54.1

5.3.1.7. Use of acetophenone as the carbonyl compound.

TABLE 5.32.

Run 3.39. Temperature = 20°C.

Quantity of $C_6H_5COCH_3$ = 400 ml. Quantity of CH_3OH = 100 ml.

Duration of run = 47 minutes. Chlorine flow rate = 25 ml per min.

Ammonia flow rate = 950 ml per min. Nitrogen flow rate = 350 ml per min.

R_A = 38.0 X_c = 0.067.

YS = 64% Y_T = 62%

Run 3.86. Temperature = 17°C.

Quantity of $C_6H_5COCH_3$ = 400 ml. Quantity of CH_3OH = 100 ml.

Duration of run = 45 minutes. Chlorine flow rate = 41.3 ml per min.

Ammonia flow rate = 1150 ml per min. Nitrogen flow rate = 420 ml per min.

R_A = 27.8 X_C = 0.0897.

Y_S = 70% Y_T = 43.5%

Run 3.107. Temperature = 5°C.

Quantity of $C_6H_5COCH_3$ = 500 ml. Quantity of CH_3OH = 200 ml.

Duration of run = 30 minutes. Chlorine flow rate = 39.1 ml per min.

Ammonia flow rate = 950 ml per min. Nitrogen flow rate = 420 ml per min.

R_A = 24.3. X_C = 0.085.

Y_S = 73.5% based on azine. Y_T = 23.1%.

Y_S = 35.6% based on isohydrazone.

5.3.1.8. Use of Liquid Ammonia.

Two experiments were carried out in which a nitrogen-chlorine mixture was bubbled into the liquid phase which consisted of liquid ammonia and a ketone.

TABLE 5.33.

Run 3.109. Temperature = - 60°C.

Volume of Liquid Ammonia = 35 ml.

Volume of acetone = 70 ml.

Nitrogen flow rate = 420 ml per min.

Chlorine flow rate = 44 ml per min. Duration of run = 20 mins.

X_C = 0.0948. R_A = 36.2.

Y_S = 35% Y_T = 36.1%

Run 3.116. Temperature = - 60°C.

Volume of Liquid Ammonia = 35 ml.

Volume of methyl isopropyl ketone = 80 ml.

Nitrogen flow rate = 420 ml per min.

Chlorine flow rate = 29.3 ml per min.

Duration of run = 15 mins.

X_C = 0.0652. R_A = 54.2.

Y_S = 46.8% Y_T = 41.7%

5.3.1.9. Miscellaneous Experiments.

This series of experiments was carried out using unusual systems as the reactor feed. It was impossible to detect organic hydrazine compounds in any of these tests by the detection procedures developed in chapter 4.1.3.

TABLE 5.34.

Run No.	Reactor charge	Observations during the run.	Y_S per cent	Y_T per cent
3.63	500 ml of Benzaldehyde.	Temperature increased to 50°C in 12 mins.	A very low value of optical density ⌊ 0.1 ⌋ was obtained. This was with samples of high concentration of reactor effluent.	No $N_2H_4H_2SO_4$ was obtained.
3.70	540 ml of Cyclohexanone + 60 ml methyl alcohol.	Temperature increased to 35°C in 19 mins.	The samples were a very dark reddish-brown colour and thus no reliance could be put on any value of optical density measurement.	No $N_2H_4H_2SO_4$ was obtained.
3.93	250 ml of MEK + 250 ml of a 33% W/W solution of methylamine in ethanol.	White fumes appeared above the liquid but there was no sign of precipitation in the liquid phase. After 15 mins. reactor liquor turned a green colour.	Samples developed a dark red colour and thus no conclusions could be drawn.	No precipitation of substituted hydrazine sulphate was obtained.
3.98	500 ml of MEK + 100 ml of ethylamine.	White fumes appeared above the liquid, but there was no sign of precipitation in the liquid phase.	Samples developed a dark red colour and thus no conclusions could be drawn.	No precipitation of substituted hydrazine sulphate was obtained.

5.3.1.10. Synthesis of Azines.

In this series of experiments the reactor liquid was a mixture of sodium hydroxide solution and a ketone.

TABLE 5.35.

Temperature = 20°C.

Ketone = MEK except in run 3.94 where diethyl ketone was employed.

Nitrogen flow rate = 420 ml per min.

Ammonia flow rate = 950 ml per min. except in run 3.108 where it was 1150 ml per min.

Run No.	X_C	R_A	C_W. moles of water per litre.	C_B. moles of sodium hydroxide per litre.	C_K. moles of ketone per litre.	Y_S per cent	Y_T per cent
3.94	0.112	17.9	27.8	0.400	4.740	-	-
3.95	0.1125	17.7	48.5	0.500	1.735	22.5	17.0
3.96	0.125	15.9	55.6	0.218	1.515	33.0	26.6
3.108	0.116	20.9	45.0	0.154	2.370	23.8	34.5

5.3.2. Column Reactor.

This series of experiments was carried out in the apparatus shown in figure 3.11. Several different means of injecting the gases into the system were employed and in some experiments photographs were taken of the reactor in operation in order to estimate the size of the nitrogen-chlorine bubble. Recirculation of the ketone was employed in some cases and the rate was approximately 1.5 litres per minute. All the experiments were carried out at 20°C and methyl ethyl ketone (MEK) was used in all cases.

As in chapter 5.3.1. a few experiments were performed in which the product was an azine and not the isohydrazone. In most experiments the usual gas injection system was two $\frac{1}{8}$" jets situated about 1 cm apart.

5.3.2.1. Packed Column.

TABLE 5.36.

Recirculation was employed in all experiments except runs 3.40 and 3.41. The packing was 6 mm glass ballotini except in runs 3.43 and 3.46 where carbon chips were used.

Quantity of MEK in the column = 600 ml.

Run No.	Duration of run. mins.	Chlorine flow rate ml per min.	R_A	X_C	Y_S per cent	Y_T per cent	Total Flow
3.40	25	13.6	84.6	0.0314	75.6	73.4	a 1583.6
3.41	16	21.0	54.8	0.0475	81.5	79.8	1593.0
3.43	25 —c	23.2	49.6	0.0524	41.7	-	(b) 1596.2
3.44	30	20.5	56.1	0.0465	71.5	-	(a) 1584.5
3.46	24	13.5	85.2	0.0312	48.2	37.8	(b) 1586.5
3.48	30 —c	43.2	35.8	0.0932	57.5	54.2	(a) 2013.2

method of data reporting
confusing

5.3.2.2. Separate entry jets in a horizontal position.

TABLE 5.37.

Empty Column.

Recirculation was employed in all experiments except runs 3.73 and 3.75.

Quantity of ketone = 600 ml. except in runs 3.73 and 3.75 where it was 200 ml.

N_2 flow a 420 ml/min
throughout table

Run No.	Duration of run. mins.	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.45	30	13.43	70.6	0.0309	95.2	-
3.47	26	61.0	21.4	0.1265	68.0	-
3.68	30	31.0	30.6	0.0688	64.8	63.8
3.73	65	53.0	17.9	0.1120	27.2	-
3.75	22	43.4	21.9	0.0936	41.5	-

5.3.2.3. Separate entry jets in a vertical position.

TABLE 5.38.

Empty Column.

Recirculation was employed in all experiments.

Quantity of ketone = 600 ml.

Run No.	Duration of run. mins.	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.64	30	34.6	33.2	0.0762	59.0	57.3
3.65	30	26.1	44.1	0.0586	62.2	58.4
3.67	30	24.2	47.5	0.0544	67.4	64.8

5.3.2.4. Use of annular jets.

TABLE 5.39.

Recirculation was employed in all experiments.

Quantity of ketone = 600 ml.

Run No.	Duration of run mins	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.90	17	48.2	28.0	0.127	66.2	60.1
3.92	14	47.0	28.8	0.101	76.5	73.1
3.106	16	83.0	18.7	0.165	65.0	58.6

5.3.2.5. Other methods of gas injection.

TABLE 5.40.

Recirculation was employed in both experiments.

Quantity of ketone = 700 ml.

In run 3.110 the nitrogen-chlorine mixture was bubbled through a sintered glass disc.

In run 3.111 the nitrogen-chlorine mixture was bubbled through fine holes drilled in a P T F E plug.

In both experiments the ammonia was bubbled through a separate hole which was close to the nitrogen-chlorine entry.

Run No.	Duration of run mins	Chlorine flow rate ml per min	R_A	X_C	Y_S per cent	Y_T per cent
3.110	23	27.0	42.6	0.0674	82.3	81.8
3.111	22	62.5	21.6	0.1240	57.6	49.0

5.3.2.6. Synthesis of Azines.

TABLE 5.41.

Recirculation was employed in all experiments.

The same quantities of reactants were used in all experiments.

Concentration of MEK = 1.515 moles per litre.

Concentration of water = 55.6 " " "

Concentration of sodium hydroxide = 0.218 " " "

Run No.	Duration of run mins	Chlorine flow rate ml per min.	R_A	X_C	Y_S per cent	Y_T per cent
3.103	31	52.0	22.1	0.110	11.8	7.8
3.104	30	53.6	21.5	0.113	14.2	12.7
3.105	23	82.5	16.35	0.164	16.1	12.8

Sample Calculation.

Example; Run 3.53.

Air flow rate = 425 ml per min.

Ammonia flow rate = 1150 ml per min.

Duration of run = 35 minutes.

Volume of solution of ammonium chloride washings. = 1980 ml.

Volume taken for titration = 20 ml.

Volume of 0.1 M $AgNO_3$ added = 12 ml.

Volume of 0.1 M KCNS used in back-titration. = 5 ml.

∴ Weight of ammonium chloride deposited. $= 1.98 \times \frac{(12 - 5)}{20} \times 5.35$

= 3.71 gms.

Quantity of chlorine used = (3.71 x 0.664) gms.

= 2.46 gms.

Chlorine flow rate = $\frac{2.46}{35}$ = 0.0703 gm per min.

= $\frac{0.0703}{0.00298}$ = 23.6 ml per min.

$\therefore R_A = \frac{1150}{23.6} = 48.7.$

$X_C = \frac{23.6}{425 + 23.6} = 0.0526.$

But

1 mole Cl_2 ≡ 1 mole $N_2H_4H_2O$

$\therefore$ 1 gm Cl_2 ≡ 0.684 ml $N_2H_4H_2O$

Similarly

1 gm Cl_2 ≡ 1.835 gms $N_2H_4SO_4$

Thus if in run 3.53 a yield of 100 per cent of isohydrazone was obtained, then this would be equivalent to the following quantities of $N_2H_4H_2SO_4$ and $N_2H_4H_2O$.

$N_2H_4H_2SO_4$ = (1.835 x 2.46) gms

= 4.52 gms.

$N_2H_4H_2O$ = (0.684 x 2.46) ml

= 1.68 ml.

Potassium Iodate method of analysis.

Total volume of recovered solution from reactor. = 590 ml

50 ml of this solution was taken and placed on a watch glass. 5 ml of H_2SO_4 (50 per cent W/W) was added. The hydrazine sulphate formed was recovered and made up to a 87 ml solution.

Now if the yield of isohydrazone was 100 per cent, the quantity of hydrazine sulphate in the 50 ml sample would be $(\frac{50}{590} \times 4.52)$ gms

= 0.382 gms.

If this were made up to a 0.05 M solution the volume would be

$$\left(0.382 \times \frac{20}{130.124}\right) \text{ ml}$$

$$= \quad 58.7 \text{ ml.}$$

$\therefore$ Molarity of solution made up (assuming 100% yield). $= \quad \frac{58.7}{87} \quad \frac{M}{20}$

$$= \quad 0.675 \quad \frac{M}{20}$$

20 ml of this solution were taken and titrated with potassium iodate in the manner described in chapter 4.1.3.1.

Volume of 0.05M KlO_3 required $= \quad 9.3$ ml

$\therefore$ Yield based on KlO_3 method (Y_T) $= \quad \frac{9.3}{20 \times 0.675} \times 100$

$$= \quad 69\%$$

Colorimetric method of analysis.

If the yield of isohydrazone was 100 per cent, the dilution of equivalent hydrazine hydrate in the reactor effluent would be

$$\frac{1.68}{590} \quad = \quad \frac{285}{10^5}$$

Several dilutions were made and the corresponding colour sample was made up as described in chapter 4.1.3.2. The following values of optical density, and therefore yield, were obtained.

Concentration assuming 100% yield parts per 10^5	Optical density after 75 hours	Concentration parts per 10^5	Yield Y_S per cent
5.70	0.924	3.88	68.0
2.85	0.474	1.94	68.2
1.425	0.240	0.985	69.1

Average value of Y_S $= \quad 68.2\%$

CHAPTER SIX

DISCUSSION OF RESULTS

6. DISCUSSION OF RESULTS

In this chapter the results presented in chapter 5 are discussed. For convenience of reference the various headings and sub-headings of chapters 5 and 6 are the same.

6.1. Electrochemical Investigation.

6.1.1. Continuous system.

This series of results is shown in tables 5.1 - 5.3. In all the results tabulated the anode was of platinized titanium /Type 1/ and the cathode was of either the same material or stainless steel; preliminary results had shown that heavy corrosion of the anode occurred if it was constructed of nickel or stainless steel. Earlier experiments were carried out using ammonium nitrate as the electrolyte, but since it was later found that this compound interfered with the detection procedure, the results have not been presented.

As has been stated the detection procedure employed was that involving p - dimethylaminobenzaldehyde and the samples were made up in the same proportions as in the method described in chapter 4.1.3. Thus if Y ml of filtered effluent were obtained, then Y ml of a 2.5 per cent by weight solution of p - dimethylaminobenzaldehyde in methanol and 8Y ml of glacial acetic acid were added.

It can be seen from tables 5.1 - 5.3 that hydrazine was detected in only four of the experiments. This is probably due to the fact that in some experiments in the continuous system the residence time in the cell was very small. However it is likely that the most important reason is that the anode was corroded. It was found in later experiments on the batch system that the number of times the anode had been employed was a critical factor in determining if hydrazine was formed. The reason why the two experiments in which MEK was employed gave no indication of hydrazine formation is again probably due to the fact that the anode was corroded by previous use. Unfortunately at this stage of the investigation no record was kept of the anode condition and the results did not show sufficient promise to justify repetition. In run 1.13 no ketone was used and hydrazine was detected; this system was similar to that described by Pursley [52].

In the above series of experiments the surface areas of the anode and cathode were 4.1 cm^2 and 3.3 cm^2 respectively. If 0.1 gm of K Br were used as the electrolyte and the total volume of liquid was 40 ml the solution was 0.021 M.

6.1.2. Batch system.

The results obtained for this part of the investigation are shown in tables 5.4 - 5.11. A variety of different conditions were employed and their affect on the formation of hydrazine noted. For the results shown in tables 5.6 - 5.11 the condition of the anode before each run was also observed.

