A study of the process of nitration

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"A STUDY OF THE PROCESS OF NITRATION".

Being an account of work carried out at the Science Laboratories, Durham University (Durham Division), under the Direction of Professor I. Masson, M.B.E., D.Sc., F.I.C.

Photographs of solid model constructed to represent the shape of the area of dinitration after a given time interval. Flat triangular surface represents composition (in mols.%) of "nitrating acid". Vertical height represents time of nitration; total height = 16 hours.

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SUMMARY OF WORK.

A systematic investigation of the process of nitration and an attempt to determine and classify the factors governing this reaction has been made.

The reaction between ternary acids (consisting of mixtures of sulphuric acid, nitric acid and water) and mononitrobenzene was selected for special study on account of the comparative simplicity of the system and the absence of consecutive reactions. There is reason to believe, however, that many of the effects noticed for this special nitration may well be applied to the general process of nitration.

By expressing results on a triangular diagram (giving the composition of ternary nitrating acid) it has been possible to define a limiting area including all compositions of acids which will nitrate mononitrobenzene to dinitrobenzene. The authenticity of this area has been tested from many standpoints.

The position of "THE LIMITING LINE OF DINITRATION" (which is the boundary of the dinitration area) is determined almost exclusively by the composition of the nitrating acid. It depends very little, if ~~any~~ at all, upon the relative quantities used, provided there is sufficient M.N.B. present for the reaction, and that sufficient time is allowed for the system to reach its end point when no further nitration takes place.

From the position of the limiting line of dinitration, it is proved that the chemical activity of the nitric acid present, as determined by its ability to nitrate, is quite different from its thermodynamic activity, as measured by its partial vapour pressure.

A study of heterogeneous or two layer nitrations proves that reaction velocity diminishes with increasing degree of heterogeneity.

Sulphuric acid increases the velocity of nitration in an additive manner.

The function of the sulphuric acid is probably, to remove water from hydrates of nitric acid until it has formed sulphuric acid monohydrate. After monohydrate formation, further dehydrating action is either absent or very small.

Separation into two layers, determined by solubility of nitro compounds in nitrating acids can be predicted by a triangular diagram.

When a nitration system produces two layers the acid is distributed in such a manner that the greater part of the nitric acid, together with small quantities of sulphuric acid and water are contained in the organic layer whilst the acid layer residue contains nearly all the sulphuric acid. This acid-layer-acid is the layer which performs nitration.

The facts suggest that sulphuric acid when dissolved by the organic layer might form an additive molecular compound with nitrobenzene, thus becoming unable to dehydrate the nitric acid present.

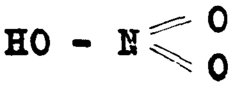
PART 1.

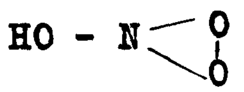
§ 1. NITRIC ACID, ITS PROPERTIES AND CONSTITUTION.

(a) According to V. H. Veley and J. J. Manley, E. W. Kuster and S. Münch, alsolute nitric acid exists only in snow-white crystals stable below -41°; on melting it partly decomposes into water and nitrogen pentoxide which dissolves in the melted acid to form a yellow solution. The red fuming liquid known as "fuming nitric acid" is a solution containing a variable amount of N_2O_4 and NO_2 in concentrated acid.

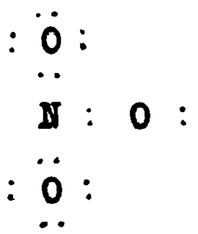
(b) Many investigations on the physical properties of solutions of nitric acid showed the existance of discontinuities which have been interpreted to mean that definite hydrates are formed. Freezing points were investigated by V. H. Veley and J. J. Manley, heat of solution by M. Berthelot, J. Thom~~p~~sen and S. U. Pickering, viscosity by C. Chéneveau, absorption spectra by W. N. Hartley, and electrical conductivity and refractive indices by V. H. Veley and J. J. Manley. The curves showed singularities corresponding with hydrates with 14, 7, 4, 3, 1½, and 1 H_2O. H. Erdmann claimed to have isolated by freezing at low temperatures hydrates with 2, 1½, 1 and ½ H_2O. For the present purpose we are not concerned with the extensive range of hydrates supposedly formed by nitric acid, it is sufficient to know that the evidence indicates that nitric acid may behave in solution as a very complex substance undergoing a number of changes which are only partially comprehended.

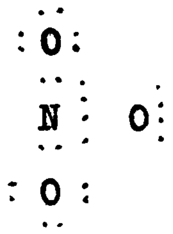
(c) <u>Constitution</u>:- Nitric Acid is nearly always regarded as being constituted with quinquevalent nitrogen but I. I. Kanonnikoff inferred that the refractive indices of a number of nitrates agreed better with tervalent nitrogen. These two hypotheses are symbolized :-





A number of workers have discussed the electronic structure, and from observations on the absorption spectra of sodium and potassium nitrates in different solvents, G. Scheibe inferred that the nitrate ion is dipolar, and that the electronic structure is such that the first of the following forms exists in equilibrium with a small proportion of the second :-





(d) The constitution of the nitric acid molecule in solution is not yet definitely fixed but the weight of evidence suggests that the molecules in aqueous solution are complex $(HNO_3)n$, and in some cases form the equivalent of mesonitric acid H_3NO_4 --- W. N. Hartley, E. Aston and W. Ramsay, W. H. Perkin, S. U. Pickering and V. H. Veley and J. J. Manley. Anhydrous nitric acid is probably bimolecular $H_2N_2O_6$; and with acids between 78 and 100% HNO_3 there is a mixture of mesonitric acid H_3NO_4 and the bimolecular acid $H_2N_2O_6$. The former is supposed to be active and the latter inert.

(e) Further light is shown on the constitution of nitric acid by absorption spectra. K. Schaefer and co-workers found that solutions of the nitrates exhibit selective absorption, while the alkyl nitrates cut off only the ultra-violet end of the spectrum. Dilute nitric acid has a spectrum like that of the salts, but with a concentration above 2N - HNO_3, the ester type appears and with the concentrated acid there is only continuous absorption. According to A. Hantzsch the optical properties indicate that two types of molecules can exist, the ordinary true acid molecule $H.NO_3$ which is ionizable and gives rise to electrical conductivity and the "pseudo acid" molecule $HO.NO_2$; by a pseudo acid he means one which is homopolar with respect to hydrogen, but whose hydrogen atoms do not exercise an acid function, which in the case of oxyacids, are linked with oxygen in the form of hydroxyl. When water is added the pseudo acid becomes a true acid changing its constitution and optical properties. D. D. Karve found that the heat of solution of nitric acid in alcohol and ether supports this hypothesis. It is assumed therefore that solutions of nitric acid contain equilibrium mixtures of the pseudo acid $HO(NO_2)$ and the true acid $H.NO_3$ which is assumed to be present as oxonium nitrate, $(H.OH_2)(NO_3)$.

(f) The absorption spectrum and electrical conductivity of nitric acid led to the inference that yet a third type of molecule is present. Solutions of nitric acid in absolute sulphuric acid contain a largely ionized electrolyte which is more transparent than an equally concentrated ethereal or aqueous solution of nitric acid. Since solutions of acetic acid in absolute sulphuric acid producing an acetylium cation, behave similarly, it is inferred that a nitronium cation is formed by dissolving nitric acid in absolute sulphuric acid and the solution contains nitronium hydrosulphate $\left\{NO(OH)_2\right\} (HSO_4)$, and $\left\{N(OH)_3\right\} (HSO_4)_2$. This hypothesis is confirmed by the isolation from solution of the nitronium salts :-

$\left\{N(OH)_3\right\} (ClO_4)$, $\left\{N(OH)_3\right\} S_2O_7$.

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§ II SULPHURIC ACID AND ITS HYDRATES.

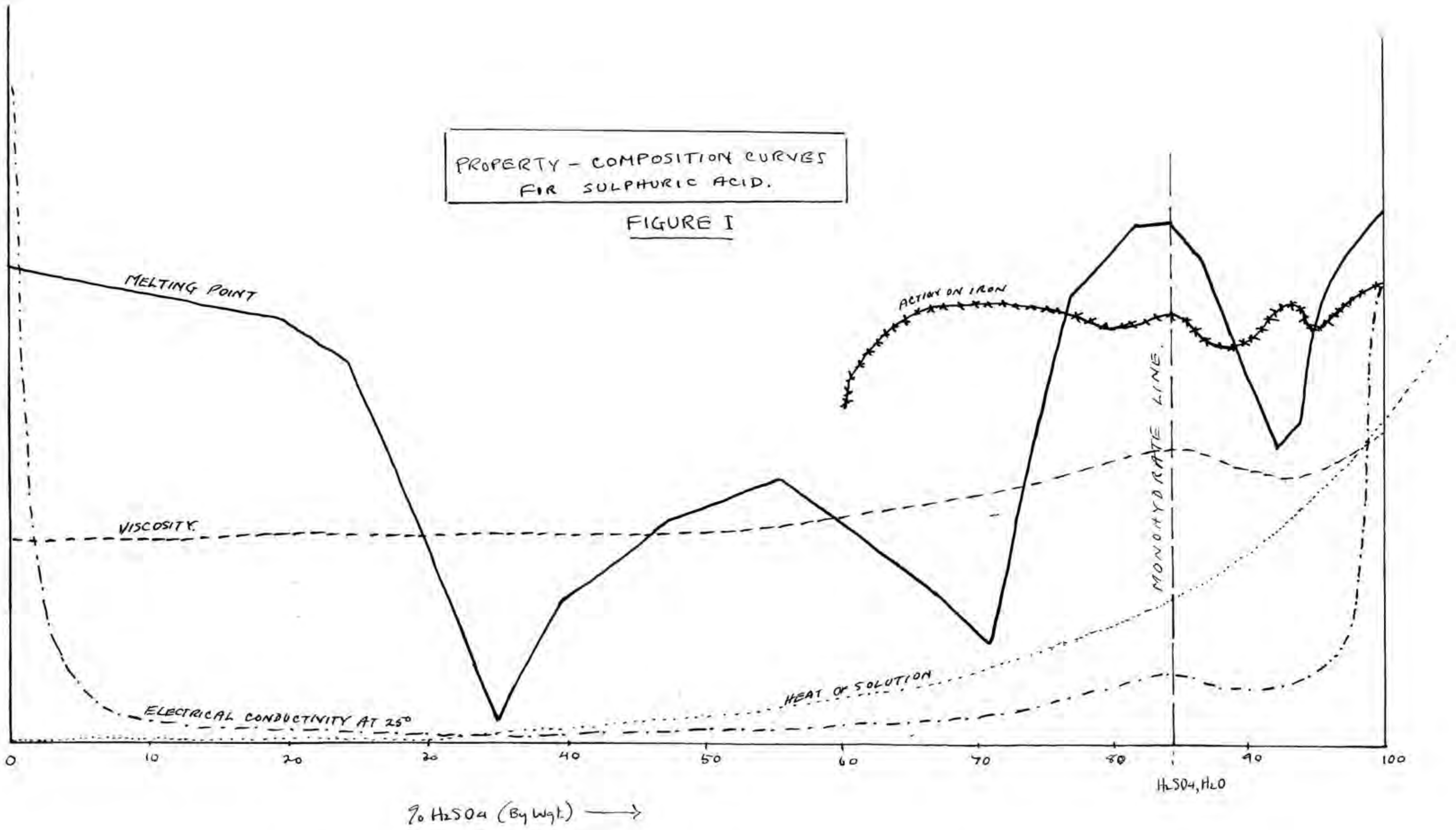
(a) While the existence of a large number of hydrates of sulphuric acid has been surmised from the properties of its aqueous solution, only the monohydrate and the tetrahydrate have been definitely isolated. The absolute acid fumes at temperatures above 30° due to a partial dissociation into SO_3 and H_2O.

(b) A number of physical properties of aqueous solutions of sulphuric acid are shown in the accompanying diagram (Fig. I) which appeared in Ephraim's "Anorganische Chemie". It will be seen that marked changes of direction in the curves occur at intervals and these are interpreted as pointing to formation of definite hydrates in solution.

Sulphuric Acid Monohydrate:-

(c) In the present work which is described in part II of this thesis the significance of an equimolecular mixture of sulphuric acid and water is very noticeable and leads to the belief that this particular mixture is a very important entity in the study of nitration mixtures. For the existance of this particular hydrate, a wealth of evidence is available.

