"The Mechanism of Nitramine Formation"

by

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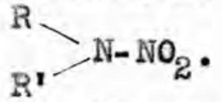
Part I. - Introduction

(i) NITRAMINES

A nitramine is the compound formed by the substitution of a nitro group for an amine hydrogen. The N-nitro compound thus formed may be designated as



$$R(R')N\text{-}NO_2.$$

Where R is an alkyl group, and R' is hydrogen, the compound is a primary nitramine; where both R and R' are alkyl groups the compound is a secondary nitramine. Substitution by an acyl group is also possible, the compound is then the corresponding nitramide. A less extensive series of compounds exists in which substitution by aryl groups has been effected. The nitramines form a limited, but interesting group of organic compounds. The chemistry of these compounds has not been extensively investigated, but their interest as explosives has led to much research regarding possible methods of synthesis.

The first recorded instance of a nitramine being isolated was in 1869. In that year P. Griess prepared a mixture of isomeric carboxyphenylnitroureas by treating 2-carboxyphenylurea with cold concentrated nitric acid (1). In 1877 K.H. Mertens prepared N,2,4,6-tetranitro-N-methylaniline by the action of boiling nitric acid upon dimethyl aniline (2). In the following thirty years a large number of nitramines were synthesised, and their chemistry investigated (3,4,5,6,7,8).

Relatively little work was done in this field during the years 1914-1939, but the increasing importance of nitramines as explosives has led to a considerable amount of research in the past decade. The greater part of this work, however, remains unpublished.

There are three common methods of synthesis of N-nitro compounds, namely, direct nitration, nitrolysis, and catalysed nitration. Direct nitration may be used for the preparation of nitramides from the corresponding amides. Very few primary nitramides are known; the rigorous conditions of nitration may well prevent the isolation of others. Direct conversion of the monoalkylated amides, $R.CO.NHR'$, into the secondary nitramides, $R.CO.N(NO_2)R'$, is generally readily effected by absolute (98-100%) nitric acid alone, although mixtures of nitric acid with sulphuric acid or acetic anhydride have also been used. In a review of nitramine chemistry (9) A.H. Lamberton concedes that the use of the acetic anhydride is often advantageous, but expresses a doubt as to whether the sulphuric acid exercises an influence comparable with that shown in aromatic nitration.

Aliphatic primary nitramines are rapidly decomposed by concentrated acids, and cannot be prepared by direct nitration of the corresponding amines. The most usual method of preparation is nitration of the acylated amine to form a secondary nitramide, followed by decomposition to give the salt of the required nitramine.

The classical method of preparing aliphatic secondary nitramines is to use the nitrolysis of suitable dialkylamides. In nitrolysis, as opposed to nitration, rupture of a carbon-nitrogen bond occurs: there are thus two possible products to the reaction.

$$X.CO.NR_2 \xrightarrow{HNO_3} X.CO_2H + R_2N.NO_2$$

$$\xrightarrow{HNO_3} X.CO.N(NO_2).R + ROH$$

The methods of preparation mentioned above cannot generally be applied to the aromatic series. The direct nitration of suitable (usually weakly basic) anilines can be effected by successive addition of absolute nitric acid and acetic anhydride to a suspension of the aniline in acetic acid (10). A similar method of preparation is the "dehydration" of the solid base nitrate salt by adding it to acetic anhydride (11). Aryl primary nitramines without nuclear nitro groups are best prepared by oxidation of the appropriate diazotates (12).

$$C_6H_5.N{:}NOK \xrightarrow{O} C_6H_5.NK.NO_2$$

The work of G.F Wright and others at Toronto has resulted in the third method of preparing nitramines (13). When N,N-dichloroamines in an excess of acetic anhydride are treated with anhydrous nitric acid, the N-chloronitramine may be isolated.

$$R.NCl_2 \xrightarrow{HNO_3 - Ac_2O} R.N(NO_2)Cl \xrightarrow{Na_2S_2O_3} R.NH.NO_2$$

The halogen in compounds of this type is positive in nature, and can be removed by simple reducing reagents to give the primary nitramine.

Wright et al. found that nitration via the chloramine could also be applied to secondary amines (14,15). It was found easier to synthesise the chloramine in situ than to isolate it. The addition of a small amount of a chloride salt to a mixture of the amine nitrate and acetic anhydride caused continuous formation of the intermediate chloramine. The role of the chloride salt led to this process being designated as "catalysed nitration".

The nature of the catalytic action was investigated in a series of papers (15,16,17,18,19). It was found that electropositive chlorine existed in the reaction mixtures, and that this positive chlorine, probably in the form of chlorine acetate, converted the secondary amine into the corresponding chloramine. The action on dialkylchloramines of nitric acid, or of nitric acid-acetic anhydride mixtures, was also investigated. In most cases a satisfactory conversion into the nitramine was accomplished. Since electropositive chlorine was regenerated, the catalysed nitration of the parent amines could be considered as a self sustaining chain reaction.

$$CH_3CO.OCl + R_2NH \longrightarrow R_2NCl + CH_3CO.OH$$

$$R_2NCl + HNO_3 \longrightarrow R_2N.NO_2 + HOCl$$

$$HOCl + CH_3CO.O.CO.CH_3 \longrightarrow CH_3CO.OH + CH_3CO.OCl$$

Examination of the by-products resulting from the nitration of chloramines seemed to indicate that chloramine nitration, rather than chloramine formation, was the rate determining step in the reaction.

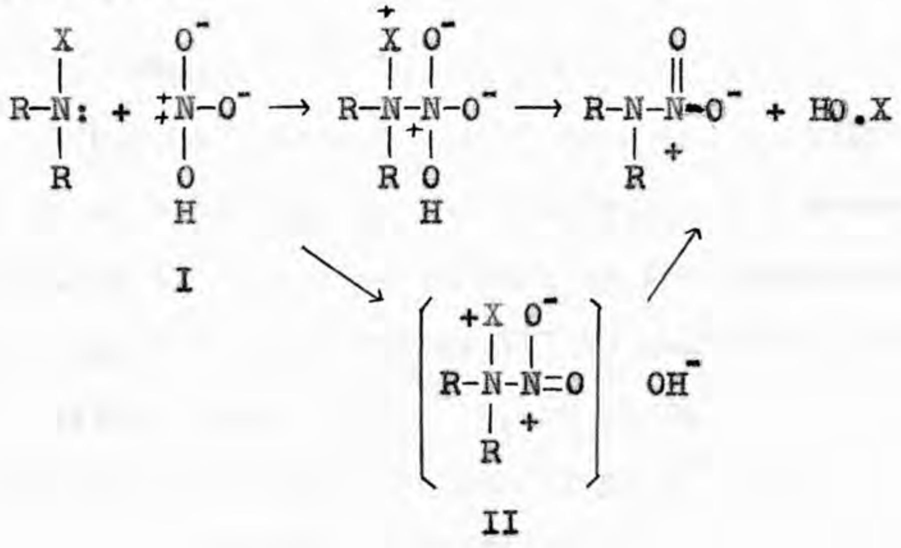
Wright has shown that the formation of an N-nitro compound from an amine is dependent upon the basicity of the amino group (15,20). The basicity in acetic acid of a series of secondary amines was determined, and compared with the ease of nitration. It was found that amines which were nitrated in good yield without the necessity of a catalyst were weaker than morpholine. Amines with a base strength greater than that of morpholine could not be nitrated without a catalyst, while strong amines, such as di-n-butylamine, were nitrated best when the catalyst was present in equimolecular proportion. Three conclusions were drawn from these observations: (i) The customary representation of the proton-accepting tendency of an amine is shown in the following equilibrium arrangement

$$R_2NH + HNO_3 \longleftrightarrow R_2NH.HNO_3 \longleftrightarrow R_2NH_2^+ + NO_3^-$$

Since ease in nitration is inversely proportional to the proton-accepting tendency of the amine it would seem that the normal electrovalent ammonium salt is not the reactive species in the nitration. (ii) Since such amines as diphenylamine and diacetamide cannot be nitrated, the capacity to form a salt is essential for nitration.

(iii) The action of the chloride catalyst must be to decrease the proton-acquiring tendency of the amine.

Wright suggested that the nitration of secondary amines proceeded through the formation of a nitrogen-nitrogen bonded complex of the amine and nitric acid (20,17). The nitric acid, in the form I, is depicted as reacting with the lone pair of electrons of the amino nitrogen. The nitramine is then formed by trans elimination of HOX, X being equivalent to Cl in the catalysed, and H in the uncatalysed reaction. The complex can be regarded as an ionic form II if desired, here loss of X produces the nitramine.



It was held that such a complex would not be formed by the non-basic diacylamines, and that the strongly basic amines would form electrovalent salts rather than complexes of this type.

In postulating this mechanism Wright discounted recent evidence of the existence of the nitronium ion as a nitrating entity. A.H. Lamberton has pointed out (9) that it is possible to reinterpret the mechanism in the light of recent developments. Union of the free amine base with the nitronium ion NO_2^+ would yield, directly, the cation of Wright's complex II. If this is possible, then amine nitration may well be considered as the result of two competing bimolecular reactions, A and B. The ejection of a hydrogen ion from the complex III results

$$R_2NH + NO_2.OH \Longleftrightarrow NO_2.OH....NH.R_2 \Longleftrightarrow NO_3^- + H_2\overset{+}{N}R_2 \quad (A)$$

$$R_2NH + NO_2^+ \quad \Longleftrightarrow \quad \underset{III}{R_2\overset{H^+}{N}.NO_2} \quad \Longleftrightarrow \quad R_2N.NO_2 + H^+ \quad (B)$$

in the formation of the N-nitro compound.

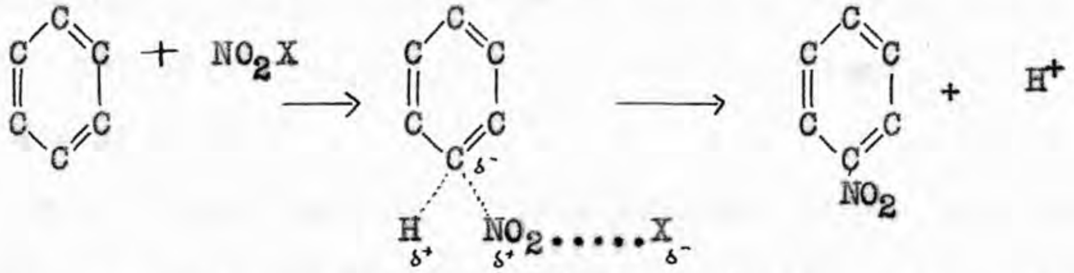
This mechanism differs from that postulated for aromatic nitration in the existence of a competing reaction A. It also differs in the comparative stability attributed to the complex III in contrast to either the transition state  , or to the intermediate compound $Ar^+H(NO_2)$ postulated by Ingold _et al._ (21). The existence of the two competing reactions furnishes an explanation for the effect of amine basicity upon nitration. Strong bases are probably converted almost entirely into the quaternary ammonium form by means of reaction A. On the other hand it is likely that bases weaker than acetamide are unable to react with the nitronium ion. Experimental evidence for the reversibility of the nitration process B is furnished for such compounds as nitrourethane (22), N-methylnitrourethane (9), N,2,4,6-tetranitro-N-methylaniline (23), nitroguanidine (24), and others.

From the foregoing it will be seen that in order to accomplish successful nitration it is necessary to reduce the proton acquiring tendency of an amine to below a critical level. The process of catalysed nitration accomplishes this by substituting a chloramine for the parent amine. An interesting commentary on this theory is afforded by the work of E.D. Hughes and his collaborators (25). In an investigation of the nitration of dimethyl aniline it was found that nuclear substituted phenylmethylnitramines were produced as intermediates in the preparation of N,2,4,6-tetranitro-N-methylaniline. Such nitramines suffered "denitration" of the N-nitro group under acid conditions, followed by subsequent further nuclear nitration. Hughes et al. concluded that the rearrangement of the nitro group took place through an intramolecular mechanism. This conclusion was based, among other things, upon the observations (i) that in the rearrangement of p-nitrophenylmethylnitramine, nitric acid is not produced to a detectable extent, and not fast enough to enable it to be considered a possible intermediate: (ii) that in the rearrangement of 2,4-dinitrophenylmethylnitramine, nitric acid is produced quickly enough to enable it to be considered as a possible intermediate, (iii) but, that nitric acid cannot be an intermediate of any importance, because it does not effect the necessary nuclear nitration with sufficient facility: (iv) in the rearrangement of 2,4,6-trinitrophenylmethylnitramine nitric acid is produced quickly and in large quantities. In this context nitric acid is used to designate entities capable of effecting nitration, no definition of the actual form (viz. nitronium ion, molecular nitric acid) is attempted. It can be observed that the ease of "denitration" to yield nitric acid increases with decreasing base strength of the aniline compound. This is fully in accord with the idea that reaction B takes predominance as the base strength of the amino group decreases.

(ii) NITRATING AGENTS

Investigation of the effect of substituents upon reactivity and orientation in the benzene nucleus has led to an extensive amount of theory regarding the mechanism of aromatic nitration.

An acceptable theory in the light of modern knowledge is that nitration is an electrophilic displacement reaction. In such a reaction the nitro group from the nitrating reagent becomes attached to a carbon atom, whilst the hydrogen atom attached to the carbon atom is either simultaneously or subsequently expelled as a proton. Writing the nitrating agent as NO_2X the reaction is



The suggestion that the nitrating agent under certain conditions might be the nitronium ion NO_2^+ was first made by H. von Euler in 1903 (26), and was subsequently reiterated by other workers (27,28,29). In recent years ample evidence has been adduced by physical methods to confirm the existence of the nitronium ion as a stable entity. The kinetics of a number of nitrations under different conditions have been investigated, and shown to be consistent with the concept that the nitronium ion is the actual nitrating agent.

The nature of solutions of nitric acid in anhydrous and in concentrated aqueous sulphuric acid has been the subject of many investigations. G.M. Bennett, J.C.D. Brand, and Gwyn Williams have carried out a survey of the available evidence concerning the possible existence of an active form of nitric acid, present in sulphuric acid media, that could be responsible for nitration (30). From this they concluded that an ionisation took place that resulted in the formation of a nitronium cation, according to the equation

$$NO_2OH + 2H_2SO_4 \rightleftarrows NO_2^+ + OH_3^+ + 2HSO_4^-$$

This reaction thus postulates the reversible formation of water prior to the actual irreversible nitration; this concept had also been adopted by F.H. Westheimer and M.S. Kharasch (31).

The evidence leading to this view was drawn from many sources. The ultra-violet absorption spectra for solutions of nitric acid in concentrated sulphuric acid had been measured by A. Hantzsch (32,33), and by H. von Halban and J. Eisenbrand (34). These workers had found that the absorption bands characteristic of the nitrate ion, and those of the undissociated nitric acid molecule were either absent, or greatly reduced in intensity under such conditions. Investigation of the Raman spectra of solutions of nitric acid in sulphuric acid had led J. Chédin (35,36) to the consideration of two characteristic lines, at 1050 cm.$^{-1}$

and 1400 cm.$^{-1}$. These lines were not characteristic of either the nitric acid or the sulphuric acid molecule. Chédin attributed these two lines to dinitrogen pentoxide, but since solutions of dinitrogen pentoxide in organic solvents gave a different Raman spectra, assumed that such dinitrogen pentoxide was present in nitric acid or sulphuric acid in some special form.

The vapour pressure of nitric acid in solution in sulphuric acid had been measured by A. Saposchnikov (37) and other workers (38,39). It had been found that the vapour pressure of nitric acid reached a maximum over a solution containing equimolecular proportions of sulphuric acid and water. The vapour pressure of the nitric acid declined to zero above solutions that contained a large excess of either water or of sulphuric acid. These variations could be accounted for by the conversion of molecular nitric acid into nitrate ion in the more aqueous solutions, and into some other less volatile form in the more acid region. Thus the maximum concentration of molecular nitric acid would be in that solution where the ratio of water to sulphuric acid (H_2O/H_2SO_4) is unity; such was the case.

A series of cryoscopic measurements upon solutions of nitric acid in sulphuric acid had been carried out by Hantzsch (40,41,42,43,44), and later by C.R. Robles and E. Moles (45). Both sets of measurements showed that when nitric acid was dissolved in sulphuric acid the van t'Hoff factor i was greater than two, thus indicating the production of more than two particles per added molecule of nitric acid. After noting that solutions of nitric acid in sulphuric acid had a high electrical conductivity, thus indicating ion formation (37,46,47), Hantzsch had suggested that nitric acid was converted into some new species of ion when in solution in sulphuric acid. Hantzsch had further suggested that these ions were produced by nitric acid acting as a base in sulphuric acid, and thus forming the nitracidium cations $H_2NO_3^+$ and $H_3NO_3^{++}$.

In an effort to provide a more concrete proof for the presence of the nitracidium ions Hantzsch had made an unsuccessful attempt to isolate the salts $(H_2NO_3^+)(HSO_4^-)$ and $(H_3NO_3^{++})(HSO_4^-)_2$. A partial confirmation of this theory was provided by the isolation of two crystalline salts formed by the direct combination of nitric and perchloric acids. To these salts Hantzsch had assigned the formulae $(H_2NO_3^+)(ClO_4^-)$ and $(H_3NO_3^{++})(ClO_4^-)_2$. The ionic nature of these salts had been confirmed by investigation of the electrical conductivity and transference phenomena of their solutions in nitromethane (48). The results obtained definitely established the conversion of nitric acid into a positive ion in solutions of these compounds.

Other theories that had been suggested concerning the nature of solutions of nitric acid in sulphuric acid were that they contain $NO_2.O.SO_3H$ (49) or NO_2^+(26,28). P. Walden had suggested that the nitronium ion existed in the anhydrous acid, pointing out that the specific electrical conductance at 25°C. requires that the nitric acid should be considerably self ionised (27). As an explanation for this Walden had suggested that nitric acid might be regarded as an amphoteric electrolyte, and that the following equilibrium was set up

$$HNO_3 \longleftrightarrow H^+ + NO_3^- \longleftrightarrow OH^- + NO_2^+$$

In reviewing this work, Bennett, Brand, and Williams recalculated the cryoscopic factors of Hantzsch. Hantzsch had reported a van t'Hoff factor of 3 for solutions of nitric acid in sulphuric acid, but Bennett et al. noted that some of the best results were obtained for solutions of potassium nitrate in sulphuric acid. After allowance has been made for the potassium hydrogen sulphate formed, these solutions have an i factor more nearly equal to four.

Summarising the possible methods of ionisation in sulphuric acid:

(1) $2HNO_3 + H_2SO_4 \longleftrightarrow N_2O_5 + H_3O^+ + HSO_4^-$ $i = 1.5$

(2) $HNO_3 + 2H_2SO_4 \longleftrightarrow NO_2OSO_2OH + H_3O^+ + HSO_4^-$ 3

(3) $HNO_3 + H_2SO_4 \longleftrightarrow H_2NO_3^+ + HSO_4^-$ 2

(4) $HNO_3 + 2H_2SO_4 \longleftrightarrow H_3NO_3^{++} + 2HSO_4^-$ 3

(5) $HNO_3 + 2H_2SO_4 \longleftrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ 4

it will be seen that the reaction producing the nitronium ion (5) uniquely has an i factor of four. R.J. Gillespie and collaborators have recently repeated the cryoscopic work of Hantzsch, using a more accurate technique (50), and obtained a van t'Hoff factor of 3.83 for solutions of nitric acid in sulphuric acid. Solutions of dinitrogen pentoxide and dinitrogen tetroxide in sulphuric acid were also examined cryoscopically by the same authors, and found to have i-factors of 6, which is in accord with the ionisations

(6) $N_2O_5 + 3H_2SO_4 \Longleftrightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^-$

(7) $N_2O_4 + 3H_2SO_4 \Longleftrightarrow NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$

L.P. Kuhn has confirmed the cryoscopic measurements for solutions of nitric acid in sulphuric acid (51), and has also found an i-factor of 5 for solutions of ethyl nitrate in sulphuric acid, which is consistent with the ionisation

(8) $Et.O.NO_2 + 3H_2SO_4 \Longleftrightarrow NO_2^+ + H_3O^+ + 2HSO_4^- + Et.O.SO_3H$

This interpretation is supported by the similarity in the ultra-violet absorption spectra of such solutions to that of solutions of nitric acid in sulphuric acid.

Bennett, Brand, and Williams made a study of the Raman spectra results of Chédin (30), and as a result assigned the line at 1400 cm.$^{-1}$ uniquely to the nitronium ion. The accompanying line at 1050 cm.$^{-1}$ was assigned either to the nitrate ion NO_3^-, or, in the presence of sulphuric acid, to the bisulphate ion. This interpretation of the spectra has been confirmed, and extended, by the work of D.J. Millen on the Raman spectra of solutions of nitric acid in other strong acids (52).

A. Hantzsch made an unsuccessful attempt to demonstrate the transport of nitric acid to the cathode during the electrolysis of solutions of nitric acid in sulphuric acid (52). This work was repeated, with some degree of success by Bennett, Brand, and Williams (53), who while unable to isolate nitric acid at the cathode, were able to demonstrate the migration of nitric acid away from the anode. The failure to isolate nitric acid at the cathode was attributed to excessive reduction occurring there. Confirmation of this theory is found in that the authors were able to isolate nitric acid at the cathode after electrolysis in oleum: in this case the sulphur trioxide had been preferentially reduced.

The formation of salts of nitric acid has also been reinvestigated; D.R. Goddard, E.D. Hughes, and C.K. Ingold having studied in detail the solid phase formed between nitric acid and perchloric acid (54). A vacuum technique was used to ensure the complete absence of water, and to prevent contamination by solvents. By these means a dry solid corresponding to the composition $(H_3NO_3^{++})(ClO_4^-)_2$ was obtained. This solid was shown to be an equimolecular mixture of nitronium perchlorate $(NO_2^+)(ClO_4^-)$, and the well known perchloric acid hydrate $(H_3O^+)(ClO_4^-)$. These workers were unable to obtain a dry solid of the composition

$(H_2NO_3^+)(ClO_4^-)$, but pointed out that compositions approximating to this could result from the occlusion of nitric acid to the mixture obtained above. The ionic nature of the nitronium perchlorate was demonstrated by the Raman spectra of the solid salt, which consisted of the known spectra of the nitronium and perchlorate ions (55), and was confirmed by an X-ray study of the crystal structure of the solid (56).

Using the same technique Goddard <u>et al</u>. were able to prepare and isolate a number of other nitronium salts (54). Thus in addition to nitronium perchlorate $(NO_2^+)(ClO_4^-)$, nitronium hydrogen disulphate $(NO_2^+)(HS_2O_7^-)$, nitronium disulphate $(NO_2^+)_2(S_2O_7^{--})$, nitronium trisulphate $(NO_2^+)_2(S_3O_{10}^{--})$, and nitronium fluorosulphonate $(NO_2^+)(FSO_3^-)$ were prepared as crystalline salts. The assigned ionic structures were spectroscopically established for all these compounds, with the exception of nitronium trisulphate. In the same work crystalline dinitrogen pentoxide N_2O_5, was shown to be nitronium nitrate $(NO_2^+)(NO_3^-)$, and thus a member of the same series. Other nitronium salts, such as nitronium hydrogen sulphate, nitronium chlorosulphonate, and nitronium polyselenates could be isolated, but not in a pure, or stable, form.

The evidence given above clearly establishes the existence of the nitronium ion under certain conditions in the nitric acid-sulphuric acid-water system. Chédin has quantitatively investigated this system by observation of the intensity of the 1400 cm.$^{-1}$ line in the Raman spectra of such solutions. The triangular diagram, Fig. 1, was constructed by Bennett <u>et al</u>. from the data of Chédin and illustrates the concentration of the nitronium ion in such a system. It will be seen that in 100% sulphuric acid, solutions of less than 18 moles % of nitric acid are practically completely ionised. This conclusion is based upon the fact that the frequencies of the nitric acid are not detectable in solutions within these concentrations. The diagram also shows that the nitronium ion formed by a solution of nitric acid in an excess of sulphuric acid is not completely destroyed by the addition of water until sufficient has been added to form the monohydrate of sulphuric acid. These spectroscopic results have been confirmed by measurement of the partial vapour pressure of nitric acid in this system (39). For those solutions in which molecular nitric acid is undetectable, the vapour pressure of nitric acid is too small to measure. The addition of water to a solution of nitric acid in sulphuric acid initially raises the vapour pressure of the nitric acid; this is due to the repression of the ionisation of the nitric acid by the mass effect of the hydroxonium and bisulphate ions.