Initially acetone was used as the carbonyl compound and the results obtained with this ketone are shown in table 5.4. Hydrazine was detected in experiments where high and low concentrations of potassium bromide and acetone were employed. In experiments where the anode was stainless steel, the effluent from the cell at the end of the run had suspended in it reddish brown particles which were found to give a positive test for iron. Hydrazine was not detected in these examples; probably bromine, discharged at the anode, preferentially reacted with the electrode instead of the solvent ammonia. However it was possible to detect hydrazine when the cathode was of stainless steel as shown in run 1.23.

Similar results were obtained with methyl ethyl ketone as shown in table 5.5. In tables 5.6 - 5.9 the effect of the anode material is presented. It is apparent that when brand new platinized titanium [type I] was employed, hydrazine was detected in almost every experiment.

Initially with this material the cell effluent contained a small amount of suspended yellow particles, but after the anode had been used a few times the number of particles increased and their colour appeared to be more brown than yellow. It would therefore appear that anodic products such as bromine had attacked the anode and removed the platinum layer, thus exposing the titanium. It can be seen from the results that when the platinum layer had been removed, hydrazine was not detected in any subsequent experiment using this electrode. Normally this occurred after about three experiments or $1\frac{1}{2}$ - 2 hours.

When carbon and platinum were employed as anode materials, hydrazine was detected in most experiments. However it was found that with platinum a yellow layer had formed on the anode by the end of the run which could possibly be a complex ammoniated platinum halide. The greyish colour in the cell effluent in runs 1.70, 1.78 and 1.79 was caused by particles of carbon being removed by the solution. Three types of carbon were used ranging from graphite to gas carbon and in the latter case, corresponding to run 1.79, hydrazine was not detected.

In some of the later experiments potassium bromide was replaced by rubidium bromide and the results are shown in table 5.8. Hydrazine was detected when platinized titanium /Type 1/ was used, but not with platinized titanium /Type 2/. It would therefore appear that the surface of the anode played an important role in determining the products of electrolysis. The only apparent difference between the two kinds of platinized titanium is that type 2 had a smoother surface than type 1.

The results obtained by using electrolytes other than potassium or rubidium bromide are presented in table 5.9. It was decided to employ only the alkali metal halides because according to the literature survey discussed in chapter 2.2.2 they offered the best prospect of hydrazine being synthesised either as an azine or an isohydrazone. They are also simple compounds and attempts can therefore be made to predict the various products of electrolysis, and furthermore it was possible to detect hydrazine, in the form of an organic intermediate in their presence. As can be seen from table 5.9 hydrazine was not detected in any of the experiments carried out. In run 1.61 sodium chloride caused more corrosion of the platinized titanium /Type 1/ anode than corresponding quantities of potassium or rubidium bromide.

The reverse polarity switch was used in two experiments but it did not have the desired effect; no hydrazine was detected with either carbon or platinized titanium /Type 2/ electrodes. However hydrazine was detected when the rotating carbon disc was employed as the anode.

6.1.3. Summary.

From the above series of experiments it was concluded that hydrazine can be formed by electrolysis, but the concentration and overall yield obtained in this investigation were extremely low. Optical density measurements were made on some samples and the highest concentration of equivalent hydrazine hydrate detected was estimated to be in the region 5 - 10 parts per 10^5. From observations of the manner in which the colour developed it was likely that hydrazine was synthesised in the form of the isohydrazone.

It is impossible to give any indication of optimum values of temperature, concentration of electrolyte or quantity of ketone in the cell as the results were not quantitative. It is possible, however, that the best results were obtained when new platinized titanium /Type 1/ electrodes were employed. Practical difficulties prevented any study of the gaseous products of electrolysis or the surface of the anode before and after each experiment. Thus although hydrazine was detected in low concentrations in some experiments, this process did not offer much promise compared with the possibilities offered from the chlorine-ammonia chemical reaction fixed by a ketone. Consequently it was decided to investigate the synthesis of hydrazine by the fixation process using an alternative method.

6.2. Gas Phase Investigation.

These experiments were carried out in two parts. Initially the formation of chloramine was investigated and in these cases a ketone was not present in the reactor. Secondly the gas phase formation of acetone isohydrazone was investigated.

6.2.1. Chloramine Synthesis.

The results obtained in this series of experiments are presented in tables 5.12 - 5.15. It is apparent that even when the chlorine stream was considerably diluted with nitrogen and large excesses of ammonia were employed the yield of chloramine was still quite low. This was true for either a vertical or a horizontal reactor. Furthermore it was extremely difficult to run the reactor for very long periods because the chlorine jet persistently blocked with ammonium chloride. For an experiment lasting ten minutes it would be usual to unblock the jet at least four times.

In all the experiments tabulated the diameter of the chlorine jet was 3/16". However smaller jets, including a stainless steel syringe, were used but it was found that these blocked almost at once with ammonium chloride. If the reactor was in a vertical position and the 3/16" chlorine jet was employed, it was observed that when the ammonia flow rate was increased past a certain limit, turbulence in the reactor was greatly increased. Thus referring to run 2.4 it was noted that when the ammonia flow rate was 1150 ml per min, the reactor operated normally with the chlorine jet gradually blocking up, but when the flow rate was raised to 3380 ml per min great turbulence appeared in the reactor, especially in the vicinity of the chlorine jet. This recirculation around the chlorine jet was considered undesirable and therefore the flow rate was cut back to 1150 ml per min.

In all the experiments carried out the yield of chloramine was very low; the highest value obtained was only 38.2 per cent. The reason for this was due to bad mixing in the primary reaction between chlorine and ammonia, or to chloramine being carried back into the reaction zone where it further reacted to form ammonium chloride.

$$6\ NH_3 + 2\ Cl_2 + NH_2Cl \longrightarrow N_2 + 5\ NH_4\ Cl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ 6.1.$$

It was not possible to repeat the work of Sisler et al [68] who claimed to have run their reactor almost indefinitely without the chlorine jet blocking. Furthermore the yields of chloramine obtained in this investigation were much lower than those obtained by Sisler. Although it is possible that differences in reactor design account for these discrepancies, it was also found to be extremely difficult to run the reactor with small chlorine jets as used by Sisler and Drago [68, 71].

From the results obtained it was concluded that, because the yields were low and the chlorine jet blocked so rapidly with ammonium chloride, this process in its present form did not offer much promise from an industrial viewpoint. Therefore a reactor was constructed in which a ketone was introduced into the reaction zone; by this means it was hoped that the chloramine would be fixed in the form of an isohydrazone and therefore improve the yields obtained in the process.

6.2.2. Isohydrazone Synthesis.

In this part of the investigation four experiments only were carried out and they are presented in Tables 5.16 and 5.17. This was because similar trouble to that described above was encountered, with the chlorine jet blocking with ammonium chloride. However higher yields than in the previous section were obtained and in run 2.15 a yield of 84 per cent was measured. It therefore appears that the acetone helped to prevent further reaction of chloramine to ammonium chloride by fixing it in the form of acetone isohydrazone.

It was found that when the contents of the two dreschel bottles containing the reactor condensate were analysed separately, most of the isohydrazone was recovered in the first bottle. Thus in run 2.16 the volume of condensate collected in the first bottle was 69 ml and in the second bottle 4.4 ml. In addition the concentration of isohydrazone in the first bottle was 1.37 times that in the second bottle. The operating temperature of the reactor fluctuated as the experiment progressed, but in most cases it was maintained between 75 - 130°C, which is a similar temperature range to that used by Abendroth and Henrich [16, 20].

The results obtained in this investigation were also similar to those quoted by Abendroth and Henrich for atmospheric pressure. In this work the reactor was not run at reduced pressures and therefore the high yields obtained by the above authors under these conditions could not be compared. However it can be seen from run 2.15 that reasonable yields could be realised at atmospheric pressure providing adequate mixing of the reactants was obtained. In practice this was difficult to achieve in the gas phase and in addition it was not possible to run the reactor for more than a few minutes without the chlorine jet blocking. Therefore it was decided to construct a reactor in which chlorine and ammonia were bubbled into liquid ketone. In this way it was hoped to obtain better mixing in the reactor and at the same time eliminate the problem of ammonium chloride blocking the chlorine jet.

6.3. Gas-Liquid Investigation.

This investigation was carried out on two types of reactor. Initially a stirred tank reactor was employed, but the results obtained showed that stirring was not essential for high yields. Therefore the reaction was also carried out in a column reactor.

6.3.1. Stirred Tank Reactor.

The apparatus shown in figure 3.9. was constructed for this investigation and the results are presented in tables 5.18 - 5.35.

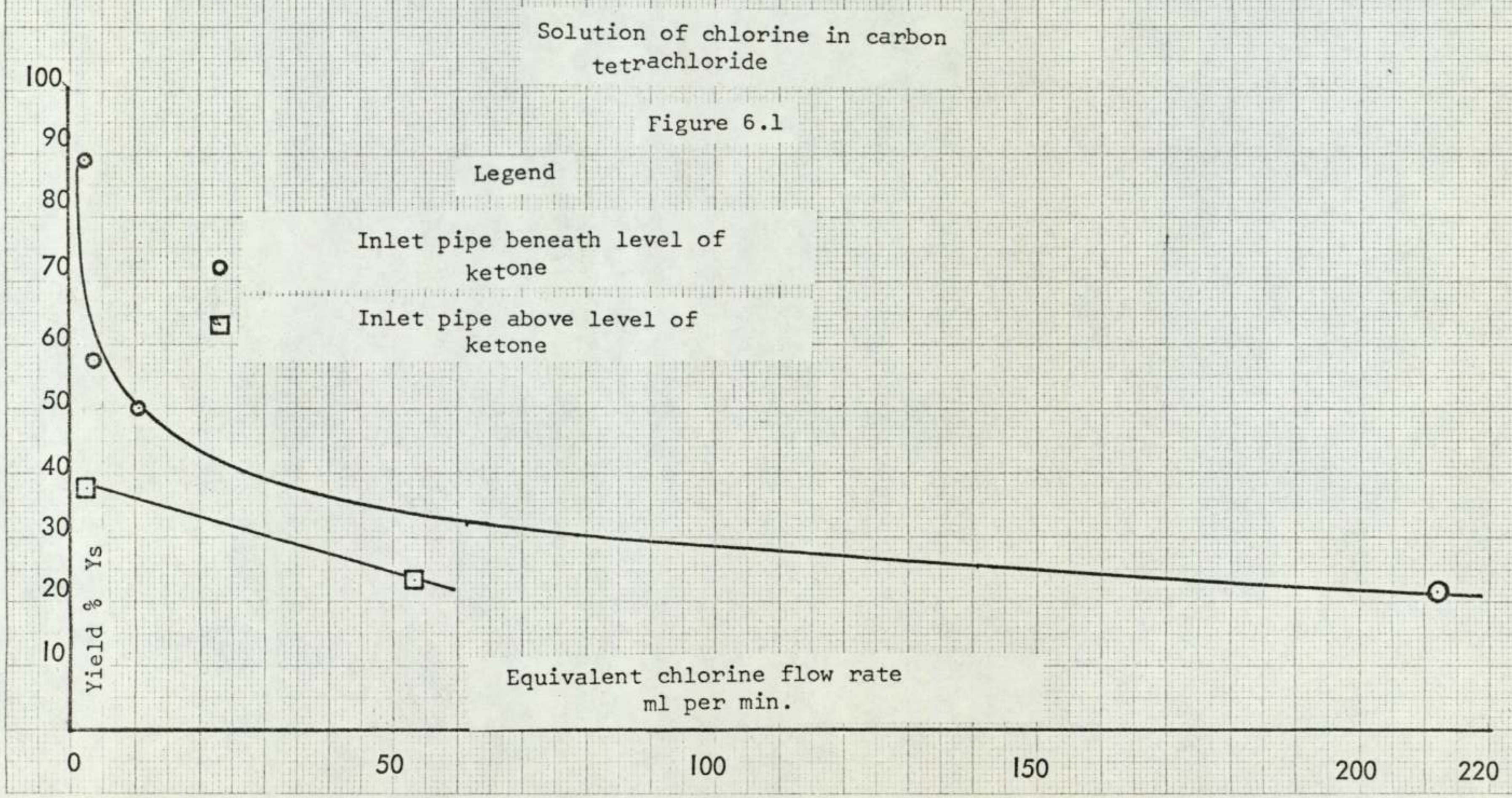
6.3.1.1. Solution of chlorine in carbon tetrachloride.

Chlorine was dissolved in carbon tetrachloride and the mixture was subsequently allowed to flow into the reactor where it reacted with ammonia. The ammonia was bubbled in at the same time. The results are presented in table 5.18 and plotted in figure 6.1. It is apparent that the yield of isohydrazone was higher when the inlet pipe dipped beneath the surface of the ketone. This was expected because, when the inlet pipe terminated above the level of the ketone it was probable that some of the chloramine was carried out of the reactor without coming into contact with the liquid phase.

In most experiments the yield of isohydrazone was low. An exception was run 3.114 where the equivalent chlorine flow rate was only 2.19 ml per min. Thus this system did not give good yields at reasonable chlorine flow rates and so it was decided to introduce the chlorine into the reactor in a stream of nitrogen or air.

6.3.1.2. Effect of temperature and dilution of chlorine stream.

The results obtained in this investigation are presented in tables 5.19 - 5.24 and plotted in figures 6.2 and 6.3. Experiments were carried out at five different temperatures and at various values of X_C and RA. It can be seen that the yield of isohydrazone was increased by reducing the concentration of chlorine in the nitrogen carrier gas.



Solution of chlorine in carbon tetrachloride

Figure 6.1

This is seen quite clearly in figure 6.2. In addition it can be seen that although there is some scatter in the points plotted, it appears that there is an optimum temperature in the region of 0°C. Results obtained at similar values of X_C and R_A are plotted in figure 6.3., and these also indicate a maximum temperature in the same region. The reason why there is such considerable scatter is probably due to the fact that the actual values of X_C and R_A often differed markedly from the average value quoted. Differences in the values of R_A could also account for the scatter in figure 6.2., although the results indicated that providing this ratio was 20-25 or greater it did not unduly affect the yield.