(d) S. U. Pickering in his classic work on "The Nature of Solutions" found no discernible change at the point 84.5% H_2SO_4 (which is the percentage by weight in the monohydrate mixture) in the heat of dissolution curve, in the expansion curve it was but feebly marked, and in the first differential of the densities it was by no means prominent. In all these curves, however, it was found that a repeated application of differentiation showed a very prominent change at the monohydrate point. Its being partially masked in the experimental curves may be due to the fact that this hydrate is really exceptionally stable while liquid, acting as an entity and forming compounds in the same way as the other stable liquids, water and pure acid, containing several fundamental molecules of itself with a single water molecule~~s~~ on the one hand, and a single sulphuric acid molecule on the other; the proximity of the minor changes due to such compounds would in the absence of a very large number of experimental points, result in the rounding off of the change which shows the monohydrate itself.



PROPERTY - COMPOSITION CURVES FOR SULPHURIC ACID.

FIGURE I

(e) R. Lespieau fractionally crystallised a large quantity of sulphuric acid monohydrate until the melting point rose to and remained stationary at 8.53°; a temperature identical with that determined by Pickering. The constants in the equation :-

$$Mx/p = ax + K$$

where x = lowering of freezing point,

p = percentage of dissolved substance,

M = Molecular weight of dissolved substance,

a = Constant for solid,

K = Constant for solvent, ---

were determined for acetic, pyruvic and uric acids.

a = 1.2, - 2.7, 13.3

K = 48.1, 47.5, 48.0

K may therefore be taken as 48.

The value of K calculated from the latent heat of fusion is 49.5 taking Berthelot's value 31.7 Cal., and 39.3 taking Pickering's value 39.9 Cal. Thus from the cryoscopic point of view, $H_2SO_4.H_2O$ behaves as an individual.

(f) The refractive indices of sulphuric acid at different concentrations were determined very accurately by V. H. Veley and J. J.Manley. The maximum value of the refractive indices and of the first constant of Cauchey's dispersion formula ($\mu = A + B/\lambda^2 + C/\lambda^4$) occur at a point which corresponds with the composition of a hydrate $H_2SO_4.H_2O$, but otherwise, any indication of the existance of hydrates is doubtful. Livingston, Morgan and Davis found that both the addition of sulphuric acid to water and of water to sulphuric acid caused an increase in surface tension so that different concentrations of sulphuric acid may have the same surface tension at the same temperature. The property - composition curve again indicated a discontinuity at the point $H_2SO_4.H_2O$.

(g) According to Sir D. O. Masson there is very definite evidence of monohydrate formation in solution. He studied the relation between solute molecular volumes and solvation and ionization and showed that in the molecular volume curve a discontinuity occurs at the point 84.2% H_2SO_4. It is noteworthy that acetic acid which may be used as a solvent for nitration shows a similar change in molecular volume at its monohydrate point.

These and many other facts prove conclusively that sulphuric acid forms a stable hydrate with one molecule of water.

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§ III TERNARY MIXTURES OF H_2SO_4, HNO_3 and H_2O.

(a) A study of the properties of ternary mixtures of H_2SO_4, HNO_3 and H_2O yields facts which throw a certain amount of light on the process of nitration in the presence of sulphuric acid.

(b) A. A. Saposchnikoff determined the vapour pressure of different strengths of nitric acid dissolved in sulphuric acid. His data obtained by mixing nitric acid of specific gravity 1.52, 1.48 and 1.4 respectively with different quantities of absolute sulphuric acid enabled him to draw curves in which the partial pressure of the nitric acid is plotted against the acid composition. From these curves he was able to plot vapour pressure points on the ternary acid diagram, expressing the composition of the mixed acid in terms of its three components HNO_3, H_2SO_4 and H_2O. By joining up on the triangular diagram, points having the same vapour pressure he obtained a series of curves or isobars of pressure showing at a glance how the vapour pressure varies with acid composition over the whole range of acid mixtures. A reproduction from Saposchnikoff's data appears in Fig XI page 92, employing the method of triangular co-ordinates (about which a special section has been compiled in this thesis --- see page 16), to represent the molecular composition of the acids. A study of this diagram yields many interesting facts which Saposchnikoff has utilized in explaining the mechanism of formation of cellulose nitrates.

(c) It will be seen that on adding water to nitric acid in increasing proportions, the HNO_3 partial vapour pressure is rapidly diminished, the volatility of the nitric acid being decreased by formation of hydrates coupled with simple dilution. In the same way a diminution in vapour pressure occurs when we dilute pure nitric acid with pure sulphuric acid, but in this case the process is much more gradual and probably due simply to straightforward solution effects, the vapour pressure obeying Henry's Law being proportional to the amount of nitric acid present over a very wide range of concentration. If, instead of absolute nitric acid we use a more dilute (say 60%) acid for mixing with sulphuric acid, we first of all encounter a rapid rise in vapour pressure, the value reaching a maximum and then gradually decreasing on further addition of sulphuric acid. The Isobars of vapour pressure show optimum values, changing direction at points which lie very near to the line joining pure nitric acid with an equimolecular mixture of sulphuric acid and water. Saposchnikoff explains these maximum vapour pressure points by supposing nitric acid when treated with increasing quantities of sulphuric acid, to gradually deliver water of hydration, finally attaining the almost anhydrous state on the line of equal molecular ratios of water and sulphuric acid. Further additions of sulphuric acid beyond this point only serve to diminish the concentration of the already anhydrous nitric acid and consequently a gradual fall is then encountered. Thus those acids containing the least quantity of nitric acid whilst holding the highest vapour pressures are situated on the line of equal molecular ratios of sulphuric acid and water.

(d) Saposchnikoff's conclusion, that sulphuric acid when added to a solution of nitric acid is hydrated and produces an increased concentration of free anhydrous nitric acid molecules, was supported by the work of Paschal and Garnier on the distillation of ternary acid mixtures.

On the other hand, Berl and Samtleben in a similar study obtained fundamentally different boiling point and vapour composition curves and concluded that for ternary mixtures with over 32% water, there was no evidence of any water binding action of the sulphuric acid at the boiling point.

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§ IV NITRATION.

(1) Influence of Nitrous Acid:-

(a) It has been suggested by a number of workers that nitration takes place through the formation of intermediate compounds with nitrous acid. This is true in certain cases but cannot be accepted as the general mechanism in nitration of any aromatic body.

(b) Denizes observed that certain hydroxybenzoic acids can be nitrated by nitrous acid alone and assumed that a nitroso compound is first formed and then either decomposed by nitric acid or oxidized by nitric oxide, arising in either case from decomposition of the nitrous acid. (Thus the action of metals on nitric acid is probably analagous, a nitrite being formed first and then decomposed by nitric acid). Orton in 1907, employing acetic anhydride as solvent, excluded the possibility of free HNO_2 arising by adding a little carbamide, and obtained a 90% yield of nitroamines.

(c) Martinsen found that nitrous acid plays an important part in the nitration of phenol, the rate of production of HNO_2 and the rate of nitration running parallel. When nitrous acid was excluded, no nitration took place and curiously, although addition of nitroso phenol increased the velocity of the reaction its effect was almost independent of its concentration. Arnall confirmed the view that nitrous acid autocatalyses the nitration of phenol and since in his opinion nitrosophenol was not formed he suggested the following mechanism :-

$$HNO_3 + HNO_2 \rightleftharpoons N_2O_4 + H_2O$$

$$C_6H_5OH + N_2O_4 \rightleftharpoons NO_2.C_6H_4.OH + HNO_2$$

(The prevention of the reaction by addition of hydrazine to remove nitrous acid reminds us of the way that nitric acid refuses to react with metals when urea is added).

(d) Nitrous acid plays no part in the nitration of simple hydrocarbons such as nitro-benzene, nitrotoluene and 2:4-dinitro xylene, which in the presence of sulphuric acid give excellent bimolecular velocity constants.

(2) Effect of the Solvent.

There is a good deal of evidence in the literature of directive influence of the solvent used during nitration.

(a) Nitrations carried out in cold glacial acetic acid solutions appeared to affect the relative amounts of ortho - and para - compounds formed, e.g. Witt obtained an 87% yield from acetanilide with $\frac{3}{4}$ ortho - and $\frac{1}{4}$ para - nitro compounds. If nitric acid alone was used as a nitrating agent, the chief product was the para - compound. Sulphuric acid is <u>in general</u>, a meta - directing solvent --- Tingle and others........

Acetanilide yields m - nitroacetanilide in sulphuric acid,
" " p - nitroacetanilide in trichloracetic acid

Schwalbe also observed that the solvent had a marked orienting influence, thus benzylidene - aniline, when nitrated in concentrated sulphuric acid at 5° yields p - nitroaniline only, but in glacial acetic acid solution, with a mixture of nitric acid and acetic anhydride, a mixture of ortho - and para - was obtained.

(b) Tingle and co-workers published a series of papers dealing with the nitration of aniline and N - substituted anilines, in acid solvents ranging in strength from acetic to sulphuric and found that a certain directive influence could be traced to the acid solvent. It is well known that aniline cannot be nitrated directly, for nitric acid converts it into a tarry mass. Some workers hold that "substitution" in the nucleus is really preceded by addition or substitution in the side chain if one be present, or addition in the nucleus itself, followed in each case by subsequent rearrangement.

(c) Much work has been done with the object of studying the effect of different atoms or groups on the position assumed by entering groups. Blanksma postulates direct and indirect nitration, indirect substitution giving chiefly O - and p - compounds whereas direct gives principally the meta type. Holleman has attempted to determine the effect of relatively small quantities of water on the nature and quantities of the isomers formed.

(d) The influence of a solvent on the velocity of nitration is very marked in the case of phenol. Arnall found that nitration proceeds to the following extent :-

In acetone............	8%	after	3 weeks
" ether	68%	"	12 hours
" mixture of alcohol and acetic acid 2:1	75%	"	48 hours
" alcohol............	55%	"	48 hours

Thus by choosing a suitable medium one can conveniently accelerate or retard the velocity of nitration. It is moreover possible, that this change in velocity is somehow linked up with the change in relative proportions of the isomers produced for, in general, nitrations producing ortho- and para- derivatives are more rapid than the corresponding meta- nitrations.

(3) Nitrations in Sulphuric Acid as Solvent :-

(a) As yet, no satisfactory theory of the solvent nature of sulphuric acid has been advanced. It is indeed difficult to generalize on this matter beyond a certain very indefinite point on account of the variety of conflicting facts which must be explained.

(b) A. A. Saposchnikoff studied the nitration of cellulose in acids consisting of mixtures of nitric and sulphuric acids and found a very close parallel between the nitrating power of an acid as measured by the number of nitrate radicles introduced into the cellulose molecule and the vapour pressure of the given acid. Since he considered the vapour pressure to depend on the degree of hydration of the nitric acid present he also proposed a similar relation between the state of the nitric acid and the extent of nitration. Kullgren put forward the theory that nitric acid is only capable of nitrating when present in the unhydrated form and that the part played by the added sulphuric acid was to set free HNO_3 from its hydrate or hydrates. Berl and Klaye independently studied the nitration of cellulose and came to the conclusion that the sulphuric acid could play two opposing parts, firstly it favoured nitration by removing water, and secondly it could also hydrolyse some of the nitrate groups and thus prevent the action from going to completion. This explains why acids in the right hand corner of the diagram, rich in anhydrous sulphuric acid, are unable to nitrate cellulose and (according to Patart), naphthalene.

(c) It must be remembered however that the nitration of cellulose is a decidedly different process from the nitration of benzene, toluene and related compounds. In the first place, "nitrocellulose" contains no nitro compound at all, but is a mixture of nitric esters; the chemical rôle played by nitric acid in its formation is therefore not the same as in aromatic nitration, and ester formation is a reversible reaction; the formation of a nitro-compound is not. In any case in "nitrating" cellulose, we have a complicated heterogeneous reaction in which the mixed acid must be taken up by the cellulose thread before it is able to react. Cellulose is composed of a number of fine tubes with usually a hard, horny, exterior and a hollow interior. The outside layers are nitrated first and become more and more impermeable to the attacking acid so that it is practically impossible to nitrate the inner layers of material to the same extent as the outer layers. An analysis of the nitrated material gives only an average value for nitrogen content for the outer layers may have as many as twelve nitrate groups (per $C_{12}H_{20}O_{10}$), whilst the inner layers may have been able to attach no more than six. It may be some such process as this protection of the outer layers, that enables very strong sulphuric acid to hinder nitration of cellulose; and there is also the possibility of the formation of sulphuric esters.

(d) In the case of a simple hydrocarbon, no such complicated effects are encountered since the nitration takes place either in homogeneous solution or in a heterogeneous system consisting of two well mixed layers only. It is therefore quite reasonable to assume that a thorough investigation of such a simple system will yield facts which are quite likely to have direct bearing on the action of a ternary mixed acid.

End of Part 1.

PART 11

§I. USE OF THE TRIANGULAR DIAGRAM

(1) Expression of Compositions of Mixed Acids.