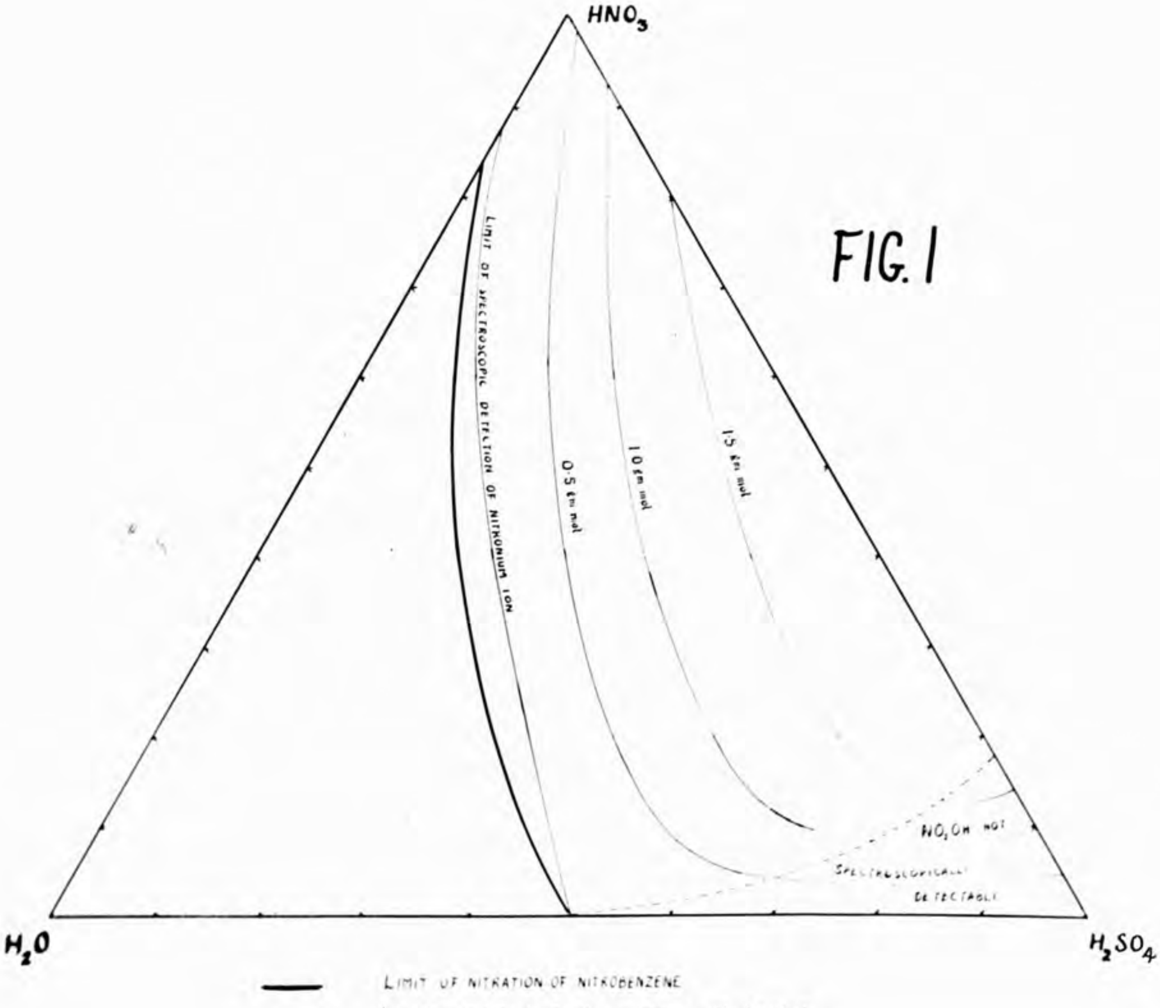

HNO_3
H_2O
H_2SO_4
LIMIT OF SPECTROSCOPIC DETECTION OF NITRONIUM ION
0·5 gm mol
1·0 gm mol
1·5 gm mol
NO_2OH NOT
SPECTROSCOPICALLY
DETECTABLE
LIMIT OF NITRATION OF NITROBENZENE
AMOUNTS OF NITRONIUM ION PER 1000 g. OF SOLUTION

FIG. I

$$H_2O + H_2SO_4 \longleftrightarrow H_3O^+ + HSO_4^-$$

$$HNO_3 + 2H_2SO_4 \longleftrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

The eventual ionisation of the nitric acid to nitrate ion finally results in a lowering of the vapour pressure of the nitric acid. It may be concluded that sulphuric acid provides a strongly acidic medium in which nitric acid acts as a base, forming the nitronium ion according to equation (5). The electronic theory of reactions requires that the nitrating agent for the benzene ring should be cationoid or electrophilic. In accordance with this concept, G.H. Benford and C.K. Ingold (57) suggested that the nitrating agent always had the form NO_2-X, where X is an electron attracting group. It follows that the nitronium ion, carrying an integral positive charge, should be the most active of all nitrating agents.

(iii) ACIDITY FUNCTIONS

In 1932 L.P. Hammett and A.J. Deyrup pointed out the need for an experimental criterion of acidity in strong acids, and of a general method of measuring such (58). When the acidity of a solution is determined by means of a simple basic indicator the quantity actually measured is the tendency of the acids present, under the conditions prevailing, to transfer hydrogen ion to a neutral organic molecule, the indicator base, converting it into a positive ion. Hammett and Deyrup emphasised that the "acidity in terms of a basic indicator" is a most significant quantity, certainly for the equilibrium in any reaction in which hydrogen ion is added to a neutral molecule, and probably for other forms of acid catalysed reactions. Making the assumption that the relative strength of two bases of the same charge type is independent of the medium in which they are compared, the authors measured the acidity of sulphuric acid and perchloric acid over a large range by employing a series of simple basic indicators. The indicators used were such that the ranges of acidity in which they had varying ionisation successively overlapped. A simple basic indicator was defined as a non-ionised or neutral substance capable of adding one hydrogen ion per molecule without any further complicating reactions, (a mobile tautomerism of either ion or base being specifically allowed), and in such a way that a colour change is determined by the extent of the ionisation. The strength of the indicator, or of any other monoacid base, entering the equilibrium

$$B + H^+ \longleftrightarrow BH^+$$

was defined by the function

$$pK' = -\log \frac{a_{H^+}\, a_B}{a_{BH^+}} = -\log \frac{(H^+)(B)}{(BH^+)} - \log \frac{f_{H^+}\, f_B}{f_{BH^+}}$$

where a is activity, ( ) is concentration, and f the activity coefficient .

The form of this function follows from the definition of pK' in terms of the strength of the conjugate acid BH^+. The activities in all solvents were referred to the same reference standard, a dilute aqueous solution. In such a solution

$$\log \frac{f_{H^+}\, f_B}{f_{BH^+}} = 0 \quad \text{and } pK' = -\log \frac{(OH_3^+)(B)}{(BH^+)}$$

From this it follows that if the ionisation ratios of two bases B and C are determined in any given solution, (where the concentrations of B and C are so small as not to affect the activities of the medium constituents)

$$pK'_B - pK'_C = -\log \frac{(B)\ (CH^+)}{(BH^+)(C)} - \log \frac{f_B\, f_{CH^+}}{f_{BH^+}\, f_C}$$

The first term of the right hand side may be measured colorimetrically, the second term is zero if the assumption that f_B/f_{BH^+} in a given solution is the same for all bases is correct.

The acidity function H_o is defined by the equation

$$H_o = \log \frac{[B]}{[BH^+]} + pK'_B = - \log \frac{a_{H^+} f_B}{f_{BH^+}}$$

In dilute aqueous solutions the acidity function H_o is equivalent to the pH, and in acetic acid to the $(pH)^{HAc.}$ of N.F. Hall and J.B. Connant (59).

A series of bases of the anthraquinone or nitroaniline type were employed to measure the acidity of sulphuric acid over the range 0-100%. Such bases ionise as

$$A + H_2SO_4 \longleftrightarrow AH^+ + HSO_4^-$$

and thus give a Van t'Hoff factor of 2: cryoscopic evidence was used as the basis of selection of indicators. The values of H_o obtained are plotted in Fig. 2 (plus an additive constant of -0.29 unit). Save in the immediate neighbourhood of pure water and pure sulphuric acid, where rapid change is to be expected on a logarithmic plot, the curve is strikingly free from sudden changes of direction, even in the region of sulphuric acid monohydrate. The limiting value of the acidity function H_o for 100% sulphuric acid was -10.60, 17.6 units more acid than water. In 1934 L.P. Hammett and M.A. Paul made a more accurate study of the acidity of dilute acids, using the stronger bases benzeneazodiphenylamine and aminoazobenzene as indicators (60). The ionisation of these bases could be measured colorimetrically in solutions of hydrochloric acid so dilute that the activity of hydrogen ion could be set equal to the molarity of the acid. As a result,

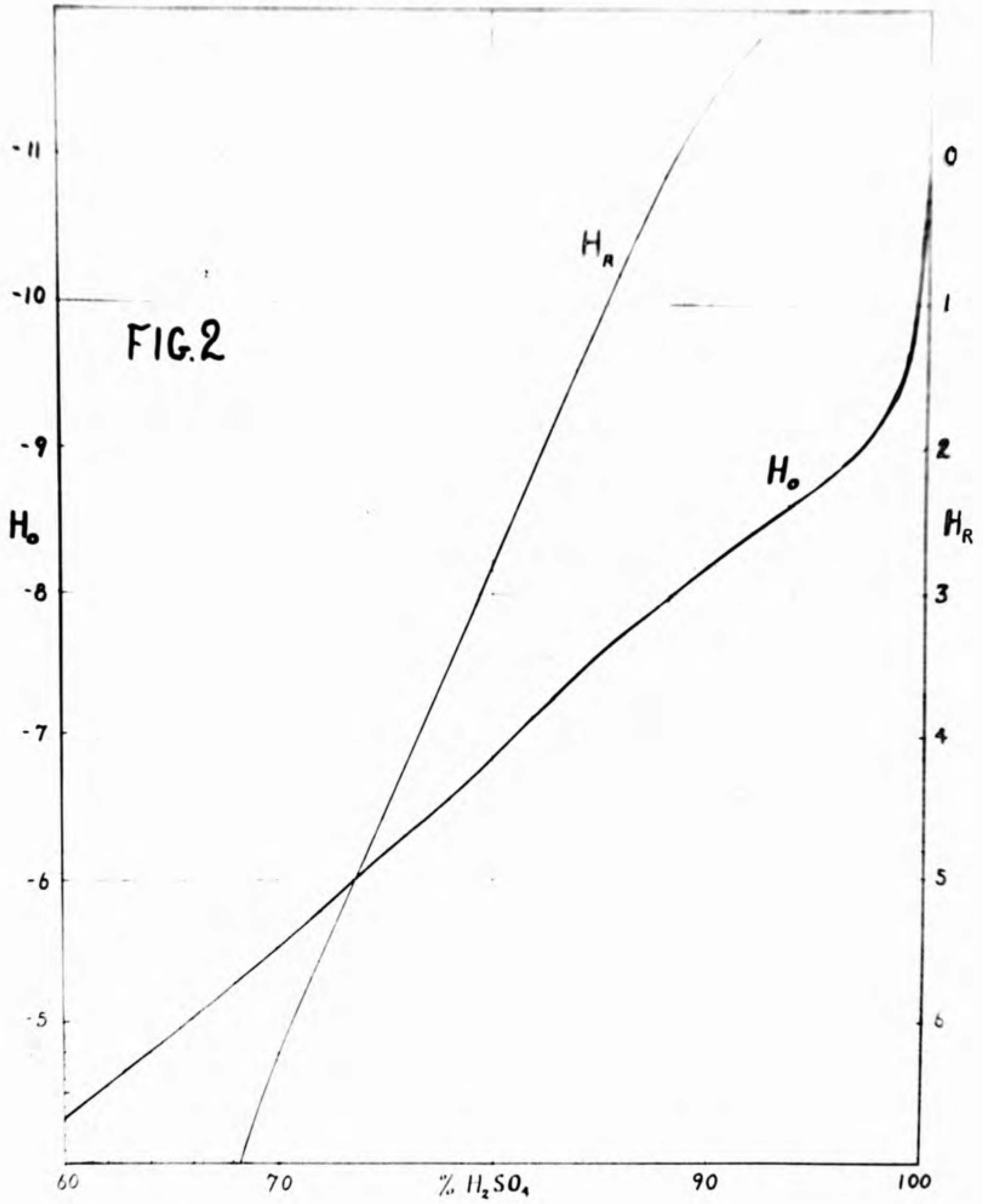


FIG.2

since the range of acidity in which these indicators could be used overlapped that of the lowest employed in previous work, an accurate value for the zero on the scale of the acidity function H_0 could be established. This zero was 0.29 unit lower than that previously provisionally adopted by Hammett and Deyrup (58). Thus all values of pK' and H_0 given in the earlier work should be corrected by the subtraction of 0.29 unit.

Hammett and Paul also observed that it was possible to correlate the behaviour of such typical acid-catalysed reactions as sucrose inversion and ester hydrolysis on the basis of the acidity of the solution (61). If the logarithm of the rate of reaction was plotted against H_0 a straight line with a unit slope was obtained. This amounts to a direct proportionality between the reaction rate and the measure of hydrogen ion concentration or activity given by the indicator method of measurement. The authors pointed out that this can only result from the fact that both the acid catalysis and the indicator reaction depend upon the addition of the hydrogen ion to a neutral organic molecule of basic properties, the substrate in one case and the indicator base in the other. According to the ionisation theory discussed by Bronsted the observed rate of reaction is the rate of further change of the ion SH^+ formed by addition of hydrogen ion to the substrate S. The rate of formation of the ion SH^+ is so rapid compared with that of further reaction that equilibrium exists between the ion and substrate. The rate of reaction r is then given by $r = k_1[SH^+] = k_2\, a_S\, a_{H^+} \frac{1}{f_{SH^+}} = k_2[S]\, a_{H^+} \frac{f_S}{f_{SH^+}}$

Since the ratio f_S/f_{SH^+} may be expected to be the same as the corresponding ratio f_B/f_{BH^+} for any other base, including the indicators, and since by definition $H_o = -\log a_{H^+} \frac{f_B}{f_{BH^+}}$,

the specific velocity $k = r/[S]$ is given by

$\log k + H_o = \log k_2$ which is the equation of the straight line previously obtained.

In 1935 L.A. Flexser, L.P. Hammett, and A. Dingwall demonstrated that ultra-violet absorption methods could be used to measure the degree of ionisation of an organic base, and hence the acidity function of suitable solutions (62)

In 1946 F.H. Westheimer and M.S. Kharasch demonstrated that the rate of nitration of nitrobenzene in 85-95% sulphuric acid could be correlated to the acidity of the nitrating medium (31). To do this they employed an indicator of the triarylcarbinol type in place of Hammett's simple base. These two types of indicators ionise in different ways in sulphuric acid

$$A + H_2SO_4 \rightleftarrows AH^+ + HSO_4^-$$

$$ROH + 2H_2SO_4 \rightleftarrows R^+ + OH_3^+ + 2HSO_4^-$$

While not explicitly designated as such, a new scale of acidity had been introduced by this work. This new acidity function was defined, and the range extended by the work of A.M. Lowen, M.A. Murray and Gwyn Williams (63,64). These authors defined K_R and K_S as the thermodynamic equilibrium constants, defined in terms of activities, for two carbinol indicators ROH and SOH. If the two indicators are placed in the same sulphuric acid-water medium, in concentrations so small as not to affect the activities of the medium constituents, then, independently of the form of K

$$pK_R - pK_S = \log \frac{[R^+]}{[ROH]} - \log \frac{[S^+]}{[SOH]} + \log \frac{f_{R^+}\, f_{SOH}}{f_{ROH}\, f_{S^+}}$$

It was shown, experimentally, that for the carbinol indicators used $f_{R^+}/f_{ROH} = f_{S^+}/f_{SOH}$. Since pK_R and pK_S are thermodynamic constants, independent of medium

$$\log \frac{[R^+]}{[ROH]} - \log \frac{[S^+]}{[SOH]} = \text{Constant (independent of medium).}$$

The ionisation of triarylcarbinol indicators is similar to that observed for nitric acid

$$HNO_3 + 2H_2SO_4 \Longleftrightarrow NO_2^+ + OH_3^+ + 2HSO_4^-$$

It is reasonable, therefore, to expect that

$$\log \frac{[R^+]}{[ROH]} - \log \frac{[NO_2^+]}{[NO_2.OH]} = \text{Constant (independent of medium).}$$

If the rate of nitration of a compound ArH is given by

$$\begin{aligned} r &= k[NO_2^+][ArH] \\ &= k[NO_2.OH][ArH]\frac{[NO_2^+]}{[NO_2.OH]} \end{aligned}$$

Then, if $[HNO_3]$ denotes the stoichiometric concentration of total nitric acid

$$r \sim k\ [HNO_3][ArH]\frac{[NO_2^+]}{[NO_2.OH]}$$

providing that the extent of ionisation of nitric acid is small (e.g. in sulphuric acid-water media below 85% sulphuric acid). Experimentally it has been shown that

$$r = k_2\ [HNO_3][ArH]$$

in which k_2 varies with the medium composition. Therefore

$$\begin{aligned} \log k_2 &= \log r - \log [HNO_3][ArH] \\ &= \log k + \log \frac{[NO_2^+]}{[NO_2.OH]} \\ &= \log k + \log \frac{[R^+]}{[ROH]} + \text{Const. (independent of medium).} \end{aligned}$$

Providing that k is constant over the medium range examined, the variation of log k_2 with medium composition should run parallel with that of log $\frac{[R^+]}{[ROH]}$. This was found to be the case for those organic molecules whose kinetics could be examined in the medium range 72-85% sulphuric acid. There was no parallelism between these lines and Hammett's acidity function H_o.

Williams <u>et al</u>., without specifying the form of either K_R or H_R explicitly, other than in terms of a_{R^+}/a_{ROH} , defined the acidity function H_R which measured the capacity of a medium to ionise a triarylcarbinol indicator.

$$H_R = +pK_R - \log \frac{\{R^+\}}{\{ROH\}}$$

So long as nitric acid ionises in the same way as a triarylcarbinol

$$H_R = +pK_{NO_2.OH} - \log \frac{\{NO_2^+\}}{\{NO_2.OH\}}$$

Therefore $\log k_2 = \log k + pK_{NO_2.OH} - H_R$

where $K_{NO_2.OH}$ is a thermodynamic equilibrium constant for the ionisation of nitric acid. Being defined in terms of activities $pK_{NO_2.OH}$ is invariant with change of medium. Provided that k does not vary over the medium range examined, $\log k_2$ should therefore be linear with respect to H_R , and a line connecting the two should have a unit slope. Without knowing pK_R for some carbinol indicator, H_R cannot be determined in absolute values; values relative to an arbitrary zero may, however, be computed. When values for k_2 for the nitration of trimethylaniline ion and trimethyl-p-tolylammonium ion were plotted against such values of H_R a straight line with a slope of 1.20 was obtained.

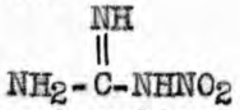
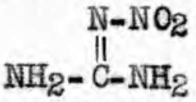
The nature and range of the triarylcarbinol type indicators has since been extended (65).

(iv) Guanidine and Nitroguanidine

Guanidine was first isolated by W. Strecher, as an oxidation product of guanine (71). The chemical literature records three main sources of guanidine salts, namely, from dicyandiamide, from cyanamide solutions, and from cyanamide salts. A review of the history, and methods of preparation of guanidine nitrate is contained in articles by G.B.L. Smith *et al.* (66) and G.F. Wright *et al.* (72). In all convenient methods of synthesis homologous by-products (ammonium nitrate, biguanide nitrate *etc.*) are formed. Unless extensive purification is carried out such by-products will affect the nitration of guanidine. As will be shown later, ammonium type salts have a marked effect upon the yield and rate of nitration in sulphuric acid.

In 1892 V. Thiele (73) prepared nitroguanidine from guanidine nitrate, and also from guanidine thiocyanate, by the action of nitric acid in fuming sulphuric acid. Thiele, and previously G. Pellizzara (74) showed that the product obtained by L. Jousselin (75) by the action of nitric or sulphuric acid on guanidine was nitroguanidine, and not nitrosoguanidine as had been reported. In 1921 T. Ewan and J.H. Young investigated possible methods of preparation of nitroguanidine (76). These authors were concerned only with the overall yield of nitroguanidine, and used concentrations similar to those used commercially. The failure to specify accurately the % sulphuric acid used robs this work of much of its value, but the final conclusion, namely that the action of 92-98% sulphuric acid on guanidine nitrate (1cc./gm. salt) for a period of 48 hours before dilution is the most satisfactory process (yield $>$ 80%), is valid. Ewan and Young also studied the nitration of guanidine nitrate in concentrated nitric acid. Using a "reddish coloured" nitric acid (87.6%, 3cc./gm. salt) a 64.5% yield of nitroguanidine was obtained in 96 hours. Less time, or a lower ratio of acid/salt resulted in lower yields.

T.L. Davis, A.A. Ashdown, and H.R. Crouch were able to isolate two different crystal forms of nitroguanidine (77), which however possess identical chemical properties. Davis also studied the nitration of substituted guanidines (78) and concluded that only those alkyl guanidines which contain an unsubstituted amino group can form N-nitro compounds by direct nitration. Concluding that the mechanism of nitration was not a straightforward dehydration of the nitrate salt, Davis treated guanidine nitrate with phosphoric acid and phosphorous pentoxide. After 30 minutes at 65°C., or 30 hours at room temperature 95% of the guanidine was recovered; after 48 hours at room temperature an 82% yield of nitroguanidine was obtained. The authors explain these results as being due to the formation of nitric or nitrophoric acid, but they make no suggestion as to the actual mechanism of the reaction.

T.L. Davis and A.J.J. Abrams studied the behaviour of nitroguanidine in sulphuric acid (79), and found that it dearranges in two modes, to form nitroamide and cyanamide, or to form ammonia and nitrocyanamide. They also found that a solution of nitroguanidine in concentrated sulphuric acid was an excellent nitrating agent. Thiele, after due consideration (80), assigned the structure  $NH_2\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NHNO_2$ (I) to nitroguanidine but Wright <u>et al</u>. have advanced evidence to support the alternate structure  $NH_2\text{-}\overset{\overset{N\text{-}NO_2}{\|}}{C}\text{-}NH_2$ (II). Both arguments are adduced from evidence obtained in dilute aqueous solutions, and as will be seen later neither structure has a strict physical meaning when applied to solutions of nitroguanidine in concentrated sulphuric acid.

II.

II. The Kinetics of Nitration of Guanidine in Sulphuric Acid.

The object of this research was to study the mechanism of the conversion of guanidine nitrate into nitroguanidine in a sulphuric acid medium.

(i) Reversibility of the reaction.

When guanidine nitrate is dissolved in sulphuric acid the nitric acid concentration falls very rapidly to a constant value which is not zero. This behaviour is illustrated by the two experiments given in Table I.

Table I

Initial concentration guanidine nitrate 0.2000 M.

Temp. 25°C.

Expt. 78 Medium 100% H_2SO_4		Expt. 82 Medium 87.8% H_2SO_4	
Time	Conc. HNO_3	Time	Conc. HNO_3
min.	M.	min.	M.
0	(0.2000)	0	(0.2000)
8.7	0.1674	9.2	0.0126
12.2	0.1672	13.0	0.0122
17.0	0.1679	16.5	0.0124
20.8	0.1671	21.4	0.0127
27.6	0.1666	27.2	0.0124
34.1	0.1650	36.3	0.0125
67.4	0.1672	52.3	0.0125

On the basis that the disappearance of the nitric acid is connected with the formation of nitroguanidine the results suggest that guanidine nitrate and nitroguanidine enter into an equilibrium in sulphuric acid solution, the composition of the equilibrium mixture being dependent on the medium composition. This suggestion is confirmed by experiments with nitroguanidine as a starting material. When nitroguanidine is dissolved in a sulphuric acid medium nitric acid is formed, the concentration of which rapidly rises to a constant value, identical with that obtained from guanidine nitrate (in appropriate concentration) as a starting material. Thus, the same equilibrium composition may be approached from either side, from initial guanidine nitrate, or from initial nitroguanidine. In media below 83% sulphuric acid the rate of attainment of equilibrium is small enough to permit the progress of the reaction to be followed. Experiments illustrating the identity of this equilibrium are given in Table II, and in Fig. 11.

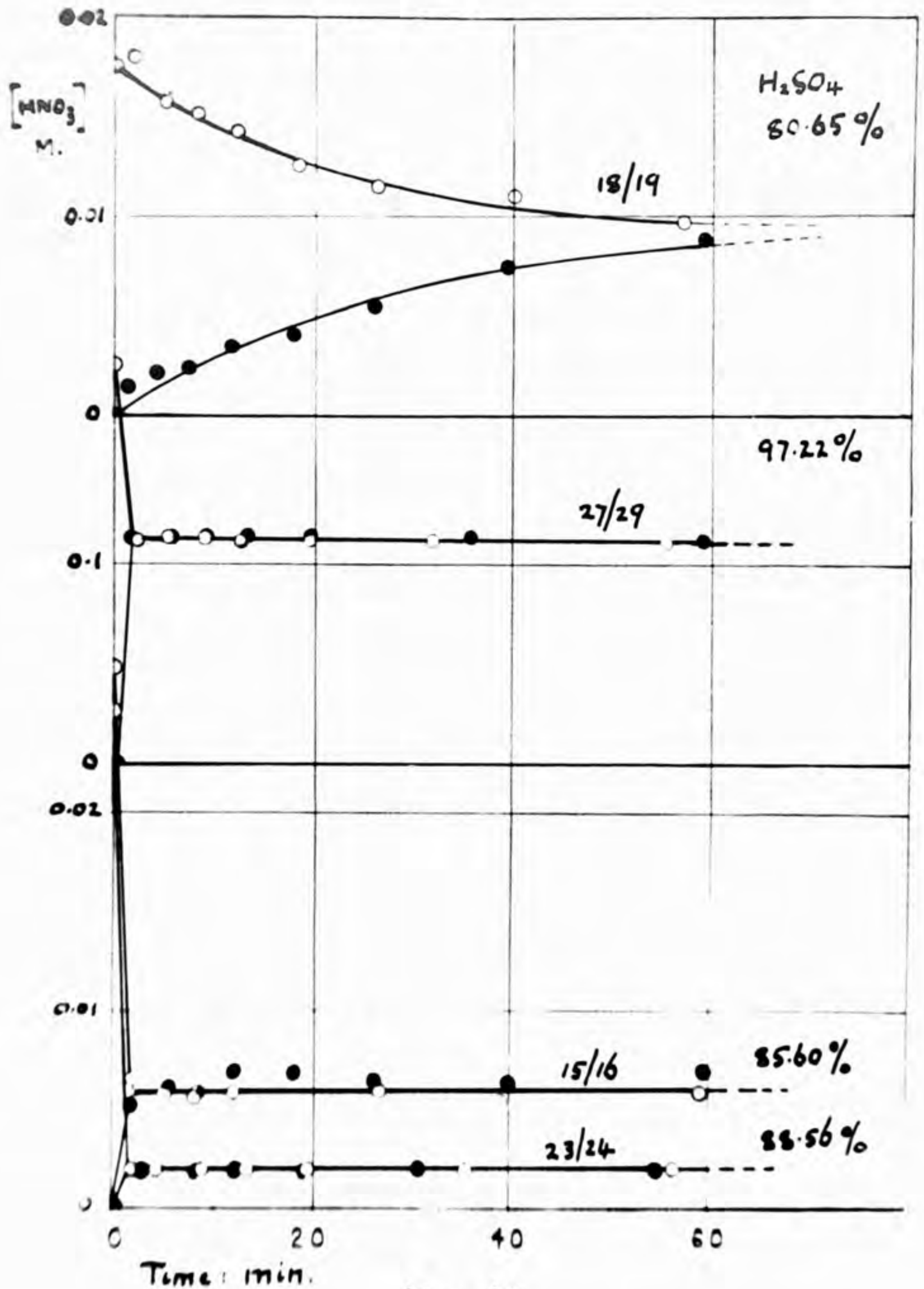


Fig 11

○ Initial guanidine nitrate

● Initial nitroguanidine

Table II

Medium 97.2% H_2SO_4 Temp. 25°C.