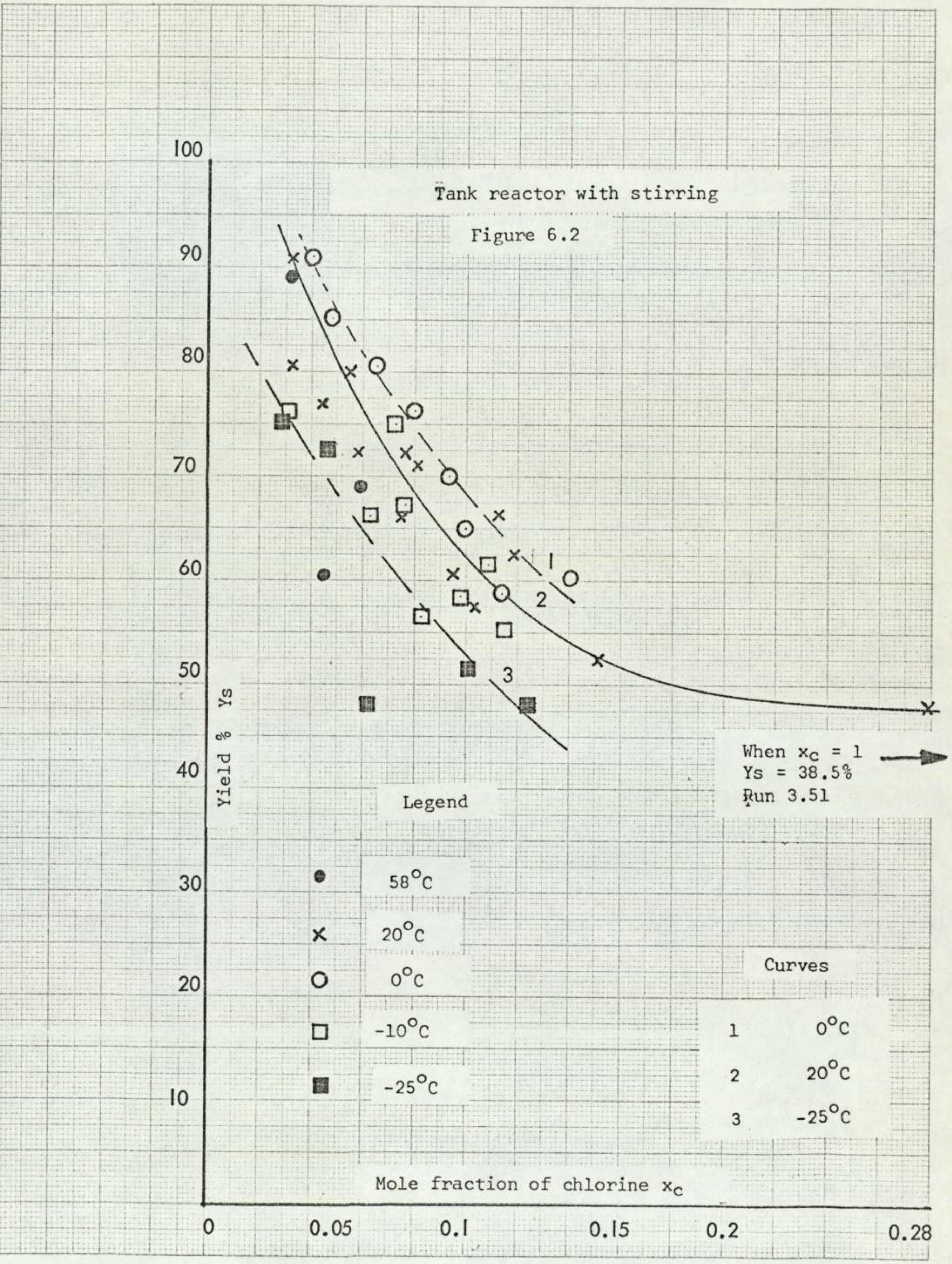
It can be seen that when the value of X_C was increased past 0.2 the yield fell off slowly to a value of 38.5 per cent. In addition to obtain yields in the region of 90 per cent the value of X_C had to be less than 0.04. This completely contradicts the work of Paulsen and Huck [18, 21, 22, 43] who claimed yields of over 90 per cent at much higher concentrations of chlorine in nitrogen. In fact in some of their examples only the ammonia stream was diluted; chlorine being added undiluted. The conflicting nature of these conditions was discussed in chapter 2.5.1.

Paulsen and Huck used annular jets as a means of injecting the gases into the reactor and this does help to increase the yield. However as will be seen in chapter 6.3.2., where the results obtained on the column reactor are discussed, values of X_C of the order of 0.1 were still necessary to obtain yields over 75 per cent. Therefore the yield data presented by Paulsen and Huck [18, 21, 22, 43] must be considered as erroneous. The temperature of the reaction fluctuated by a few degrees during an experiment and thus the values quoted in chapter 5 are average values. This also explains some scatter in the points plotted. However it is obvious from figure 6.2. that decreasing the temperature to -25°C considerably reduced the yield of isohydrazone. This could possibly be due to increased stability of the addition compound (ketone - ammonia intermediate), thus reducing the concentration of ketimine in the reactor. It is also possible that the overall rate of reaction between chloramine and ketimine was reduced at these lower temperatures.

It is difficult to give a reason why the yield decreased at higher temperatures. This affect is not so marked as that at low temperatures, and there are examples of higher yields being obtained at 20°C than under similar conditions at 0°C. In addition one of the three runs carried out at 58°C compared favourably with similar experiments at 20°C and 0°C. It is possible that 0°C was the optimum temperature for the formation of chloramine by the ammonia-chlorine reaction or, that at higher temperatures the rate of yield reducing side-reactions was increased.

The formation of azines was not detected, either by their unique colour development or by any discrepancy in the two methods of analysis, in any of the experiments carried out in this section of the investigation. Although it was possible that the azine was present in trace quantities, it would appear that the only important product formed when just a ketone was employed as the liquid phase was the isohydrazone. Acetone was used instead of MEK in some runs and similar yields were obtained.

It is seen in tables 5.19 - 5.24 that activated carbon (Caldacarb K.45/6/16) was placed in the reactor in some experiments. This did not effect any increase in yield. In addition, increasing the quantity of ketone in the reactor from 500 ml to 600 ml did not affect the yield. It can therefore be assumed that the hold-up time in the reactor was sufficient for the reaction of chloramine with ketimine to proceed to completion when the quantity of ketone was only 500 ml. The amount of ammonium chloride carried out of the reactor was determined in some experiments and these measurements were used to indicate in which phase the various reactions were taking place. This will be discussed in detail in chapter 7.



Tank reactor with stirring

Figure 6.2

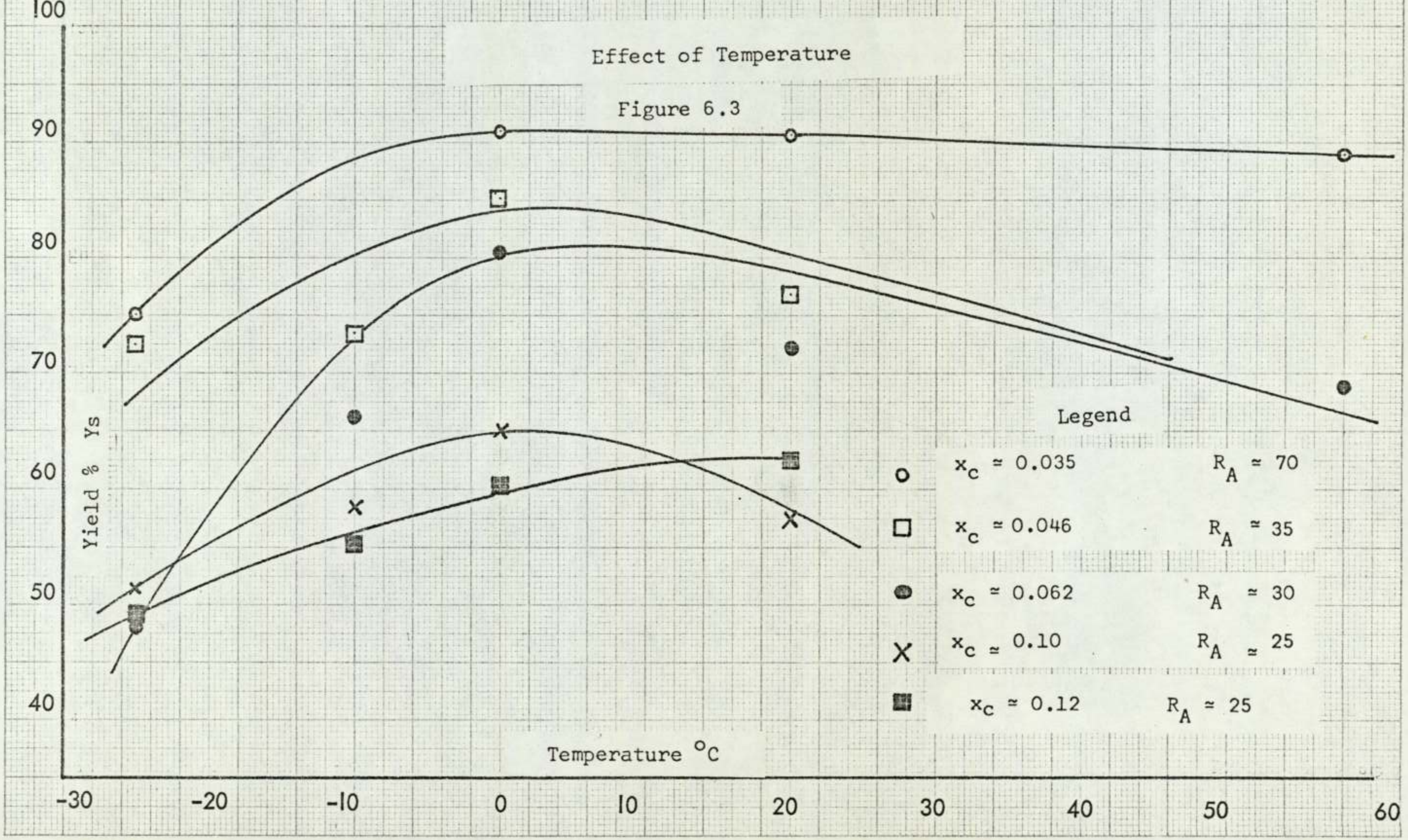


Figure 6.3

Effect of Temperature

6.3.1.3. Unstirred reactor using either air or nitrogen as the chlorine diluent.

The results obtained in this investigation are presented in tables 5.25 - 5.28 and plotted in figure 6.4. Experiments were carried out at $0^{o}C$ and $20^{o}C$ using both air and nitrogen as the chlorine diluent. It can be seen in figure 6.4. that the yields at $0^{o}C$ were higher than those at $20^{o}C$ under corresponding conditions by between 5-10 per cent. In addition the results obtained without stirring were similar to those obtained with stirring. This suggested that the overall rate controlling parameter was the value of the mass transfer coefficient in the liquid phase. Thus Calderbank and Moo-Young /160/ found that k_L was substantially independent of power input. Furthermore it will be shown in chapter 7 that the chloramine was formed in the gas phase and subsequently diffused into the liquid where it reacted with the ketimine to form the isohydrazone.

Valentin and Preen /161/ correlated the power consumption of an agitator with a dimensionless expression equivalent to the Flow Number. This expression was

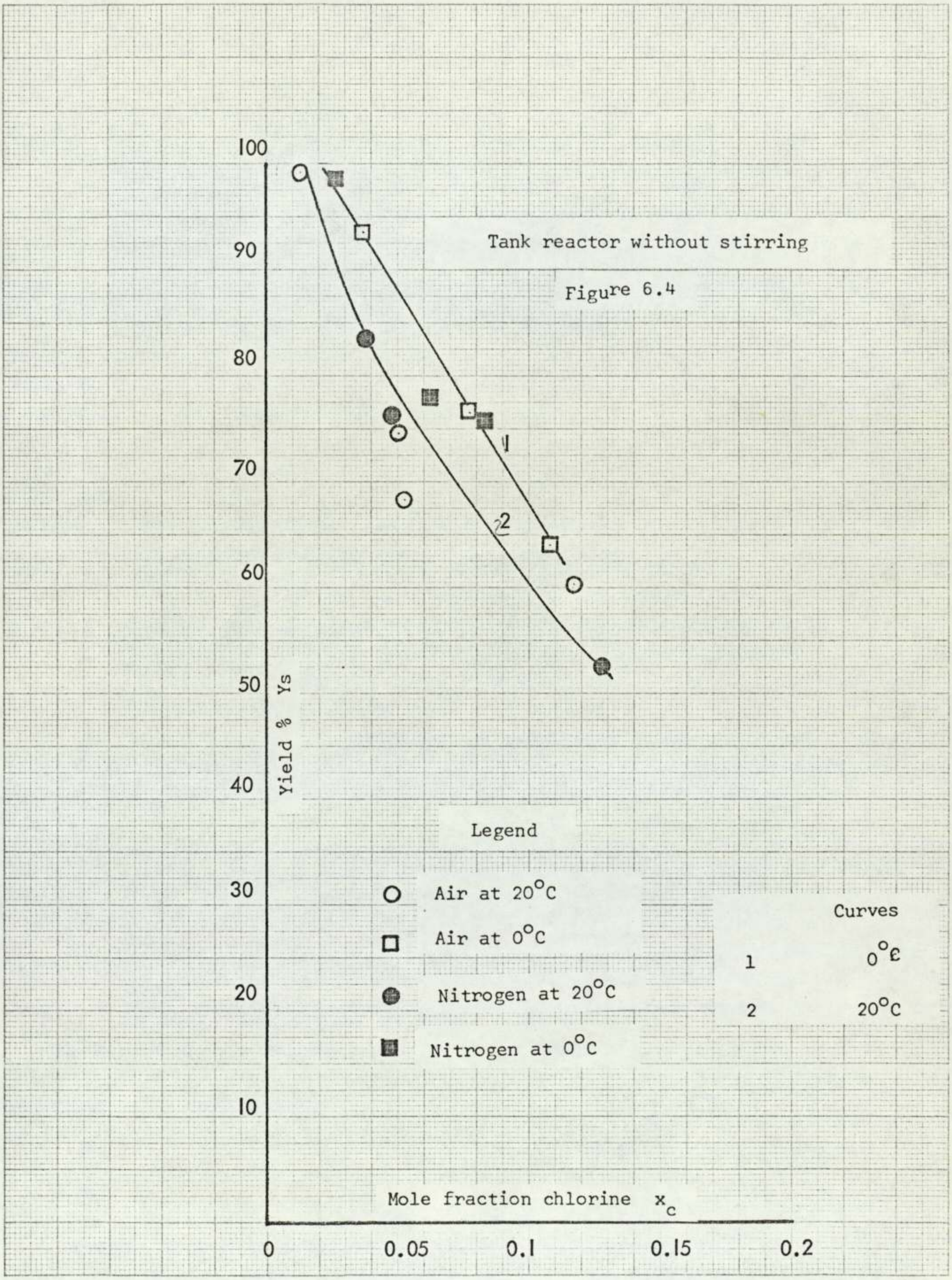
$$\frac{Q}{N\, d_s^3}$$

where Q = Gas flow rate

N = Speed of rotation of agitator.

d_s = Agitator diameter.

It was found to equal 0.0371 under normal conditions and this indicated that the agitator was operating in the transition region where "flooding" begins to occur. However it was still likely that the interfacial area was increased by agitation. The results obtained on this unstirred system are compared with those obtained from the stirred tank reactor and the column reactor in figure 6.10.



Tank reactor without stirring

Figure 6.4

It is apparent from figure 6.4 that similar results were obtained when either air or nitrogen were used as the chlorine diluent. This is important from the commercial point of view because of the lower cost of supplying air. However in most of the experiments carried out on both the stirred tank reactor and the column reactor, nitrogen was used as the diluent in order to standardise the results.