(a) In dealing with the properties of ternary mixtures of sulphuric acid, nitric acid and water, it is necessary to have some convenient method of expressing results graphically, by means of which one can corelate the change in a certain physical or chemical property with variation of the composition of ternary mixed acid. The triangular method of expressing three variables in one plane is perhaps most convenient and is very easily manipulated and interpreted by virtue of the simple geometrical properties of an equilateral triangle. If we represent pure sulphuric acid, pure nitric acid and pure water at the three corners of an equilateral triangle then the composition of any mixture of these three is represented by one point in the triangle.

(b) In an equilateral triangle the sum of the perpendiculars from any point to the sides is constant and equal to the height of the triangle. If we therefore represent the height of the triangle as 100 units then the co-ordinates, (perpendicular distances from the sides) at any point, will always give a total of 100. Thus to represent the mixed acid --

$$\left\{\begin{array}{l} x\%\ H_2SO_4 \\ y\%\ HNO_3 \\ z\%\ H_2O \end{array}\right\}$$

a point is plotted which is x units distant from the sulphuric acid zero axis, y units distant from the nitric acid zero axis and consequently z units distant from the water axis; (refer to Fig. II , page 23). The sulphuric acid zero is most conveniently represented by the side opposite the corner "H_2SO_4", i.e., by the line joining the points marked "HNO_3" and "H_2O", similarly y is the perpendicular on the side opposite HNO_3 and z the perpendicular on the side opposite H_2O so that $x+y+z$ always equals 100.

(c) The composition of any mixture made from two different acids, whether they be ternary, binary, or simply pure single compounds, lies somewhere on the straight line joining the compositions of these two. This property holds good on the ternary diagram whether we are expressing molecular - percentage - compositions or cpmpositions by weight. Thus in making up a series of mixed acids for use in nitrations by mixing a stock strength of nitric acid with a stock strength of sulphuric acid in various proportions, all the mixed acids have compositions lying on the straight line joining these two.

(d) Another very useful property of the trianglar system of representation is to be found by considering the CHANGE IN COMPOSITION OF A TERNARY MIXED ACID DURING NITRATION.

So far as the acid is concerned, the process of nitration consists of abstracting HNO_3 and replacing it by H_2O in molecularly equivalent amounts, the sulphuric acid being unchanged in weight. During nitration therefore, the total number of molecules ($H_2SO_4 + HNO_3 + H_2O$) remains constant; the number of molecules of H_2SO_4 does not change and consequently, by expressing compositions of acids in Molecular percentages on the triangular diagram the "Line of Change" of the Acid Composition must run parallel to the side $HNO_3 - H_2O$; (see Fig. IIa page 23). This principle will constantly be utilized in this thesis.

(e) In a Weights percentage diagram, on the other hand, this property no longer holds, since the total weight (excluding the organic material), is decreasing as nitration proceeds. There is, however, a constant weight of sulphuric acid present and a constant ratio exists between the weight of nitric acid decomposed by the organic material and the weight of water returned to the acid. It is interesting to elucidate the direction of lines of acid change in a weights - percentage diagram. For this purpose the compositions of a number of mixed acids and their ideally corresponding waste acids have been calculated and plotted on the triangular diagram for weights - percentages (Fig. II page 23). A table of the calculated compositions is here appended :-

TABLE I

Gms. H_2SO_4 in M/A	0	20	10	30	40	50	60.	70	80	90
" HNO_3 " "	100	80	90	70	60	50	40	30	20	10
" H_2O " "	0	0	0	0	0	0	0	0	0	0
Total wgt. of M/A	100	100	100	100	100	100	100	100	100	100
Grms. H_2SO_4 in W/A	0	20	10	30	40	50	60	70	80	90
" HNO_3 " W/A	0	0	0	0	0	0	0	0	0	0
" H_2O " "	28.61	22.89	25.75	20.03	17.17	14.31	11.45	8.58	5.72	2.86
Total wgt. of W/A	28.61	42.89	35.75	50.03	57.17	64.31	71.45	78.58	85.72	92.86
Compn. of W/A (Wgts %)										
% H_2SO_4	0.00	46.63	27.99	59.98	69.96	77.76	83.98	89.08	93.33	96.92
% H_2O	100.00	53.37	72.01	40.02	30.04	22.24	16.02	10.92	6.67	3.08

(Abbreviations; Initial Mixed Acid -- M/A.
Waste Acid -- W/A.)

In the weights percentage diagram (Fig. II), any one red line inside the triangle signifies a series of acid mixtures having a fixed molecular percentage of sulphuric acid; i.e. it shows the direction in which the act of nitration alters composition when this is expressed in weights percentage. It will be seen that when the red lines are produced they all intersect at one point, lying outside the triangle. This point is easily obtained by producing the side H_2O - HNO_3 and measuring off along this extension two-fifths of the length of the side. Actually the height of the point P above the base of the triangle (H_2O - H_2SO_4) in terms of the height of the triangle as unity, is expressed by $\frac{63}{63-18}$, i.e. by :-

$$\frac{\text{Molecular weight of HNO}_3}{\text{Change in weight when 1 mol. H}_2\text{O replaces 1 mol. HNO}_3}$$

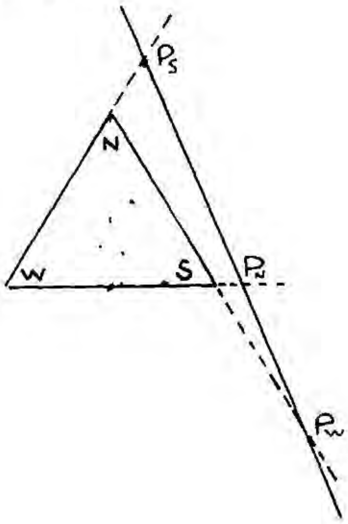
(f) By calculating the whole range of ternary mixed acids in weights-percent, one can show an extension of this principle together with a corroboration of the numerical reckoning of the external convergent points.

(g) If one reckons and plots the radiant point~~s~~ for fixed molecular percentages of HNO_3 similarly, it falls on the prolongation of the (weight) triangle base H_2O - H_2SO_4 --- and turns out to stand at a height (from the zero sulphuric acid line) of 1.225 units, which $= \frac{98}{98-18}$;
$= \frac{\text{Molecular weight of sulphuric acid}}{\text{Mol. weight H}_2\text{SO}_4 - \text{Mol. weight H}_2\text{O}}$

(h) Again, the radiant point for fixed molecular percents of water is a long way off, lying on the prolongation of the HNO_3 - H_2SO_4 --- line; and it is, on drawing it, apparently at the predicted distance (from zero H_2SO_4 line) of

$\frac{98}{98-63}$, i.e. 2.80 units.

(i) Thus calling these three radiant points respectively Ps, Pn, and Pw, the more complete nomogram is something like :-



Where WPs = 1.4 units
WPn = 1.225 "
NPw = 2.80 " and
WN = NS = SW taken as 1 unit.

From graphical work it was concluded that the points Ps, Pn and Pw lie on one straight line.

(j) In order to further extend this principle a general system was tested graphically in which nitric acid, sulphuric acid and water were replaced by three hypothetical compounds of molecular weights 3, 2 and 1 respectively. Again, on determining the radiant points P_1, P_2, and P_3, they were found to lie on a straight line the distances being given by $3/(3-1)$, $2/(2-1)$, and $3/(3-2)$ respectively.

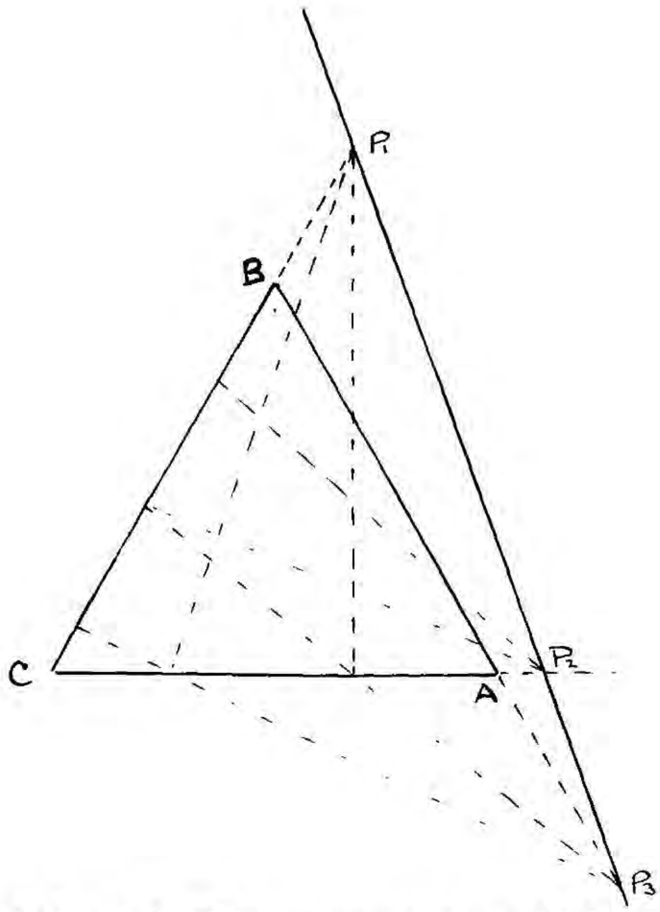
(k) The General Statement of the Nomogram is as follows :- --- If we represent the compositions of any ternary system A, B and C on a weights-percentage triangular diagram, then if we consider the process $x.A + y.B + z.C \overset{-C}{=} x.A + (y+z)B$ taking place, the lines of weight composition change during the process when produced backwards meet at a point P_1 which we will call "radiant point of the system". This radiant point lies on the prolongation of the side of the triangle joining the points C and B and the distance of this point from C is a function of the molecular weights of C and B respectively and is equal to Molecular weight of compound B divided by the difference between the molecular weights of compounds B and C, (where the side of the triangle is taken as unit length.)

Similar considerations apply to the changes

$$x.A + y.B + z.C \overset{-A}{=} y.B + (x+z)\,C$$

and $$x.A + y.B + z.C \overset{-A}{=} (x+y)B + zC$$

The three radiant points lie in one and the same straight line.



The principle of this nomogram, while useful for a number of purposes, will only occasionally be involved in the descriptions which follow.

(2) Quantity of Organic Material involved in Nitration:-

(a) Since (in this work) each molecule of nitric acid which disappears converts one molecule of aromatic compound into one molecule of nitrated product, it is possible and proves convenient to read off, upon the triangle showing molecular composition of the acids, the molecular quantities of the organic material concerned. For example, if, in a given nitration of mono - to di-nitrobenzene, the amount of M.N.B. (mononitrobenzene) taken is chemcially equivalent to the nitric acid initially present, then the vertical height in the triangle which measures the HNO_3 - content (mols. %) of the particular acid will also measure the number of mols. of M.N.B. taken per 100 mols. of initial mixed acid.

It also measures the M.N.B. mols. taken per 100 mols. of spent acid, since the number of mols. of total acid plus water remains unchanged during nitration, as has been pointed out.

(b) If, further, the whole of this M.N.B. is attacked chemically, then the same vertical height measures the quantity (in mols. per 100 mols. of ternary acid) of D.N.B. (dinitrobenzene) formed. If the M.N.B. is only partly nitrated the quantity of D.N.B. formed is measured by a proportional length of the same vertical co-ordinate. This principle will be used later on, particularly in §II,(10.)

(3) Solid Models :-

(a) By employing a third dimension in space it is possible to express another variable, such as the time element; and an attempt to depict the change of acid composition at any time during a nitration has been made by constructing, from experimental data to be given later, a solid model showing the acid composition on a triangular flat plane, and the time of nitration by vertical height above this flat triangle. Thus by cutting slices parallel to the base, one can obtain an approximate idea of the progress of a nitration after any time interval has elapsed. A photograph of this model appears in the front of this thesis.

(II) §II AREA OF DINITRATION.

(1) The Meaning of the Term - "Area".

(a) The present work was designed to ascertain the shape of an area, (drawn on a triangular diagram expressing the percentage compositions of nitrating mixed acids), such that all acids inside this area, are capable of nitrating mononitrobenzene to dinitrobenzene and all acids outside this area are incapable of performing this reaction.

(b) It is a well known fact that any mixture of absolute nitric acid with 100% sulphuric acid is capable of nitrating M.N.B. (mononitrobenzene) to D.N.B. (dinitrobenzene) but that in adding water, to gradually dilute such a mixed acid, the ability to nitrate, gradually diminishes and, presumably, at a certain dilution nitration can no longer be performed. This is what happens during a nitration, water is formed and nitric acid is removed from the nitrating acid until the acid becomes too dilute to attack more M.N.B. and at this stage, nitration ceases. By ascertaining the exact composition at which the ability to nitrate ceases one is able to plot this point in the triangular diagram of acid compositions and by plotting a number of these points, all representing limiting acid concentrations, one can draw a limiting line across the triangle which represents the boundary between dinitrating acids and acids unable to dinitrate. Acids more concentrated than these limiting acids, i.e., acid compositions lying to the right of the

FIGURE II

Ternary diagram expressing compositions of Mixed Acids in weights-percent

Red lines indicate lines of change in compositions of Mixed Acids during nitration.