Expt. 27 Initial guanidine nitrate 0.2000 M.		Expt. 29 Initial nitroguanidine 0.2000 M.	
Time min.	Conc. HNO_3 M.	Time min.	Conc. HNO_3 M.
2.4	0.1124	1.8	0.1129
5.3	0.1133	5.7	0.1133
9.0	0.1130	9.2	0.1134
12.7	0.1122	13.3	0.1140
19.1	0.1121	19.7	0.1140
32.1	0.1121	36.0	0.1138
55.8	0.1105	59.3	0.1119

The data used in establishing the equilibrium compositions was obtained by analysing the residual nitric acid by the modified Kolthoff method of nitrate analysis (see experimental section). If a solution of guanidine nitrate in sulphuric acid is analysed by the Treadwall and Vontobel method of nitrate analysis (69) a value corresponding to 100% nitric acid is obtained. Similarly, when nitroguanidine is used as the starting material, the value obtained for the nitric acid concentration is that which would be expected if the equilibrium

Guanidine + Nitric acid ⟷ Nitroguanidine + Water (I) lay 100% to the left.

The explanation of this anomaly lies in the fact that the Treadwall and Vontobel method of analysis is done in sulphuric acid of a strength greater than 90%. In such an acid the rate of attainment of equilibrium is very great, and the result of titrating the original residual nitric acid will be to shift the equilibrium in such a manner as to produce more nitric acid. Since the equilibrium shifts very rapidly the process continues until all the potential nitric acid has been used up. Typical experimental values are given in Table III.

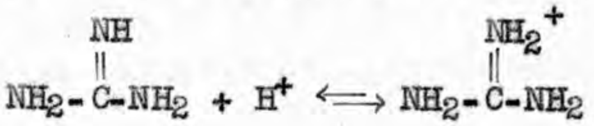
Table III

Weight Nitroguanidine	gm. HNO_3 found	$\frac{\text{Moles } HNO_3 \text{ found}}{\text{Moles nitroguanidine}}$
0.0741 gm.	0.0448	0.998
0.1067	0.0643	0.995
0.0841	0.0508	0.997

Aqueous solutions are used in the Kolthoff method of analysis; below 70% sulphuric acid the rate of attainment of equilibrium is so low that solutions can be analysed without inducing a change in the equilibrium composition.

(ii) Ionisation of guanidine and nitroguanidine.

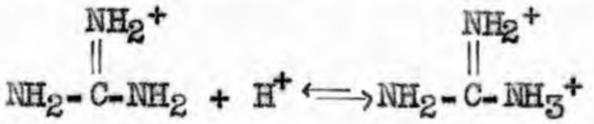
In view of the strong basic properties of guanidine (82), it must exist as a charged ion when in solution in sulphuric acid. Such an uptake of a proton may be represented as



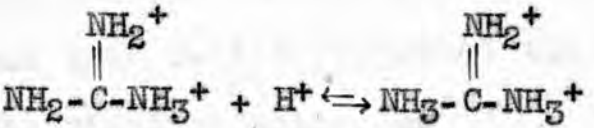
$$NH_2-\overset{\overset{NH}{\|}}{C}-NH_2 + H^+ \rightleftarrows NH_2-\overset{\overset{NH_2^+}{\|}}{C}-NH_2 \qquad (\mathrm{II})$$

or more concisely $G + H^+ \rightleftarrows GH^+$

A. Hantzsch and W. Geidel measured the cryoscopic depression of a solution of guanidine in 100% sulphuric acid, and found that guanidine was present as a triply charged ion (81). If this is so, then there are the further equilibria



$$NH_2-\overset{\overset{NH_2^+}{\|}}{C}-NH_2 + H^+ \rightleftarrows NH_2-\overset{\overset{NH_2^+}{\|}}{C}-NH_3^+ \qquad (\mathrm{III})$$

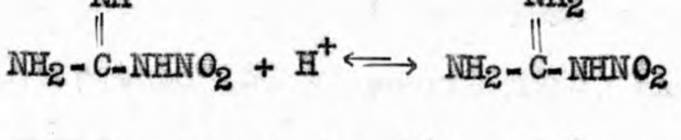


$$NH_2-\overset{\overset{NH_2^+}{\|}}{C}-NH_3^+ + H^+ \rightleftarrows NH_3-\overset{\overset{NH_2^+}{\|}}{C}-NH_3^+ \qquad (\mathrm{IV})$$

There is no evidence as to the concentration of sulphuric acid in which these ionisations occur; it would seem likely that the degree of further ionisation does not become extensive until high concentrations of sulphuric acid are reached, since no simple double salt has ever been isolated.

When a saturated solution of nitroguanidine in concentrated sulphuric acid is diluted with water the nitroguanidine is precipitated as a sulphate salt, which is stable in concentrations of sulphuric acid greater than 30%.

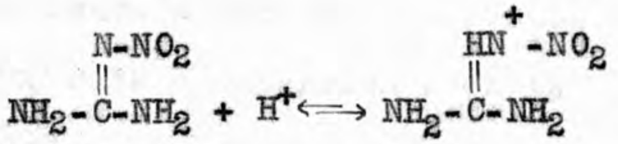
Nitroguanidine is therefore present in an ionised form when in solution in strong sulphuric acid, although it is normally considered as being lacking in basic properties (82). This ionisation may be represented as



$$NH_2-\overset{NH}{\overset{\|}{C}}-NHNO_2 + H^+ \longleftrightarrow NH_2-\overset{NH_2^+}{\overset{\|}{C}}-NHNO_2 \qquad (V)$$

or more concisely $R + H^+ \longleftrightarrow RH^+$

or



$$NH_2-\overset{N-NO_2}{\overset{\|}{C}}-NH_2 + H^+ \longleftrightarrow NH_2-\overset{H\overset{+}{N}-NO_2}{\overset{\|}{C}}-NH_2 \qquad (VI)$$

Leaving the consideration of which is the most appropriate form of nitroguanidine ion until later, we may thus better represent the reversible reaction (1), (in the simplest case), as

$$GH^+ + HNO_3 \longleftrightarrow RH^+ + H_2O \qquad (VII)$$

(iii) Bimolecular nitration.

Expts. 15/6 and 23/4 in Fig. 11 show that the attainment of equilibrium is very rapid in 85.6% sulphuric acid with 0.027 M. reagents (c.f. expts. 27/9 at 0.2 M.). With 0.018 M. reagents in 80.7% sulphuric acid (expts. 18/9), however, the approach to equilibrium takes a measurable time, being incomplete after one hour. It may be assumed, therefore, that the actual chemical reaction is very rapid in media of greater than 85% sulphuric acid, and normal kinetic measurements are impossible. Below 85% sulphuric acid it is possible to follow the attainment of equilibrium, and thus to measure the rate of reaction.

The rate of approach from the left hand side to equilibrium in the reversible system (VII) has been measured in sulphuric acid in the media range 71-83% sulphuric acid. The rates were measured by mixing a solution prepared by dissolving guanidine carbonate in a given medium with a solution of anhydrous nitric acid in the same medium, and then following the fall of nitric acid with time. The methods of mixing, and of analysis, are described in the experimental section. Guanidine carbonate, $G_2.H_2CO_3$, is not an ideal material for the preparation of solutions of guanidine ion, inasmuch as the reaction

$$G_2.H_2CO_3 + 2H_2SO_4 \rightarrow 2GH^+ + 2HSO_4^- + H_2O + CO_2$$

results in the production of one half mole of water per mole of guanidine ion. The failure to obtain a pure guanidine sulphate, $G_2.H_2SO_4$, rather than the hemi-hydrate, $G_2.H_2SO_4.\frac{1}{2}H_2O$, left no alternative to its use. Some specimen results of the reaction curves obtained are shown in Fig. 11.

When 1/ $[HNO_3]$or log $\dfrac{[HNO_3]}{[GH^+]}$, (according to whether the initial reactant concentrations are equivalent or not), is plotted against time, the plot is initially linear, as is shown in Figs. 13,14. This circumstance suggests that the equation

$$-d\ [HNO_3]\ /dt = k_2\ [HNO_3][GH^+] \qquad \text{(VIII)}$$

is valid for the nitration process. The progressive deviation from linearity may be attributed to the increasing influence of the reverse reaction (denitration). In the reactions with guanidine salt and nitric acid as starting materials, the equilibrium end-point generally corresponds to a 60-95% conversion of the initial reagent present in defect, that is, equilibrium VII lies substantially to the right. In consequence the initial stage of nitration may be considered to be relatively little disturbed by the reverse reaction, and the test applied to the nitration in Figs. 13, 14 is more reliable than the analogous test applied to the denitration (see Part II (iv)). Confirmation of the validity of equation VIII is found in that plots of log $[HNO_3]$ against time are initially curved (Fig.14). The evidence from the initial stages of individual nitration

FIG. 13

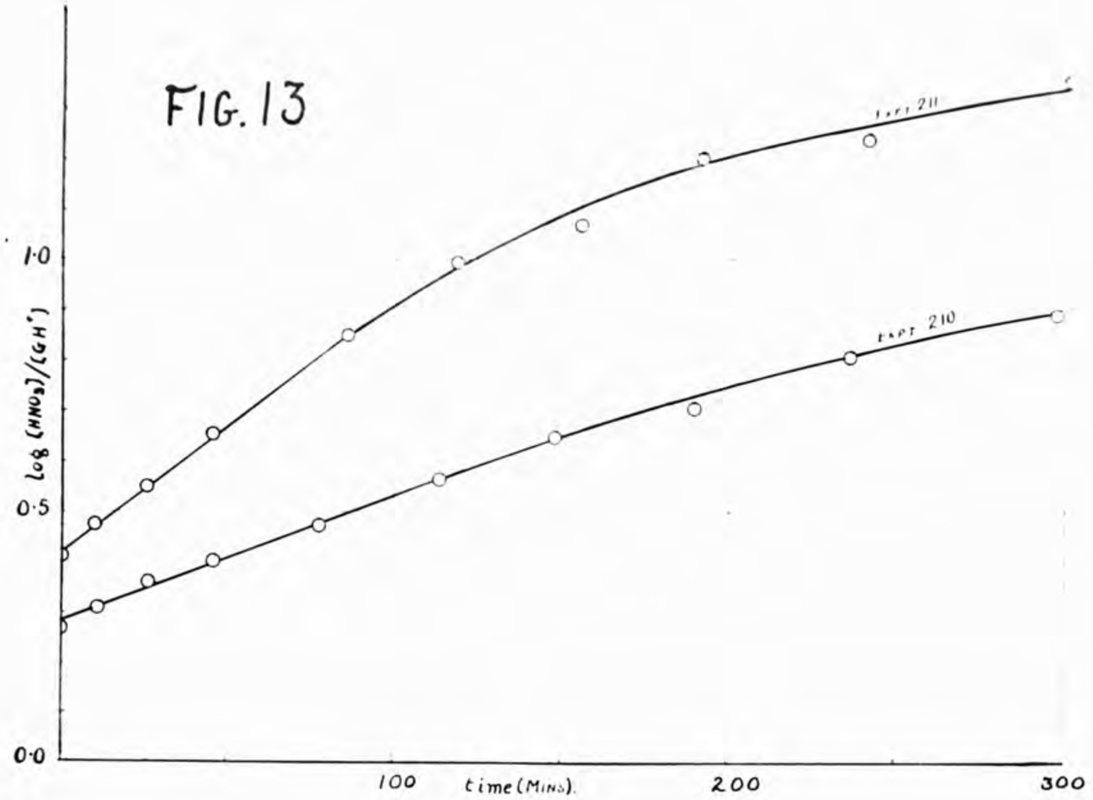

Expt 211
Expt 210
log [HNO3]/[GH']
1·0
0·5
0·0
100
time (Mins).
200
300

FIG. 14


Expt 204
1/[HNO3] ~ time
Expt 211
log [HNO3] ~ time
1̄·7
1̄·6
log [HNO3]
20
15
1/[HNO3]
100
time (Mins).
200
300

experiments is therefore in favour of the bimolecular equation VIII, and against a unimolecular equation in which the rate is represented as being independent of the guanidine ion concentration. These conclusions are supported by the results of varying the initial concentrations of the reactants in a given medium.

(a) Influence of initial nitric acid concentration.

The values of velocity coefficients, k_2, set out in Table IV, which were derived graphically from equation VIII for the initial stages of nitration, show that k_2 is constant for a 13-fold variation of the initial nitric acid concentration. The rate of nitration is thus proportional to the nitric acid concentration, which is in accordance with equation VIII.

Table IV

Variation of Initial Nitric Acid Concentration

Medium 75.47% H_2SO_4 Temp. 25°C.

Expt. No.	Guanidine - initial conc. M.	HNO_3 - initial conc. M.	$k_2 \times 10^2$
206	0.2024	0.0509	3.56
203	0.2025	0.0815	3.62
202	0.2027	0.0996	3.55
198	0.2020	0.1481	3.60
190	0.2025	0.2037	3.60
208	0.2026	0.2446	3.73
209	0.2019	0.2974	3.79
210	0.2022	0.3744	3.59
211	0.2019	0.5190	3.60
212	0.2023	0.6649	3.91

(b) Influence of Initial Guanidine Concentration.

The values of velocity coefficients, k_2, set out in Table V were derived graphically from equation VIII for the initial stages of nitration. In any one medium the coefficient k_2 falls substantially with rising initial concentration of guanidine ion. Nevertheless, k_2 is not inversely proportional to the initial concentration of guanidine ion, hence the variation does not mean that the reaction is first order (i.e. with the rate independent of the guanidine concentration). The varying coefficients, k_2, of Table V would seem to be inconsistent with equation VIII, but this discrepancy may be explained. It is known that variation of the guanidine ion concentration alters the acidity of the sulphuric acid medium. As will be discussed later, there is some evidence that the induced change in acidity is sufficient to account for the variation in the coefficients k_2 under varying initial concentrations of guanidine ion.

Table V

Variation of Initial Guanidine Concentration Temp. 25°C.

Medium % H_2SO_4	Expt. No.	Guanidine - initial conc. M.	HNO_3 - initial conc. M.	$k_2 \times 10^2$
81.14	162/163	0.0957	0.1923	369
	160/161	0.1907	0.1930	209
	164/165	0.3822	0.1923	158
78.33	182/183	0.0494	0.1988	25.4
	177/178	0.0987	0.1990	23.0
	181	0.1486	0.1985	18.5
	175/176	0.1979	0.1985	18.9
	179/180	0.2951	0.1997	15.2
75.47	194	0.0508	0.2028	6.52
	193	0.1013	0.2038	5.02
	192	0.1525	0.2030	4.36
	190	0.2025	0.2037	3.60
	191	0.3034	0.2040	2.85

(c) Influence of Initial Equimolecular Guanidine and Nitric Acid Concentrations.

The values of velocity coefficients, k_2, set out in Table VI were derived graphically from equation VIII for the initial stages of nitration. In the experiments thus summarised guanidine and nitric acid were kept in equimolecular proportions while the initial concentrations were varied. In any one medium the coefficient k_2 falls with rising initial concentration of the reagents. The variation of the coefficient k_2 is not so great as in Table VI, although probably caused by the same effect.

Table VI

Variation of Initial Guanidine - Nitric Acid Concentration
Temp. 25°C.

Medium % H_2SO_4	Expt. No.	Guanidine - initial conc. M.	HNO_3 - initial conc. M.	$k_2 \times 10^2$
78.33	185	0.1040	0.1049	18.1
	186	0.1335	0.1345	19.9
	175/176	0.1979	0.1985	18.9
	184	0.2349	0.2374	16.6
75.47	205	0.0506	0.0509	4.15
	204	0.0812	0.0812	4.44
	201	0.0993	0.0994	4.26
	200	0.1329	0.1331	4.07
	199	0.1469	0.1480	4.00
	197	0.1752	0.1773	3.53
	190	0.2025	0.2037	3.60

(d) Influence of Sulphuric Acid Medium.

The values of velocity coefficients, k_2, set out in Table VII were derived graphically from equation VIII for the initial stages of nitration. With a constant initial concentration of guanidine and nitric acid (0.2 M.) the velocity coefficient k_2 varies by an order of 4×10^3 over the sulphuric acid range 71.5-83.0%. The variation of k_2, subject to experimental error, is linear with regard to the % sulphuric acid: the implications of this will be discussed later.

Table VII

Variation of Sulphuric Acid Medium Temp. 25°C.

Medium % H_2SO_4	Expt. No.	Guanidine - initial conc. M.	HNO_3 - initial conc. M.	k_2
82.94	225/226	0.2004	0.2023	9.95 ?
81.14	160/161	0.1907	0.1930	2.59 ? — 2.09
79.24	221/222	0.2070	0.2093	0.730 ✓
78.33	175/176	0.1979	0.1985	0.189 ✓
75.47	190	0.2025	0.2037	0.0360 ✓
71.48	223/224	0.2099	0.2081	0.00254 ✓

(iv) Unimolecular Denitration.

The rate of approach from the right hand side to equilibrium in the reversible system (VII) has been measured in sulphuric acid in the medium range 71-83% sulphuric acid. The rates were measured by dissolving a known amount of nitroguanidine in a given medium and then following the rise of nitric acid with time. The method of mixing, and of analysis, is described in the experimental section. If log $[RH^+]$ is plotted against time, then for the initial stage of denitration the plot is approximately linear (Fig. 15). This suggests that the equation

$$-d\,[RH^+]/dt = k_1\,[RH^+] \qquad (IX)$$

is valid for the denitration process. The progressive deviation from linearity may be attributed to the increasing influence of the forward reaction (nitration). In this media range the equilibrium VII lies substantially to the right, and the process of denitration, (which at the equilibrium end-point amounts to 40% at most) cannot proceed far before being heavily interfered with by the nitration process. Thus the reasonable range of validity of plots such as Fig. 15 extends over so small a conversion range that the linear plot is far from reliable as a criterion for the applicability of equation IX. Nevertheless, when the initial concentration of nitroguanidine is multiplied eight-fold in a given medium, the time taken for 5% denitration rises by no more than 50%; it would seem

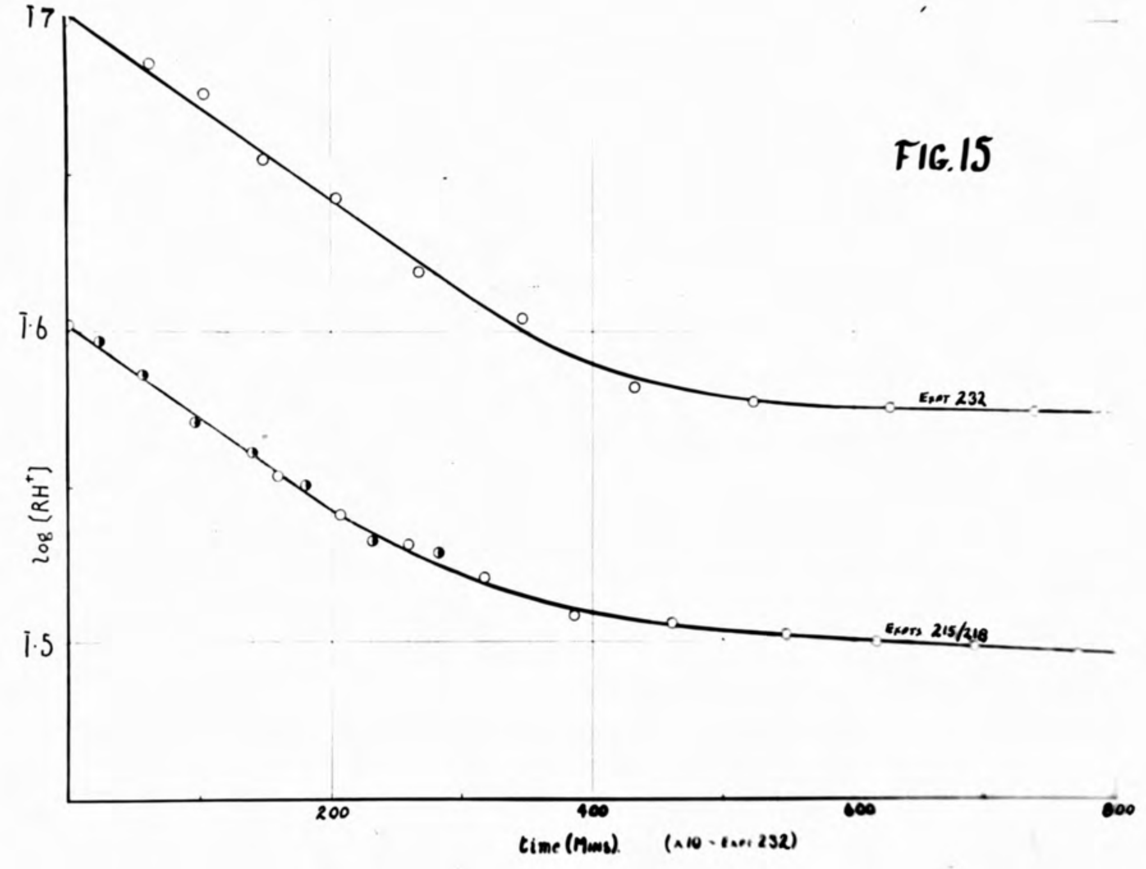

Ī7
Ī·6
Ī·5
log (RH⁺)
200
400
600
800
time (Mins).
(×10 - Expt 232)
Expt 232
Expts 215/218

FIG. 15

therefore that equation IX is the best simple expression for the rate of denitration.

(a) Influence of Initial Nitroguanidine Concentration, and of Sulphuric Acid Media.

The values of velocity coefficients, k_1, set out in Table VIII, were derived graphically from equation IX for the initial stages of denitration. In any one medium the velocity coefficient k_1 falls substantially with rising initial concentration of nitroguanidine ion, but it is not inversely proportional to the initial concentration of nitroguanidine ion. While a variation in the coefficient k_1 would seem to be inconsistent with equation IX, the discrepancy may, like that of k_2 with increasing initial guanidine ion concentration, be explained as a result of the inherent change in the acidity of the sulphuric acid medium.

The velocity coefficient for denitration, k_1, like the velocity coefficient for nitration, k_2, falls with decreasing sulphuric acid concentration. The variation in k_1 is linear with respect to % sulphuric acid, but the magnitude of the change ($= 1 \times 10^2$) is not so great as in the case of k_2.

Table VIII

Variation of Initial Nitroguanidine. Temp. 25°C.

Medium % H_2SO_4	Expt. No.	Nitroguanidine - initial conc. M.	k_1	Time for 5% Denitration (min)
82.94	235/237/238	0.2084	0.0277	
79.24	232	0.0500	0.00682	8.0
	231	0.1041	0.00645	8.5
	230	0.1562	0.00576	9.7
	228/229	0.2084	0.00555	8.7
	233	0.3047	0.00480	9.7
	234	0.4146	0.00415	12.3
75.47	216/217	0.1000	0.00106	50
	207/213/214	0.2024	0.000945	57
	215/218	0.4000	0.000680	77
71.48	239/240	0.2082	0.000180	

(b) Equilibrium Constants

A further example of the validity of equation VIII for nitration and equation IX for denitration is afforded by comparison of the values of the empirical equilibrium constant K of equation VII (determined from end-point measurements, the suffix e denoting equilibrium concentrations)

$$K = \frac{[RH^+]_e}{[GH^+]_e [HNO_3]_e} \qquad (X)$$

with values of equilibrium constant calculated from the initial reaction rates by the relation $K = k_2/k_1$. This has been done in Table VIIIa; a good measure of agreement is shown if due allowance is made for the size of the experimental error. Fig. 19 shows that the equilibrium constants K obtained in this manner are in good agreement with those obtained by end-point measurements over the range 83-100% sulphuric acid.