6.3.1.4. Effect of high chlorine flow rates.

The results obtained are presented in table 5.29 and plotted in figure 6.5. Chlorine flow rates ranging from 107-406 ml per min. were investigated. In order to accommodate the copious quantities of ammonium chloride produced, a larger filter was inserted into the system. Apart from run 3.29 the results are somewhat lower than those presented in chapter 5.3.1.2 for the stirred tank reactor. In the case of run 3.52 the value of R_A was below the stoichiometric requirement and this explained the extremely low yield obtained. The temperature in the reactor increased to $52^{\circ}C$ in seven minutes in this experiment; this was caused by the formation of nitrogen trichloride. Normally the temperature increased only a few degrees in thirty minutes.

Thus it would appear that with the reactor in its present form, the upper limit for the chlorine flow rate for reasonable yields was 150 ml per min. If a manifold was inserted into the chlorine supply and separate inlets employed it is possible that higher flow rates of chlorine could have been tolerated. In this way local excess of chlorine could possibly be avoided.

6.3.1.5. Use of higher ketones.

These results are presented in table 5.30 and plotted in figure 6.6. Several different ketones were employed at various temperatures. This variation in temperature was probably the main reason for the scatter encountered in figure 6.6. The results were in general agreement with

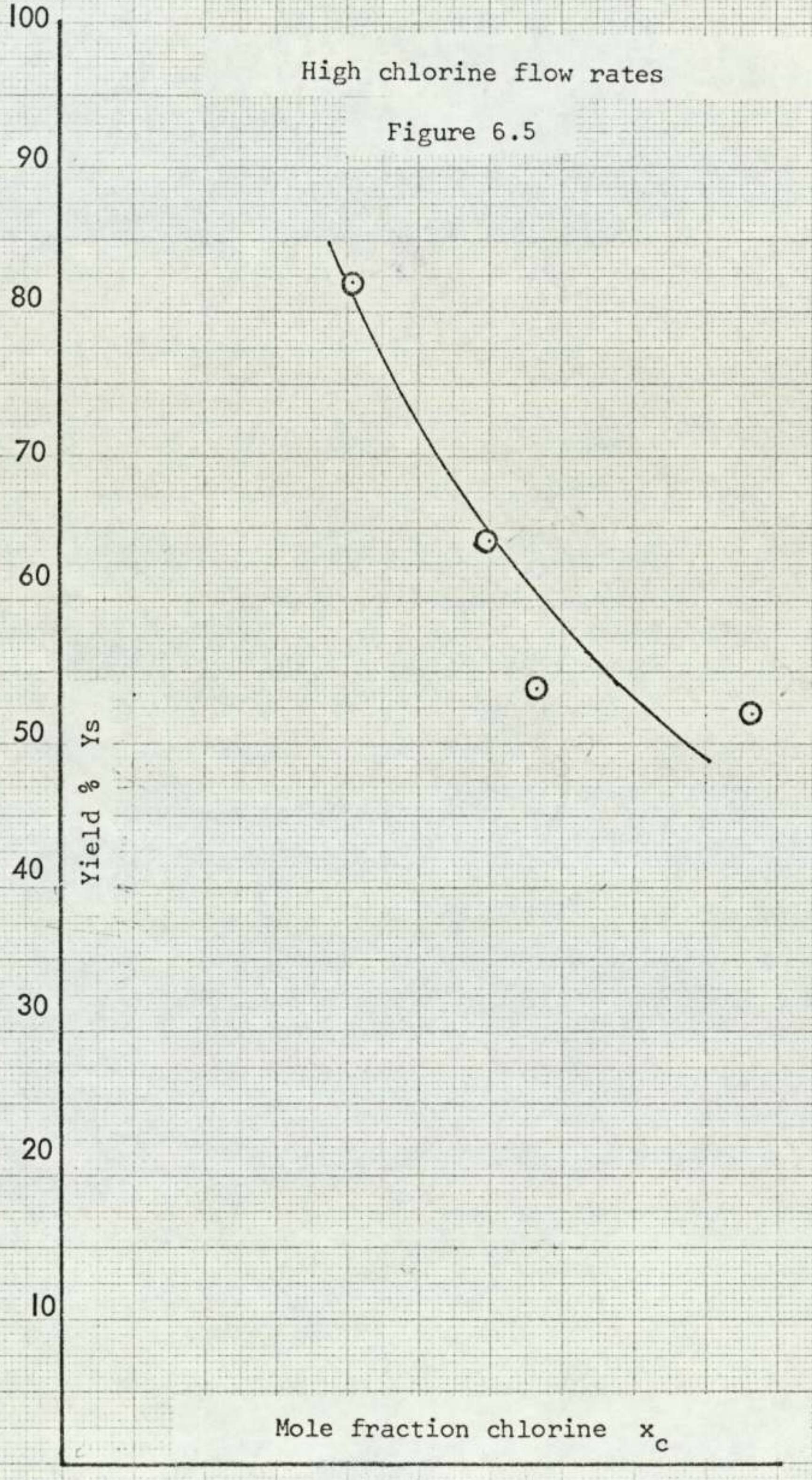
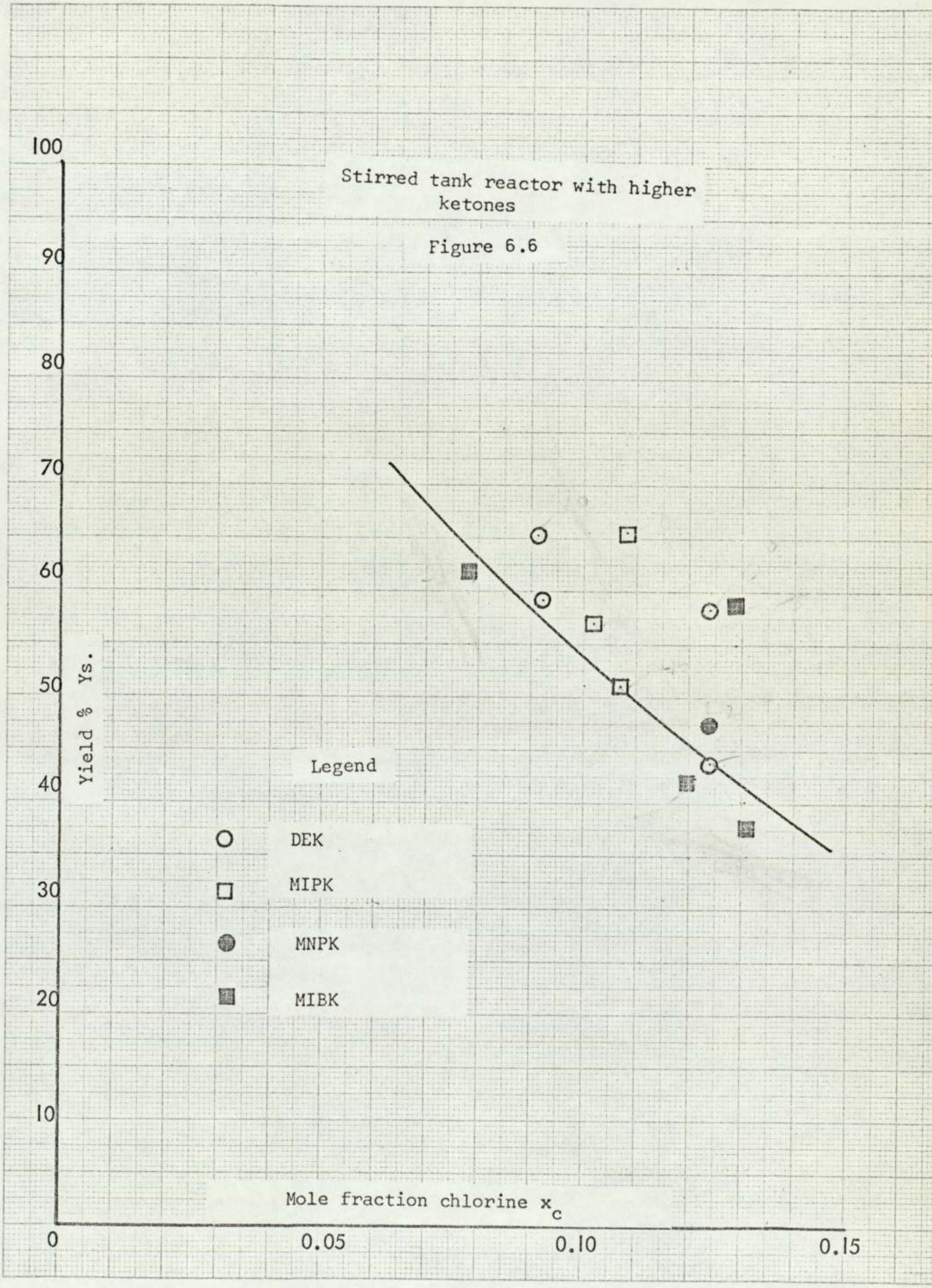

High chlorine flow rates
100
90
80
70
60
50
40
30
20
10
0
Yield % Ys
0.05
0.10
Mole fraction chlorine x_c

Figure 6.5



Stirred tank reactor with higher ketones

Figure 6.6

those plotted in figure 6.2 but it was possible that the optimum temperature was different for each ketone.

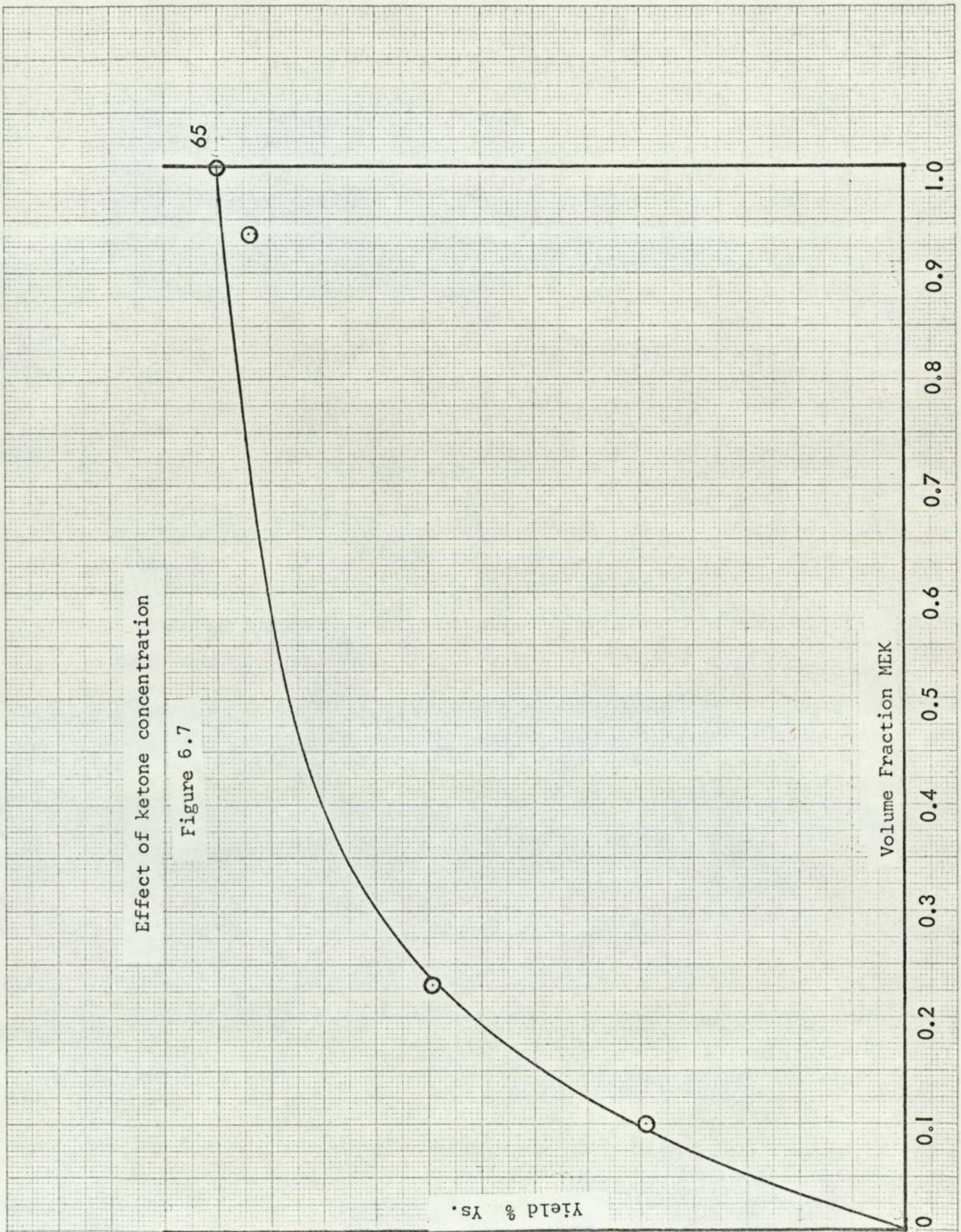
In this series of experiments the reactor was run for much longer periods and in some cases up to three hours. Because the results were similar to those obtained for shorter duration it can be assumed that operating the reactor for long periods does not affect the yield. However it is probable that this will only be true at low concentrations because of the yield reducing reaction between chloramine and isohydrazone.

6.3.1.6. Effect of ketone concentration.

The results obtained are presented in table 5.31 and plotted in figure 6.7. Three experiments were carried out at similar values of X_C and R_A but at different ratios of water to ketone. The ketone concentration was expressed as a volume fraction in order to help draw figure 6.7 accurately. This was because if mole fractions were used the points would be very near to the yield axis. No data was obtained in the immiscible region formed by MEK and water, although by the end of run 3.113 a concentrated aqueous solution of ammonium chloride had separated out from the ketone.

In figure 6.7 the origin is an extra point because the yield must be zero when the concentration of MEK is zero. The yield when the volume fraction of MEK was unity was obtained from figure 6.2. Paulsen and Huck [43] claimed good yields in a water-ketone emulsion at 0-20°C but as no data was presented it was impossible to compare their work with the results obtained in this investigation.

It is apparent from figure 6.7 that the yield of isohydrazone decreased when the concentration of ketone was reduced or correspondingly the concentration of water increased. This could have been due to the reduced ketimine concentration in the reactor, caused by the lower ketone concentration, which allowed the chloramine to participate in other yield reducing reactions. Another possible explanation was that as the



Effect of ketone concentration

Figure 6.7

ketimine concentration was reduced, the mass transfer rate was reduced and therefore unreacted chloramine left the reactor in the nitrogen stream. Furthermore it was likely that the presence of such considerable quantities of water affected the equilibrium of the MEK-ammonia system and further reduced the ketimine concentration. In this set of experiments the formation of azines was not detected.

6.3.1.7. Use of acetophenone as the carbonyl compound.

Three experiments were carried out to investigate the type of compound formed when acetophenone was employed as the carbonyl compound, and they are presented in table 5.32. In runs 3.39 and 3.86 the value of Y_S is based on a calibration graph for azines and in run 3.107 the value is given for both azine and isohydrazone calibrations. This was because the latter run was conducted at a much lower temperature than the first two, and under these conditions it appeared that the isohydrazone was preferentially formed. It was also observed that the temperature rise in the reactor was slightly higher than that normally encountered with the MEK system.