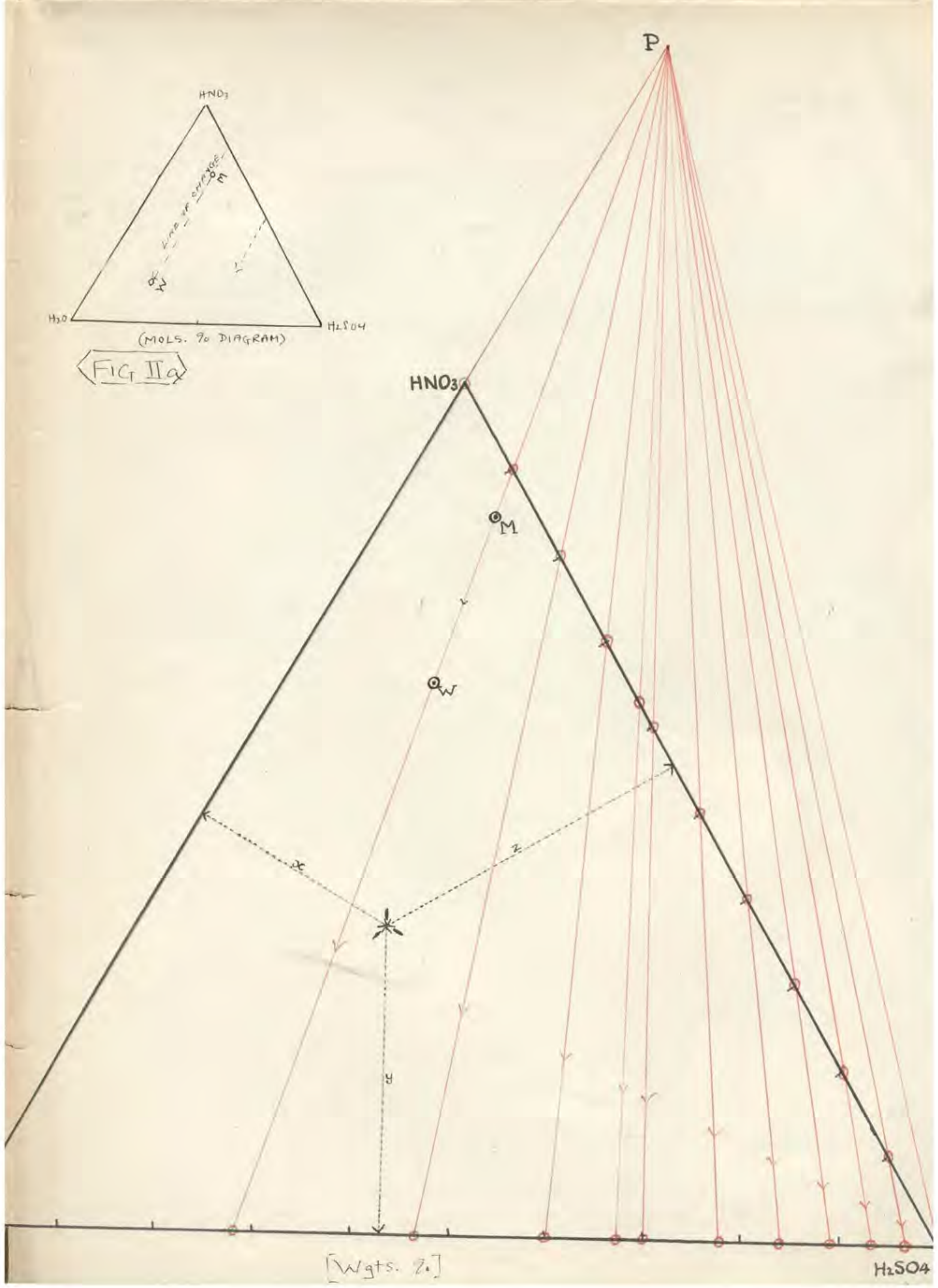


FIG IIa

limiting line of dinitration are all able to perform dinitration even if it is to an infinitesimally small extent whilst acids to the left cannot dinitrate even a trace of mononitrobenzene.

(c) In the literature there seems to have been some uncertainty about the meaning of the term "area" or "zone" of Nitration. A. A. Saposchnikoff in studying the "nitration" of cellulose was able to draw three limiting lines across his triangle of nitrating acids each line representing the limit of a certain stage in the "nitration" of cellulose. Patart, studying the nitration of naphthalene also recognised a division into definite zones of nitration; by recalculation, his results can be expressed on a triangular diagram dividing the triangle into four zones, --- a zone of tetranitronaphthalene, a zone of trinitro --- naphthalene, a zone of dinitronaphthalene and final zone of mononitronaphthalene.

(d) Both these investigators employed the same method. They took a fixed amount of initial mixed acid, of known composition, say 300 grams, and with it nitrated a fixed small amount, say 10 grams of the organic material. By measuring the nitrogen content of the final organic product they were able to plot points on their diagrams, grouping together acid compositions giving approximately the same nitro content in the nitrated material. Thus, for instance, the area containing all acids producing a nitro product whose nitro - content indicated the presence of approximately two nitro groups was called the "Zone of Dinitration".

(e) From the industrial point of view, which no doubt was their chief consideration, this method of dividing into "zones" has its uses but its shortcomings in the realm of pure chemistry are many. In the first place the nitro product produced is only known by an average figure, its composition not being completely defined by its total nitrogen content since it may be a mixture of many different nitro compounds. In the second place the initial mixed acid used has a different composition from the acid which is actually doing the nitration. The actual nitrating acid is continually varying in composition becoming more and more dilute as nitration proceeds. This complication is only partly excluded by taking an excess of initial acid. Finally, the division into zones is only approximate.

(f) The present method of defining a "zone" or "area" of nitration has many advantages over this older method. The general principle is similar, but the experimental method is capable of much greater accuracy. A diagram showing the limiting lines of Saposchnikoff, Patart and Kostevitch (for nitrotoluene) is given near the end of this thesis and a short section is devoted to a comparison of the results of these workers with the results of the present work.

(2) General Plan of present Method.

(a) In order to find the compositions of acids where dinitration ceases, a series of mixed acids are allowed to nitrate nitrobenzene, under strictly defined experimental conditions, until sufficient water has been produced and no further action takes place. By determining the compositions of the spent acids obtained in this manner one obtains a direct estimate of the required limiting concentration which marks a definite property of the acid mixture analysed. By joining the compositions of spent acids one can establish the limiting line of dinitration provided that the limiting composition, reached, is independent of other variables. It will be shown that the composition of an acid in which nitration ceases at 35° is, in fact, but little affected by the conditions of the experiment.

----

(3) Choice of Materials.

(a) It was pointed out in Part I of this thesis (§IV,(3)(d) page 15) that one can minimise the chance of consecutive actions taking place, during nitration, by choosing a suitable material in which there is room for only one entering nitro group.

The simple hydrocarbons benzene and toluene are very convenient on this account, and of the two, benzene offers the most straightforward type of nitration.

(b) In the transition from toluene to trinitrotoluene the three steps are not sharply marked for in attempting to make dinitrotoluene, the formation of some trinitrotoluene is hardly avoidable, and if only sufficient nitric acid has been taken to provide for the formation of dinitro compound, the formation of some trinitrotoluene is necessarily accompanied by the equivalent residue of unitrated material.

(c) It was chiefly for this reason that nitrobenzene was chosen as a starting material for nitration; because the transformation of mononitrobenzene into dinitrobenzene is a definite step since trinitrobenzene is only formed with great difficulty and in poor yield by using fuming sulphuric acid under high temperature. Mononitrobenzene also possesses the advantage of having no oxidisable side-chain and the chief product of nitration is the meta-dinitro derivative. The present work has not attempted to differentiate the isomeric dinitrobenzenes obtained; doubtless there is some variation in their proportion and this will need further study after the main lines have been cleared up. For the present it is only necessary to indicate that the dinitro products under the most favourable conditions will only consist of about10% of a mixture of ortho - and para - dinitrobenzene, while the majority of nitrations will produce considerably over ninety percent meta-compound.

The present work refers to the nitration of benzene. A few points have also been obtained for the corresponding nitration of toluene.

---

(4) EXPERIMENTAL.

Methods of Analysis.

General:- Both strong "mixed acids" and dilute "waste acids" were analysed by the same method. Nitric acid was directly estimated in a Lunge Nitrometer, in the ordinary way. The figure obtained includes the small quantity of nitrous acid which is always present at the end of the nitration. Nitrous acid was also determined separately by means of potassium permanganate and back titration with oxalic acid. The quantity of nitrous acid varied throughout but was always very small and less than one percent. The total acidity was measured with standard sodium hydroxide solution using methyl red as indicator (since small quantities of nitrous acid quickly decolourise methyl orange). Knowing the concentration of nitric acid, sulphuric acid was calculated by difference from total acidity. The concentration of D.N.B. in M.N.B. at the end of a nitration was estimated by a density determination, carried out upon the isolated nitro-body.

Detail:-

(a) Determination of Nitric Acid.

To ensure maximum accuracy in acid analysis it was necessary first to determine the conditions for maximum efficiency of the nitrometer. The yield of nitric oxide from a given quantity of nitric acid varies considerably with the concentration of sulphuric acid present whilst shaking with mercury. A general mixed acid was made up, small quantities of which (weighed out with the Lunge pipette) were shaken up in the nitrometer with quantities of 8 ccs. of different strengths of sulphuric acid. The maximum yield of gas was obtained when the total water content lay between 17 and 23%. If the acid was more concentrated than this a gradual reduction in volume was registered, resulting in too small a figure for nitric acid content. On diluting below 77% H_2SO_4 no nitric acid was formed for a considerable time, oxides of mercury rapidly form and the whole mixture became sticky. It was also found that a slight loss of accuracy amounting to 0.1 or 0.2% was effected by taking readings too quickly after shaking, the contents of the nitrometer should be allowed to stand for half an hour in order to liberate any NO which has been dissolved through excess pressure caused by shaking. Shaking is best carried out, as far as possible at atmospheric pressure. Two effects are at work during a nitrometer estimation of nitric acid, the physical or solubility effect and the chemical effect which is analogous to the action of nitric acid on various metals, when different products can be obtained by varying the dilution. This latter effect depends upon the concentration of acid and between the limits of 17% and 23% water, the formation of products other than nitric oxide is negligible. The solubility effect can be corrected by tables drawn up by Lunge; he suggests adding 0.2 ccs. nitric oxide at 25°c. and 0.3°ccs. at 0°c. At the given strength, however, the solubility of nitric oxide in sulphuric acid must be very nearly equal to the solubility of air already dissolved in the acid before addition. The following results, obtained in an analysis of pure potassium nitrate show that a surprising degree of accuracy can easily be obtained in nitrometer estimations :-

0.0896 grams of pure KNO_3 yielded 20.90 ccs. of NO at 757.9 mms. pressure and 13.4°C.

Vol of NO at N.T.P. = 19.86 ccs.

This amount of nitric oxide is theoretically equivalent to .0897 grams of KNO_3. Error = 1 part in 897.

For each acid analysed, two or three nitrometric determinations were made showing in all cases good agreement.

Specimen Nitric Acid Determination :-

	Wgt of Acid used.	Vol of NO.	Pressure.	Temp.	HNO_3 content.
(1)	0.3352 grams	24.53 ccs.	763.6 mms	19.0°	19.34%
(2)	0.3776 "	27.70 "	763.6 "	19.5°	19.36%

Average for two determinations = 19.35% HNO_3

(b) Total Acidity Determination.

Little need be said about this as the method employed was simply to titrate the acid against standard 0.1 normal sodium hydroxide solution. This in turn was referred to an ultimate standard made up from a weighed quantity of ignited pure sodium bicarbonate. The acids in all cases were weighed by difference from a Lunge weighing pipette which minimises transference losses by fuming. A sharp end point was obtained as nitrous acid only very slowly decolourises the methyl red indicator. The burette was read to 0.01 cc. Each determination was duplicated.

Specimen Determination :-

	Wgt of Acid used.	CCs. of NaOH required.	1 cc NaOH is equivalent to:-
(1)	5.7238 grams	5.15	1.111 grs acid
(2)	35.1113 "	31.50	1.114 " "

Average of two determinations; 1 cc NaOH = 1.113 gms acid.