Table VIIIa

Medium % H_2SO_4	k_2/k_1	K
82.94	359	324
79.24	132	115
75.47	38.1	40.7
71.48	14.1	13.8

(v) The Reversible Kinetic Equation

Combination of equations VIII and IX gives us an equation which is an expression of the reaction rate in the reversible reaction for a given medium.

$$-d[HNO_3]/dt = k_2[GH^+][HNO_3] - k_1[RH^+] \qquad (XI)$$

Let a be the initial concentration of guanidine ion, and b the initial concentration of nitric acid; and let x and z be the concentrations of nitroguanidine at time t and at equilibrium respectively. Then equation XI takes the form

$$dx/dt = k_2(a-x)(b-x) - k_1x \qquad (XII)$$

and this can be integrated to the form (*cf.* Walker and

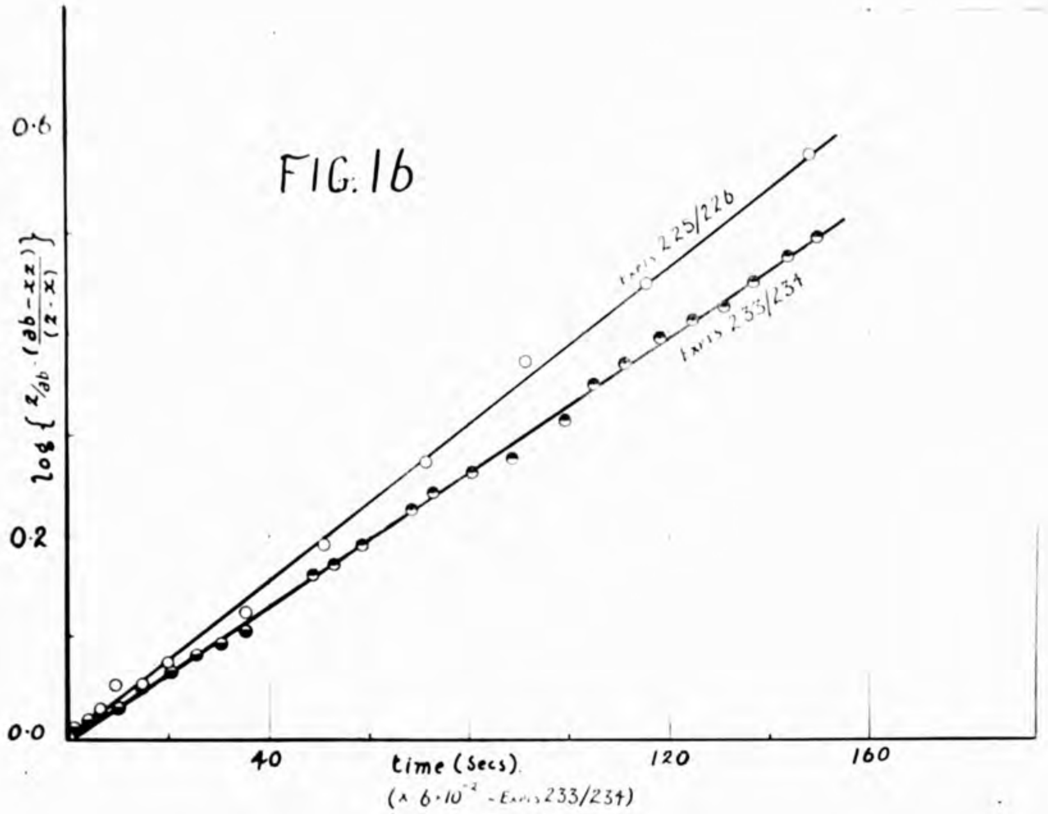


FIG. 16

0·0
0·2
0·6
$\log\left\{\frac{z}{ab}\cdot\frac{(ab-xz)}{(z\cdot x)}\right\}$
40
120
160
time (Secs)
(× 6·10⁻² – Expts 233/234)
Expts 225/226
Expts 233/234

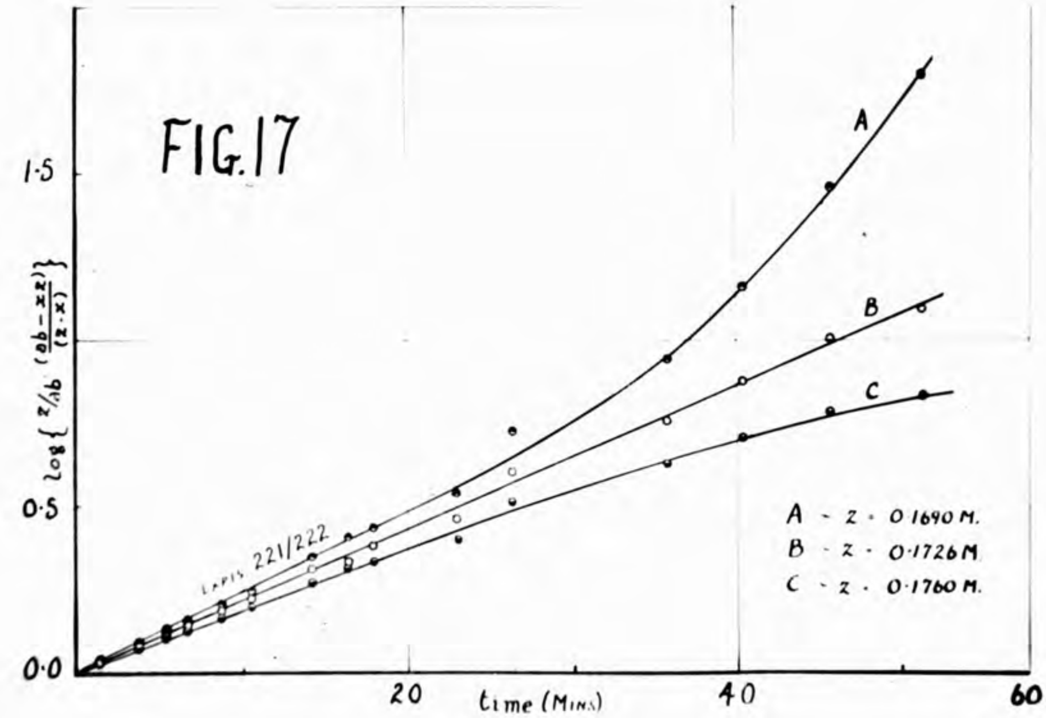


FIG. 17

0·0
0·5
1·5
$\log\left\{\frac{z}{ab}\cdot\frac{(ab-xz)}{(z\cdot x)}\right\}$
20
40
60
time (Mins)
Expts 221/222
A
B
C
A – z = 0·1690 M.
B – z = 0·1726 M.
C – z = 0·1760 M.

Appleyard (83))

$$k_2t = \frac{2.303z}{(ab-z^2)} \log \left\{ \frac{z}{ab} \cdot \frac{(ab-xz)}{(z-x)} \right\} \qquad \text{(XIII)}$$

Equation XIII can be tested by plotting log $\{(ab-xz)/(z-x)\}$ against time. Fig. 16 shows that linear plots result when this is done for experiments in which the equilibrium concentration z is known. In those experiments wherein the reaction was not followed to equilibrium, a judicious extrapolation enables one to plot the function above. This has been done for a number of experiments; Fig. 17 shows how the shape of the plot indicates the validity of the extrapolated value of z. More accurate values of the velocity coefficient k_2 obtained from equation XIII are summarised in Table IX; values which depend upon extrapolation are shown in brackets. In order to differentiate from values of the velocity coefficient obtained from the initial stages of nitration, those values of the velocity coefficient obtained by use of equation XIII have been designated as k_2(corr.). It will be noted that the values of k_2(corr.) do not show the discrepancies in variation exhibited by values of k_2. In some instances there is a substantial difference between the two values of the velocity coefficient (e.g. values for 75.47% sulphuric acid). The alternative values given for k_2 in Expt. 204 show that much depends upon the chosen section of the plot of equation VIII, if this is borne in

Table IX

Medium % H_2SO_4	Expt. No.	c.f. Table No.	k_2	k_2 (corr.)
82.94	225/226	VII	9.95	(11.0)
81.14	162/163	V	3.69	3.74
	160/161	V, VII	2.09	2.59
	164/165	V	1.58	1.61
79.24	221/222	VII	0.730	0.648
78.33	185	VI	0.181	(0.217)
	186	VI	0.199	(0.209)
	175/176	V, VI, VII	0.189	(0.171)
	184	VI	0.166	(0.162)
	182/183	V	0.254	0.272
	177/178	V	0.230	0.241
	181	V	0.185	0.228
	175/176	V, VI, VII	0.189	(0.171)
	179/180	V	0.152	(0.156)
75.47	205	VI	0.0415	--
	204 }	VI	{0.0444	(0.0555
	204 }	VI	{0.0480	0.0555)
	201	VI	0.0426	(0.0530)
	200	VI	0.0407	(0.0517)
	199	VI	0.0400	(0.0489)
	197	VI	0.0353	(0.0434)
	190	IV, V, VI, VII	0.0360	0.0410
	194	V	0.0652	0.0691
	193	V	0.0502	0.0607
	192	V	0.0436	(0.0484)
	190	IV, V, VI, VII	0.0360	0.0410
	191	V	0.0285	(0.0366)
	206	IV	0.0356	--
	203	IV	0.0362	--
	202	IV	0.0355	(0.0362)
	198	IV	0.0360	--
	190	IV, V, VI, VII	0.0360	0.0410
	208	IV	0.0373	--
	209	IV	0.0379	--
	210	IV	0.0359	--
	211	IV	0.0360	0.0435
	212	IV	0.0391	--
71.48	223/224	V, VI, VII	0.00254	(0.00310)

mind together with the error introduced by an extrapolation, then probably the discrepancy is not too marked.

(vi) The Probable Mechanism of N-nitration.

The velocity coefficient k_2 of equation VIII or XII falls by a factor of 4×10^3 in the media range 83-71.5% sulphuric acid. The effective nitrating entity in this range of media could be the residual nitronium ion NO_2^+ (the nitronium ion concentration formed by ionisation of nitric acid in sulphuric acid media of this range is extremely small, see Fig. 1), the nitric acid molecule NO_2OH, or, possibly, the nitracidium ion H_2NO_3 (84).

The N-nitration of the guanidine ion takes place at measurable speeds in the same media range as does the nuclear nitration of the p-tolyltrimethylammonium ion (85). The rates of nitration for the two ions are almost identical in the media range studied, and nitration by the nitric acid molecule is unlikely, since the rate of nitration falls far more steeply than does the vapour pressure of nitric acid over solutions of nitric acid in the same media. Nitration by the nitracidium ion would involve a simple relation between the velocity coefficients k_2 for nitration and the acidity function H_0; similarly nitration by the nitronium ion would involve a simple relation between the velocity coefficients k_2 for nitration and the acidity function H_R. Inspection of Fig. 18 shows that the plot of log k_2 against H_R is a straight line of unit slope. The equation of this straight line may

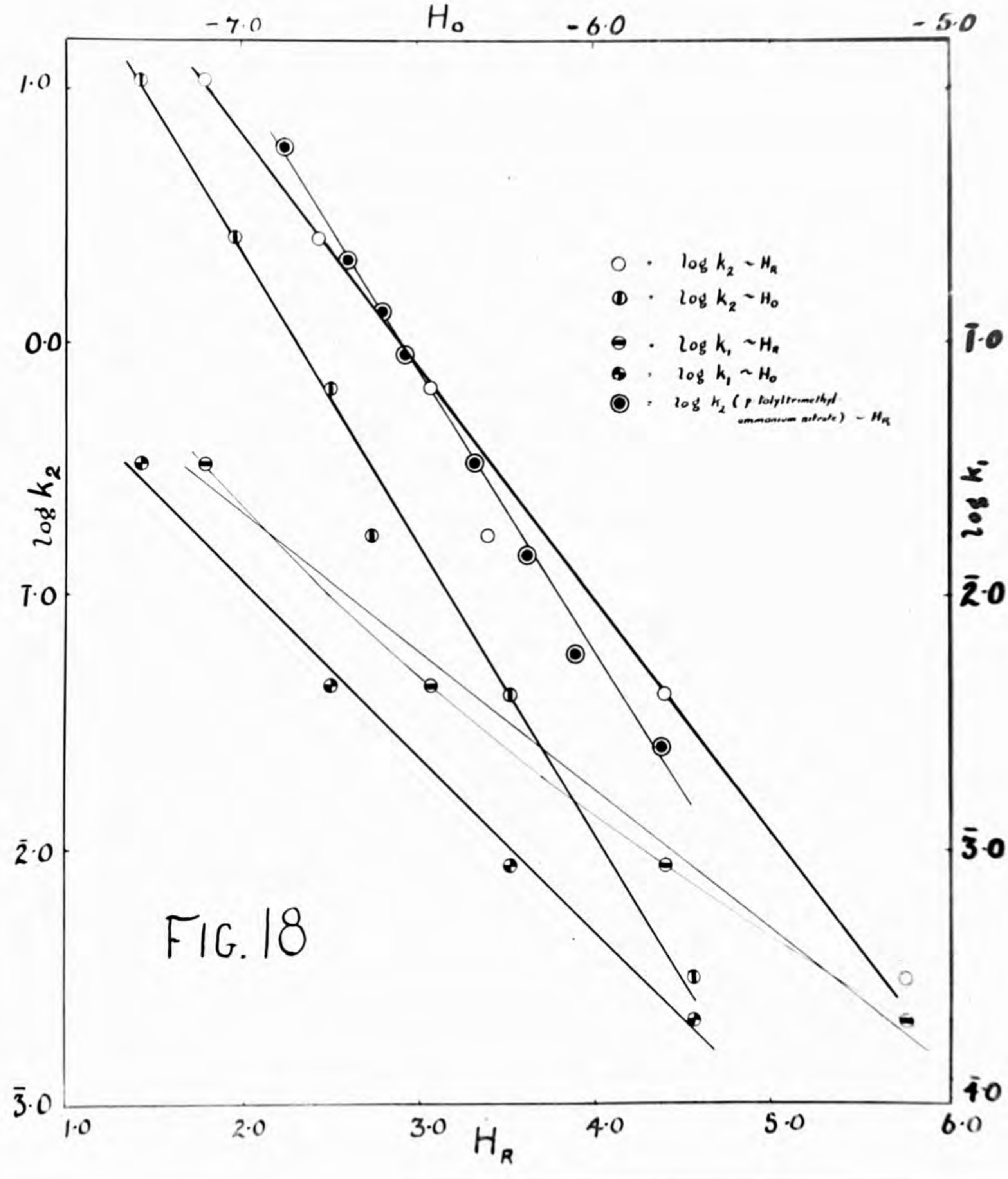

-7.0
H₀
-6.0
-5.0
1.0
0.0
1̄.0
2̄.0
3̄.0
log k₂
1̄.0
2̄.0
3̄.0
4̄.0
log k₁
1.0
2.0
3.0
4.0
5.0
6.0
H_R
○ · log k₂ ~ H_R
◐ · log k₂ ~ H₀
⊖ · log k₁ ~ H_R
● · log k₁ ~ H₀
◉ · log k₂ (p tolyltrimethyl ammonium nitrate) ~ H_R

FIG. 18

be derived simply:

If the experimental equation for r, the rate of nitration of a compound YH, in a given medium, is

$$r = k_2[YH][HNO_3] = k_2[YH][NO_2^+ + NO_2OH] \qquad (XIV)$$

and if the theoretical equation is

$$r = k^{\circ}_2[YH][NO_2^+] \qquad (XV)$$

then

$$k_2 = k^{\circ}_2 \frac{[NO_2^+]}{[NO_2^+ + NO_2OH]} \qquad (XVI)$$

$$\log k_2 = \log k^{\circ}_2 + \log \frac{[NO_2^+]}{[NO_2OH]} - \log\left\{1 + \frac{[NO_2^+]}{[NO_2OH]}\right\} \qquad (XVII)$$

From the definition of H_R

$$H_R = +pK_R - \log \frac{[R^+]}{[ROH]} \qquad (XVIII)$$

$$\log k_2 = \log k^{\circ}_2 + pK_{NO_2OH} - H_R - \log\left\{1 + \frac{[NO_2^+]}{[NO_2OH]}\right\} \qquad (XIX)$$

If $[NO_2OH] \gg [NO_2^+]$,

then $\log k_2 = \log k^{\circ}_2 + pK_{NO_2OH} - H_R \qquad (XX)$

All available evidence points to the fact that $[NO_2OH]$ is very much greater than $[NO_2^+]$ in 70-85% sulphuric acid, and one would therefore expect equation XX to be valid if nitration in this region is effected by the nitronium ion. That this is the case may be seen in Fig. 18, where the logs of the velocity coefficients k_2 for the nitration of p-tolyltrimethylammonium ion, phenyltrimethylammonium ion, and guanidine ion are plotted against H_R.

The points for the plot of the nitration of the guanidine ion are rather scattered, but the slope, calculated by the method of least squares, for the best straight line through them, is -1.04: this is in good agreement with equation XX. By similar arguments it can be shown that if the nitracidium ion were the nitrating agent the plot of log k_2 against H_0 should be a straight line with unit slope, this plot in Fig. 18 has a slope of -2.2. Fig. 18 shows clearly that the concept of N-nitration by the nitronium ion is preferable to that of nitration by the nitracidium ion, but the conformation of the experimental points to the best line

$$\log k_2 = 1.04\ (-H_R) + 3.005 \qquad \text{(XXI)}$$

is not exact, for it would be possible to draw a shallow curve through the points. The curvature (if real) could be due (a) to experimental error, (b) to a variation of the ratio of indicator ionisation with media, (c) to a medium variation of $k^{o}2$ in equation XX. Insufficient information is available at present to decide between these possibilities.

(vii) Influence of Constituents on Acidity

It has been shown above that the major variations in the velocity coefficients k_2 are directly related to changes in the acidity of the medium, as measured by the acidity function H_R. The addition of reagents to a sulphuric acid medium must influence the acidity of it, and it is probable that the varied effects of initial concentrations of reagents may be accounted for by the resultant change of acidity.

(a) Effect of Added Salts.

The effect upon the velocity coefficient, k_2, of induced changes in acidity may be most simply studied in the case of added salts. The values of velocity coefficients, k_2, set out in Table X were derived graphically from equation VIII or XIII for the reaction of equimolar quantities of guanidine ion and nitric acid in a sulphuric acid medium to which either potassium acid sulphate, or ammonium sulphate had been added.

Table X

Medium 81.14% Sulphuric Acid. Temp. 25°C.

Initial Reagent Concentrations 0.2 M.

Expt. No.	Added Salt	Conc. Salt	k_2	k_2 (corr.)
160/161	-	-	2.09	2.59
168	$KHSO_4$	0.299	1.63	2.15
169	"	0.557	1.54	1.94
172	$(NH_4)_2SO_4$	0.285	1.14	
173	"	0.599	0.787	
174	"	0.861	0.475	

Only preliminary measurements have been made of the effect of added materials upon carbinol indicator ionisation, and the values given in Table XI must be accepted with reserve. These values, however, may be used to calculate

Table XI

Added Substance	Medium - % H_2SO_4	ΔH_R/Mole.
Guanidine Carbonate $(GH_2)_2CO_3$	71.48	-1.98 ($\Delta H/2 \simeq -1.0$)
	82.94	-1.82 ($\Delta H/2 \simeq -0.9$)
Potassium Bisulphate $KHSO_4$	78-83	-0.2
Ammonium Sulphate $(NH_4)_2SO_4$	79.79	-0.62
	83.64	-0.97
Nitric Acid HNO_3	71-83	0.2

the acidity, as measured by H_R, for the solutions used in the experiments in Table X. The log of the velocity coefficient k_2 has been plotted against the calculated acidity H_R (Fig.18a), and a close approach to a straight line with unit slope has been achieved. This shows that the main effect of added salt on the velocity coefficient k_2 is accomplished by the alteration of the degree of ionisation of the nitric acid.

(b) Effect of Initial Concentrations.

Because of the inaccuracies involved in (i) the

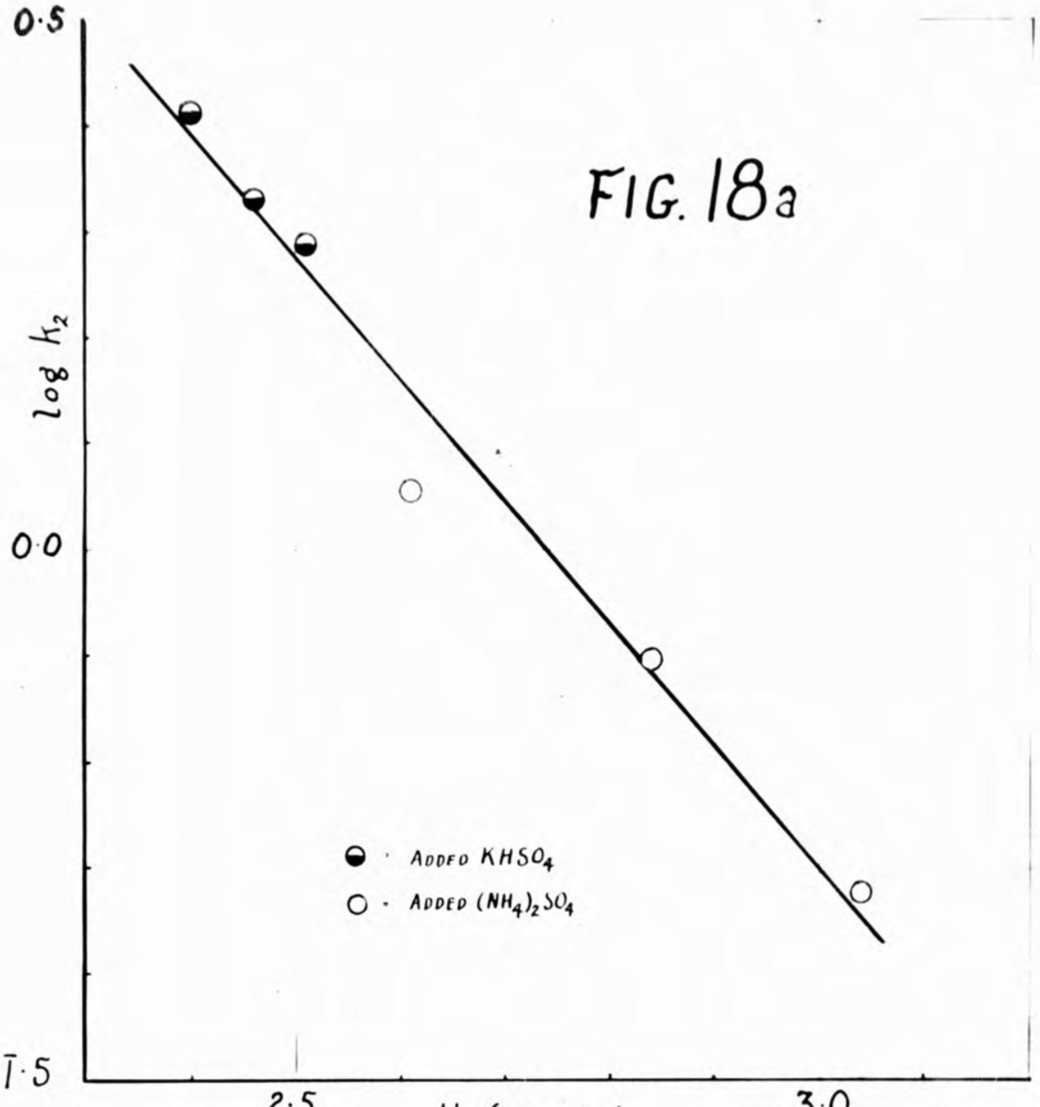

0·5
0·0
$\bar{1}$·5
log k_2
2·5
3·0
H_R (Calculated)
● · Added $KHSO_4$
○ · Added $(NH_4)_2SO_4$

FIG. 18a

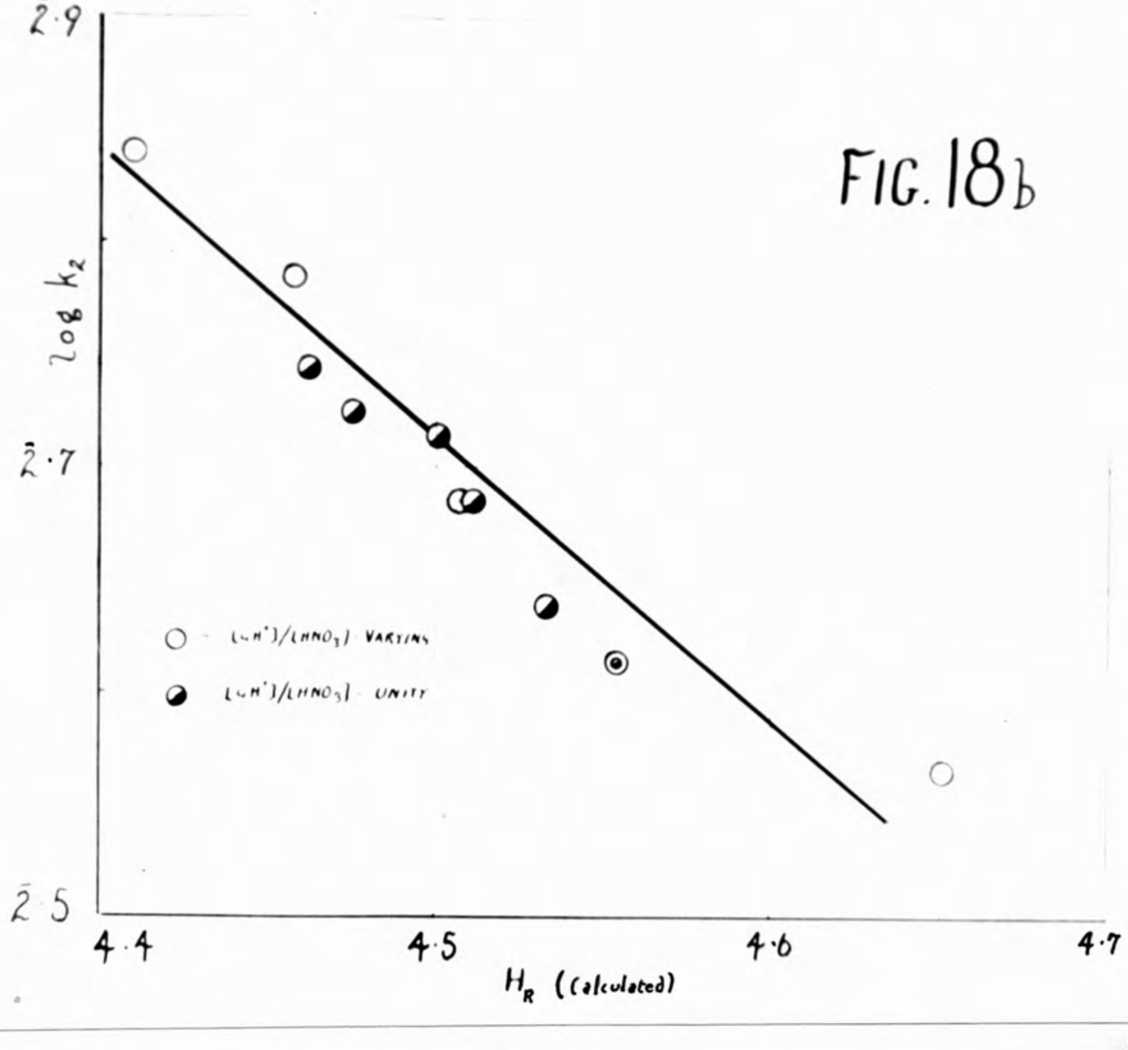

$\bar{2}\cdot9$
$\bar{2}\cdot7$
$\bar{2}\cdot5$
$\log k_2$
4·4
4·5
4·6
4·7
H_R (calculated)
○ $[_sH^+]/[HNO_3]$ VARYING
◐ $[_sH^+]/[HNO_3]$ UNITY

FIG. 18b

determination of k_2, (ii) the determination of H_R, and (iii) the values of ΔH_R/Mole, any calculation seeking to correlate the effect of initial concentration upon the velocity coefficients, k_2, must at best be extremely approximate. It is, however, possible to indicate that the variations of k_2 involved might be accounted for in terms of the induced change in the degree of ionisation of the nitric acid (acidity). From the values given in Table XI it is possible to calculate the decrease in acidity caused by the addition of the initial guanidine, to this value is added the increase in acidity caused by the addition of the initial nitric acid; one then has a value for the acidity of the medium in which the reaction actually took place. This has been done for the experiments carried out in 75.47% sulphuric acid, and log k_2 plotted against the resulting values. As can be seen in Fig.18b the scatter of points is bad, but it is possible to consider them being grouped around a straight line with a slope of -1.3. This would seem to indicate that some of the effect of initial concentration upon the velocity coefficient k_2 is accomplished by the alteration of the degree of ionisation of the nitric acid.