Paulsen and Huck [43] claimed that at 10°C the azine was the major product, but it was also stated by Paulsen [21] that at 0°C the isohydrazone was obtained in good yields. The results obtained in this investigation support the above authors in their claim that when the temperature is reduced the isohydrazone is preferentially formed, but it was not possible to synthesise this compound in the same yields.

The experiments were carried out at similar values of X_C and R_A and thus the difference in yields was almost certainly due to temperature effects. Excellent agreement between Y_S and Y_T was obtained in run 3.39. In this experiment the acetophenone azine formed was recovered and used in calibration 9. Its infra-red spectrum is shown in figure 4.14 and it is similar to that obtained for the compound prepared from the reaction of acetophenone and hydrazine shown in figure 4.15. This conclusively proved that the azine was formed in run 3.39. In run 3.86 it was deduced, by inspecting the values of Y_S and Y_T, that a mixture of the two compounds was formed but in run 3.107 it appeared that the isohydrazone was the major product.

6.3.1.8. Use of liquid ammonia.

Two experiments were carried out on this system and they are presented in table 5.33. In both experiments a gas stream consisting of nitrogen and chlorine was bubbled into the liquid. Even at the end of the experiment ammonia was still present in considerable excess. The value of R_A quoted was the average value during the experiment.

It can be seen that the yields were lower than those obtained for the stirred tank at -25°C; run 3.116 was slightly lower but run 3.109 was considerably less. These results do not agree with those quoted by previous investigators /17, 19/ who claimed yields of over 90 per cent using this system. In addition it was found to be extremely difficult to operate this reactor as the chlorine jet tended to block with ammonium chloride far more readily than with the stirred tank reactor. The low yields obtained with this system were probably due to the low temperature as it was shown in chapter 6.3.1.2. that the yield fell off markedly when the temperature was reduced below -10°C. Another possible reason for the low yields was the reduced diffusivity of ammonia at the low temperatures employed.

6.3.1.9. Miscellaneous experiments.

These experiments were carried out on unusual systems and are presented in table 5.34. Runs were carried out using amines, cyclohexanone and benzaldehyde in the reactor but in no case was it possible to detect an organic intermediate of hydrazine. However this could have been caused by the analytical procedure not being adequate for these particular conditions.

Where amines were used in place of ammonia there was no precipitate in the reactor but white fumes appeared in the vapour space above the liquid level. It was impossible to obtain any value of yield by the two analytical procedures developed. Thus either the methods developed in chapter 4.1.3 did not apply to N- substituted isohydrazones or the yield was very low. Abendroth /107-109/ carried out this reaction in the gas phase and therefore no comparison can be made between his results and those obtained in this investigation.

When cyclohexanone and benzaldehyde were employed as the carbonyl compound it was also impossible to detect an organic hydrazine derivative. In both experiments the temperature rose very rapidly and in the case of benzaldehyde it was probable that the ammoniated complex was formed. Paulsen /18/ obtained his results for cyclohexanone and benzaldehyde at low temperatures and claimed yields of the isohydrazone of 36 per cent and 41 per cent respectively. Because of the difference in temperature it is impossible to compare Paulsen's results with those obtained in this investigation.

6.3.1.10. Synthesis of azines.

The formation of azines was investigated in four experiments and the results are presented in table 5.35. In run 3.94 where diethyl ketone was employed the yield was so low that it was impossible to determine by either method of analysis. Because of the low solubility of diethyl ketone in water there were two liquid phases present in the reactor.

In the other three runs, MEK was employed in sufficiently low quantities that the reactor liquid formed one homogeneous phase. Low yields were obtained in all cases and although the agreement between the two methods of analysis was not good they did indicate values of the same order of magnitude. The low yield was almost certainly caused by the presence of considerable excess sodium hydroxide which reacted with some of the chloramine formed. The mechanism of the azine formation reaction was different to that of the isohydrazone formation reaction. In the former case chloramine reacted with ammonia to form hydrazine which subsequently reacted with ketone to form the hydrazone and eventually the azine. There were several other possible decomposition reactions and these also were partially responsible for the low yield obtained.

It therefore appeared that it was essential to maintain strict control of the pH in this system and to ensure that only sufficient alkali to prevent the formation of ammonium chloride, which in turn prevented the formation of the ketimine [162], was present. It was also observed that the temperature rise was greater in the azine system than in the isohydrazone system. This was caused by the high heat of solution of ammonia in water.

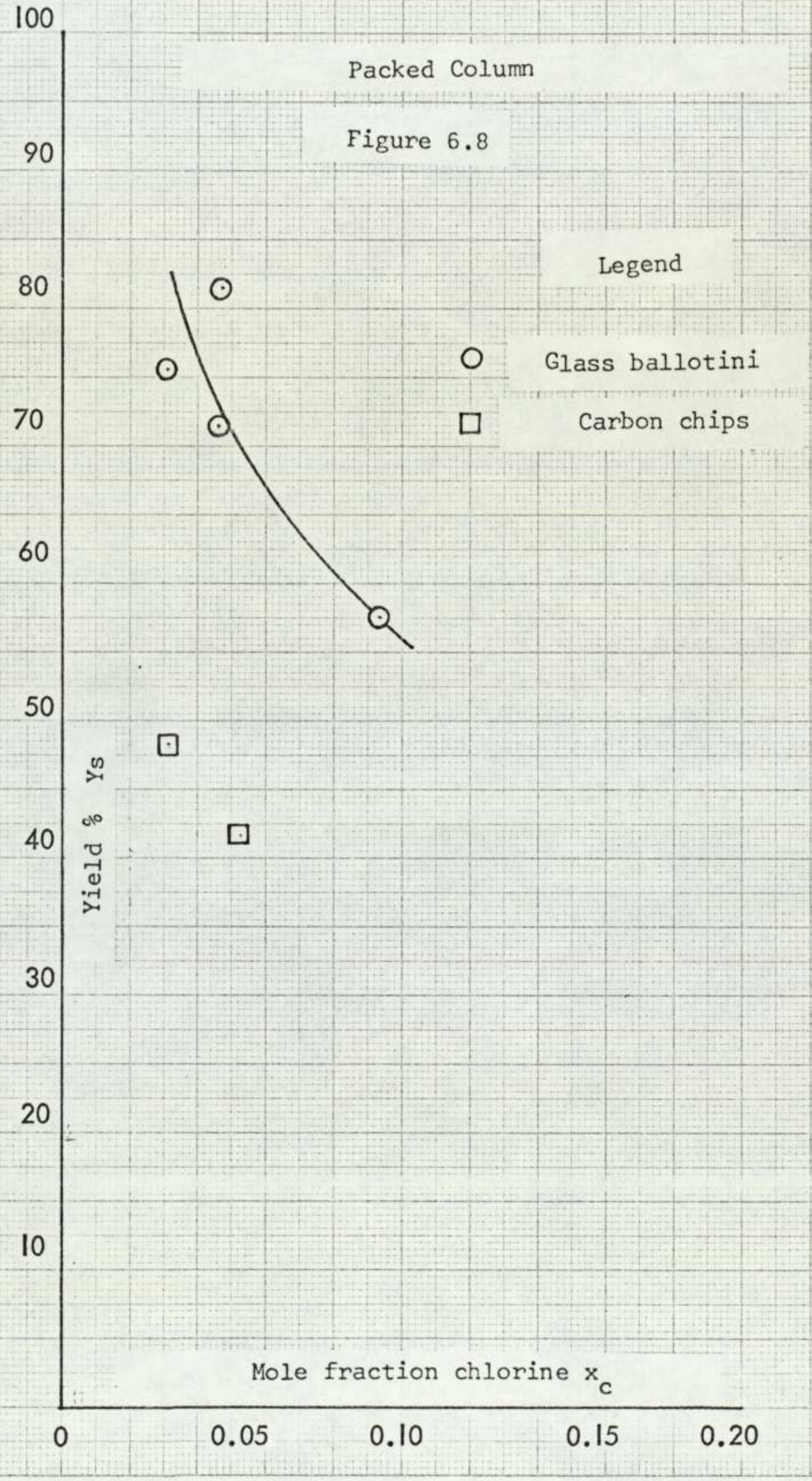
Most of the previous work on the formation of azines by the fixation process was carried out in aqueous solutions of sodium hypochlorite and ammonia. High yields were claimed [85-88, 125] and this was probably due to the fact that there was no excess alkali present in the reactor. Crosskinsky et al [41] employed chlorine but used a two stage process; the first stage taking place in the gas phase and the second stage taking place in the liquid phase.

6.3.2. Column Reactor.

The apparatus shown in figure 3.11 was used in this investigation and the results are presented in tables 5.36 - 5.41.

6.3.2.1. Packed Column.

The results obtained are presented in table 5.36 and plotted in figure 6.8. Two types of packing were employed, namely, carbon chips and 6 mm diameter glass ballotini. The yields obtained using the ballotini



Packed Column

Figure 6.8

were comparable with those obtained on the tank reactor but when carbon was used as the packing the yields were considerably lower, and in addition there was a rapid increase in temperature in the vicinity of the gas inlet jets.

The reason for this was that in the latter case the pressure drop over the column was large and therefore when the pump was switched on the ketone drained from the column and formed a reservoir of liquid at the top of the packing. Thus a gas phase reaction instead of a gas-liquid reaction was taking place. Furthermore the mixing of the reactants was extremely poor because recirculation of the gas stream around the chlorine jet took place which caused nitrogen trichloride to be formed and thereby resulted in a rise in temperature and a drop in yield. The results obtained using carbon were similar to those obtained for the gas phase reactor presented in chapter 5.2.

When glass ballotini was used as the packing it was found that recirculation of the ketone did not affect the yield. This was probably because there was adequate mixing in the column and also because the isohydrazone was formed in dilute solutions. Although reasonable yields were obtained with this system it was found that ammonium chloride tended to bridge between individual packings and thus impede the flow of liquid down the column and also cause channelling of the gas stream up the side of the column. It was therefore decided to employ an empty column.

6.3.2.2. Empty column.

The results obtained in this investigation are presented in tables 5.37 - 5.40 and plotted in figure 6.9. Several types of gas injection system were employed and the affect on yield was noted.

It is obvious from figure 6.9 that the best results were obtained when annular jets were employed. This conforms with the mechanism proposed in chapter 7 which requires local excess of ammonia around the nitrogen bubble in order that chloramine be formed in stoichiometric quantities.

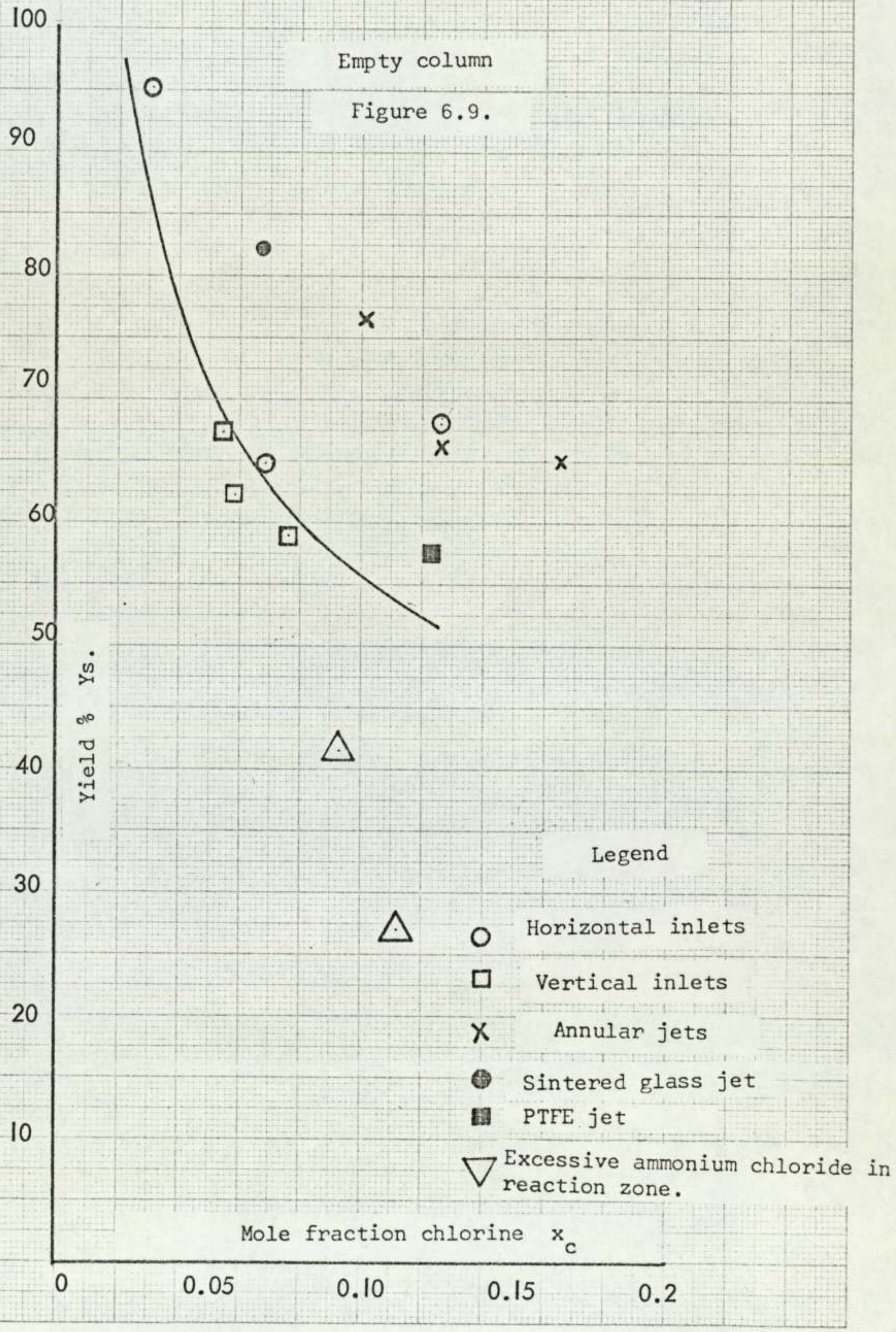
There was probably a slight increase in yield when horizontal inlets as opposed to vertical inlets were employed, probably caused by better mixing of the ammonia and chlorine. The sintered glass jet and the P T F E jet gave yields intermediate between the annular jet system and the usual vertical or horizontal system.

The yields obtained with the sintered glass jet and the P T F E jet corresponded with the stirred tank results. However the yields obtained with the packed column and the usual vertical or horizontal inlets on the empty column, although comparable with the stirred tank results, were slightly lower. It was assumed that the smaller nitrogen bubbles obtained with the sintered glass jet and the P T F E jet were of a similar size to those obtained in the stirred tank reactor. The bubbles obtained in the other column systems were larger and were calculated and measured to be 0.8 - 1.0 cm diameter. Thus decreasing the interfacial area in the column did slightly reduce the yield.