(In previous standardisation, 1 cc. NaOH is equivalent to 0.05884 gms Na_2CO_3 and the acid under analysis contains 5.58% HNO_3.

therefore HNO_3 accounts for 0.05223 grams Na_2CO_3

and H_2SO_4 " " 0.00361 " "

therefore Stength of sulphuric acid = 0.30%)

(c) Determination of Nitrous Acid.

To a sample of waste acid, standard potassium permanganate was added drop by drop until the pink colour persisted. The solution was then gradually heated, excess of $KMnO_4$ being rapidly added together with 20 or 30 ccs. dilute sulphuric acid. The solution was kept at 70° for five minutes. Excess of standard oxalic acid solution was then added and the solution back titrated with $KMnO_4$ until a faint permanent pink colouration developed. Nitrous acid was in nearly all cases considerably less than 1% and is expressed in acid compositions as Nitric acid, since it has been proved to play no part in accelerating or retarding the nitration of nitrobenzene (H. Martinsen) the reastion being truly bimolecular. Its presence is merely dependent on the decomposition of a small part of the nitric acid by heating effects and final dilution of the waste acid.

In the preparation of mixed acids ordinary laboratory fuming nitric acid of a pale yellow colour was used in solution with the purest commercial concentrated sulphuric acid.

(d) Determination of Organic Material.

Preliminary experiments were executed with pure redistilled nitrobenzene but the actual results recorded were obtained with commercial nitrobenzene, suitably purified. A generous quantity of this was supplied by British Dyestuffs Corporation, to whom we are indebted. The mononitrobenzene contained in an iron drum was transported during the heavy frosts of 1929 and consequently was subjected to a very useful fractional crystallisation on the route. The dark brown liquid portion (a)was drained off (it contained a sediment consisting chiefly of impurities from the metal drum), whilst the yellow crystalline fraction (b) on melting yielded a liquid gradually changing in colour from dark brown to yellow. An average sample was tested in the following manner :-

(1) 200 grams of fraction (b) shaken up with boiling water. Aqueous layer separated off and titrated against standard caustic soda solution using phenolphthalein as indicator. Only 0.46 ccs. of normal NaOH solution was required for neutralisation so the acid content is negligibly small.

(2) A quantity of the (b) fraction was distilled. Very little moisture was present and all the liquid distilled over at 206 - 208°, giving an amber coloured distillate.

(3) A sample of fraction (b) was gradually frozen out

in an ice chest and the remaining small quantity of liquid drained off.

The following table shows the results of tests performed on these refined products :-

Material.	Setting Point.	Density at 15°
Pure M.N.B. twice redistilled	4.6°	1.209
Commercial (b), dried over $Ca(NO_3)_2$	5.2°	1.209
Commercial (b), redistilled	4.9°	1.209
Commercial (b), after fractional crystallisation	4.9 to 5.0°	1.209

Thus in all the nitrations described in this paper the organic starting material was the (b) fraction of commercial nitrobenzene which has been further purified by a second fractional freezing at 0°c, melting down and allowing to stand over anhydrous calcium nitrate in order to ensure dryness.

Calcium nitrate is quite insoluble in nitrobenzene as a sample which had been standing over $Ca(NO_3)_2$ for six months was tested but gave no indication of calcium or nitric acid. The material is coloured a light brown and contains small traces of aniline or amino bodies since a trace of azo dye is given on diazotising and coupling with β. Naphthol.)

(e) Estimation of dinitrobenzene :-

An elaborate estimation of the nitro content of organic material after nitration is not necessary since we are concerned only with waste acids. It is important however to have a check on the waste acid composition by estimating the amount of nitric acid used in combination with nitrobenzene. The analysis of the nitro product is therefore a very suitable control test. Two physical methods of estimation suggest themselves, the refractive index and the specific gravity. The former is ruled out on account of the small differences observed in refractive indices of widely different mixtures of M.N.B. and D.N.B. and also because of the variation in colour of the nitro product. The density method is sensitive to a surprising degree the only disadvantage being that in determinations with a Westphal Balance, at least 150 grams of nitro product must be available whereas the refractive index method using a refractometer requires only a few drops of material.

(f) Calibration of the Westphal Balance.

A quantity of meta dinitrobenzene was prepared and purified by recrystallising from alcohol, M.Pt. 90°c. A number of artificial mixtures were then made up with mono nitrobenzene (specific gravity 1.209 at 15°) and their densities determined by means of a Westphal Density Balance. There was a small but noticeable fall of temperature on dissolving D.N.B. and during the density determinations, the mixture under examination was surrounded by a water bath at 15°c. The following data were used to draw up a curve showing the variation in density with composition:-

Wgt of D.N.B. in 100 grams M.N.B.	Density at 15°
0.00	1.2088
2.08	1.2133
7.702	1.2237
12.90	1.2326
19.74	1.2427
29.23	1.2564
35.73	1.2647

The curve is very nearly a straight line and by drawing to a large scale the concentration of D.N.B. in M.N.B. can be easily measured to 0.1 gms per 100 grams.

The method of determining an organic nitro product was to wash well with water, dry over $Ca(NO_3)_2$ and measure the density. On comparing with the previous calibration and knowing the total weight of nitro product, the D.N.B. formed during nitration can be easily estimated. In most cases nitro products were already liquid containing below 30% D.N.B. but if any solid was present extra mononitro benzene was added to dissolve up for the density determinatio A correction was then applied for the extra nitrobenzene introduced.

---

(5) ~~De~~tails of Nitration Method.

(a) The method of nitration was that which is ordinarily employed in the laboratory, carried out in a careful routine manner. A known weight of mixed acid is introduced into a large round bottomed flask and the calculated quantity of nitrobenzene weighed out into a graduated dropping funnel. 5 ccs. of M.N.B. is added and the mixture well shaken, heat is developed and the temperature kept below 35° by cooling under the tap. The contents of the flask are separated from the outside atmosphere by a cork (through which the thermometer passes) thus losses through fuming and errors through moisture absorption are minimised. Additions of M.N.B. are at first slow and it is necessary to cool between additions so that the temperature does not exceed 35°. When most of the reaction is complete M.N.B. may be added at a much quicker rate the total time of addition being between ½ hour and an hour, depending on the amount of nitration taking place. Finally the nitration mixture is well shaken the temperature being kept constant at 35°c by immersing the flask in a large beaker of water, until the expiration of the given time (usually 2 hours). A complete log of each nitration is kept showing the time, temperature and condition of the nitration throughout. A note is also made of the appearance of a second phase when the solubility limit of nitro compound in mixed acid is passed and also any observations on precipitation of solid D.N.B. etc.

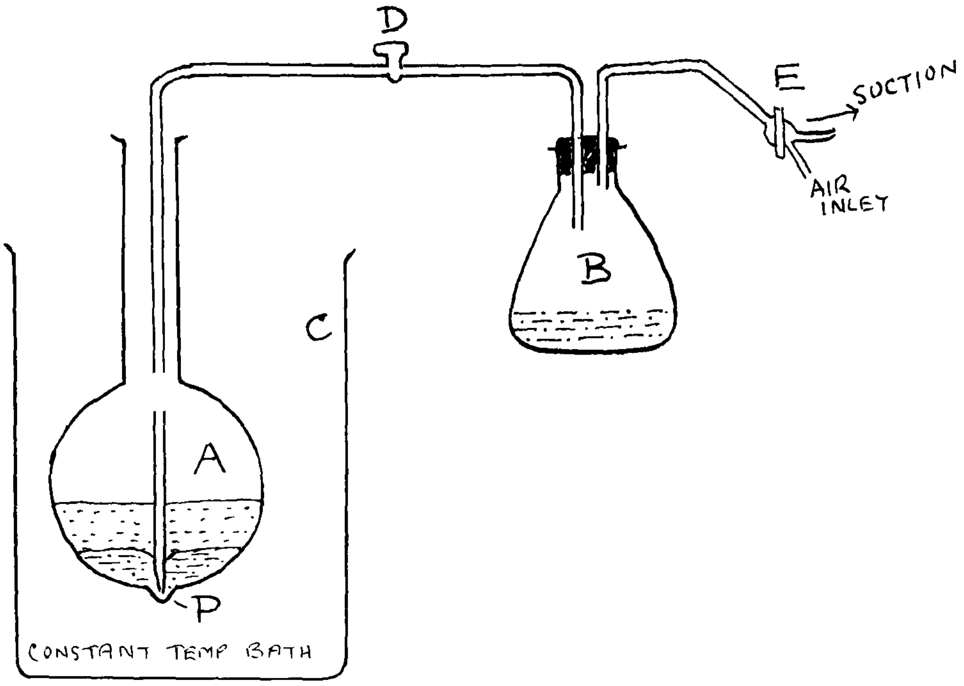
(b) After completion of the reaction, the nitration mixture is cooled and a large quantity of water carefully added, cooling all the while under a tap. This final dilution is to extract acid from the organic layer and nitro-compounds from the acid layer. After shaking for ten minutes the contents of the flask are allowed to stand for twenty four hours when two clear layers result, (if any solid D.N.B. is present after nitration, a further quantity of M.N.B. is added as solvent -- after dilution; this further quantity is labelled "M.N.B.II" in the tables.

(c) The two layers are separated by a special method described below, and analysed in the usual way for nitric acid, total acidity, nitrous acid and dinitrobenzene. Water is obtained by difference after corrections have been applied for the addition of extra diluting water.

---

(6) Special Method of Separation.

The diagram shows the arrangement for separation of two layers. A small pip P is previously blown in the round bottomed litre flask used as nitrating vessel; c is a narrow tube of cappillary bore drawn out to a narrow diameter at the end which just dips into the small trough P. D is a single bore stop-tap and B the weighed receiver. The pressure in B is lowered by suction and the three way stop-cock E can be used either to connect up the filter pump with B or as an air inlet to either the flask B or the filter pump. Before separating, the nitrating flask and contents are allowed to stand for an hour, the temperature being kept constant at 35°c by emmersing it in a large water bath with suitably adjusted



flame; (on account of the large bulk of water, the temperature can easily be maintained between the limits 34° and 36°). When two clear layers have settled out the stopcock D is closed and the capillary tube introduced, B is partially evacuated until a head of about 25 cms. of mercury is realised then D is opened and the bottom layer slowly drawn off. The last drops of acid layer collect in P and care must be taken to shake the flask two or three times, dislodging any acid clinging to the sides which can be coaxed into the pip by a gentle tapping of the flask. The final separation is best accomplished by drawing the surface of separation up to the stop-cock D, then by suddenly removing the tap the remaining acid is drawn into B whilst the nitrobenzene runs back into A. In this way a very accurate separation can be accomplished.

Separation without previously diluting after nitration is often made difficult by production of a deep red colour formed during nitration; this arises from traces of amino impurities present in the nitrobenzene which couple up with nitro compounds producing a deep red condensation product, soluble in both layers. Thus it is often difficult to see the surface of separation unless a bright light is suitably arranged behind the vessel A. After separation the second layer is drawn off into another weighed receiver in the same manner.

---

(7) Control Tests.

(a) Acid Analysis:- The analysis was occasionally checked by estimating sulphuric acid gravimetrically. Good agreement was found, e.g.; -

Experiment E

By Difference (Total acidity method).. 83.48% H_2SO_4
Average of 2 determinations

By gravimetric method (weighing as $BaSO_4$) 83.47% H_2SO_4
Average of 2 determinations.

(b) Repetition of Nitration with different total mass :-

In nitration test (a), test (b), test (c), the starting conditions were identical except that the total mass involved varied in the ratio 1: 3: 9; the relative amounts of M.N.B. and mixed acid remaining constant. The initial starting acid contained 47.95% HNO_3 (molecular percentage) and the final spent acids a, b and c, contained respectively 16.1, 15.8 and 14.7% HNO_3 (molecular percentages). The variation is very small and unimportant and is a consequence of the difference in time between the three nitrations because nitration (c) had to be allowed a longer time than (a) and (b) on account of the great mass of material present and, as will be shown later, this small reduction in final nitric acid content is to be expected on velocity considerations.

(c) Reaction Balance Sheet :-

This is a crucial test of analytical figures and gives, at once, a measure of accuracy of the analytical figures. The total gram molecules of material (acid and water and nitrobenzene) are calculated before nitration and balanced against the total gram molecules found after nitration. To obtain perfect agreement would be next to impossible since the number of additive small errors involved in so large, and since water is only determined by difference, but has a very low molecular weight. A rough test is to compare the molecular figures for sulphuric acid before and after nitration, they should be equal --- and also to compare the loss of nitric acid with the amount of D.N.B. formed. Quite good agreement was found in the later experiments I, II, III ----- XX, but some of the earlier two hour nitrations 10 -- 25 reveal discrepancies which can be explained by incomplete washing of the nitro compound since most of these nitrations were carried out before the important experiments on distribution.