On the basis that nitric acid has a ΔH/Mole of 0.2 one would not expect the velocity coefficient k_2 to remain constant for a 13-fold variation of the initial nitric acid concentration (Table IV). Careful examination of the values obtained, however, indicates that k_2 is actually increasing slightly with increasing initial concentration of nitric acid. Since nitric acid is the only constituent present that could increase the acidity of the medium any increase in the velocity coefficient may be safely attributed to the effect of the nitric acid on the acidity. The sign and smallness of Δ H/Mole of nitric acid would account for its effect not being readily noticeable.

(viii) Effect of Temperature upon N-Nitration.

The progress of the reaction between guanidine ion and nitric acid in sulphuric acid was followed, for given media, over a 20° range of temperature; the velocity coefficients calculated graphically from these observations are given in Table XII. On plotting log k_2 against 1/T straight lines were obtained (Fig. 24), and from the slopes and intercepts of these lines it was possible to calculate the constants in the equation

$$k_2 = A.e^{-E_A/RT}$$

for the given media. The values obtained are given in Table XII.

Table XII

Variation of the Velocity Coefficient k_2 with Temperature

Initial Concentration of Guanidine Nitrate 0.2000 M.

Medium % H_2SO_4	T°C.	k_2	k_2 (corr.)	E_A Cal/Mole.	A Moles^{-1} - Litres^{-1}. Sec
81.14	14.83	1.03	2.59	8,940	8.15×10^5
	24.91	2.09			
	35.03	3.09			
78.33	14.83	0.0726	0.171	13,230	1.60×10^7
	24.91	0.189			
	35.03	0.370			
75.47	14.83	0.0156	0.0410	13,790	7.71×10^7
	24.91	0.0360			
	35.03	0.0872			

(ix) A Limiting Rate of Nitration.

It can be seen in Fig. 18 that the nitration of guanidine and of p-tolyltrimethylammonium ion proceed at almost identical rates. Inasmuch as p-tolyltrimethylammonium ion was synthesised as a compound that would nitrate at an observable rate in 75-85% sulphuric acid, similar rates of reaction may be only a coincidence. There is a possibility, however, that the rates of reaction observed in these cases could represent a lower limit to the rate of nitration. The ionisation of nitric acid has always been assumed to be a fast reaction, and hence of no

$$NO_2OH + 2H_2SO_4 \leftrightarrow NO_2^+ + OH_3^+ + 2HSO_4^-$$

kinetic significance. It is possible, however, that in media of the range 70-80% sulphuric acid the ionisation of nitric acid has become a slow reaction, and thus the rate determining step in nitration. If this is the case the nature of the organic compound cannot cause a nitration faster than the limiting rate. In an attempt to show that the rate of nitration of guanidine is not determined by the limiting case the progress of the nitration of toluene-*p*-sulphonic acid was observed. When a 0.08 Molar solution of toluene-*p*-sulphonic acid in 79% sulphuric acid was mixed with a 0.2 Molar solution of nitric acid in sulphuric acid, at 30°C., the introduction of the first nitro group was so rapid as to be complete by the time the first sample was taken (1.5 mins). Inasmuch as guanidine takes over 30 minutes to nitrate under similar conditions, it would seem that the rate of production of nitronium ion is not the rate determining step in the nitration of guanidine. The relevant experiments are summarised in Table XIIa.

Table XIIa.

Nitration of Guanidine.
Expt. No. 221.
Initial Concentration
Guanidine = 0.2070 M.
Initial Concentration HNO_3 = 0.2096 M.

Nitration of Toluene-*p*-sulphonic Acid.
Expt. No. 242
Initial Concentration
Toluene-p-sulphonic Acid = 0.08494
Initial Concentration HNO_3 = 0.2089

t(mins)	T°C.	Concn.HNO_3 M	t (mins)	T°C.	Concn.HNO_3 M.
0.0	25.0	0.2096	0.0	30	0.2089
5.4	24.90	0.1224	1.5	33.2	0.0615
8.8	25.00	0.0997	3.1	29.5	0.0620
16.4	24.98	0.0703	4.7	27.4	0.0605
26.8	24.93	0.0530	6.5	26.25	0.0586
40.4	24.92	0.0447	8.4	25.80	0.0587
51.3	24.90	0.0415	10.4	25.50	0.0590
76.1	24.88	0.0414	12.2	25.40	0.0601

(x) A Possible Mechanism of Denitration.

The velocity coefficient k_1 of equation IX or XII falls by a factor of 10^2 in the media range 83-71.5% sulphuric acid. Denitration may be caused by either the decomposition of the nitroguanidine ion, or, more likely, by the decomposition of a complex formed from the nitroguanidine ion. The decomposition of the nitroguanidine ion into uncharged guanidine and the nitronium ion is a most

$$RH^+ \longleftrightarrow G + NO_2^+ \qquad (XXII)$$

unlikely process for a highly polar medium, such as sulphuric acid in the media range under consideration. A more probable mechanism is the uptake of a proton by the nitroguanidine ion to form the unstable nitroguanidonium ion, which then breaks down into a guanidine ion and a

$$RH^+ + H^+ \longleftrightarrow RH_2^{++} \longleftrightarrow GH^+ + NO_2^+ \qquad (XXIII)$$

nitronium ion. If such is the case, the rate-determining step may be either (a) the uptake of the proton to form the nitroguanidonium ion, or (b) the breakdown of the nitroguanidonium ion.

(a) If proton uptake is the slow, rate-determining step, then the rate of denitration, r, for a given medium, is

$$r = k'_2 [RH^+][H^+] \qquad (XXIV)$$

and the experimental equation for r is

$$r = k_1 [RH^+] \qquad (IX)$$

then

$$k_1 = k'_2 [H^+] \qquad (XXV)$$

From the equation $H_2SO_4 \rightleftarrows H^+ + HSO_4^-$ (XXVI)

we may substitute

$$k_1 = k'_2 . K_c . \frac{[H_2SO_4]}{[HSO_4^-]} \qquad \text{(XXVII)}$$

$$\log k_1 = \log k'_2 - \log \frac{[HSO_4^-]}{[H_2SO_4]} + \text{constant}$$

$$= \log k'_2 - H_o + \text{constant} \qquad \text{(XXVIII)}$$

Thus, a plot of log k_1 against the acidity function H_o should be a straight line with negative unit slope.

(b) If the breakdown of the nitroguanidonium ion is the slow, rate-determining step, then the rate of denitration, r, for a given medium, is

$$r = k^o{}_1 [RH_2^{++}] \qquad \text{(XXIX)}$$

and the experimental equation for r is

$$r = k_1 [RH^+] \qquad \text{(IX)}$$

then $$k_1 = k^o{}_1 \frac{[RH_2^{++}]}{[RH^+]} \qquad \text{(XXX)}$$

$$\log k_1 = \log k^o{}_1 - \log \frac{[RH^+]}{[RH_2^{++}]} \qquad \text{(XXXI)}$$

$$= \log k^o{}_1 - H_+ \qquad \text{(XXXII)}$$

where H_+ is an acidity function defined as

$$H_+ = \log \frac{[BH^+]}{[BH_2^{++}]} + pK'_{BH^+} \qquad \text{(XXXIII)}$$

Thus, a plot of k_1 against the acidity function H_+ should be a straight line with negative unit slope.

As is shown in Fig. 18, the plot of log k_1 against H_0 approaches a straight line with a slope of -1.4. There is no information available about acidity functions of the type H_+, although their existence has long been postulated (58); but H_+ undoubtedly varies with the strength of sulphuric acid in a similar manner to H_0. If such is the case, then the sign of the slope of the log k_1 plot is correct, and the numerical value may well be closer to unity. Without further information it is impossible to make a choice between these two mechanisms.

(xi) Equilibrium Constants.

In media of greater strength than 83% sulphuric acid, the rate of reaction is too great to permit normal kinetic measurements to be made. As was shown in part (i) the only stoichiometric measurement that can be made is that of the equilibrium composition. The equilibrium concentrations determined in this fashion may be used to calculate an empirical constant

$$K = \frac{[RH]_e}{[GH]_e[HNO_3]_e} = k_2/k_1 \qquad (X)$$

Measurements of K (for constant initial equimolecular concentration) were made in media over the range 75-100% sulphuric acid; measurements were also made with varying initial equimolecular concentrations. The values are given in Tables XIII and XIV.

Table XIII

Initial Concentration Guanidine Nitrate 0.2000 M. Temp. 25°C.

Medium % H_2SO_4	K	k_2/k_1	log K	$\log k_2/k_1$
100	1.17		0.0682	
98.95	1.92		0.2833	
98.87	2.50		0.3980	
98.64	2.03		0.3075	
98.40	2.74		0.4371	
97.22	7.08		0.8500	
97.11	5.64		0.7510	
95.74	14.1		1.1526	
93.95	51.2		1.7093	
93.85	58.3		1.7656	
91.60	255		2.4072	
90.96	387		2.5877	
90.91	398		2.5999	
88.61	1027		3.0115	
87.84	1121		3.0496	
87.16	1115		3.0472	
86.70	915		2.9614	
85.03	629		2.7987	
84.90	543	from	2.7348	
83.79	441	corr	2.6441	
83.09	385	k_2'/k_1'	2.5855	
82.94	294	333	2.4676	2.5220
81.84	235	--	2.3711	--
81.14	212	225	2.3259	2.3515
79.24	114	148	2.0557	2.1638
78.33	--	110	--	2.0424
75.47	44.6	47.1	1.6508	1.6733
71.48	--	14.7	--	1.1664

Table XIV

Varying Initial Guanidine Nitrate or Nitroguanidine Temp.25 C.

Medium % H_2SO_4	Initial Concn. Guanidine Nitrate	Initial Concn. Nitroguanidine	log K
98.95	0.2000	--	0.2833
	0.3991	--	0.5051
	0.6000	--	0.7067
97.22	0.1000	--	0.7160
	0.2000	--	0.8500
	0.4792	--	1.1367
95.74	0.2000	--	1.1526
	0.4000	--	1.2891
	0.6000	--	1.4548
93.95	0.2000	--	1.7093
	0.4000	--	1.8899
90.91	0.2000	--	2.5999
	0.4000	--	2.7235
	0.6000	--	2.8293
87.84	0.2000	--	3.0496
	0.4000	--	3.0522
	0.6000	--	3.0043
	0.8000	--	2.9708
83.09	0.2000	--	2.5855
	0.4000	--	2.5502
	0.6000	--	2.4969
79.24	0.2082	--	2.0256
	--	0.0500	2.3404
	--	0.1041	(2.1641)
	--	0.1562	2.2310
	--	0.2088	2.0857
	--	0.3047	2.1081
	--	0.4146	(2.1184)
75.47	--	0.1000	(1.7565)
	--	0.2024	1.6508
	--	0.4000	1.6222

(a) Variation of Equilibrium Constant K with Medium.

The values of the equilibrium constant K given in Table XIII have been plotted as a function of the % sulphuric acid (Fig. 19). The shape of the curve obtained is similar to that obtained when the rate of nitration of aromatic substances is plotted against % sulphuric acid.

The equilibrium constant K is the ratio of the velocity coefficients for nitration and denitration, and will thus be a function of sulphuric acid with two dependent variables. The velocity coefficient, k_2, for nitration will vary with the strength of sulphuric acid in a similar manner to those of such compounds as nitrobenzene, dinitrotoluene and anthraquinone. There is no precedent to predictthe continued behaviour of the velocity coefficient, k_1, for denitration, but it might be reasonable to assume that it will continue to be linear with respect to % sulphuric acid (acidity). The variation of K with % sulphuric acid should therefore be similar to the variation of the rate of nitration of aromatic compounds in sulphuric acid, but more extreme in its behaviour.

The phenonemon of a maximum speed of nitration in a sulphuric acid medium of about 90% was first noted by H. Martinsen (86,87), and has been subject to various explanations by different authors. The presence of a maximum rate of nitration may be explained by the concept, first

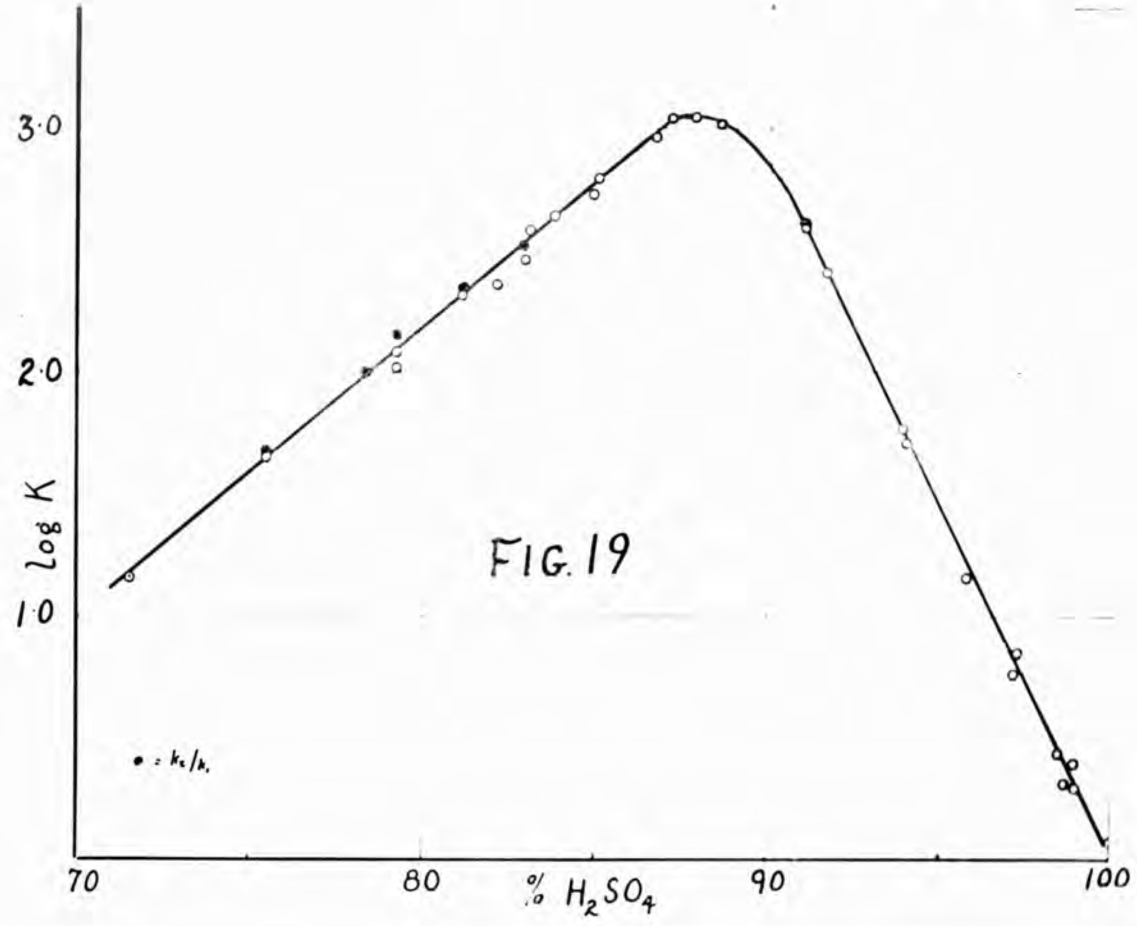

3·0
2·0
1·0
log K
● = k_2/k_1
70
80
90
100
% H_2SO_4

FIG. 19

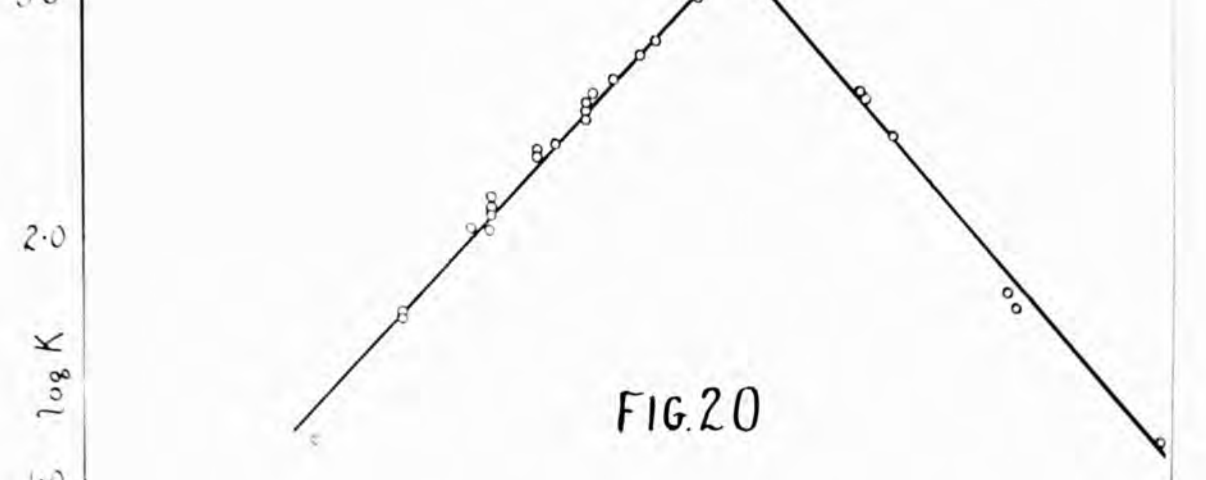

3·0
2·0
1·0
log K
-1·0
-2·0
-4·0
-5·0
log $(P/P_0)_{H_2O}$

FIG. 20

advanced by R. Robinson (88) of nitration as a dual process of attachment of the cation to, and removal of a proton from, a carbon atom. This concept requires that the speed of nitration be mutually dependent upon both factors, and Robinson further suggested that the composition of the medium in which the rate of nitration is a maximum might represent a balance between the acid function of the solvent, (to give the nitronium ion), and its basic function as a proton acceptor. Bennett and Williams (89) ascribed the basic action of the medium principally to the bisulphate ion, although also assuming that the sulphuric acid molecule was a proton acceptor, if less effective. From this theory it follows that an increase in water content increases the bisulphate ion concentration, and thus enhances proton removal from the organic compound. An increase in water content, however, simultaneously decreases the acidity of the medium, which in turn results in a lowered nitronium ion concentration. There will thus be an optimum medium, representing a balance between these two factors. The work of L. Melander and others (91) has shown that this theory was based on false concepts; as an empirical treatment of the variation of the rate of nitration it is still valid.

This explanation was specific for nitration in sulphuric acid media, but C.K. Ingold and collaborators have advanced an alternate theory, which, it is claimed, is extensible to nitration in the solvent series , sulphuric acid, nitric acid, nitromethane, acetic acid, and water. According to this theory the polarity of the medium has a large part in determining the speed of nitration. The decrease in the rate of nitration of the aqueous side of the maximum is held to be due to the decrease in nitronium ion concentration. The decrease in the rate of nitration in the medium range 90-100% sulphuric acid, where the nitronium ion concentration is largely constant, is attributed to two factors. Increasing sulphuric acid concentration is accompanied by increasing solvating power; but an increase in solvation will result in a lower rate of reaction. Overlaying this effect is a stronger factor, due to the formation of salt-like complexes in strong sulphuric acid. There is evidence that many organic compounds behave as bases in sulphuric acid, forming hydrogen bond complexes with the acid, which may then undergo ionisation into the conjugate acid and bisulphate ion. It might be expected that the positive field induced in the aromatic nucleus by the formation of the hydrogen bond would retard nitration, while the stronger field arising from the free pole produced by ionisation of the complex should retard nitration still further. Once the ionisation of the nitric acid is complete these two factors must result in a decrease in rate of nitration; unfortunately no quantitative evidence is available.

The overall reaction in the nitration of guanidine is, in the simplest case,

$$GH^+ + NO_2^+ \leftrightarrows RH^+ + H^+ \qquad \text{(VII)}$$

which may also be expressed as

$$GH^+ + NO_2^+ + HSO_4^- \longleftrightarrow RH^+ + H_2SO_4 \qquad (XXXIV)$$

From equation XXXIV, an equilibrium constant, K_o, may be defined, in terms of concentrations, by the equation

$$K_o = \frac{[RH^+][H_2SO_4]}{[GH^+][NO_2^+][HSO_4^-]} \qquad (XXXV)$$

To introduce the stoichiometric nitric acid concentration $[HNO_3]$, write

$$Q = \frac{[NO_2^+]}{[HNO_3]} = \frac{1}{1 + \frac{[OH_3^+]}{K_c}\left\{\frac{[HSO_4^-]}{[H_2SO_4]}\right\}^2} \qquad (XXXVI)$$

K_c being the concentration equilibrium constant of the system

$$NO_2OH + 2H_2SO_4 \longleftrightarrow NO_2^+ + OH_3^+ + 2HSO_4^- \qquad (XXXVII)$$

Then $$K_o = \frac{[RH^+]}{[GH^+][HNO_3]} \cdot \frac{[H_2SO_4]}{[HSO_4^-]} \cdot \frac{1}{Q} \qquad (XXXVIII)$$

$$= K/rQ \qquad (XXXIX)$$

in which $r = [HSO_4^-]/[H_2SO_4]$, and K is the empirical constant given by equation X Therefore

$$\log K_o = \log K - \log r - \log Q \qquad (XL)$$

or

$$\log K = (H_o + \log Q) + \text{constant}. \qquad (XLI)$$

If the degree of ionisation of nitric acid is small, then $[HNO_3] = [NO_2OH]$ and $\log Q = - H_R$. In sulphuric acid media below 85% the degree of ionisation of nitric acid is small, and thus this substitution is valid. Therefore, for aqueous sulphuric acid media

$$\log K = H_o - H_R + \text{constant} \qquad (XLII)$$

V. Gold has shown that

$$H_R = H_o + \log (H_2O) = J_o \qquad (XLIII) \quad (90)$$

where (H_2O) is the activity of water.

Thus, for aqueous sulphuric acid media,

$$\log K = - \log(H_2O) + \text{constant} \quad (XLIV)$$

and a plot of log K against the log of activity of water should be a straight line with negative unit slope. Fig. 20 shows that a straight line is obtained, the slope of which is -1.04.

When the degree of ionisation of nitric acid is large the above substitution is invalid, this is the case in sulphuric acid media above 90% sulphuric acid. T.G. Bonner has calculated values of Q for media in the range 85-100% sulphuric acid (68). Using these values, one might expect a positive asymptotic curve if one plotted log K against the combined function $(H_o + \log Q)$; in practice, as Fig. 21 shows, a curved line is obtained. In view of the small variation of Q the plot seems excessively curved. Possible reasons for this discrepancy are, (i) the form of the combined function $(H_o + \log Q)$, (ii) the effect the ionisation of guanidine nitrate will have upon the acidity of a strong sulphuric acid medium, or (iii) varying ionisation of either, or both, guanidine or nitroguanidine; because of insufficient data Fig. 21 was plotted on the

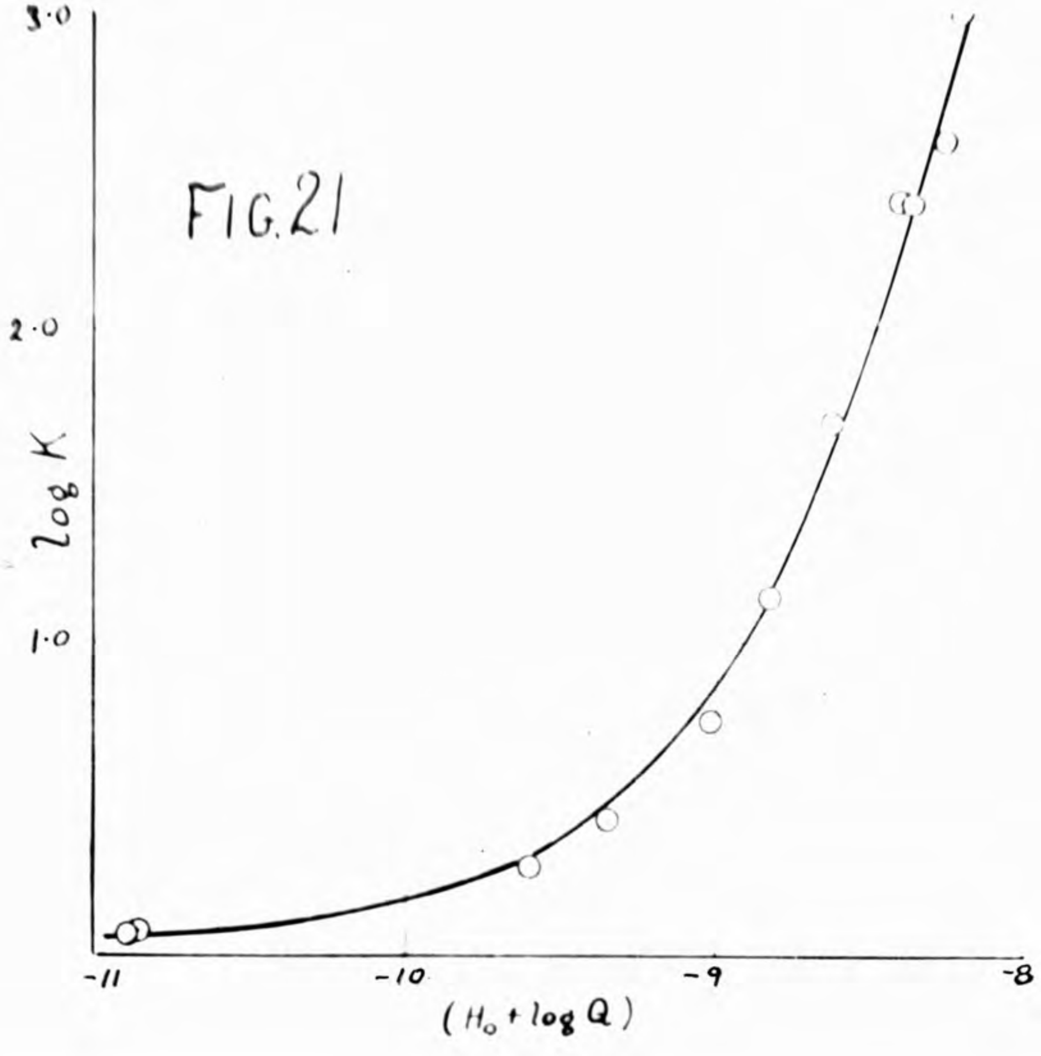


FIG. 21

basis of the acidity of sulphuric acid media before the addition of guanidine nitrate.