It was apparent from runs 3.73 and 3.75 that when excessive quantities of ammonium chloride were present in the reaction zone the yield fell off sharply. These conditions were achieved by employing only 200 ml of ketone in the column without any recirculation. A comparison of the results obtained on the column reactor, the stirred and unstirred tank reactor is shown in figure 6.10 and a reasonable agreement between the systems was obtained.

6.3.2.3. Synthesis of azines.

Three experiments were carried out on this system using the same concentrations of MEK, water and sodium hydroxide that were employed in run 3.96 on the stirred tank reactor. Lower yields were obtained with the column reactor and this was probably caused by the lower interfacial area in this system. Thus as with the stirred tank reactor it would appear that strict control of the pH was necessary before high yields could be realised.



Empty column

Figure 6.9.

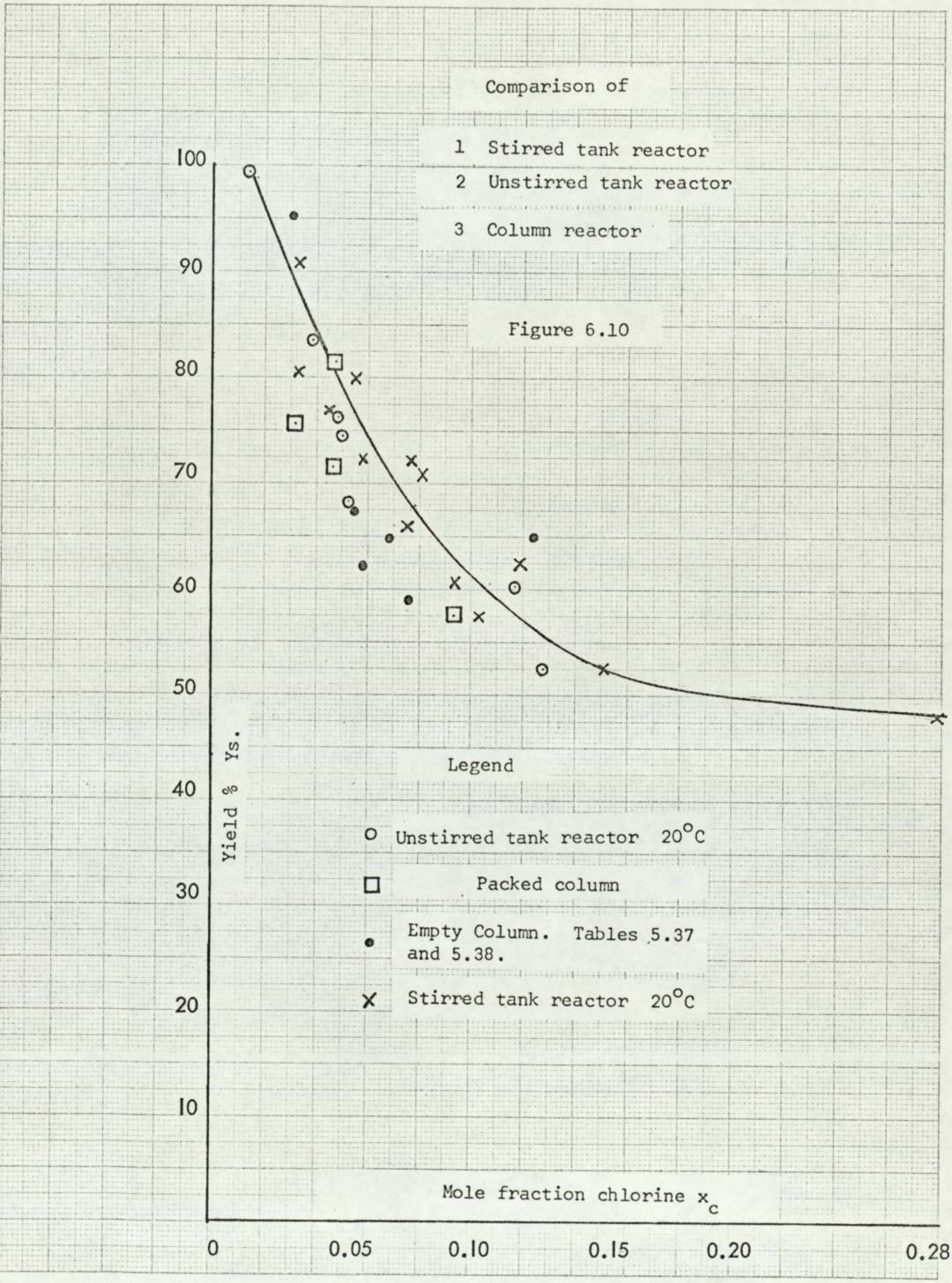


Figure 6.10

Comparison of

1 Stirred tank reactor
2 Unstirred tank reactor
3 Column reactor

CHAPTER SEVEN

MASS TRANSFER PROCESSES IN THE REACTOR

7. MASS TRANSFER PROCESSES IN THE REACTOR.

7.1. Reaction Path.

A nitrogen-chlorine mixture and ammonia were introduced into the reactor through separate jets. Nitrogen was insoluble in the ketone and therefore bubbles of nitrogen containing chlorine passed through the ammonia/ketone solution. By this time the chlorine had reacted to form chloramine and ammonium chloride, and the effluent gas stream contained fine particles of the latter compound. The chloramine subsequently reacted with the ketimine to form the isohydrazone. It was possible that:-

1. Ammonia dissolved in the ketone and diffused into the nitrogen bubble where it reacted to form chloramine which then diffused into the liquid to react with the ketimine.
2. Ammonia and nitrogen-chlorine bubbles coalesced and formed chloramine which then diffused into the liquid to react with the ketimine.
3. Chlorine diffused into the liquid phase where it reacted to form chloramine which subsequently reacted with the ketimine.

The reactions taking place were:-

$$2\ NH_3 + Cl_2 \longrightarrow NH_4Cl + NH_2Cl \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 7.1.$$

$$NH_3 + R_1R_2CO \rightleftharpoons R_1R_2C(OH)NH_2 \rightleftharpoons R_1R_2CNH + H_2O \quad \ldots\ldots\ 7.2.$$

$$NH_2Cl + NH_3 + R_1R_2CNH \longrightarrow R_1R_2CN_2H_2 + NH_4Cl \quad \ldots\ldots\ldots\ 7.3.$$

Thus if case 3 was true and reaction 7.1. took place in the liquid phase, then it was unlikely that ammonium chloride would be present in the effluent gases unless the gas stream actually picked up solids as the bubbles rose through the reactor. This was tested by bubbling nitrogen through a well stirred suspension of MEK and ammonium chloride. It was found that even after an hour there were no solids removed from the suspension. Thus the reaction between ammonia and chlorine appeared to have taken place in the gas phase.

Several experiments were carried out in which the yield of isohydrazone was in excess of 80 per cent and in some of these runs the quantity of ammonium chloride carried out of the reactor was determined. These results are presented in table 7.1. where it can be seen that in three of the experiments the yield was in excess of 90 per cent.

TABLE 7.1.

Determination of R_c.

Run	NH_4Cl left in reactor W_L - gms	NH_4Cl taken out of reactor W_G - gms	Y_s per cent	$R_c = \frac{W_G}{W_G + W_L}$
3.69	2.464	0.786	80.0	0.242
3.9	2.18	1.005	91.0	0.316
3.88	1.37	0.510	89.0	0.271
3.55	0.76	0.173	99.4	0.188
3.58	2.09	0.885	93.6	0.297
3.61	1.578	0.698	83.5	0.307

average value of R_c = 0.27.

R_c was the ratio of ammonium chloride that left the reactor in the gas phase to the total amount formed.

If reaction 7.1. took place completely inside the nitrogen bubble then 50 per cent of the total amount of ammonium chloride would be formed in the gas phase. This, of course, assumed 100 per cent yield and the runs considered in Table 7.1. reasonably conformed to this requirement. Thus since R_c was 0.27 at least 50 per cent of this reaction took place inside the nitrogen bubble.

However when ammonia and chlorine reacted to form chloramine and ammonium chloride in the gas phase, the ketone wetted the nitrogen bubble and therefore transfer of ammonium chloride to the liquid phase took place. An attempt was made to estimate the quantity of ammonium chloride so retained by the liquid.

The stirred tank was employed and the effluent gases were passed into a dreschel bottle, maintained at -70°C, to condense out any ammonia or ketone vapour. The effluent stream from this dreschel bottle consisted of a stream of nitrogen and ammonium chloride. This was then passed into a dreschel bottle containing MEK to a level 6.5 cm above the level of the gas inlet, i.e. the same level as in the stirred tank reactor. The quantity of ammonium chloride retained by the liquid and the quantity that passed through were determined. The results are presented in Table 7.2. In run 4.3. the ammonia and ketone were not condensed out of the stream prior to entering the dreschel bottle containing MEK. It can be seen from Table 7.2. that the average ratio (R_P) of the quantity of ammonium chloride retained to the total quantity initially in the gas phase was 0.40.

Consider the gas-liquid reaction in the stirred tank reactor at 100 per cent yield.

TABLE 7.2.

Determination of R_P.

Run	NH_4Cl passed through dreschel bottle W_P gms.	NH_4Cl retained in dreschel bottle W_C gms.	$W_P + W_C$ gms.	$(W_P + W_C)$ per unit time / then won't req'd here. gms/min.	$R_P = \frac{W_C}{W_P + W_C}$
4.1.	0.2555	0.1565	0.4120	0.01373	0.38
4.2.	0.0718	0.041	0.1128	0.00564	0.364
4.3.	0.185	0.145	0.330	0.022	0.44

Take average value of R_P = 0.40.

Total quantity of NH_4Cl formed by reaction	=	W_T gms.
Initial quantity of NH_4Cl formed in gas phase	=	W_1 gms.
Amount transferred to liquid phase	=	W_2 gms.
Final quantity in gas phase	=	W_3 gms.

Thus if reaction 7.1. took place completely in the gas phase then the ratio $\frac{W_1}{W_T}$ would equal 0.5.

By definition.

$$R_c = \frac{W_3}{W_T} \qquad \text{and} \qquad R_P = \frac{W_2}{W_1}$$

In addition $W_1 = W_2 + W_3$

$$\therefore \quad W_1 = R_P W_1 + R_c W_T$$

$$W_1 (1 - R_P) = R_c W_T$$

$$\frac{W_1}{W_T} = \frac{R_c}{1 - R_P} = \frac{0.27}{1 - 0.4} = \frac{0.27}{0.6}$$

$$= 0.45$$

Thus 90 per cent of reaction 7.1. took place in the gas phase. There are two small errors inherent in the above calculation.

1. There was a thin layer of ammonium chloride at the top of the reactor which should have been analysed as part of W_G. However for the sake of convenience it was analysed with W_L.

2. In the experiments where R_P was determined, the liquid was not stirred and thus the conditions were not exactly the same as those prevailing in the stirred tank reactor in most of the runs.

Correcting for the first error would make R_c larger and for the second error would also make R_P larger. Both of these corrections would make the ratio $\frac{W_1}{W_T}$ even closer to 0.5 which further indicates that reaction 7.1. took place in the gas phase.

7.2. Kinetics.

It was impossible to obtain any precise information regarding the kinetics of the system. The first reaction [7.1.] took place instantly, and there was no information available regarding reaction 7.2. However it was claimed [163] that for the acetone-ammonia system the intermediate $(CH_3)_2C(OH)NH_2$ deposited in a 35 per cent yield at -50°C.

The chloramine formed in reaction 7.1. subsequently diffused into the liquid phase where it reacted with the ketimine to form the isohydrazone. No information was available concerning this reaction so it was not known if it was slow, moderate or fast. However similar results were obtained with the stirred tank reactor as with the column reactor where the residence time was greater. Furthermore in the tank reactor stirring, which causes an increase in residence time, produced no increase in yield. Thus it could be assumed that the chloramine - ketimine reaction proceeded to completion in the stirred tank reactor and was therefore also a fast reaction. It was not known if this reaction always proceeded stoichiometrically and thus an investigation of the chloramine-ketimine reaction independently of the chlorine-ammonia reaction is proposed in Chapter 9 as a suggestion for future work. This would then give some indication at which step losses in yield occurred.

An attempt was made using the method of initial rates to determine the order of reaction 7.3. in ketimine. The results presented in Table 5.31 were used and a value of approximately 0.4 was obtained. This would indicate that the reaction was half order in ketimine but assumptions were made which could well invalidate this method. These were:-

1. The concentration of ketimine was directly proportional to the concentration of ketone and that the large quantities of water did not affect the equilibrium of the ammonia-ketone reaction.
2. The presence of water did not cause any other yield reducing reactions.

It was observed in figures 6.2. and 6.3. that at low temperatures the yield dropped and this was attributed to the affect of temperature on the ammonia-ketone system. However it was also possible that the rate of reaction 7.3. was reduced thus lowering the yield. However no exact information regarding the kinetics of the system could be obtained. This was because the process was investigated from the industrial viewpoint and therefore determining the reaction mechanism and the conditions for maximum yields were considered to be more important in this study. Furthermore since some of the reactions taking place were fast it would appear that sophisticated methods would be necessary to investigate them in detail. It would also be advantageous to investigate separately the various reactions taking place. Finally it appears that the overall reaction is very fast and therefore the process would be expected to be mass transfer controlled which would be the basis of the design of a reactor.

7.3. Discussion.

It is obvious from the above sections that the system under consideration was very complex. Thus apart from elucidating in which phase the various reactions were taking place, it was difficult to obtain any other information regarding the mass transfer processes in the reactor. It was probable that any loss in yield was caused by reaction 7.1. not proceeding stoichiometrically. This is in agreement with the mechanism proposed, that the chloramine formation reaction took place in the gas phase. Furthermore the results obtained with annular jets on the column reactor also indicated that the loss in yield was caused by stoichiometric quantities of chloramine not being formed. In this latter instance it was probable that coalescence of ammonia and nitrogen-chlorine bubbles occurred to some extent. However in most cases it was likely that ammonia dissolved in the ketone and then diffused into the nitrogen-chlorine bubble.

When the column reactor was employed with vertical jets an attempt was made to determine the size of the bubble using photographic methods. Some of the photographs taken are shown in Plate 8. The size of the nitrogen-chlorine bubble was measured and calculated [164] to be in the region 0.8 - 1.0 cm, and using the method outlined by Gorring and Katz [165] the rising velocity of the bubble was calculated to be 20 cm per second. This was equivalent to a residence time in the reactor of 3 seconds. However it must be stressed that the above calculations were at best extremely approximate.

Using the above values the gas and liquid phase mass transfer coefficients due to physical absorption were calculated by the following equations.

$$k_L^o = 2\left(\frac{D}{\pi\ t_D}\right)^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 7.4.$$

$$k_g^o = \frac{2\ D\ \pi^2}{3\ d_B} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 7.5.$$

An attempt was then made to estimate the critical concentration of chlorine in the gas phase such that if it was increased beyond this value the chlorine would diffuse into the liquid phase. If this critical concentration was in the region of 0.02 (mole fraction basis) which is approximately the value at which the yield began to decrease sharply then it would indicate that low yields were caused by the chloramine formation reaction taking place in the liquid phase.