These molecular balance sheets are fully laid out in the tables at the end of this thesis and the following example gives some idea of the type of agreement found :-

Nitration X, Molecular Balance.

		Before	After	Difference (Theory = 0)
Mols.	H_2SO_4	.5798	.5800	.0002
"	HNO_3	.4343	.0778	.0032
"	H_2O	.2031	.5564	
"	M.N.B.	1.7377	1.3850	.0001
"	D.N.B.	0.0	.3528	
Total Mols.		2.9549	2.9520	.0029

(Error is approximately 1 part per 1000)

(d) Variation in Time of Operation :-

In experiments I, II ----- XX an investigation has been made into the time element. Velocity curves which will be discussed later will prove that the process of nitration at 35°c may take anything from one to sixteen hours for completion depending upon the composition of the mixed acid used. In general; a nitration takes more than two hours for completion and hence a number of the two hour points must be regarded as intermediate acids governed largely by the conditions of experiment. A full investigation has been made into this time effect.

(e) Variation in Relative Quantities :-

Results go to prove that the velocity of nitration depends upon the relative quantities used but the composition of the final spent acid (reached after 16 - 24 hours nitration) is very little, if at all, affected by this condition.

The effect of changing the relative quantities is noticed, of course, in incomplete (or two hours) nitrations where the velocity of nitration determines the end acid composition. Sections under the headings "Distribution Effects" and "Homogeneous and Heterogeneous Nitrations" deal fully with this question and it is pretty certain that the chief influence at work is the variation in the extent of heterogeneity produced by varying the relative quantities of mixed acid and nitrobenzene which is directly connected with the intimacy of mixing separate phases during nitration.

(f) Reversal of Method of Addition :-

An experimental nitration (IV) was performed by adding mixed acid to nitrobenzene instead of vice-versa. A slightly different waste acid results after two hours of nitration but this again is only a velocity change effect which also will receive consideration in later sections.

The results of nitrations are fully laid out in two sets of tables at the end of this thesis. The first set 10 -- 25 includes early nitrations performed in two hours and the second set I --- XX includes a number in which the conditions of time, relative quantities etc are varied. In the first table in each set the experimental observations are given; the second table is calculated from this and shows the quantities of constituents, by weight, present before and after nitration; the third table gives a similar summary in terms of molecular quantities and the final table gives the molecular percentage compositions of mixed acids and waste acids respectively. We cannot attach much finality to the first set of nitrations and merely include them for the sake of completeness, they are all two hour nitrations in which the reaction has not gone to dompletion. In the second set I --- XX, all nitrations give good "quantity" and "molecular" balance sheets.

---

(8) Discussion of the Experimental Facts.

(a) For the purpose of discussion, the nitrations may be divided into three main classes.

(1) 2 Hour Heterogeneous Nitrations.
(2) 2 Hour Equimolecular Nitrations.
(3) 16 - 24 Hour Nitrations.

Table XVIII page 106 shows the chief experimental data of nitration series I, II, III, ---- XX, including the molecular composition of the mixed acid used, the ratio of the quantity of M.N.B. (mononitrobenzene) used to the quantity of nitric acid present in the initial mixed acid (in molecular quantities) the temperature of the experiment and the duration; the type of nitration i.e. two-phase or one-phase which is also described in places as heterogeneous or homogeneous; and finally the composition of the waste acid in molecular percentages. These acid compositions have been plotted on a triangular diagram of molecular compositions Fig. III page 50 .

(b) Thus in class (1) we have the points XIV, XVI, XI, II, and X. In class (2) we have VI, XII, I, and VIII (VI is not actually in this class but we will include it in order to bring out important points) whilst the acid compositions 50, XV, VII, XVIII, XIII, V, and IX belong to the third class --- (3). Three curves have been drawn through points in corresponding classes so that the first black curve (nearest the side HNO_3,- H_2SO_4) represents the concentrations of acids after 2 hours nitration in the heterogeneous way, two layers always being present at the end on account of the large excesses of M.N.B. employed. The second black curve is the locus of acid compositions after 2 hours nitration, the molecular equivalent of M.N.B. being used; on this curve most of the points represent heterogeneous ends but all points above VI end up in the homogeneous, or one layer manner. The red curve, joining acids in the third class represent the end conditions after at least 16 hours nitration, this includes both one layer and two layer nitrations.

(c) The paths traced out by the changing molecular compositions of the mixed acids during nitration are marked in dotted lines. These should theoretically run parallel to the HNO_3 - H_2O side as pointed out in the section on properties of the triangular diagram and since their actual divergence from the sulphuric acid parallels is in all cases hardly noticeable one can conclude that the experimental results are in very satisfactory accordance with theory.

(d) From the position of the curves on the triangle it is at once seen that heterogeneity has a very marked retarding influence on the nitration velocity since in every case, an equimolecular 2 hour nitration goes further than a more heterogeneous 2 hour nitration. In the region of point I and II there is only a slight difference whilst as we increase the nitric acid content the divergence of the two black lines steadily increases reaching a maximum somewhere near the points VI and XVI when there is a difference of nearly 7% of nitric acid between the two. As we increase the nitric acid still further, the two lines approach one another very rapidly.

(e) The reason for this curious maximum divergence is not far to seek when we remember that nitration VI was completed in one phase whilst nitration XVI became heterogeneous very early. We have therefore the case of a given acid nitrating easily, since the material undergoing nitration is dissolved by it and therefore in very intimate contact with it, and on the other hand in experiment XVI we have the same mixed acid nitrating under great difficulty because two layers are present and even the most vigorous shaking cannot establish such an intimate contact between nitrating acid and the material which it is attacking.

(f) Now in experiments I and II we have a given mixed acid whose ability to nitrate is hampered in both cases by formation of two layers. Both are therefore heterogeneous nitrations and the difference in nitrating velocity is to be attributed only to a difference in the degree of heter-

-ogeneity which would not have such a big effect as the difference between a one layer and a two layer nitration. Why there should be such a large difference between the points X and VIII is rather difficult to understand, since nitrations I and VIII were equimolecular with respect to nitric acid content whilst II and X were heterogeneous to the same extent each, having a molecular excess of 3 mols. M.N.B. per mol. HNO_3. There is evidently some other effect apart from heterogeneity influencing nitration velocity in the region of VIII, for even if we allow for the experimental discrepancy in sulphuric acid content, (which is larger for the point VIII than for any other point), there still remains a considerably greater distance between the two black lines at VIII and X than at I and II. It may be that this disappearance of a small amount of sulphuric acid is somehow connected with the apparent increase in velocity of nitration or it may be because two liquid layers are not present in nitration VIII, the organic layer coming out as solid D.N.B. whilst in nitrations I, II and X two liquid layers were present at the end and, as will be shown later, the distribution of acids between the two liquid layers, which distribution effect being absent when the organic layer is solid, could easily account for this divergence. This experimental fact is worthy of particular notice as it has important bearing on later discussion dealing with distribution of components during nitration.

(9) The Sixteen Hour Curve:-

(a) The curve marked in red on the triangular diagram is very probably the limiting curve of dinitration. The extent of this probability cannot be measured without further experiments, and considerations which will be gradually brought out in the rest of this thesis. It would not be wise at this stage to anticipate results brought out in the later matter for we must first of all look into the following,as yet unanswerable questions.

(b) Is there any such thing as a stoppage of nitration or do our 16 hour points merely represent places where the velocity of nitration has become so small that a very long time elapses before appreciable change in the nitric acid content takes place ?. Granting this point for the moment and assuming that our 16 hour nitrations represent true finalities, it is still questionable whether acid concentration is the sole factor dediding such stoppage, or whether (e.g.) the amount of excess M.N.B. may not have a share in this. If acid concentration is not the sole factor, then there is no such thing as a limiting curve in the triangular diagram, excepting for arbitrarily specified other conditions. For instance, suppose the ratio M.N.B. : M/A (mixed acid) affects the end-concentration : then the limiting line becomes a family of lines, each line corresponding with some fixed excess of M.N.B.

(c) Next, is the stoppage a stoppage?. Admittedly the 16 hour nitrations show that it is practically so;

since the change in nitric acid content between the first two hours and the next fourteen is very small, but there is a big difference between a very low velocity and none at all. Now if it were only a matter of sluggish velocity at 35^{0}, then raising the temperature to say 70^{o}c, would make a manifold increase in speed - it should do, (according to Martinsen's figures), in one hour at 70^{0} what would take a day or several days at 35^{o} thus by performing a high temperature experiment any change in the "final" spent acid should be easily observed.

(d) This was precisely the reason for performing experiments XVIII and XIX. Both were carried out with the same inital mixed acid, the weights of acid and M.N.B. being the same in each case. Both were carried out under exactly the same conditions for the first eight hours the operations of additions of M.N.B. and shaking being accurately duplicated. After the first eight hours of nitration at 35^{o}c, the nitration mixture XIX was raised to a temperature of 65 - 70^{0}c and well shaken at this temperature for four hours whilst nitration mixture XVIII remained at 35^{o} for another eight hours, In brief --- experiments XVIII and XIX were identical except that XVIII received sixteen hours nitration at 35^{o}c whilst XIX had the equivalent of at least seventy hours at 35^{o}c. It was found that a little more nitric acid (3%) had been used in the very long nitration but the amount is so small in comparison with the tremendous increase in duration of nitration that we can safely say that <u>for all practical purposes our sixteen hour points represent stoppages and not merely sluggish reaction velocities.</u>

(e) Since we have established the authenticity of nitration stoppages in the heterogeneous type of nitration, it follows that our "end points" for homogeneous reactions are also true stoppages because, as the curves indicate, even after two hours nitration in the homogeneous or one layer region, (see point VI), the composition of the nitrating acid has approached much nearer to the limiting curve (red line) than in the heterogeneous region (see point XII).

----

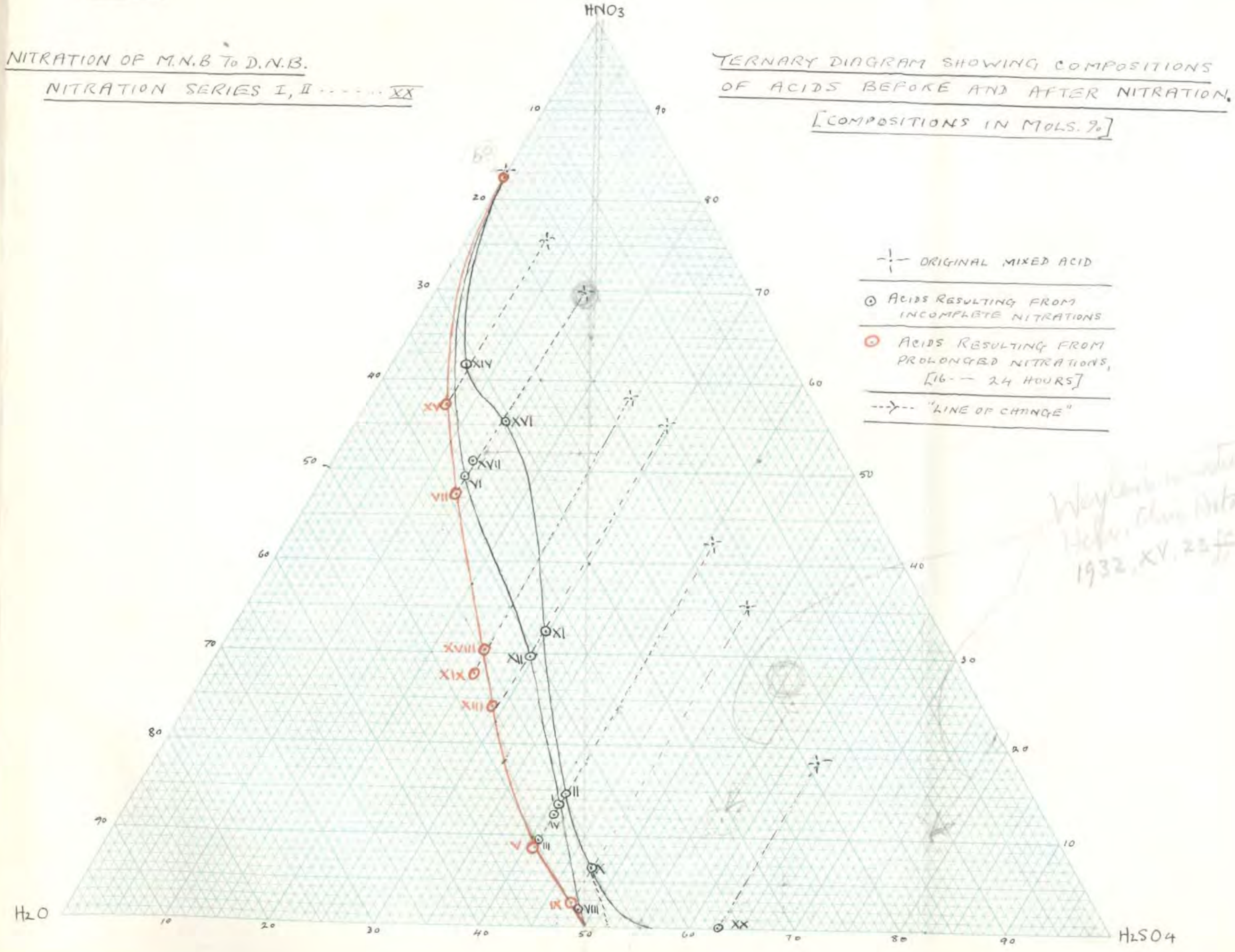
10 Homogeneous and Heterogeneous Nitrations.