(b) Variation of Equilibrium Constant K with Added Salts.

The theory of Bennett and Williams contains an inherent explanation of the effect of added bisulphate salts upon the rate of nitration. On the basis of the theory, addition of bisulphate ion should accelerate nitration in media containing a higher sulphuric acid concentration, and retard nitration in media containing a lower sulphuric acid concentration, than the optimum. On the acid side of the optimum such addition will increase the bisulphate ion concentration without sensibly affecting the degree of completeness with which the nitronium ion is formed. On the aqueous side of the maximum the rate of nitration will be decreased because the dominating effect of added bisulphate will be to repress the formation of nitronium ion. As a corollary to this, increasing the nitric acid concentration should have a similar effect, since this increases the bisulphate ion concentration. Such effects have been observed by a number of authors.

Similar effects were also found in this work. As Table XV shows, the effect of added bisulphate in media greater than 88% sulphuric acid is to increase the value of the equilibrium constant K, while addition of bisulphate to a medium below 89% sulphuric acid lowers the observed value of K. Some support for the validity of equation XLI is provided by this work; in media above 95% sulphuric acid Q equals unity, and addition of bisulphate salts will not affect the ionisation of the nitric acid appreciably. Any change in K caused by the addition of bisulphate salts must therefore be due to the effect of the salts on the acidity H_o. In 98.64% sulphuric acid ΔH_o per mole of added potassium bisulphate is 0.45; it is thus possible to calculate the resultant acidity (H_o) when potassium bisulphate is added to media of this strength. In Fig. 22 the observed log K is plotted against the calculated H_o; the plot is a straight line with unit slope, as is called for by equation XLI.

Table XV

Variation of Equilibrium Constant K with added Bisulphate Ion.

Initial Concentration Guanidine Nitrate 0.2000 M. Temp.25°C.

Medium % H_2SO_4	Molarity $KHSO_4$	K	log K
85.03	0.00	628	2.7980
	0.44	621	2.7931
	0.65	643	2.8082
	0.88	568	2.7543
98.64	0.000	2.03	0.3075
	0.222	3.06	0.4857
	0.446	3.80	0.5798
	0.748	5.13	0.7101
	1.071	7.43	0.8710
	1.428	9.49	0.9773
	1.658	15.41	1.3738

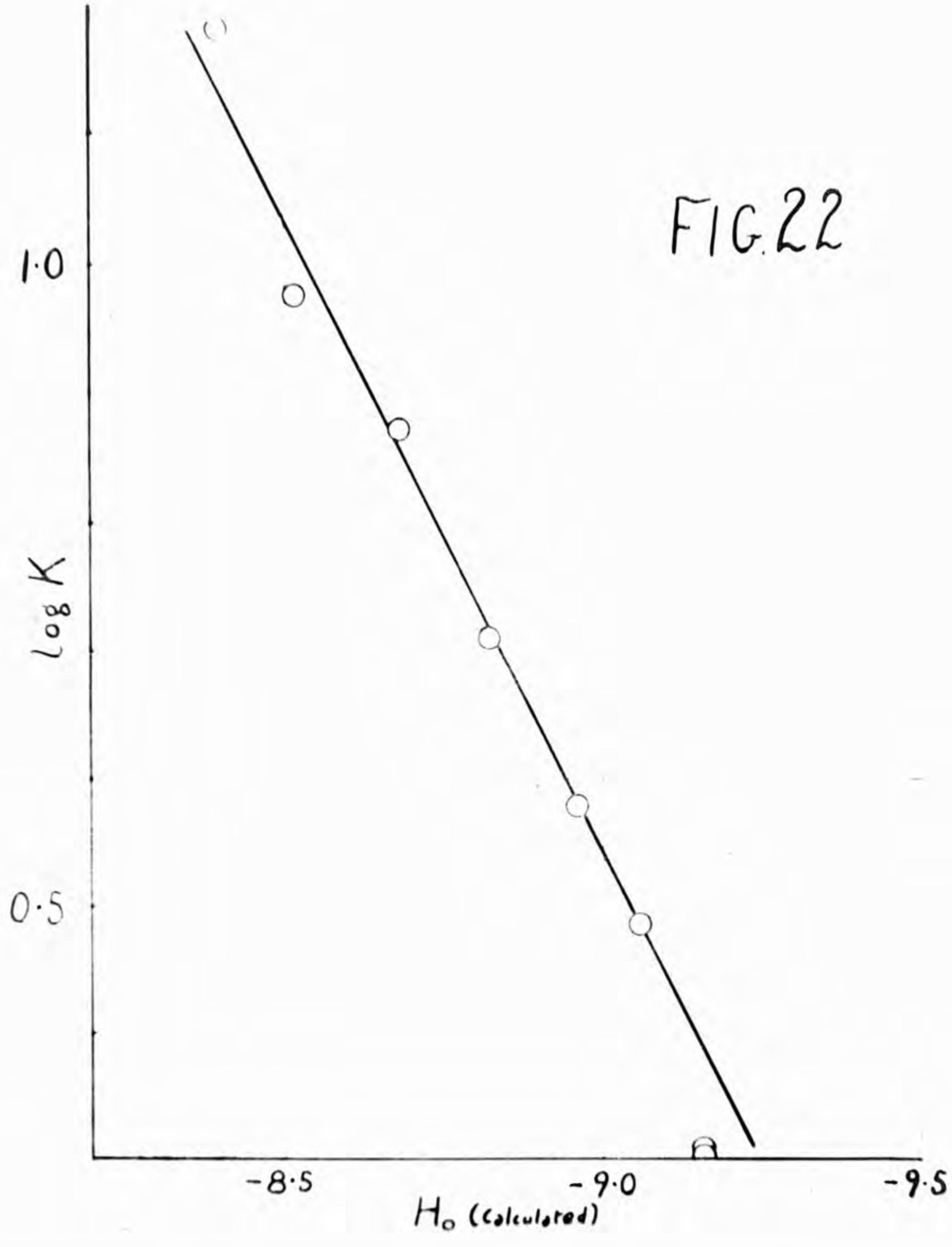


FIG.22

The effect of added nitric acid on the equilibrium constant was not studied as such, but there are figures available for the effect of increasing initial guanidine nitrate upon the equilibrium K (Table XIV). Since the action of the guanidine will be to form bisulphate ion, the effect upon the equilibrium constant will be additive. As was predicted, above the optimum increasing initial concentrations increase the equilibrium constant K, and below the optimum decrease it. It is interesting to note that almost at the maximum (87.84% sulphuric acid) the equilibrium constant remains almost constant with increasing initial concentration of guanidine nitrate.

(c) Variation of Equilibrium Constant K with Large Increases in Initial Concentrations of Guanidine Nitrate.

It has been shown that the maximum value for the equilibrium constant K occurs at a definite strength of sulphuric acid. In view of the variation of the equilibrium constant with the constituents of the solution it is better to say that the maximum value occurs at a definite acidity, (*c.f.* Westheimer and Kharasch (31)). It has also been shown that the effect of adding guanidine nitrate to a sulphuric acid medium is to lower the acidity. It might therefore be predicted that in a medium of high acidity, (*e.g.* one greater than 90% sulphuric acid), as the initial concentration of guanidine nitrate was raised the equilibrium constant K would rise to a maximum value and then fall again. Table XVI and Fig. 23 show that this prediction has been

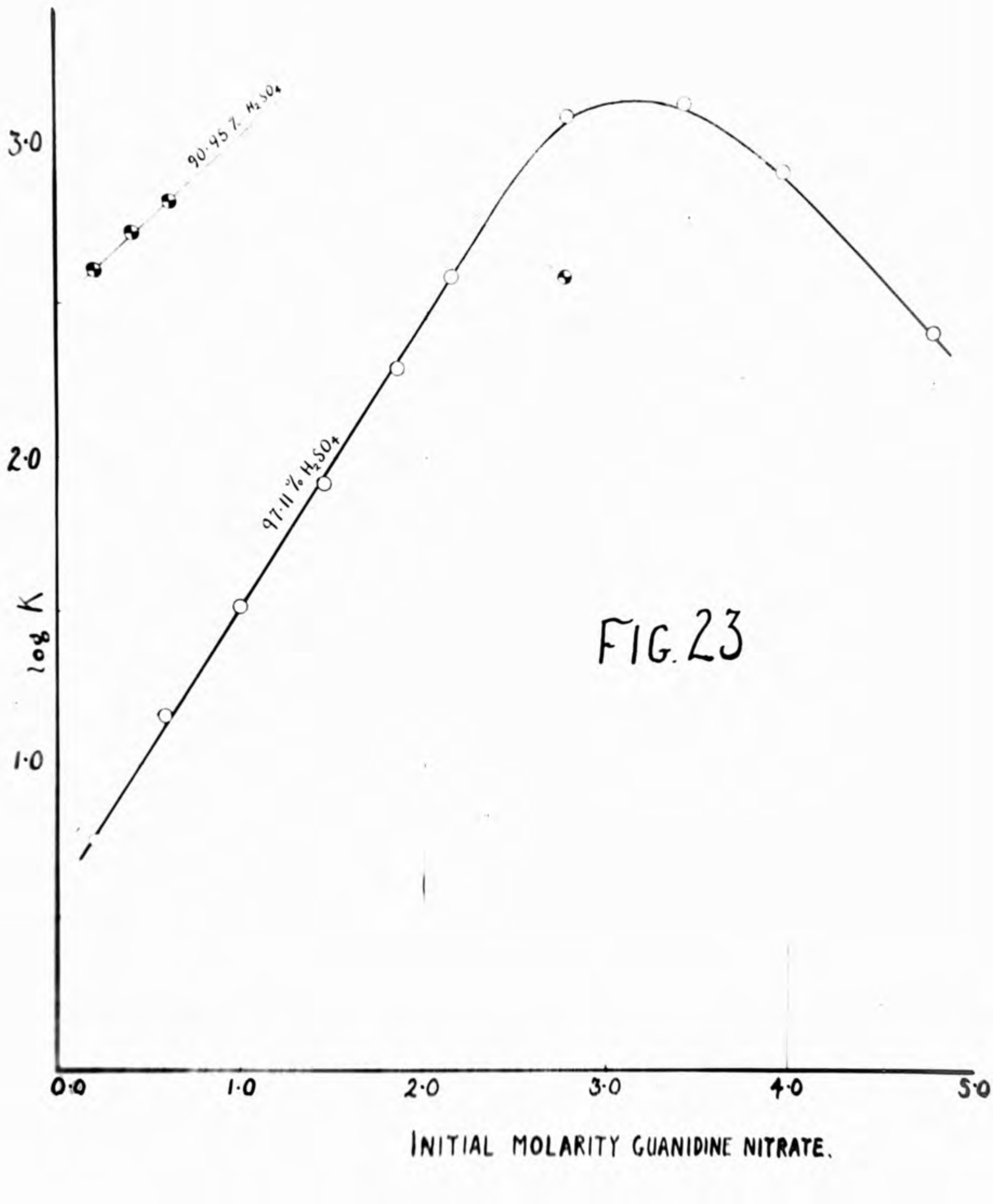

3·0
2·0
1·0
log K
90·45 % H_2SO_4
97·11 % H_2SO_4
0·0
1·0
2·0
3·0
4·0
5·0
INITIAL MOLARITY GUANIDINE NITRATE.

FIG. 23

confirmed experimentally. As might have been expected, the maximum value of the equilibrium constant, K, found, is identical with that obtained with constant initial concentrations and varying sulphuric acid media.

Table XVI

Variation of Equilibrium Constant K with Initial Concentration

% Sulphuric Acid 97.11 Temp. 25°C.

Expt. No.	Initial Concn. Guanidine Nitrate.	K.	log K
117	0.2000 M.	5.64	0.7510
118	0.5782	14.3	1.1561
121	0.9913	33.0	1.5179
119	1.442	82.2	1.9147
120	1.835	194	2.2883
122	2.135	386	2.5865
123	2.752	1255	3.0987
124	3.381	1377	3.1391
125	3.925	843	2.9259
127	4.742	254	2.4041

From the variation of the equilibrium constant K with media one may calculate the ΔH_0 necessary to obtain the maximum value of K for any given medium. From Fig. 23 one may calculate the amount of guanidine nitrate necessary to bring about a similar change. By equating these two factors one may obtain provisional values for ΔH_0/Mole. for guanidine nitrate. On the basis that a maximum value of the equilibrium constant K occurs at an acidity of $H_0 = -7.93$

(87.84% sulphuric acid), ΔH_0/Mole. for guanidine nitrate, in 97.11% sulphuric acid, is 0.35.

(xii) Variation of the Equilibrium Constant K with Temperature.

Measurement of the equilibrium concentrations in the system guanidine nitrate-nitroguanidine were carried out, for given media, over a 45° range of temperature; the equilibrium constants based on this data are given in Table XVII. It was found that log K was linear with respect to 1/T for any given media (Fig. 24), and it was thus possible to calculate values for ΔH for the reaction. It is possible that the plot of log K has a slight curvature with regard to 1/T in acids of a strength greater than 97%, but in view of the multiplication of errors introduced in calculating K too much reliance should not be placed on this fact. The values obtained for ΔH, which are given in Table XVIII, show a linearity with respect to the strength of the sulphuric acid medium (Fig. 25); the values involved, particularly in the more acid regions, are low, a fact which suggests that relatively little disturbance of structure is taking place.

Table XVII

Variation of Equilibrium Constant with respect to Temperature.

Initial Concentrations of Guanidine Nitrate 0.2000 M.

Medium % H_2SO_4	Expt. No.	T°C.	K	log K
83.79	145	14.83	639	2.8053
	144	24.91	441	2.6441
	143	35.03	307	2.4871
	142	45.08	235	2.3707
91.60	137	-0.10	447	2.6501
	138	14.83	316	2.4995
	139	24.91	255	2.4072
	140	35.03	213	2.3291
	141	45.08	178	2.2504
93.85	147	-0.10	77.8	1.8911
	148	14.83	68.7	1.8368
	149	24.91	58.3	1.7656
	150	35.03	51.8	1.7146
	151	45.08	47.5	1.6764
97.11	130	14.83	6.79	0.8320
	117	24.91	5.84	0.7662
	128	35.03	5.77	0.7611
	129	45.08	5.38	0.7309
98.40	156	-0.10	3.55	0.5510
	155	16.30	3.03	0.4820
	154	24.91	2.74	0.4371
	153	35.03	2.70	0.4314
	158	45.08	2.72	0.4343
98.87	135	14.83	2.61	0.4162
	134	24.91	2.50	0.3980
	133	35.03	2.39	0.3783

Table XVIII

Variation of ΔH with respect to Medium.

Medium - % H_2SO_4	Slope log K/(1/T)	ΔH(Cal./Mole.)
83.79	1320	6040
91.60	782	3575
93.85	495	2265
97.11	287	1315
98.40	237	1085
98.87	165	754

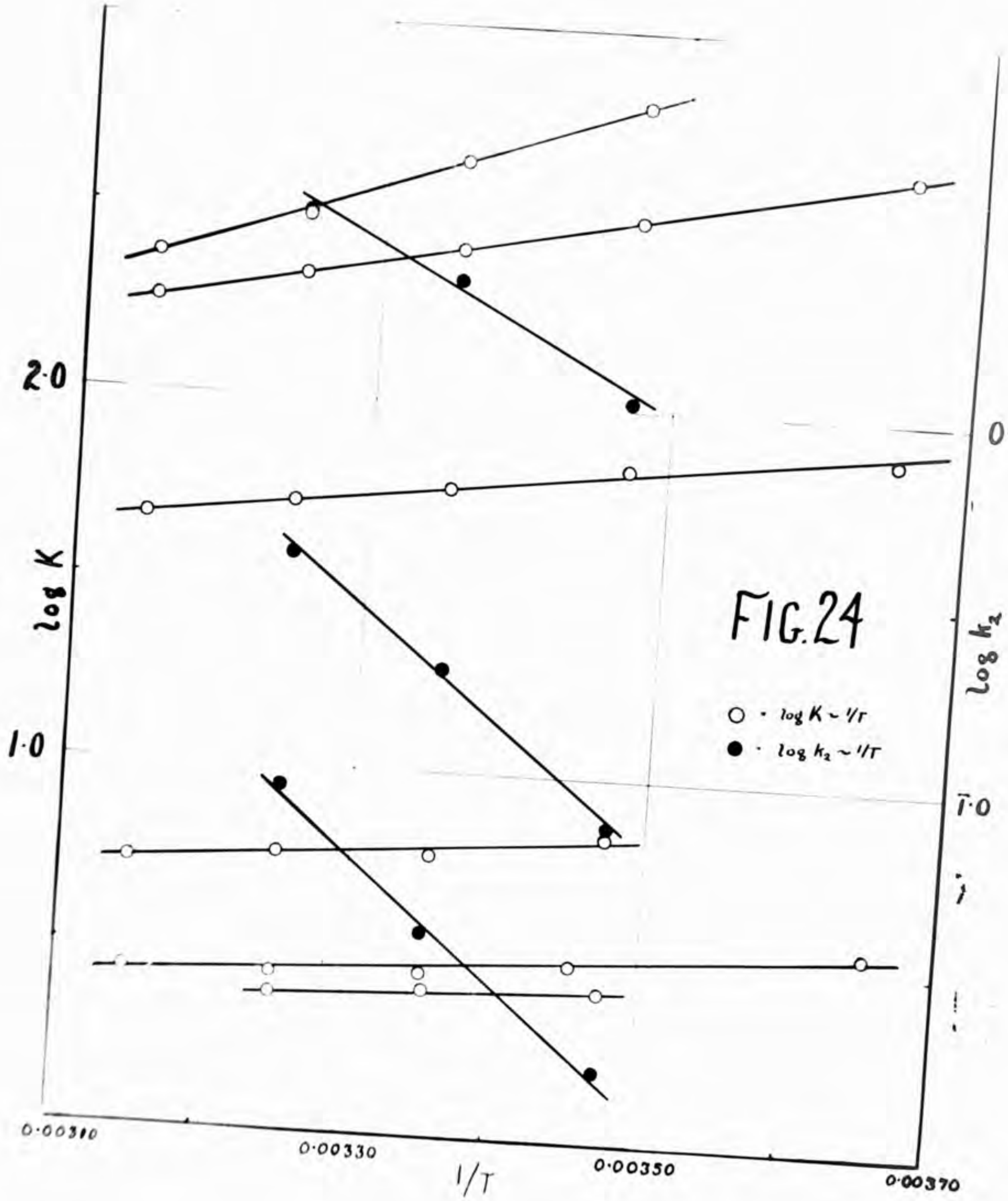

2·0
1·0
log K
0·0
1̄·0
log k₂
○ · log K ~ 1/T
● · log k₂ ~ 1/T
0·00310
0·00330
0·00350
0·00370
1/T

FIG. 24

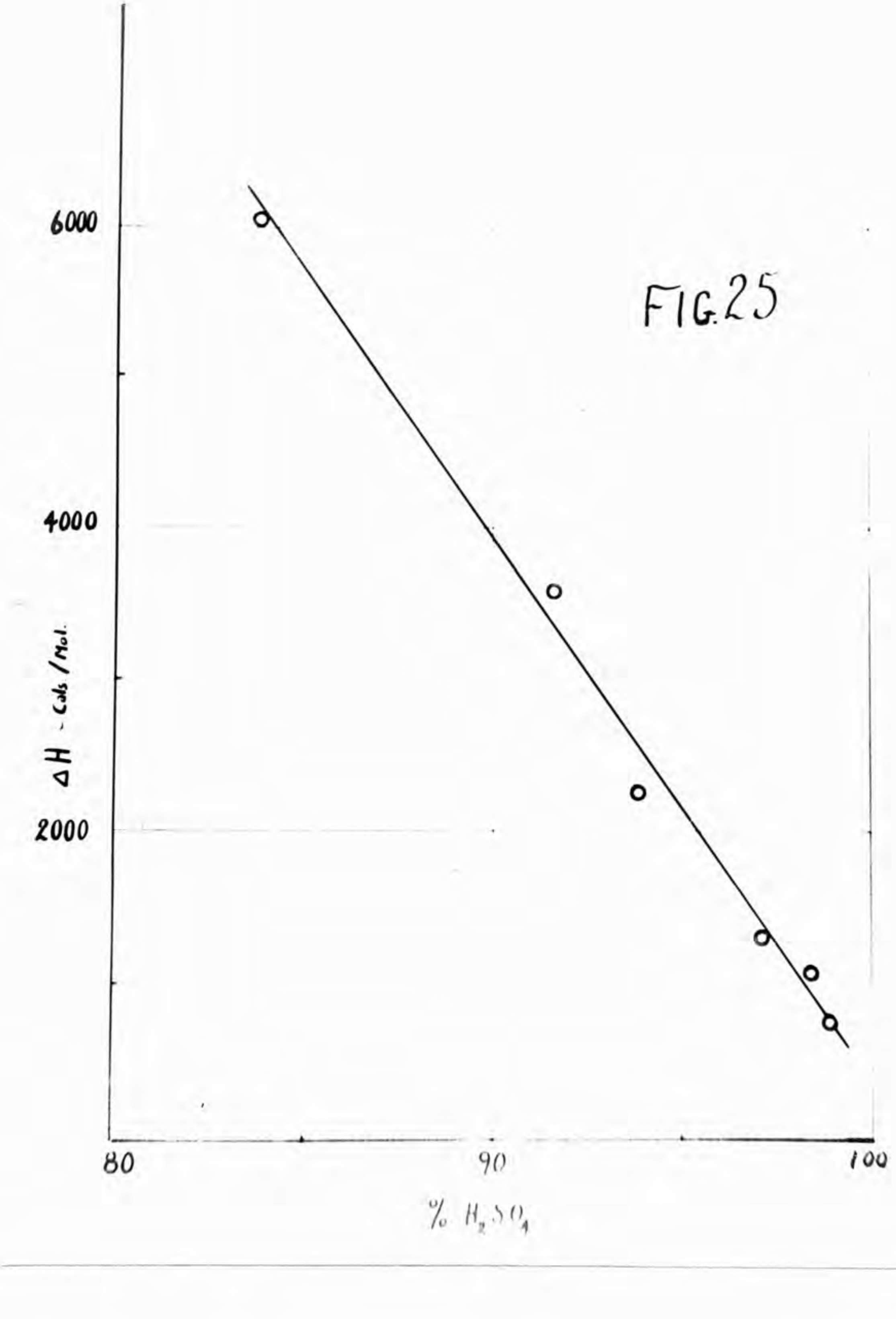
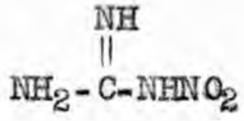


FIG. 25

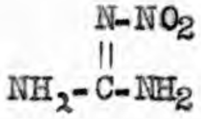
The Structure of Nitroguanidine in Solution in Sulphuric Acid.

As was discussed in an earlier section (II-ii), there are two possible structures for nitroguanidine, (A) and (B).

(A)



$$\begin{array}{c}\text{NH}\\ \| \\ \text{NH}_2\text{-C-NHNO}_2\end{array}$$

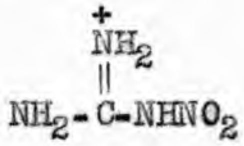


$$\begin{array}{c}\text{N-NO}_2\\ \| \\ \text{NH}_2\text{-C-NH}_2\end{array}$$

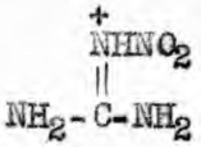
(B)

These structures, however, are based upon reactions in relatively non-polar media, and there is adequate evidence that in strong sulphuric acid nitroguanidine takes up a proton and adopts an ionised form. The ionised forms, (C) and (D), of structures (A) and (B), are identical,

(C)



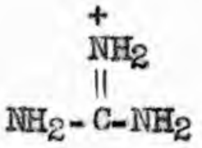
$$\begin{array}{c}\overset{+}{\text{NH}_2}\\ \| \\ \text{NH}_2\text{-C-NHNO}_2\end{array}$$



$$\begin{array}{c}\overset{+}{\text{NHNO}_2}\\ \| \\ \text{NH}_2\text{-C-NH}_2\end{array}$$

(D)

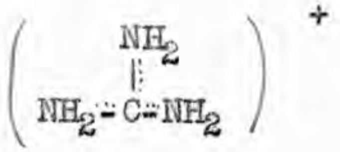
apart from the formal placement of the charge. In this form there is a direct relationship to the structure of ionised guanidine (E).



$$\begin{array}{c}\overset{+}{\text{NH}_2}\\ \| \\ \text{NH}_2\text{-C-NH}_2\end{array}$$

(E)

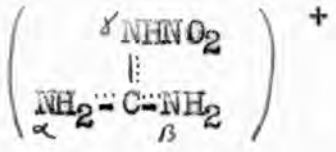
The position of the charge is probably best rationalised by considering the meaning of the structure as written. It would be a mistake to regard the carbon-nitrogen double bond as any more than a conventional representation, and the structure of ionised guanidine, possessing three degrees of resonance, would be better pictured as (F), where the



$$\left(\begin{array}{c} \mathrm{NH_2} \\ \vdots \\ \mathrm{NH_2} \cdots \mathrm{C} \cdots \mathrm{NH_2} \end{array}\right)^{+}$$

(F)

charge is spread over all the molecule. Similarly the structure of ionised nitroguanidine is best written as (G).