Secor and Southworth [166] derived an expression for the critical concentration of the liquid phase reactant and this method was reversed in order to calculate the critical concentration of the gas phase reactant. A value of 0.48 (mole fraction basis) was obtained which is higher than 0.02 by a factor of 24. However the gas phase coefficient (kg) was calculated for physical absorption and thus the actual value will be much higher because of the chemical reaction taking place. Thus the critical concentration of chlorine would be reduced. Nijsing [167] found that for the $(OH)^-/CO_2$ system the chemical acceleration factor varied from 10 to 25. Thus the critical chlorine concentration could be in the region of 0.02 although it is impossible to prove because of the lack of available data.


D

BUBBLES IN COLUMN REACTOR

PLATE 8B

CHAPTER EIGHT

CONCLUSIONS

8. CONCLUSIONS.

1. Organic hydrazine intermediates were formed by the electrolysis of solutions of ketone and liquid ammonia containing potassium bromide or rubidium bromide. However the yield obtained was very low and did not show any promise as the basis for a manufacturing process.

2. The yield of chloramine formed by the gas phase reaction of chlorine and ammonia was only of the order of 30 per cent. This was caused by bad mixing of the reactants. Furthermore this type of reactor was very difficult to control because the chlorine jet tended to block with ammonium chloride.

3. When the above gas phase reaction was conducted in the presence of acetone the yields of isohydrazone were considerably higher.

4. High yields of isohydrazone were realised when a gas-liquid reaction was carried out in a stirred tank reactor. Providing the value of the volume ratio of ammonia to chlorine (R_A) was in the region 20-25 or greater it did not unduly affect the yield. Furthermore the yield was independent of the carbonyl compound employed, if it was selected from low aliphatic ketones.

5. The concentration of chlorine in the nitrogen stream (X_c) was a critical factor in determining the yield of isohydrazone. Even when its value was reduced below 0.03 the yield was still increased. When it was increased beyond 0.2 the yield gradually fell off until at $X_c = 1.0$ the yield of isohydrazone (Y_s) was 38.5 per cent.

6. For the synthesis of isohydrazones there existed an optimum temperature range in the region of 0^oC.

7. Stirring had no affect on the yield of isohydrazones; similar results were obtained with a stirred and unstirred reactor. This would indicate that the overall rate controlling parameter was the liquid phase mass transfer coefficient.

8. Air was equally effective as nitrogen as the chlorine diluent.

9. At high chlorine flow rates the yield tended to drop and thus for the existing stirred tank reactor the maximum chlorine flow rate for reasonable yields would appear to be in the region of 150 ml per minute.

10. Low yields were obtained when the following systems were investigated:-

- i. The synthesis of azines.
- ii. Introduction of the chlorine into the reactor, in solution in carbon tetrachloride.
- iii. Use of liquid ammonia in the reactor instead of gaseous ammonia.
- iv. Use of water - MEK mixtures.

11. When acetophenone was employed as the carbonyl compound, temperature played an important part in determining if the product was the azine or isohydrazone.

12. It was impossible to detect organic hydrazine compounds, using the existing methods of analysis, in the following systems.

- i. When the carbonyl compound was benzaldehyde.
- ii. When the carbonyl compound was cyclohexanone.
- iii. Use of amines instead of ammonia.

13. Yields, similar to those given by the stirred tank reactor, were obtained with the column reactor. When annular jets were used for the gas inlets the yields of isohydrazone were higher.

A packed column was not suitable for this system as it tended to block with ammonium chloride.

14. Low yields were obtained with the column reactor when attempts were made to synthesise azines.

15. Azines and isohydrazones could be analysed at low concentrations using a colorimetric technique. However it was essential that the concentration of water and ammonia be kept to a minimum.

16. Azines and isohydrazones could be analysed by conversion at 20°C to hydrazine sulphate, followed by titration with standard potassium iodate solution.

17. The initial reaction between chlorine and ammonia to form chloramine took place in the gas phase.

18. The consecutive fast reaction between chloramine and ketimine took place in the liquid phase.

CHAPTER NINE

SUGGESTIONS FOR FUTURE WORK

9. SUGGESTIONS FOR FUTURE WORK.

There are numerous diverging fields of research into which this work could be continued and some of these are listed below.

1. The work on the stirred tank reactor should be continued at higher concentrations of isohydrazone to see if there is a critical value at which the yield falls off. If it is found that good yields can be realised at higher concentrations then it would be interesting from the industrial point of view to construct a column reactor with a continuous product take-off.

2. The design and shape of the reactor should be investigated, possibly employing multiple gas inlets of the annular jet type.

3. The synthesis of azines should be further investigated on the column reactor because of their industrial importance from the point of view of hydrazine recovery. An improvement on the existing column would be to incorporate pH control into the system.

4. The acetophenone system at 20°C should be further investigated as it has the virtues of the isohydrazone system but in this case the organic intermediate formed is the azine.

5. The recovery of hydrazine from azines and isohydrazones needs to be investigated and the allied problems solved if the fixation process is to become economically viable.

6. If further work on the fixation process is to be carried out then the analytical procedure should be looked at in greater detail. In the light of the results presented in Chapter 4.1.3.3., an obvious way to improve the method would be to employ more concentrated solutions of para-dimethylaminobenzaldehyde in methanol.

7. The chloramine fixation process in the gas phase was only looked at very briefly but a high yield was obtained in one run. Thus if a suitable reactor could be developed it is possible that this system might be more advantageous than the gas-liquid system because of the higher concentration of isohydrazone in the reactor effluent.

8. Following on from the mechanism suggested in Chapter 7, a comprehensive investigation into the various mass transfer operations taking place should be carried out. In this way a greater insight into the process would be obtained which should prove invaluable to the design of the chemical reactor.

9. The information available in the literature concerning the acetone-ammonia reaction and the MEK-ammonia reaction is negligible and thus an investigation into the various reactions occurring is necessary. This information would be helpful to any work carried out on the mass transfer processes taking place in the system.

10. There is no information available on the chloramine-ketimine reaction. Thus if chloramine was prepared in the gas phase and bubbled into the ammoniacal ketone much important information could possibly be obtained on the yields, order of reaction and velocity constants. It would be interesting to see if the yields obtained were always in the region of 100 per cent, based on chloramine. If so this would lend support to the hypothesis that the major loss in yield, based on chlorine, is due to chloramine not being formed in stoichiometric quantities.

11. Information regarding the chloramine-ketimine reaction could also be obtained by reducing the ketone concentration by dilution with inert solvents such as carbon tetrachloride and methyl alcohol.

APPENDICES

APPENDIX 1.

CALIBRATION OF ROTAMETERS.

The rotameters were initially calibrated using the method outlined in the handbook of Tri-Flat Variable-Area Flowmeters [158]. These calibrations were then checked using a Parkinson Cowan liquid sealed gas meter with nitrogen as the calibration fluid. The example of one of the nitrogen rotameters is shown below.

Tube = $\frac{1}{8}$" Scale = 8

Sapphire Float.

For $\frac{1}{8}$" tube the Size Factors are -

A = 404

B = 76·8

At STP. [1 atm, 70°F].

Density of nitrogen = 0·001160 $\frac{\text{gm}}{\text{ml}}$

Viscosity of nitrogen = 0·01756 CP.

Density of sapphire = 3·98 $\frac{\text{gm}}{\text{ml}}$

∴ Viscous Influence Number (N)

$$= \frac{404}{0{\cdot}01756}\sqrt{(3{\cdot}98 - 0{\cdot}001160) \times 0{\cdot}001160}$$

$$= 1568$$

In addition

$$W = C\,B\sqrt{(3{\cdot}98 - 0{\cdot}001160) \times 0{\cdot}001160}$$

$$\therefore \quad W = 5{\cdot}22\ C$$

where W = Flow rate (gm/min)

C = Flow coefficient.

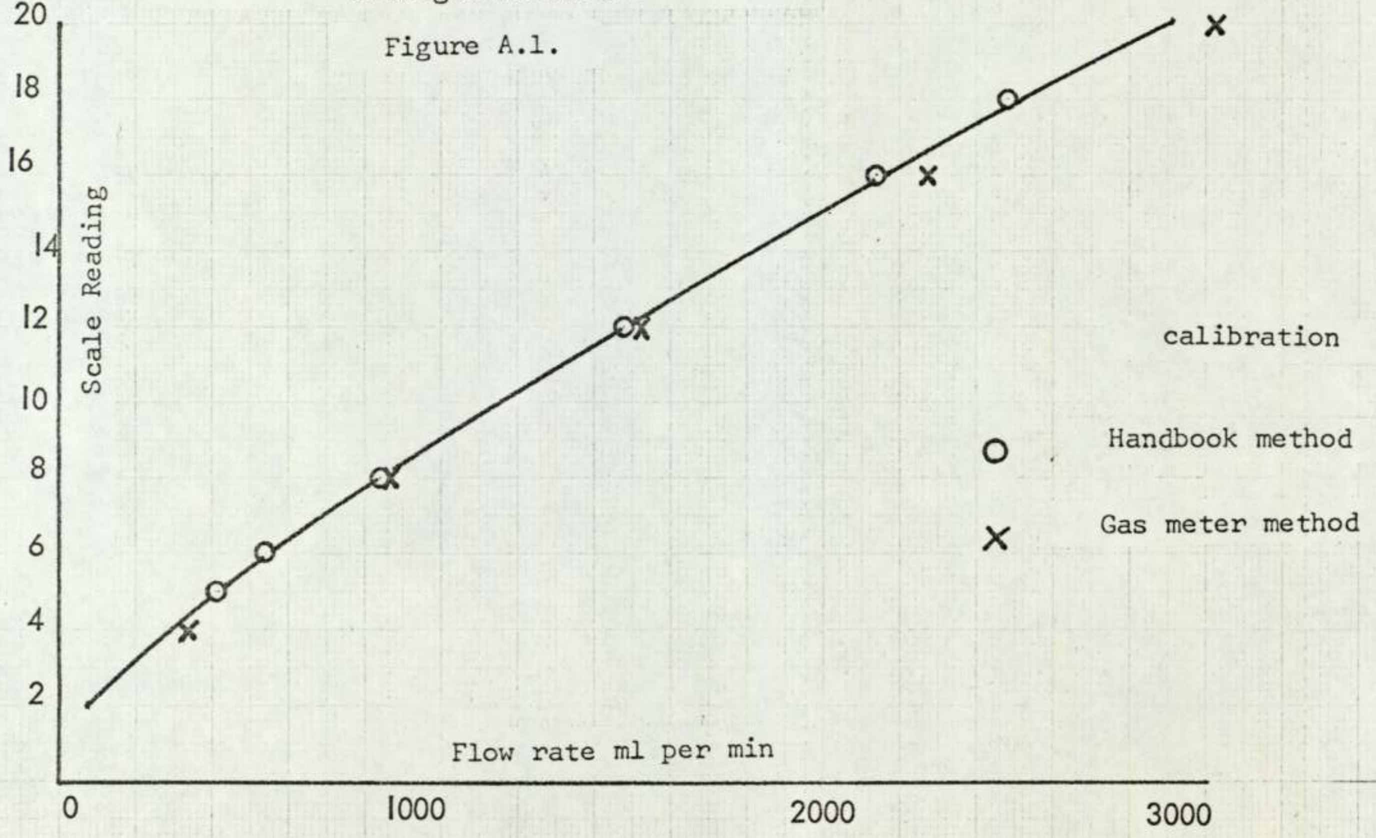
The values of C for the different scale readings, at a viscous influence number of 1568, were obtained from the appropriate table in the handbook /158/. The following table was then drawn up, showing the flow rate obtained by the handbook method and the check value obtained using the gas meter.

Scale reading	C	W gm per min	Flow rate using handbook method ml per min	Flow rate using gas meter method ml per min
1	0·0014	0.00732	6.3	
2	0.0068	0.0356	30.7	
3	0.0175	0.0915	79.0	85.5
4	0.033	0.172	148.0	140.2
5	0.055	0.287	248.0	250.7
6	0.074	0.387	334.0	338.0
8	0.118	0.617	532.0	540.0

The calibrations for the other nitrogen rotameter and the ammonia rotameter were obtained in a similar manner. The agreement was found to be reasonable in all cases. These calibrations are plotted in figures A.1. - A.3. No check was made of the calibration for the chlorine rotameters as this flow rate was determined by the weight of ammonium chloride deposited.