(a) All nitrations are homogeneous at first but even acids very strong in nitric acid can be made heterogeneous by taking a sufficiently large excess of nitrobenzene. Thus varying the relative amounts we can ensure any degree of heterogeneity. If we consider equimolecular nitrations then we can draw a sharp line between homogeneous and heterogeneous nitrations. In the first class the spent acid is sufficiently strong in nitric acid to dissolve its molecular equivalent of nitrobenzene whereas in the second class, before we reach completion, the solubility limit is passed and two layers formed. In further limiting this line of demarcation we may consider a homogeneous nitration to be one in which the acid in question is

⟨FIG. III⟩

NITRATION OF M.N.B To D.N.B.
NITRATION SERIES I, II XX

TERNARY DIAGRAM SHOWING COMPOSITIONS OF ACIDS BEFORE AND AFTER NITRATION.
[COMPOSITIONS IN MOLS. %]



able to dissolve more nitro-compound than it can nitrate and a hetergeneous nitration as one in which more material is nitrated than can be retained in solution. The following table from the results of experiments shows how the ratio of "nitratable material" to "dissolvable material" varies along the range of acids. The dissolvable material is calculated from the number of ccs of M.N.B. present when two layers form and the nitratable material is calculated from the final analysis of nitro-compound.

TABLE II

Expert.	Compn. of M/A in Mols.% H_2SO_4	HNO_3	H_2O	Mols. M.N.B. for two layers.	Mols. M.N.B. nitrated	Time in Hours.	
XX	0	84.8	15.2	all (1.22)	.026	2	HOMOGENEOUS
50	0	83.3	16.7	all (1.28)	.035	20	
23	4.9	80.6	14.5	all (1.28)	.109	2	
XIV	7.9	75.7	16.4	.14	.099		
XV	7.9	75.7	16.4	all (1.75)	.2585		
10	12.5	72.7	14.8	.45	.195	2	
XVI	14.4	70.0	15.6	.265	.127		
VI	14.4	70.0	15.6	.393	.301	2	
VII	14.4	70.0	15.6	.364	.328	24	
22	14.2	69.1	16.7	.5	.128	2	
21	22.7	64.0	13.3	.30	.251	2	
19	22.2	63.4	14.4	.23	.201	2	
XI	29.8	55.5	14.7	.177	.239		HETERO
XII	29.8	55.5	14.7	.157	.262		
XIII	29.8	55.5	14.7	.177	.391		
18	33.4	51.1	15.5	?	.242	2	

(table continued):-

Experiment	Compn. of M/A in Mols. % H_2SO_4	HNO_3	H_2O	Mols. M.N.B. for two layers.	Mols. M.N.B. nitrated.	Time in Hours
(a)	39.5	48.0	12.5	.15	.375	2
(b)	39.5	48.0	12.5	.45	.824	2
(c)	39.5	48.0	12.5	1.45	2.56	2
I	40.8	42.5	16.7	.29	.63	2
II	40.8	42.5	16.7	.16	.33	2
III	40.8	42.5	16.7	.20	.53	8
IV	40.8	42.5	16.7	Two layers throughout	.51	2
V	40.8	42.5	16.7	.15	.42	16
25a	46.2	42.0	11.8	.22	.604	2
25b	46.2	42.0	11.8	?	.513	2
24a	51.3	36.3	12.4	.27	.739	2
24b	51.3	36.3	12.4	.24	.711	2
VIII	47.6	35.6	16.8	.16	.41	2
IX	47.6	35.6	16.8	.16	.39	16
X	47.6	35.6	16.8	.15	.35	2
20	54.9	33.3	11.8	.16	.497	2

HETEROGENEOUS

According to the table the division between homogeneous and hetergeneous reactions occurs somewhere between acids containing 22 and 30 molecular percent of H_2SO_4. It will be remembered however that numbers 22, 21 and 19 are unfinished nitrations and if allowed to go to completion will nitrate to such an extent that the ratio M.N.B. "dissolvable" / M.N.B. "nitratable" becomes less than one. For finished sixteen hour nitrations therefore, the division comes

30?

between 14.4 and 20% H_2SO_4.

(b) By calculating the composition of acids when two layers appear we can divide the zone of dinitration into two areas, one area being the are of homogeneity and the other being the area of two phases thus we can predict when and where two layers will form in any nitration. The compositions of these acids are obtained by noting during the course of experiments how many gram molecules of organic material are required to produce two layers, sub~~s~~tracting this figure from the original nitric acid content and adding it to the water content. Sulphuric acid is constant and hence we can easily calculate the molecular composition of the new acid providing, ~~the~~ of course, that we assume all the mononitrobenzene to have formed dinitrobenzene at the formation of two layers. This assumption is not quite true since a certain small amount of nitrobenzene will be in the mono-state because the reaction takes appreciable time for completion.

TABLE III

Table of Acid Compositions at two layer point.

Experiment	Mols. M.N.B. to produce two layers.	Calculated compn. of "Critical" two layer acid in Mols. %		
		H_2SO_4	HNO_3	H_2O
XVIII	0.29	24.8	42.7	32.5
XIII	0.18	29.8	41.5	28.7
V	0.15	40.8	30.6	28.6
IX	0.16	47.6	22.6	29.8
XX	0.19	62.9	6.7	30.4

The calculated "critical" acids are plotted on a triangular diagram (Fig. IV page 55 .)

(c) It is evident, at the outset, that this division of the triangle is dependent on the series of initial mixed acids chosen and is only true for that particular series. It is useful however in giving a direct indication of the progress of nitrations actually met with in the present work and enables one to say exactly how far a given reaction will proceed before two layers first form. Starting with any mixed acid on the line of initial mixed acids shown, the molecular composition changes during nitration along the sulphuric acid parallel and when it reaches the line dividing the two regions "homogeneous" and "heterogeneous" it has become saturated with dissolved organic material and forms a second layer. From this point heterogeneity gradually increases until the acid ends up on the limiting curve of dinitration.

(d) It is noticeable that when between 0 and 55 molecular percent of nitric acid is present in the initial mixed acid, the dividing line between the two areas is very nearly parallel to the line of initial mixed acid compositions, then beyond this concentration it suddenly curls round to meet the limiting line of dinitration. All initial mixed acids having between about 55 and 11 molecular percent of nitric acid are able to dissolve approximately the same amount of nitro compound and the corresponding nitrations become heterogeneous before they have gone half way to completion. Above 55% nitric the nitrations rapidly become more and more homogeneous until at 65 to 70 molecular percent of nitric acid we reach nitrations which are homogeneous throughout.

(II) Division of Triangle into Areas which are independent of Initial Conditions.

(a) As was suggested in paragraph (c) in the previous section, the specification of the boundary acid at which nitrations become two layered is only partly true because it refers only to initial acid mixtures obtained by mixing stock 83.3% nitric acid with stock 82% sulphuric acid (molecular percentages).

By measuring the solubility, at 35°c, of dinitrobenzene in mixed acids whose compositions lie on the limiting curve for dinitration we can divide the dinitration area into two separate areas which are independent of the initial conditions, and which show at a glance how many nitration, using any initial mixed acid (which may be any acid within the dinitrating area) will end up when it reaches the dinitrating boundary. The following considerations will make this clear.

(b) Adopting as true the limiting curve for nitration. Consider a nitrating mixed acid of initial molecular composition marked O, on the H_2SO_4 - parallel LM, shown in the diagram given on next page. If we use 100 mols. of it to nitrate OR mols. of mononitrobenzene to dinitrobenzene, the composition of the acid will now be represented by the point Q since it has lost OR mols of HNO_3. If no

FIG IV

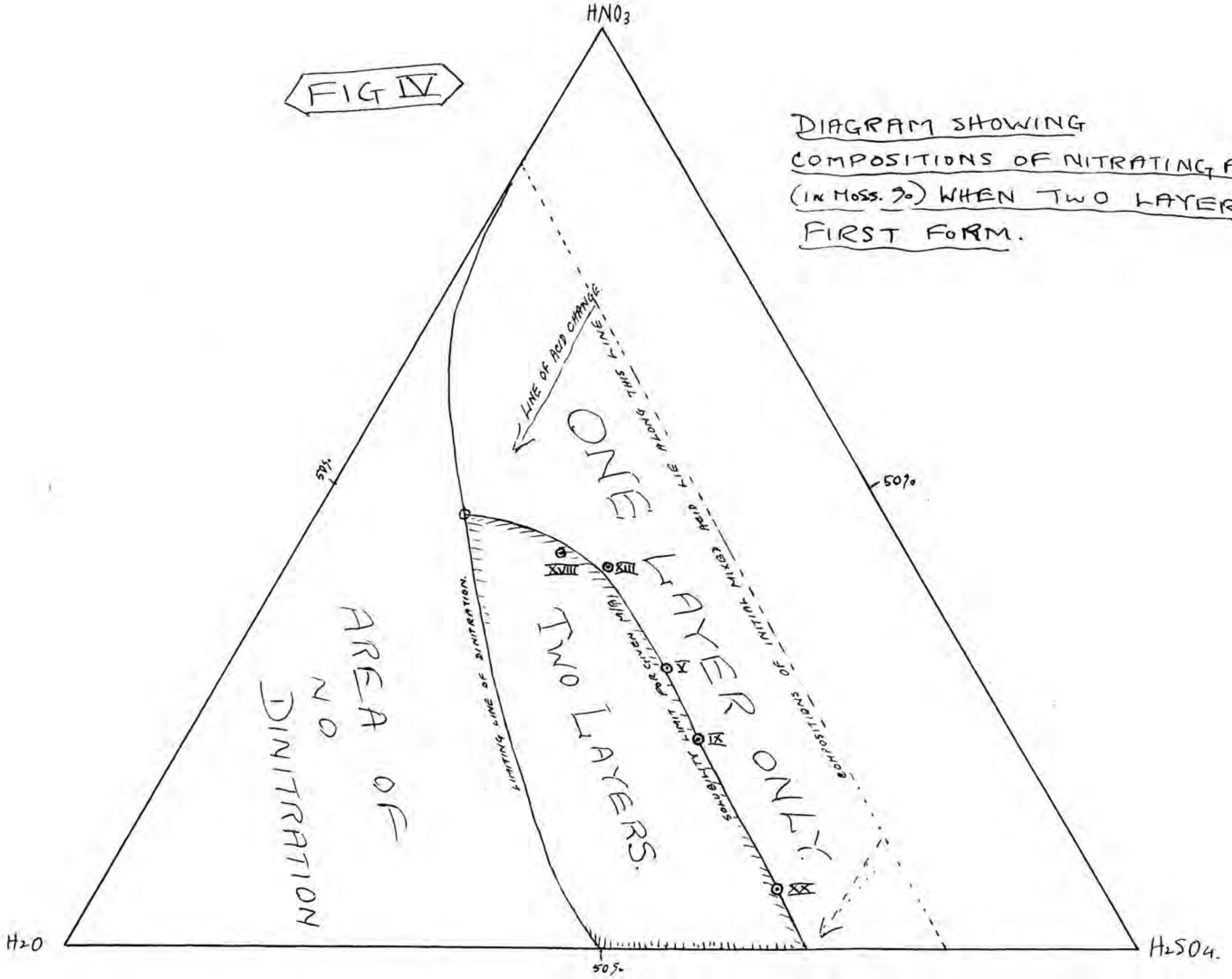
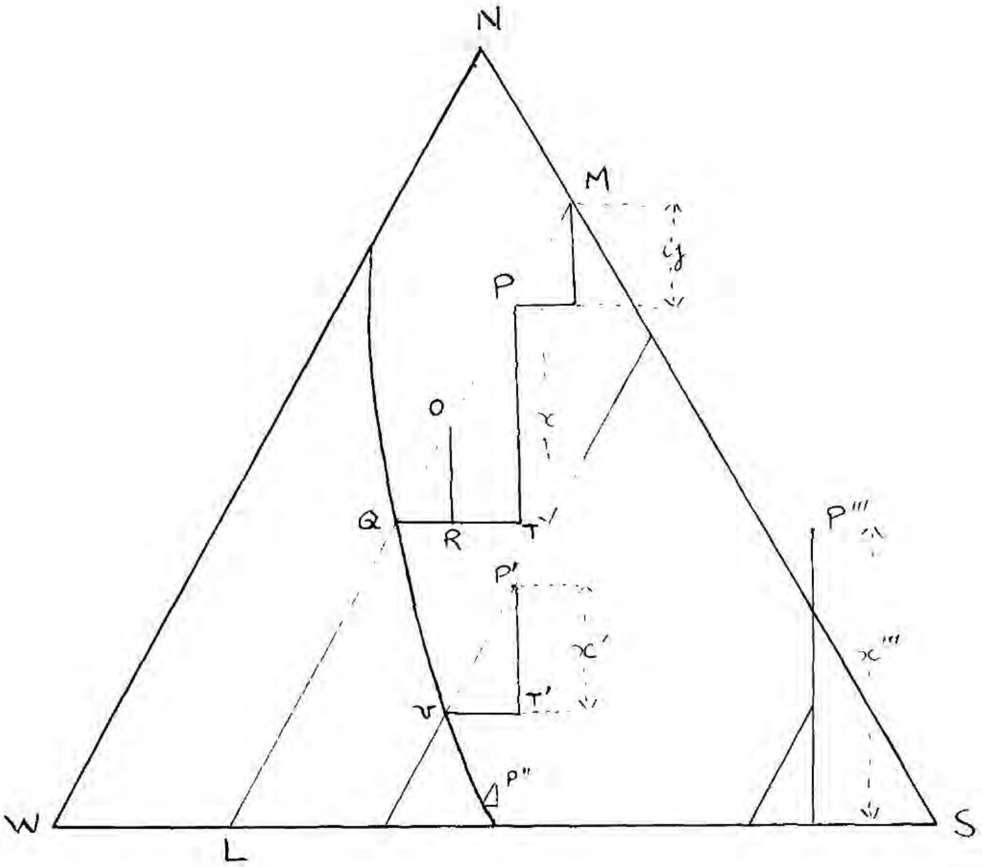