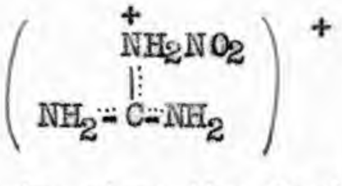


$$\left(\begin{array}{c} {}^{\gamma}\mathrm{NHNO_2} \\ \vdots \\ \underset{\alpha}{\mathrm{NH_2}} \cdots \mathrm{C} \cdots \underset{\beta}{\mathrm{NH_2}} \end{array}\right)^{+}$$

(G)

Because of the electrophilic properties of the nitro-group there will be a concentration of the charge around the α and β atoms; to the extent that it indicates this structure (C) is possibly the best classic representation.

The behaviour of structures (A) and (B) in dilute alkali solutions, is beyond the scope of this research, but it is possible to advance a theory to account for the fact that it is structure (B) that is formed by the nitration of guanidine in sulphuric acid. On the basis of the evidence that nitration takes place by attack of the nitronium ion, the guanidine ion (F) must at one point form a complex of the type (H), which will either simultaneously, or subsequently



$$\left(\begin{array}{c} \overset{+}{\mathrm{NH_2}}\mathrm{NO_2} \\ \vdots \\ \mathrm{NH_2} \cdots \mathrm{C} \cdots \mathrm{NH_2} \end{array}\right)^{+}$$

(H)

lose a proton to give the ionised form of nitroguanidine. Further loss of yet another proton will yield the uncharged nitroguanidine - this occurs when a solution of ionised nitroguanidine is diluted with water. In the ionised form (G), because of the electrophilic nature of the nitro-group, the positive charge is concentrated around the α and β nitrogen atoms, and, conversely, the resonating electrons will be close to the γ nitrogen. The hydrogen attached to the γ nitrogen is essentially the acidic hydrogen of a primary nitramine, and is much more losely bound than those attached to the α and β nitrogens. In these circumstances it will be the acidic hydrogen that is lost as a proton, leaving the structure (B) as the unionised form.

III

Part III - Experimental

(i) Preparation of materials and media

Guanidine nitrate. The material used was supplied by the kindness of Dr. T.M. Walters.

This salt was of a high degree of purity, and further recrystallisation produced no change in properties. The properties used as criteria of the purity were the melting point, and the value of the equilibrium in a specific medium. In practice the salt was recrystallised twice from boiling water, dried at 100°C. for four hours, ground to 100 mesh and then dried at 80-110°C. for twenty hours.

Some samples of commercial guanidine nitrate were heavily contaminated with sulphur compounds, but after extensive recrystallisation from water the product was identical with that above. The melting point of the purified guanidine nitrate was 215°C. (uncorrected); the recorded melting point is 217°C. (66). Calculated for $CH_6N_4O_3$: C, 9.84; H, 4.95; N, 45.90%. Found: C, 10.35, 10.42; H, 4.94, 5.03; N, 45.16, 44.44%.

Guanidine carbonate. "Analar" guanidine carbonate was dissolved in one volume boiling water and four volumes of ethanol added. The precipitated salt was filtered off and dried over P_2O_5 at 10mm. and 50°C. for forty-eight hours. The dried salt was ground to 30 mesh before use.

Calculated for $C_3H_{12}N_6O_3$: C, 20.00; H, 6.71; N, 46.66%.
Found: C, 20.50, 19.84; H, 6.55, 6.21; N, 46.57, 47.00%.

Nitroguanidine. The material used was supplied by the kindness of Dr. T.M. Walters.

Before use the nitroguanidine was dried over P_2O_5 at 10mm. and 65°C. for seventeen hours. The constancy of the equilibrium value in any specific medium was used as a criterion of the purity of the material. The nitroguanidine supplied gave an equilibrium value in agreement with that obtained when guanidine nitrate was the original constituent. Nitroguanidine that had been recrystallised from boiling water, or from other solvents, gave divergent values of this equilibrium. Thus:

% Sulphuric acid = 97.22

Molarity of initial constituent = 0.2000

Expt. No.	Initial constituent.	Equilibrium concentration HNO_3 (Mean of 7 determinations)
27	Guanidine Nitrate	0.1122
28	Guanidine Nitrate	0.1116
32	Guanidine Nitrate-1	0.1114
29	Nitroguanidine	0.1133
30	Nitroguanidine-1	0.1158
31	Nitroguanidine-1	0.1160
33	Nitroguanidine-2	0.1167
34	Nitroguanidine-3	0.1213

(Guanidine nitrate-1 and nitroguanidine-1 were the original materials after recrystallisation from boiling water.

Nitroguanidine-2 was the original material that, after recrystallisation from boiling water, had been ground under an ammonium carbonate solution, washed with water and with ether, and dried.

Nitroguanidine-3 was the original material that, after recrystallisation from boiling 5 N. ammonium acetate solution, had been washed with water and with ether, and dried.)

That the amount of decomposition caused by the recrystallisation was small is shown by the effect upon the melting point. The original nitroguanidine melted (with decomposition) at 224-226° C. The recrystallised nitroguanidine-1 melted (with decomposition) at 227-228° C. A mixture of the two (50/50) started sintering at 221.5°, and melted (with decomposition) at 224.2-225° C. Melting points recorded in the literature vary from 222° to 255° C.

<u>Nitration media</u>. Simple nitration media were prepared by adding water to 98% sulphuric acid. For analysis, 0.8 gm. samples of the medium, weighed from a Lunge pipette, were diluted into water and titrated with normal sodium hydroxide solution. Screened methyl orange was used as an indicator. A secondary standard solution of normal

hydrochloric acid was used to standardise the alkali solution.

In each analysis six titrations were made, and a geometric mean taken. In cases where there was a serious divergence of more than 0.08% in the results the analysis was repeated. A typical set of titrations for one medium gave 82.767, 82.685, 82.847, 82.893, 82.760, 82.931% sulphuric acid. Geometric mean 82.814% sulphuric acid.

Nitration media containing nitric acid were made by adding 100% nitric acid to a previously standardised sulphuric acid-water medium. The molarity of the resultant nitric acid solution was determined by the full modified Kolthoff method of analysis. In each determination five titrations were made, and the geometric mean taken. A typical set of titrations for one solution gave 0.4167, 0.4163, 0.4167, 0.4177, 0.4157 Molar nitric acid. Geometric mean 0.4166 Molar nitric acid. The nitration medium thus standardised would be used for the bulk of a series of experiments. The concentration of the standard nitric acid solution might be altered for individual experiments by the further addition of either 100% nitric acid, or of more sulphuric acid-water medium. Such individual nitration media were standardised in duplicate by the Kolthoff method. Typical analyses for such solutions were 0.1035, 0.1032 and 0.5914, 0.5913 Molar nitric acid.

Nitration media containing either potassium bisulphate or ammonium sulphate were also used. To prepare these, the salt was weighed into a volumetric flask and made up to volume after solution was complete. Ammonium sulphate dissolved in sulphuric acid-water media easily and rapidly. The solubility of potassium bisulphate is low in sulphuric acid of the range 75-95%, and the rate of solution is very small. Solutions of potassium bisulphate in sulphuric acid-water were best prepared by intermittently shaking a mixture of the salt and medium at 45°C. over a period of hours. The solutions thus obtained were yellowish in colour. Prolonged or excessive heating tended to increase the depth of discoloration.

<u>100% sulphuric acid</u> was prepared by adjusting a weak oleum to maximum freezing point by the addition of a sulphuric acid-water medium. An oleum was prepared by distilling sulphur trioxide into 99% acid. The distillation was carried out in an all glass apparatus which had previously been washed with concentrated sulphuric acid to remove all traces of organic matter. The weight of the distillate was observed, and thus the sulphur trioxide content of the oleum could be calculated. A weak oleum was made by adding to a large volume of 99% sulphuric acid slightly more of the prepared oleum than was required to neutralize all the water present. The persistence of fuming over the

surface of the medium was taken as a sign of positive sulphur trioxide content. A sample of about 250 ml. of this oleum was taken and the freezing point determined. The sample was returned to the main bulk, a known small quantity of 99% sulphuric acid added, and the freezing point redetermined. This process was continued, using decreasingly small amounts of 99% sulphuric acid, until a medium with a freezing point of 10.50°C. was obtained. The belief that this was a maximum freezing point was confirmed when a very slightly more dilute sample of the medium had a lower freezing point.

Determination of the freezing point. The freezing points of the media were determined using the apparatus shown in Fig. 4. About 250 ml. of the medium was placed in the lower half of the apparatus and the head firmly fitted on. The lower half of the apparatus and contents were cooled to near 0°C. by immersion in ice-water. Crystallisation of the oleum was initiated by rubbing the side of the flask with solid carbon dioxide. Immediately crystallisation had started the flask was placed in the air jackets, agitation started, and temperature readings taken at 30 second intervals. The thermometer used was calibrated from -11 to 50°C. in 0.1 divisions, and possessed a N.P.L. certificate of examination. The scale was read with the aid of a small lens.

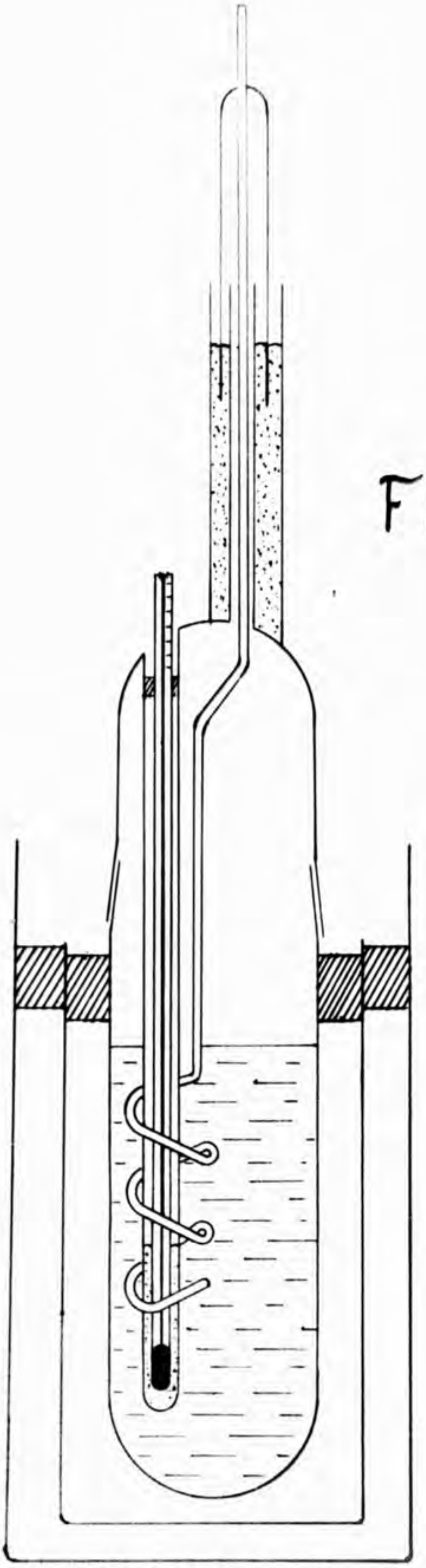


FIG. 4

The mercury sealed joint serves an additional function beyond isolating the contents of the flask. The buoyancy of the mercury acts as a spring when the agitator is depressed, and thus the solution may be stirred with a minimum of effort. Since the contents of the flask are isolated the freezing point of any sample may be repeated at wish, without fear of dilution of the medium by atmospheric water vapour.

Storage of media. Where possible media were stored in flasks that had been fitted with the male half of a cone ground joint, the female half being adapted for use as a cap. In some cases media had to be stored in flasks fitted with the normal type joints, or occasionally in ordinary glass stoppered "Winchesters". Where this was done the neck and stopper of the container were wiped dry after opening, and before closing them. This ensured that no dilution of medium occurred by acid at the neck absorbing water from the air and then running back and diluting the main stock. As a further precaution, "Winchester" bottles when used, were fitted with a glass cap seating onto a rubber gasket (Fig. 5a). This provided some protection against ill fitting ground glass stoppers. With these precautions it was found that media maintained their composition, within the limits of analysis, over a period of months.

100% nitric acid was obtained by distilling a mixture of 2 volumes of 70% nitric acid and 3 volumes of 98% sulphuric acid. The distillation was done in an all glass apparatus at 0.1 mm. and 20°C. (Fig. 6.). The condensing traps were cooled by means of a solid carbon dioxide-ethanol mixture. The first 20% of the distillate was discarded on principle, the remainder was collected as white crystals, which melted to give a limpid, colourless liquid. This nitric acid was added immediately to the requisite sulphuric acid-water mixture. No attempt was made to store 100% nitric acid as such.

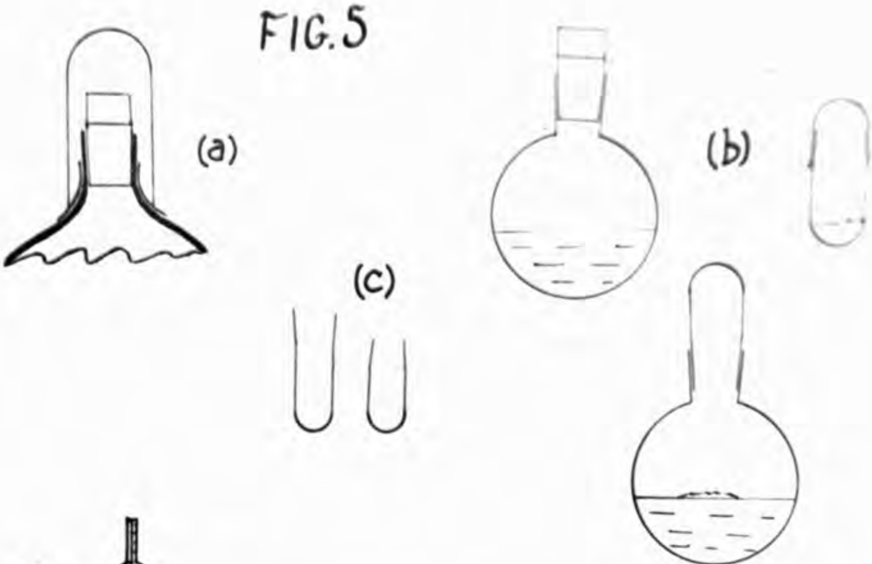
Potassium Hydrogen Sulphate. The "Analar" salt was ground to 10 mesh, dried at 110°C. for twenty four hours, and kept over calcium sulphate until use.

Potassium nitrate. The "Analar" salt was dried at 110°C. for twenty-four hours, and kept over calcium sulphate until use.

Ammonium Sulphate. The "Analar" salt was dried at 60° for eighteen hours, and kept over calcium sulphate until use.

Potassium dichromate. The "Analar" salt was ground to 20 mesh and dried at 110°C. for six hours. A standard stock solution was made by dissolving about 100 gm. of the dried salt in water and making up to 2 litres in volumetric glassware. The normality of the solution was calculated by the expression:

FIG. 5



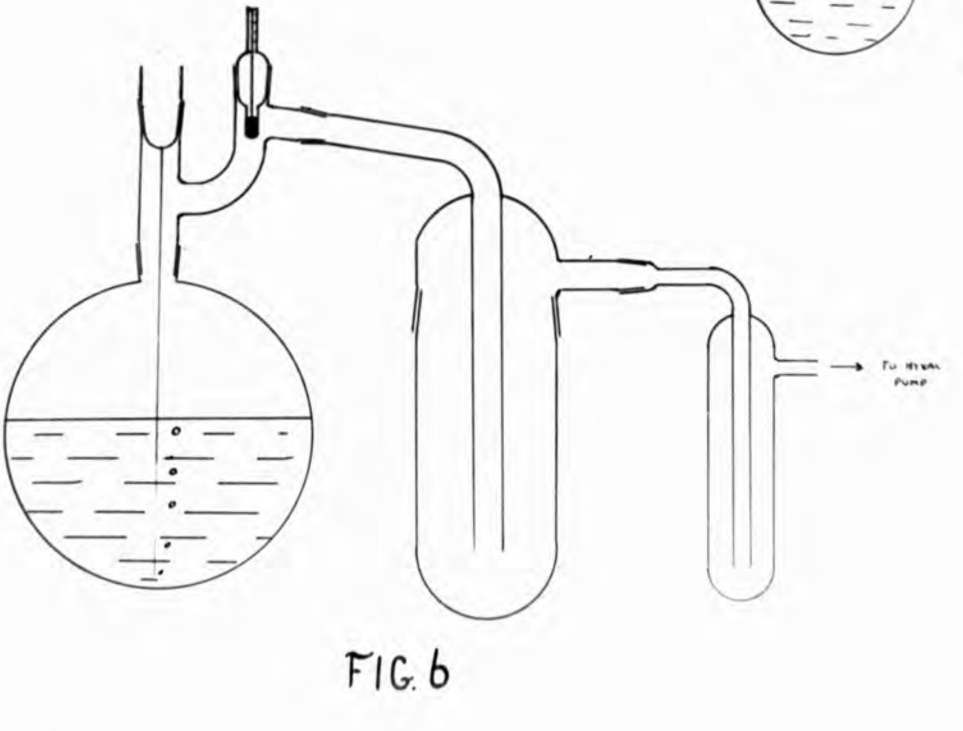


FIG. 6

$$\text{Normality} = \frac{\text{Weight of salt} \times 6000}{294.21 \times \text{Volume}}$$

Standard solutions for use in analysis, were made up, as required, by diluting 200 ml. aliquots of the stock solution to 1000 ml., using volumetric glassware; such standard solutions were kept under carbon dioxide. The normality of the analytical solution was taken as being one fifth of that of the stock solution. Potassium dichromate is itself a satisfactory primary standard, but occasionally the standardisation of the analytical solutions was checked by an alternative method. Potassium dichromate oxidises potassium iodide according to the equation

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2 \quad \text{(I)}$$

Using this reaction a potassium dichromate solution may be standardised against a thiosulphate solution, which itself has been checked against the primary standard potassium iodate. The results of a typical analysis are as follows:

97.0503 gm. of potassium dichromate were made up to 2 litres of solution.

Therefore calculated normality = 0.9900

200 ml. of stock solution were diluted to 1000 ml.

Therefore calculated normality = <u>0.1980</u>

4.919 ml. aliquots of the dilute potassium dichromate solution were used to liberate iodine, employing the reaction above. The free iodine was titrated with 0.0806 N potassium thiosulphate solution. The titres obtained were 12.10, 12.13, 12.12 ml. Mean value 12.12 ml. Therefore experimental normality = $\frac{12.12 \times 0.0806}{4.919}$ = $\underline{0.1986}$

A deviation of 0.3% is within the bounds of experimental accuracy.

Ferrous Ammonium Sulphate. A saturated solution of the "Analar" salt in 1 N. sulphuric acid was kept as a stock solution. The stock solution was diluted with 1 N. sulphuric acid to give solutions for analysis. The analytical solutions were made up to a range 0.05 - 0.5 Normal, according to the strength of the nitrate solution being analysed, such solutions were stored under carbon dioxide. The solutions of ferrous ammonium sulphate for analysis were standardised directly against the standard potassium dichromate solutions. Two end points could be used for this reaction; either the "dead stop" end point of A.T. Bowden and C.W. Foulke (67), or one using "ferroin" indicator. Identical values were obtained with either method.

Potassium Iodate. The "Analar" salt was ground to 20 mesh and dried at 65°C. for twenty hours. The dried salt was made up in volumetric glassware to give a primary standard solution.

Potassium Iodide. The "Analar" salt was used.

Potassium Thiosulphate. The "Analar" salt was made up to a

1 N. solution, which was standardised against the potassium iodate primary standard solution, using the reactions

$KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 3I_2$ (II)

and $I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$ (III)

No indicator was used. A typical analysis was:
20.00 ml. of 0.9679 N. potassium iodate solution required titres of 23.99, 23.90, 23.78, 23.96, 23.93, 23.92 ml. potassium thiosulphate solution.

Mean titre = 23.94 ml. Normality of potassium thiosulphate = <u>0.8085</u>

<u>Hydrochloric acid</u>. Concentrated hydrochloric acid (36%) was diluted to give a 1 N. solution. Using reactions II and III the hydrochloric acid was standardised against the potassium thiosulphate solution. A typical analysis was:
20.00 ml. of hydrochloric acid required titres of 18.32, 18.29, 18.30, 18.31, 18.30 ml. of 0.8085 N. potassium thiosulphate.

Mean titre = 18.30 ml. Normality of hydrochloric acid = <u>0.7399</u>
In the Kolthoff method of analysis for nitrate ion "May and Baker 36% hydrochloric acid" was used.

<u>Sodium Hydroxide</u>. The "Analar" salt was used to make up a 1 N. solution. The sodium hydroxide solution was titrated with the secondary standard, hydrochloric acid, using screened methyl orange as an indicator. A typical analysis was:

19.92 ml. of sodium hydroxide required titres of 17.70, 17.70, 17.70 ml. of 0.8754 N. hydrochloric acid.
Mean titre = 17.70 ml. Normality of sodium hydroxide = 0.9851

In the Kolthoff method of analysis for nitrate ion a 50% (w/v) solution of the "Analar" salt in distilled water was used.

Ammonium Molybdate. A 1% solution of the "Analar" salt was used as a catalyst in the Kolthoff method of analysis for nitrate ion.

Screened Methyl Orange. The commercial indicator (methyl orange screened with xylenecyanol f.f.) was adjusted by the addition of methyl orange indicator solution until a grey end point was obtained when three drops were used in an acid-base titration.

"Ferroin". One gm. of ortho-phenanthroline hydrate and 1.4 gm. of Ferrous Sulphate hepta-hydrate were made up with water to 200 ml. Five drops of this indicator would cause a colour change of orange to green in a ferrous sulphate-potassium dichromate titration.

(ii) Velocity Measurements

Temperature control. An electrically controlled water thermostat was used to maintain a constant temperature throughout the reaction. The reaction vessel and the reagents were placed in the thermostat fifteen minutes before the start of a reaction to attain thermal equilibrium. The temperature of the thermostat was recorded by an N.P.L. standardised thermometer. The thermometer was graduated from -11 to 50°C. in 0.1° divisions, and was accurate to -0.02°. The thermostat was maintained at an exact thermometer reading and corrections applied if relevant. The observed and actual temperatures were:

Observed temperature:	0.00	15.00	25.00	35.00	45.00°C.
Actual temperature:	-0.10	14.83	24.91	35.03	45.08

The thermometer was read with the aid of a small lens. A similar thermometer was used in the thermometer well in the reaction vessel.

Start of Reaction. Three methods were used to mix the reagents at the start of a reaction.

(i) The first method was used where the reaction was too fast to admit of velocity measurements. A diagram of the apparatus employed is shown in Fig. 5b. A known amount of the nitrating medium was weighed into a 100 ml.

round bottomed flask. The flask, which was fitted with a B/24 socket neck, was stoppered and placed in the thermostat. The calculated amount of solid reagent, (viz. guanidine nitrate, nitroguanidine), was weighed into a small container. This container consisted of a hollow B/24 cone, fitted with a cap.

The round bottomed flask was removed from the thermostat and the stopper replaced by the hollow cone. The solid reagent was thus precipitated upon the surface of the medium. The timing of the reaction was started from this moment. Vigorous shaking was employed to aid solution of the solid. When a homogeneous solution had been attained the contents of the flask were transferred to the reaction vessel in the thermostat.

The time taken for solution varies with the medium. In 100% sulphuric acid solution was complete within fifteen seconds. In 81.14% sulphuric acid similar solution took about nine minutes. This method of mixing the reagents could not be used for nitroguanidine in sulphuric acid of a strength greater than 98%. Above that region the heats of solution, and of decomposition of the nitroguanidine are so great as to initiate an explosion.

(ii) The second method of mixing the reagents was used for the majority of the velocity measurements. In this case separate solutions of nitric acid in sulphuric acid, and of guanidine in sulphuric acid, were mixed together to start the reaction. A 50 ml. volumetric flask was filled with a solution of nitric acid in sulphuric acid, (see preparation of materials and media), and then placed in the thermostat. Into another 50 ml. volumetric flask the calculated amount of guanidine carbonate was weighed. The flask was chilled to 0°C. in an ice-water bath, and about 40 ml. of sulphuric acid-water medium added carefully. The flask was then transferred to the thermostat, and after thermal equilibrium had been reached, made up to volume.

The solution of guanidine thus prepared was transferred to the reaction vessel and stirring commenced. This done, the solution of nitric acid was also added to the reaction vessel. Addition of the nitric acid solution was performed as rapidly as possible, generally taking about 30 seconds. The timing of the reaction was started when the addition of the nitric acid was one half completed. From the mass of the drainage residues left in the flasks the amounts of constituents present in the reaction could be calculated.

Much the same procedure was followed when a complex nitration medium, such as potassium bisulphate - sulphuric acid-water, was used. The sulphuric acid solution of the inorganic salt was first made up to volume in a 50 ml. volumetric flask. The contents of this flask were then added to the guanidine carbonate as above.

(iii) The third method of mixing the reagents was used when the rate of reaction was very high. A series of 10 ml. flasks, fitted with B/19 socket joints, were made (Fig.5c). For each flask a hollow cone joint, with a capacity of 5 ml., was made. Solutions of guanidine, and of nitric acid, in sulphuric acid, were made up as above. Five ml. aliquots of the solution of nitric acid were then placed in each cone, and 5 ml. aliquots of guanidine solution in each 10 ml. flask. The cones were fitted to the respective flasks and shaken vigorously. The timing of the reaction was started at this moment.

Withdrawal of samples. Three methods of withdrawing samples were employed.

(i) The first method was used in experiments where the equilibrium between the constituents had already been attained. Two minutes before the sample was to be withdrawn stirring was stopped in order to prevent occlusion of air bubbles. Samples were withdrawn through the male neck of the reaction vessel. A 5 ml. pipette that had been fitted with a stopcock (Fig.7a) was used for taking samples. The use of a stopcock in conjunction with a suction tube enabled the pipette to be very easily filled to about 2-3 mm. above the graduation mark. The pipette could then be very accurately levelled off at leisure. This device ensured that exposure of the reaction mixture was kept to a minimum.