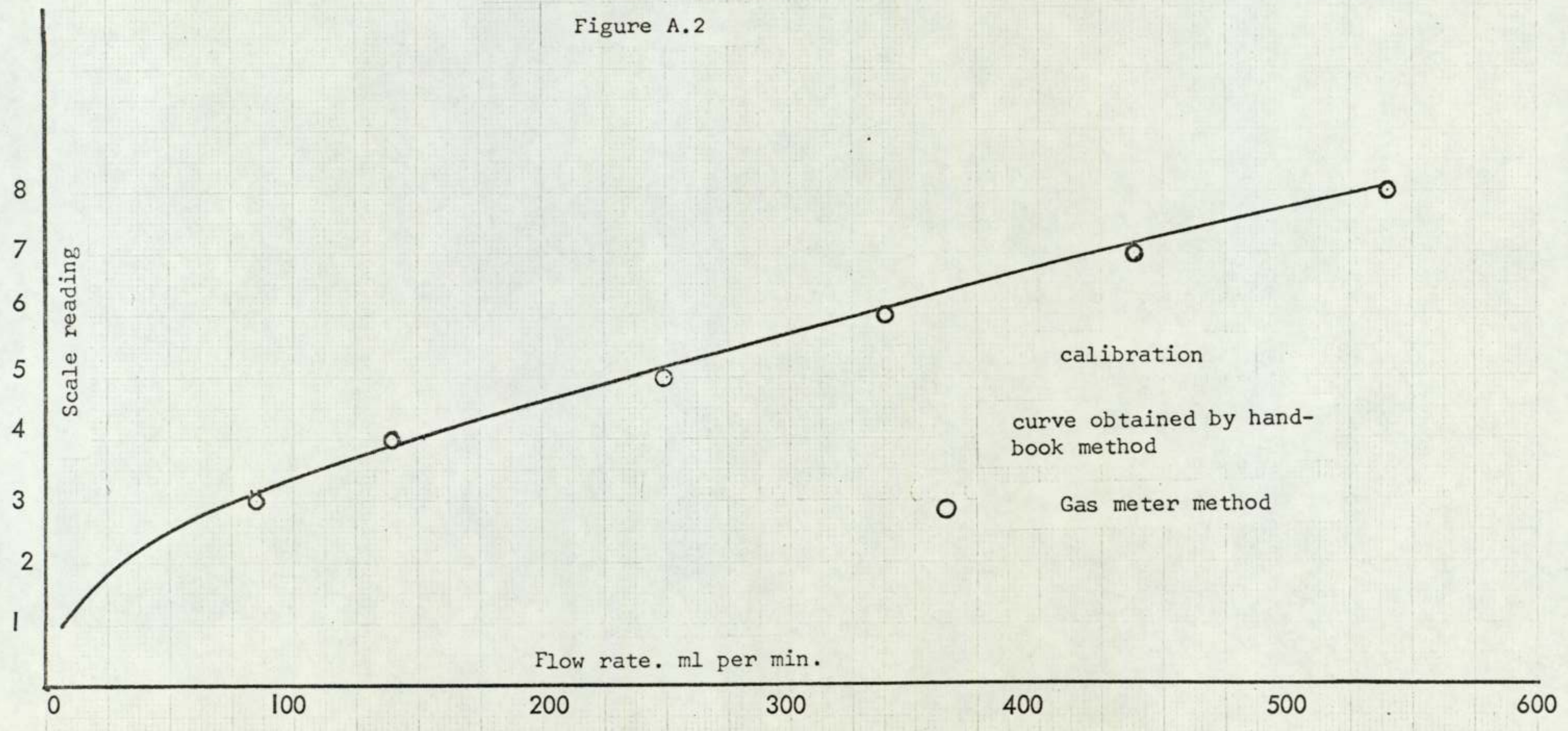
Nitrogen Rotameter

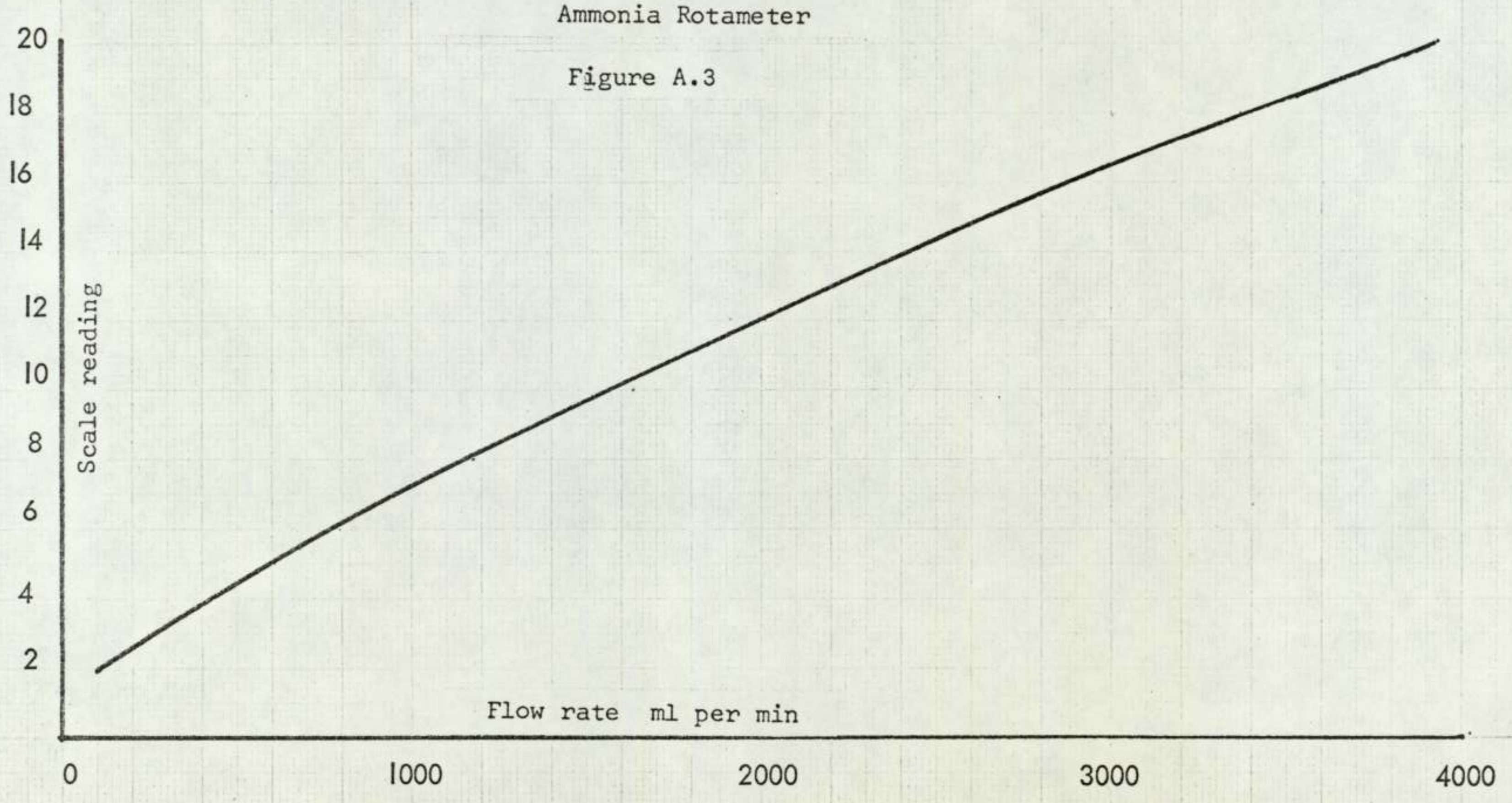
Figure A.1.



Nitrogen Rotameter

Figure A.2





Ammonia Rotameter

Figure A.3

APPENDIX 2.

ANALYSIS OF AZINES.

Calibration	7	Acetophenone azine.
Calibration	8	Benzalazine.
Calibration	9	Acetophenone azine. Run 3.39.

Calibration	Concentration of equivalent $N_2H_4H_2O$ parts per 10^5	Maximum value of optical density
7	0.51	0.075
	1.275	0.147
	2.04	0.253
	2.55	0.303
	4.08	0.474
	10.2	1.058
8	1.025	0.121
	2.050	0.280
	4.1	0.470
	6.15	0.660
	8.2	0.860
	10.25	1.050
9	2.09	0.235
	4.18	0.438
	6.27	0.650
	10.45	1.050

APPENDIX 3.

USE OF KETONES OTHER THAN ACETONE IN THE CALIBRATION OF AZINES.

Calibration	11.	Methyl ethyl ketone.
Calibration	16.	Methyl n-propyl ketone.
Calibration	17.	Diethyl ketone.
Calibration	22.	Methyl i-propyl ketone.

The samples for these calibrations were made up in the same manner as calibrations 2, 3 and 13, described in chapter 4.1.3. However acetone was replaced at all stages in the calibration by the corresponding ketone and the following results were obtained.

Calibration	Concentration of equivalent $N_2H_4H_2O$ parts per 10^5.	Maximum value of optical density.
11	2.0	0.493
	4.0	0.932
16	2.0	0.395
	4.0	0.754
	6.0	1.097
17	2.0	0.67
22	2.0	Off scale

Calibration	18.	Methyl n-propyl ketone
Calibration	19.	Methyl ethyl ketone
Calibration	21.	Methyl i-propyl ketone
Calibration	27.	Diethyl ketone.

For these calibrations 1 ml of hydrazine hydrate was made up to 100 ml with the corresponding ketone. However all the subsequent dilutions were made with acetone and the following results were obtained.

Calibration	Concentration of equivalent $N_2H_4H_2O$ parts per 10^5.	Maximum value of optical density.
18	2.0	0.222
	4.0	0.432
	10.0	0.955
19	2.0	0.220
	4.0	0.427
	10.0	0.948
21	2.0	0.205
	4.0	0.415
	10.0	0.908
27	2.0	0.198
	4.0	0.400
	10.0	0.895

APPENDIX 4.

RESULTS OBTAINED ON THE CALIBRATION OF AZINES USING METHYL I-BUTYL KETONE.

The following calibrations were obtained using the same method as that employed in Nos. 11, 16, 17 and 22.

Use of methyl i-butyl ketone.

Calibration	Concentration of equivalent $N_2H_4H_2O$ parts per 10^5.	Maximum value of optical density
10	2.0	0.221
	4.0	0.440
	6.0	0.640
	8.0	0.863
	10.0	0.970
15	2.0	0.21
	6.0	0.60
	10.0	0.93

The following calibrations were obtained using a mixture of methyl i-butyl ketone and acetone as in Nos. 18, 19, 21 and 27.

Calibration	Concentration of equivalent $N_2H_4H_2O$ parts per 10^5.	Maximum value of optical density.
23	2.0	0.09
	4.0	0.2
	10.0	0.44
24	2.0	0.098
	4.0	0.19
	10.0	0.465

APPENDIX 5.

COLOUR DEVELOPMENT OF BLANK SOLUTIONS

Calibration 14.	Usual blank.
Calibration 25.	Usual blank +0.5 ml of another ketone.
Calibration 26.	Usual blank +0.1 ml of another ketone.

Calibration 14

Time.	Hours.	21	45	95	168	264	335	390
Optical density.		0.05	0.061	0.072	0.086	0.108	0.127	0.143

Calibration 25

Methyl i-propyl ketone

Time.	Hours.	18	64.5	145	241	334	473	615
Optical density.		0.052	0.074	0.138	0.205	0.235	0.248	0.256

Methyl ethyl ketone

Time.	Hours.	18	64.5	145	241	334	473	615
Optical density.		0.048	0.062	0.092	0.125	0.152	0.200	0.238

Diethyl ketone

Time.	Hours.	18	64.5
Optical density.		0.049	0.063

Calibration 25 (continued)

Methyl n-propyl ketone

Time. Hours.	18	64.5
Optical density.	0.047	0.063

Methyl i-butyl ketone

Time. Hours.	18	64.5
Optical density.	0.049	0.063

Calibration 26

Methyl ethyl ketone

Time. Hours.	97	190	328	470	631
Optical density.	0.072	0.102	0.148	0.18	0.218

Methyl i-propyl ketone.

Time. Hours.	97	190	328	470	631
Optical density.	0.085	0.122	0.17	0.20	0.23

APPENDIX 6

Comparison of the two methods of analysis of isohydrazones.

	Run	Yield by Spekker method (Y_S)	Yield by titration method (Y_T)	$X = Y_S - Y_T$	X^2
1	3.12	71.0	69.5	1.5	2.25
2	3.28	61.5	63.5	- 2.0	4.00
3	3.37	98.7	97.5	1.2	1.44
4	3.42	76.8	74.5	2.3	5.29
5	3.49	62.5	60.0	2.5	6.25
6	3.50	48.0	50.0	- 2.0	4.00
7	3.51	38.5	38.2	0.3	0.09
8	3.52	17.0	17.1	- 0.1	0.01
9	3.53	68.2	69.0	- 0.8	0.64
10	3.58	93.6	96.0	- 2.4	5.76
11	3.74	72.3	75.0	- 2.7	7.29
12	3.82	80.5	80.0	0.5	0.25
13	3.84	73.5	69.0	4.5	20.25
14	3.100	66.2	65.2	1.0	1.0
15	3.106	65.0	58.6	6.4	40.96

$$\Sigma x = 10.2$$

$$\therefore \quad \bar{x} = \frac{10.2}{15} = 0.68$$

$$(\Sigma x)^2 = 104.04$$

$$\frac{(\Sigma x)^2}{n} = \frac{(\Sigma x)^2}{15} = \frac{104.04}{15}$$

$$= 6.936$$

$$\Sigma(x)^2 = 99.48$$

$$\sigma^2 = \text{Variance} = \frac{\left[\sum(x)^2 - \frac{(\sum x)^2}{n}\right]}{n - 1}$$

$$\therefore \quad \sigma^2 = \frac{\left[99.48 - 6.936\right]}{14}$$

$$\sigma^2 = 6.61$$

$$\therefore \quad \sigma = \sqrt{6.61} = 2.575$$

The standard deviation of the mean $\bar{x} = \frac{\sigma}{\sqrt{n}}$

$$= \frac{2.575}{\sqrt{15}} = 0.665$$

The expected value for $\bar{x} = E = 0.$

$$t = \frac{\bar{x} - E}{\sigma/\sqrt{n}} = \frac{0.68 - 0}{0.665}$$

$$t = 1.023.$$

The degress of freedom $= n - 1$

$= 14.$

according to Brownlee [159] the value of t at the 5% level of significance = 2.15

and

at the 10% level of significance = 1.76.

Thus the probability is greater than 0.1 (10%) and therefore the assumption, that there is no difference between the two methods of analysis, is in reasonable accord with the data.

APPENDIX 7.

Calculation of molar extinction coefficients.

Azines. Calibrations 2, 3 and 13

$$A = -0.00155 + 0.1196c - 0.002452c^2$$

$$\therefore \quad \frac{dA}{dc} = 0.1196 - 0.004904c.$$

The average value of c over the calibration range in equivalent parts of $N_2H_4H_2O$ (Volumetric basis) = 5 parts per 10^5.

$\therefore$ At this value

$$\frac{dA}{dc} = 0.1196 - 0.02452 = 0.09508.$$

By the Beer-Lambert Law.

$$A = K \bar{c} \; l$$

where

A = Optical density.

$\bar{c}$ = concentration in $\frac{\text{gm mole}}{\text{litre}}$

K = Molar extinction coefficient

l = Optical path.

$$\text{But} \quad \frac{dA}{d\bar{c}} = \frac{dA}{dc} \times \frac{100 \times 50}{1.03}$$

$$= \frac{dA}{dc} \times 4850$$

$\therefore$ when $c = 5$

$$\frac{dA}{d\bar{c}} = 0.09508 \times 4850.$$

Substituting

$$0.09508 \times 4850 = K \times 0.5$$

$$\therefore K = 923 \quad \frac{\text{litres}}{\text{gm. mole. cm}}$$

In a similar manner the value of K for the isohydrazone calibrations (4, 5, 6) can be determined.

In this case

$$A = -0.00927 + 0.2582c - 0.004444c^2$$

$$\therefore \frac{dA}{dc} = 0.2582 - 0.008888c.$$

The average value of c in these calibrations = 2.5

$$\frac{dA}{dc} = 0.2582 - 0.0222 = 0.23598$$

$$\therefore K = \frac{0.23598 \ \text{xx}\ 4850}{0.5} = 2290.$$

$$\therefore K = 2290 \ \frac{\text{litres}}{\text{gm. mole. cm.}}$$

APPENDIX 8

Stability of isohydrazones in acetone solution

The stability of two solutions of methyl ethyl isohydrazone in acetone was investigated. These solutions were obtained from experiments on either the column reactor or the stirred tank reactor. A 10 ml sample of these solutions was taken and made up as described in Chapter 4.1.3.2. for analysis on the absorptiometer. The optical density, relative to a blank, was measured in the time range 50-100 hrs. Several such tests were carried out over a period of about five months and the results are tabulated below.

Calibration 33. Run 3.67

Time weeks.	Optical density
0	0.43
1	0.42
3	0.405
7.5	0.372
14.5	0.38

Calibration 34. Run 3.106

Time weeks	Optical density
0	0.62
4	0.52
8	0.52
16	0.458
23.5	0.466

It is apparent that the isohydrazone does gradually decompose in acetone solution. A possible reaction taking place would be conversion to the ketazine, because ketone is present in considerable excess. This would then explain the drop in optical density that was observed.

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