The aliquot was drowned onto 55 ml. of water in a

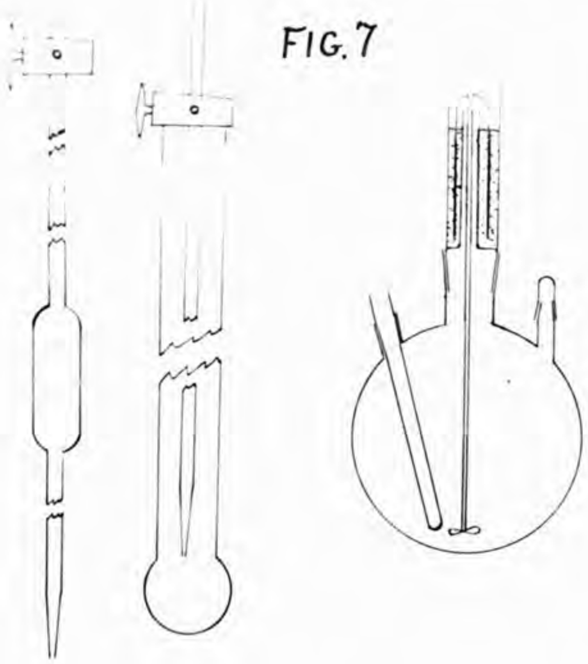


FIG. 7

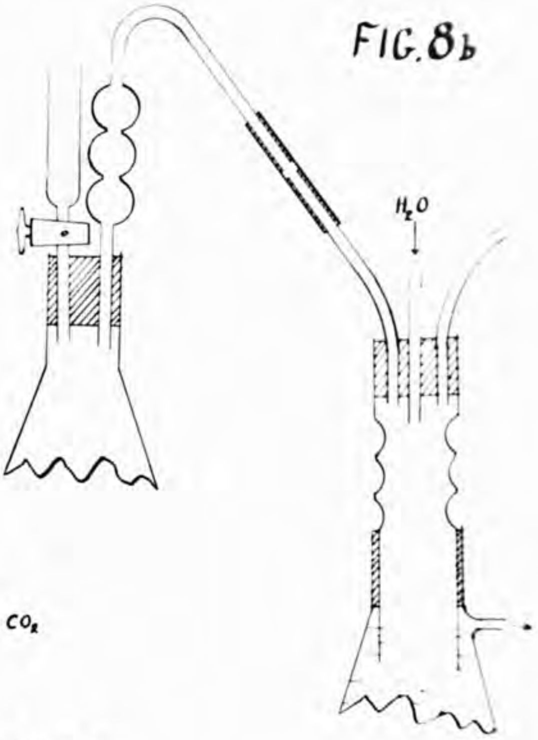


FIG. 8b

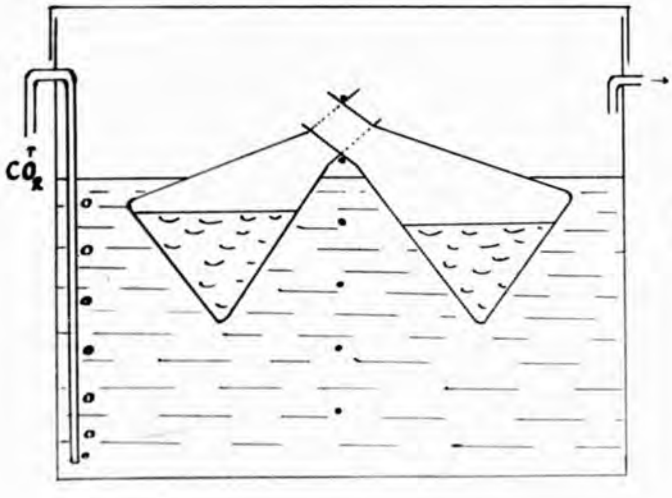


FIG. 8d

350 ml. flask, and the walls of the flask washed down with 15 ml. of water.

The timing of the sample was taken as being the moment the pipette started to empty. The pipette was empty in about 20 seconds, draining and "milking" took about another twenty seconds.

The pipette was washed three times with water, and then three times with acetone. After a final rinse with dry ether, air from a foot bellows was blown through the pipette for at least ninety seconds. This left the pipette ready for the next sample.

After the pipette had been dried, (about two minutes after drowning the sample), 30 ml. of 50% (w/v) sodium hydroxide solution were added to the contents of the flask. After adding boiling chips the basic solution could be safely left for analysis.

(ii) The second method of withdrawing samples was quicker than the first and was used in the majority of the velocity measurements. The pipette and method of withdrawal used were the same as above. In place of rinsing and drying, the pipette was hung in a vertical position to drain. A length of 16 mm. glass tubing, sealed at the lower end, was used to hold the pipette while draining. The pipette hung inside this tube, being supported by the barrel of the stopcock at the top. (Fig. 7b). The pipette holder was immersed in the thermostat, and thus the pipette was kept at the same temperature as the reaction mixture. Before taking a new sample the drainage drop at the pipette tip was blown out, and the outside of the pipette wiped dry with filter paper. Treatment of the drowned sample was the same as above. Aliquots could be taken every two minutes using this method.

(iii) The third method of taking samples was an integral part of the third method of mixing the reagents. When a sample was desired the cone and 10 ml. flask were separated and the contents poured through a short stemmed funnel into 10 ml. of water in a 350 ml. flask. The time of the sample was taken as being at this moment. The small flask and the cone were both rinsed three times with water, the washings being added to the drowned sample. It was essential that the washing be done rapidly, and the process was best performed by two people. Using this method a sample could be withdrawn within six seconds of the time of mixing. By using a series of flasks samples could be withdrawn at three second intervals if required. The difficulty of assigning the moment of drowning prevented a more rapid sampling than this.

Timing. A stopwatch calibrated in minutes and fractions of a second was used for timing the reaction. The stopwatch was accurate to within three seconds on twenty-four hours. The majority of velocity reactions were timed to the nearest decimal fraction of a minute. Very rapid reactions, viz. those sampled by method three, were timed to the nearest decimal fraction of a second.

The reaction vessel. The reactions were performed in a three necked 250 ml. round bottomed flask (Fig.7c.). The centre neck contained a mercury sealed stirrer, which was driven by a 1/50th horsepower electric motor. One of the side necks held a thermometer well, which extended close to the bottom of the flask. The third neck was used for withdrawing samples from the reaction mixture. This neck was fitted with a male ground glass joint and a cap. The male joint ensured that no drainage drops of sulphuric acid could run back to dilute the reaction mixture. The reaction vessel was kept in an electrically controlled water thermostat.

Calibration of glassware. All glassware was calibrated before use. In the case of volumetric flasks only those possessing a grade A certificate of calibration were used. All pipettes used for aqueous solutions were calibrated by weighing the amount of distilled water that they delivered at 20°C. Burettes were calibrated at 5 ml. intervals by the same method. The microburette was calibrated at 0.5 ml. intervals. Pipettes used for withdrawing samples were calibrated by weighing the amount of concentrated sulphuric acid delivered at 25°C. T.G. Bonner (68) reports that the volume of sulphuric acid delivered by a 5 ml. pipette does not vary by more than 0.02 ml. over a 12% range of sulphuric acid. In this work, because of breakages, no pipette was used over more than a 10% range of sulphuric acid. Typical figures for the calibration of a pipette are:

Weight of sulphuric acid delivered (density $_{25^\circ}$ = 1.6699)	Volume	Mean
8.2685 gm.	4.9516 ml.	
8.2782 "	4.9573 "	
8.2779 "	4.9571 "	4.9553 ml.
8.2699 "	4.9523 "	
8.2792 "	4.9579 "	

The effect of temperature upon the volume of sulphuric acid delivered was significant, and pipettes were calibrated accordingly. Thus:

Volume of 98.92% sulphuric acid delivered:	4.8249	4.8408	4.8613	4.8899	4.9091 ml.
Temperature°C.:	0.0	15.0	25.0	35.0	45.0

(iii) Methods of analysis

Two methods of analysis for nitrate ion were used.

(i) The best method of analysis of nitrate ion in concentrated sulphuric acid is that developed by W.D. Treadwall and H. Vontobel (69).

In this method the nitric acid in solution in a fairly concentrated sulphuric acid, (greater than 75%), is titrated with a ferrous sulphate solution. The end point is best observed electrometrically. The reaction goes according to the equation:

$$HNO_3 + 2FeSO_4 + H_2SO_4 = HNO_2 + Fe_2(SO_4)_3 + H_2O \qquad (IV)$$

Unfortunately, as outlined in the discussion, the removal of the nitric acid by the above reaction allows a rapid shift of the equilibrium to take place. Thus solutions of guanidine nitrate in sulphuric acid always analysed for 100% of the nitric acid present according to theory. Similarly solutions of nitroguanidine in sulphuric acid analysed for 100% of the nitric acid that would be present ~~and~~ allowing for complete conversion to guanidine nitrate.

(ii) The method of analysis that was ultimately used was a modification of that proposed by I.M. Kolthoff, E.B. Sandell and B. Moskovitz (70). Kolthoff and his co-workers employed aqueous solutions. Nitric acid, in a concentrated hydrochloric acid solution, was allowed to react with excess ferrous ammonium sulphate. In the absence of oxygen, and in the presence of an ammonium molybdate catalyst, the nitrate ion was quantitatively reduced to nitric oxide. The reaction is

$$3Fe^{++} + NO_3^{-} + 4H^{+} = 3Fe^{+++} + NO + 2H_2O \qquad (V)$$

After the nitric oxide had been expelled from the solution, the excess ferrous ammonium sulphate could be back titrated with a potassium dichromate solution.

The constituents of the solution to be analysed were, nominally, nitrate ion, the guanidine nucleus, nitroguanidine, and dilute sulphuric acid. The Kolthoff method of analysis was satisfactory for solutions of nitrate ion in sulphuric acid. Thus: A <u>0.09895</u> Molar solution of potassium nitrate in concentrated sulphuric acid was drowned onto water and analysed by the Kolthoff method.

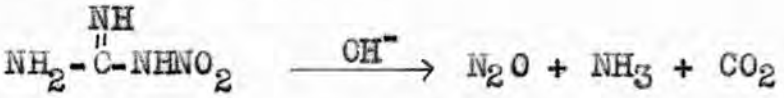
Molarity of nitrate ion found: 0.0995, 0.0993, 0.0977, 0.0999, 0.0991. Mean value: <u>0.0991</u> % error: 0.15%.

Solutions of guanidine nitrate in sulphuric acid could also be analysed with accuracy by this method. Thus: A <u>0.08704</u> Molar aqueous solution of guanidine nitrate was poured onto 10% sulphuric acid and analysed by the Kolthoff method. Molarity of nitrate ion found: 0.08752, 0.08746, 0.08746, 0.08775, 0.08789, 0.08734, 0.08752.
Mean value <u>0.08756</u> % error: 0.6%.

When nitroguanidine was added to an aqueous solution of nitrate ion the method of analysis no longer gave accurate results. Thus:

Molarity nitroguanidine:	0.22	0.26	0.10	0.24	0.47
Molarity nitrate (calc.):	0.290	0.312	0.447	0.247	0.355
Molarity nitrate (found):	0.218	0.260	0.457	0.260	0.376
% error:	24.8	8.5	2.2	5.3	5.9

Nitroguanidine can be decomposed by the action of alkali, the reaction being:



$$NH_2-\overset{\overset{NH}{\|}}{C}-NHNO_2 \xrightarrow{OH^-} N_2O + NH_3 + CO_2 \qquad (VI)$$

Thus the nitroguanidine could be completely destroyed by boiling the solution of nitrate and nitroguanidine with sodium hydroxide before starting the analysis. This procedure was completely successful. Thus:

Molarity nitroguanidine:	0.0	0.0	0.0	0.0	0.2	0.2
Molarity nitrate (calc.):	0.07925	0.07925	0.07925	0.7925	0.07925	0.07925
Molarity nitrate (found):	.07836	.07878	.07906	.07896	.07856	.07949 .07808
% Error:	1.1	0.6	0.2	0.4	0.9	0.3 1.4

Mean found value: <u>0.07875</u>

The method of analysis as finally used was a modified version of the Kolthoff version. The procedure was as follows. Diagrams of the apparatus used are given in Figs. 8,9 and 10.

The sample from the reaction mixture had been drowned and made basic, as described in the methods of sampling. In this condition the solution was perfectly stable with regard to the nitrate ion. The nitric acid had been fixed as sodium nitrate, and the nitroguanidine was being decomposed by the alkali solution. The analysis was started by boiling the basic solution. Heat was supplied by a Bunsen flame, at the rate of 22 K.cal per minute. Heating was continued for twelve minutes, the flask was then transferred to the cooling tank.

The cooling tank (Fig.8a) was a metal tank 24 x 20 x 24 cm. with a close-fitting cover. Internally a wire screen divided the bottom three-quarters of the tank into equal portions. This screen, of nine centimetre mesh, thus made two compartments, each 12 x 20 x 18 cm. The tank was filled to a depth of 15 cm. with a slurry of crushed ice and water. A constant inert atmosphere was maintained above the liquid by bubbling in carbon dioxide gas at the rate of 36 litres per hour. Flasks were placed in the ice-water with their necks supported by the wire grille, and were thus cooled in an oxygen free atmosphere.

After two and one half minutes cooling the flask was removed from the cooling tank and the contents acidified by the addition of 75 ml. of 36% hydrochloric acid. The acidification of the sodium carbonate formed by the carbon dioxide and basic solution in the cooling period ensured that the inert atmosphere was maintained above the solution in the flask. Following the acidification 15-25 ml. of approximately 0.2 N. ferrous ammonium sulphate solution was added from an automatic burette (Fig.9a). The flask was stoppered immediately, and heating recommenced. The rate of heating was the same as before.

Through the rubber stopper passed the mouth of a 7 ml. dropping funnel and a simple still head (Fig.8b). The lower end of the still head was connected to one of the inlets of a gas absorbtion cascade by means of a sleeve of rubber tubing. The gas absorption cascade consisted of a length of Vigreux column passing into a side necked flask. At the head of the column were two inlet tubes and a water jet. Water flowed down the column, through the water seal at the bottom, and out of the side arm. The hydrogen chloride and steam given off during the boiling of the acid solutions were absorbed in the constant stream of water.

After 3-4 minutes heating the yellow acid solution started to boil. About 6 ml. of a 1% solution of ammonium molybdate was run into the flask from the dropping funnel. The colour of the acid solution changed from yellow to green, and after further boiling faded to an orange. The

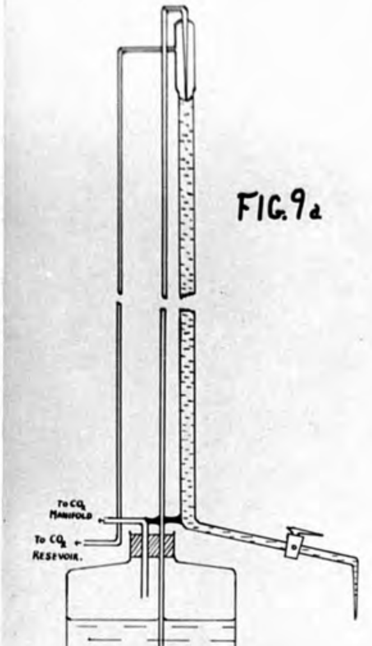


FIG. 9a

To CO_2 Manifold
To CO_2 + Resevoir.

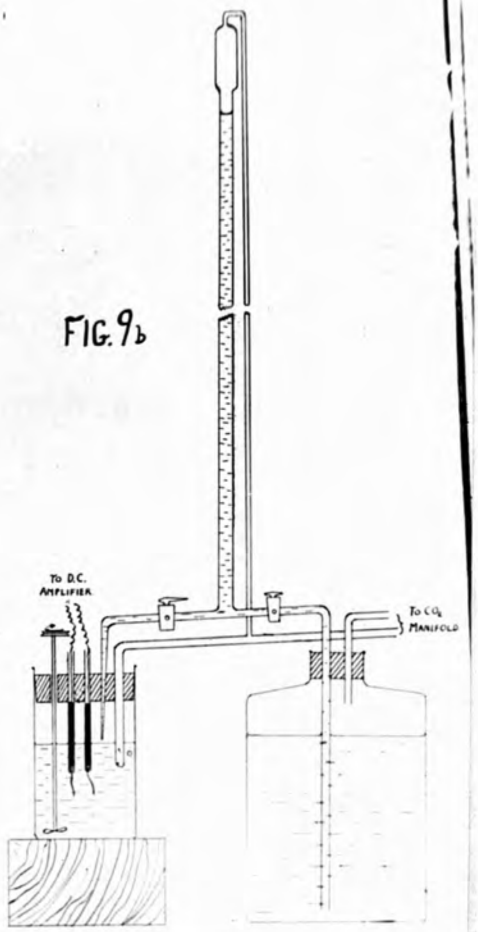


FIG. 9b

To D.C. Amplifier
To CO_2 Manifold

appearance of the orange colour signified that the reaction between the ferrous ion and the nitric acid was complete. The reaction was generally complete after about 10 minutes heating. Heating of the acid solution was continued until the volume was reduced to about 100 ml.

After being heated for 24 minutes the acid solution was placed in the cooling tank. Four minutes cooling reduced the temperature of the solution to about 10°C. At this temperature the catalysed oxidation of ferrous ion by atmospheric oxygen should be negligibly slow. For the purposes of titration the contents of the flask were washed out into a 180 ml. beaker. The cooling of the hot, concentrated, acid solution generally resulted in the precipitation of sodium salts. Any occluded ferrous salt would lead to low results in the analysis, but by making the volume of the solution up to 140 ml. the salts were found to be dissolved by the end of the titration.

The beaker was used as a reaction vessel for an electrometric titration. The excess ferrous ammonium sulphate present was back titrated with a standard potassium dichromate solution. From the amount of ferrous salt used a value for the original nitrate concentration could be calculated. The results of a typical analysis were:

Volume of 0.2299 N. ferrous ammonium sulphate added = 12.44 ml
Back titre of 0.1937 N. potassium dichromate = 8.00 ml.
Volume of sample = 4.944 ml.

Volume of ferrous ammonium sulphate used

$$= 12.44 - \frac{8.00 \times 0.1937}{0.2299}$$

$$= \underline{5.70}\ \text{ml.}$$ ✓

1 ml. of 0.1000 N. ferrous ammonium sulphate

$$= 3.370\ \text{mgm. } KNO_3$$

$$= \frac{3.370 \times 63.02}{101.1}\ \text{mgm. } HNO_3$$

Therefore Molarity of solution

$$= \frac{3.370 \times 63.02 \times 5.70 \times 0.2299 \times 1000}{101.1 \times 0.1000 \times 4.944 \times 63020}$$

$$= \underline{\underline{0.08835}}\ HNO_3$$ ✓

Allowing time for the titration, the complete analysis took about 48 minutes. Much time could be saved by analysing a series of samples consecutively. By staggering the procedures, viz. by starting the second sample while the first basic solution was cooling, a batch of ten samples could be analysed in three hours.

The Titration. A simple redox reaction was used for estimating the ferrous ammonium sulphate. The end point used was of the electrometric "dead stop" variety. When a potential difference of the order of fifteen millivolts is applied across two platinum wire electrodes in an acid ferrous salt solution, a certain amount of current passes. When titrating with an oxidising agent, as the end point is closely approached, polarisation occurs at the electrodes, and the rate of flow of current alters. As the end point is absolutely reached a definite change in current density is noticeable.

The apparatus used is shown in Fig. 9b. Agitation of the solution was effected by rapid stirring. The stirrer was driven by belt drive from a 1/50 th. horse power electric motor. The standard potassium dichromate solution was delivered from a 10 ml. microburette, modified for automatic filling. A small stream of carbon dioxide gas was kept bubbling through the surface of the ferrous solution throughout the titration. A rough guide of the approach of the end point could be had by observing the change in colour of the solution. This varied from an initial orange-yellow to a yellowish green at the actual end point.

At the beginning of this work the end point was found by using a simple galvanometer. This was suitable when the normalities of the solutions were of the order of 0.3 N. When solutions with a normality of 0.05 were used detection of an accurate end point was very difficult. Accordingly, a simple D.C. amplifier was used to amplify the change in current density.

The potential difference across the electrodes was applied as a potential to the grid of a triode thermionic valve. Thus small changes in the electrode current, when applied through the grid, caused large changes in the anode potential of the valve. The changes in anode potential could be measured by placing a galvonometer between the anode and a fixed reference point. Using the apparatus described below, and titrating with 0.1 N. solutions, the galvonometer started to "kick" over one scale division when about 0.5 ml. before the end point. The size of the "kick" increased as the end point was approached. At the end point the "kick" was about eighty scale divisions. Immediately the end point had been passed the galvonometer swung in a direction opposite to the one in which it had been previously "kicking". The behaviour of the galvonometer always followed this pattern. The magnitude of the movements of the galvonometer varied with the strength of the solutions being titrated, and the condition of the D.C. amplifier. The most notable changes were caused by variations in the filament current. The galvonometer was less sensitive to changes in the anode potential.

The circuit used for the D.C. amplifier is shown in Fig.10. The uses of switches A, B, and C ? is obvious. Switch D was used to test the circuit as a whole. The titration was normally carried out with this switch closed. Opening it put an infinite resistance between the electrode leads, and the observed effect on the galvanometer was similar to that of the end point. Switch E was incorporated to test the signal from the valve, it was only used after

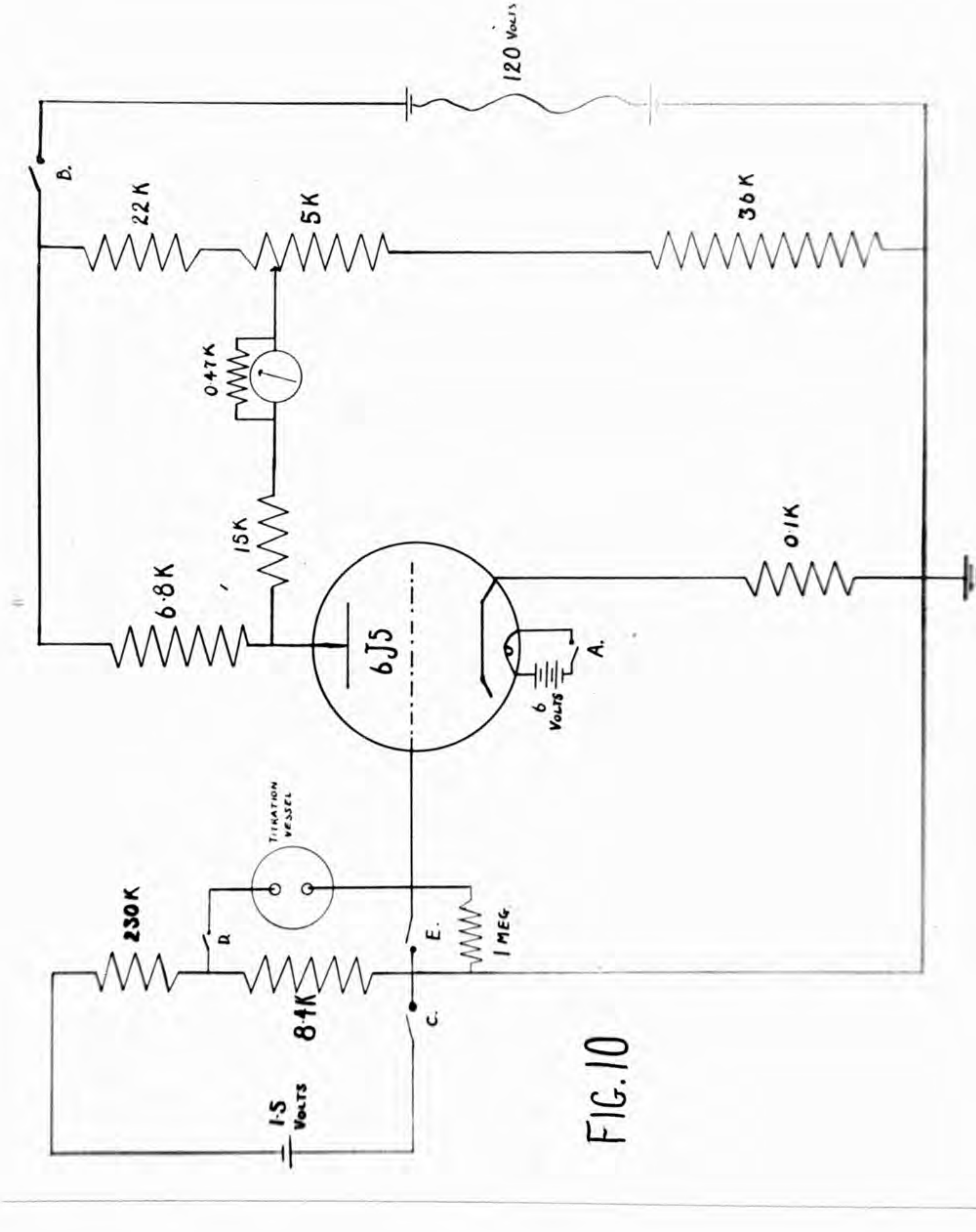

120 Volts
B.
22 K
5K
36 K
0·47K
15K
6·8K
0·1K
6J5
A.
6 Volts
Titration vessel
230K
D.
E.
1 MEG
8·4K
C.
1·5 Volts

FIG. 10

recharging the batteries. The titration is normally carried out with this switch open. The amplifier was screened, and screened cable was used for the electrode and grid leads. The galvonometer that was used was a "Cambridge spot galvonometer" - catalogue No. 41159. The characteristics were: resistance 400 ohms, critical damping 14,000 ohms, period 2 seconds, sensitivity 170 mm. per microampere. This instrument was shunted, as shown in the circuit diagram, to give an appropriate sensitivity.

Blank error. This method of analysis was suitable for estimating nitrate solutions over a large range of concentrations. At low concentration the accuracy is diminished, and it is impossible to estimate amounts of less than 1.5 mgm. of nitric acid with any degree of accuracy. Despite all refinements the method could never be made to give consistent results that were 100.0% accurate. The values obtained from the analyses were always rather less than 1% high. This error could be allowed for, but not eliminated. It was possibly due to slight impurities in the chemicals, possibly to a slight air leakage. More probably it was the result of a number of such factors. A blank error was calculated from a large number of experiments and subsequently applied to all estimations.

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