DIAGRAM SHOWING COMPOSITIONS OF NITRATING ACIDS, (IN MOLS. %) WHEN TWO LAYERS FIRST FORM.



extra mononitrobenzene has been added, only one phase will be present at the end since the acid Q is able to dissolve all the dinitrobenzene (OR mols.) formed and still be unsaturated with dissolved material.

(c) Now suppose we take 100 mols. of this waste acid Q and artificially saturate it with dinitrobenzene at the given temperature, 35°; then calling this solubility x mols. dinitrobenzene per 100 mols. waste acid Q, we can draw an HNO_3 - parallel through Q - R; and go along it until the vertical intercept between it and the H_2SO_4 - parallel measures x units. This is drawn above, the intercept~~s~~ being marked PT.

(d) We are now able to make a definite statement about the mixed acid at the point P. It has the same mols. % of H_2SO_4 as the first acid marked O, and so would end up at Q as before. If we nitrate mononitrobenzene with the acid of composition P; again avoiding any excess of mononitrobenzene, PT mols. of mononitrobenzene will be used up giving rise to PT mols. of dinitrobenzene per 100 mols. of waste acid Q. The waste acid will therefore be just saturated with dinitrobenzene. If one did a third nitration with mixed acid behind P, say M, then on its ceasing to nitrate (at Q) it would have made y too many mols. of dinitrobenzene for it to keep in stable solution. Hence for the given sulphuric acid parallel, the point P represents the limiting composition of a mixed acid for homogeneous nitration, and it is found by measuring the solubility of dinitrobenzene in the acid Q, and measuring off as indicated.

(e) Similarly, on a second sulphuric acid parallel, if the waste acid v will dissolve x'mols. of nitrobenzene then the initial mixed acid which just performs its nitration in one layer is represented by the point P'; any acid behind P' will eventually end up by producing two layers. The locus of the point P therefore is the true boundary between homogeneous and heterogeneous nitrations, if we define a "heterogeneous" nitration as one which, when it has gone to the limit marked by the limit curve with no excess of M.N.B., has produced two layers.

(f) EXPERIMENTAL:-

Determination of Solubility of D.N.B. in Final Waste Acids

A series of limiting waste acids, was made up by diluting the original mixed acids marked -:- in diagram, FIG III page 60, with water until they reached the limiting curve of dinitration marked by the red line on the same diagram.

Saturated solutions m-dinitrobenzene were made by shaking with excess of D.N.B. at 40°c and gradually cooling to 35°c with shaking. The excess D.N.B. was filtered off through glass wool and a weighed sample of saturated solution flooded with water, the precipitated D.N.B. filtered off, well washed, dried and weighed.

Sometimes on heating to 40°c, two liquid layers are formed, the melting point of dinitrobenzene being lowered by presence of dissolved acids. In these cases, only a slight excess of D.N.B. was taken and the trace of organic layer allowed to float on the surface while the clear saturated solution was drawn off and examined as above.

Experimental results of Solubility Determinations.

The experimental results are summarised in table on the following page.

The compositions of "critical" acids have been plotted on the triangular diagram, Fig. V page 60, and the curve drawn through these points represents the locus of the point P as dealt with in the previous mathematical section.

Any mixed acid in the area painted red will nitrate completely in one phase, i.e. the D.N.B. it produces during nitration will be completely dissolved by it. Any mixed acid in the green area will form two layers before

Solubility of D.N.B. in Ternary Acids lying on limiting line of Dinitration.(at 35°c). TABLE IV

		(1)	(2)	(3)	(4)	(5)
Compn of limiting acid Mols.%	H_2SO_4	50.0	17.6	30.4	82.0	67.1
	HNO_3	0.0	41.0	22.5	0.0	0.0
	H_2O	50.0	41.4	47.1	18.0	32.9
Grms Acid		112.59	51.51	88.16	51.36	74.75
Grms D.N.B. dissolved		4.52	17.14	8.08	19.52	16.42
Initial Acid consists of:- Mols.	H_2SO_4	.9697	.1793	.5107	.5034	.6990
"	HNO_3	.0000	.4179	.3780	.0000	.0000
"	H_2O	.9697	.4219	.7912	.1105	.3435
Mols. D.N.B. dissolved		.0269	.1020	.0481	.1161	.0977
"Critical" Acid consists of:- Mols	H_2SO_4	.9697	.1793	.5107	.5034	.6990
"	HNO_3	.0269	.5199	.4261	.1161	.0977
"	H_2O	.9428	.3199	.7431	(-.0056)	.2458
Compn of "critical" acid in Mols.%	H_2SO_4	50.0	17.6	30.4	82.0	67.1
	HNO_3	1.8	51.1	25.4	18.9	9.4
	H_2O	48.2	31.3	44.2	(-0.9)	23.5
State of organic layer		Solid	Liquid	Liquid	Solid	Solid

nitration has gone to the limit. Thus the majority of nitrations will be of the heterogeneous type if one chooses initial mixed acids well behind the limiting line of dinitration, but at the same time by choosing sufficiently dilute initial mixed acids, confined to the narrow red belt near to the dinitration limit, all nitrations can be made to proceed in one phase.

FIG. V

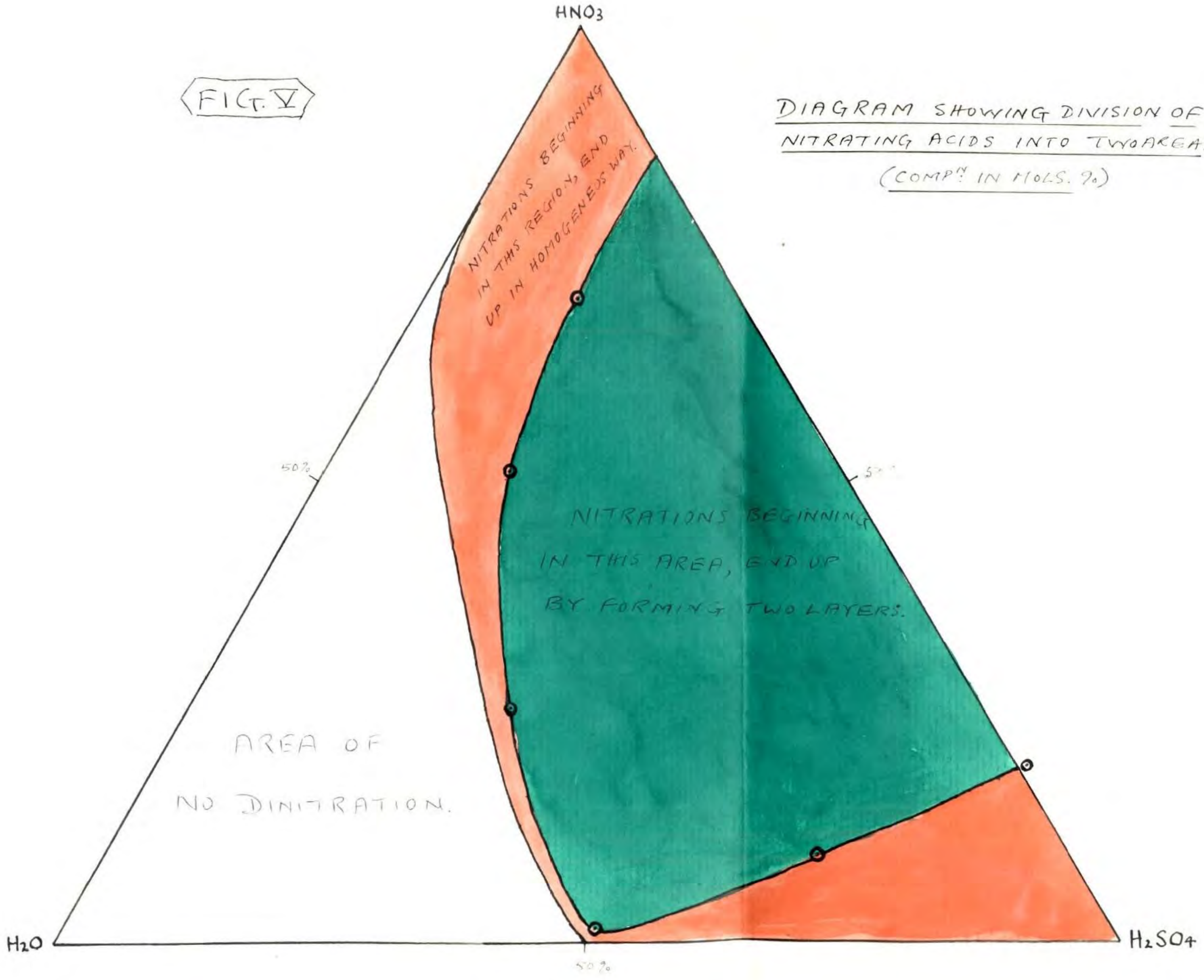


DIAGRAM SHOWING DIVISION OF NITRATING ACIDS INTO TWO AREAS (COMPN. IN MOLS. %)

(Part II) §III HYDRATE FORMATION.

(a) At the end of sixteen hours vigorous shaking with M.N.B. at 35° apparently no further change takes place in the composition of a ternary acid. The quantity of nitric acid remaining in this spent acid depends upon the concentration of sulphuric acid and water. Since there is no tendency for nitration to be reversible, we cannot perhaps strictly say that the acid is an "equilibrium" mixture, but at any rate the reaction has reached completion. The natural inference is that the nitric acid now present is no longer in the same state in which it existed in acids capable of nitration. In these, therefore, a certain modification of the nitric acid,capable of nitration,is present and the concentration of these active molecules or modifications of nitric acid must be directly controlled by the concentrations of sulphuric acid and water.

(b) All spent acids lie to the left of the line joining HNO_3 and an equimolecular mixture of H_2SO_4 and H_2O; and since the limiting line of dinitration passes through the point H_2SO_4, H_2O we have definite indication of the formation of sulphuric acid monohydrate as a factor in nitration. That this equimolecular mixture is essestially a monohydrate of sulphuric acid is well attested by a large number of other properties (which have been summarised in part I of this thesis). All the spent acids can therefore be regarded as composed of H_2SO_4, H_2O

H_2O and HNO_3. As the nitric acid content rises, the proportion of water over and above that needed to form $H_2SO_4.H_2O$ also rises; the molecular ratio of this excess water to HNO_3 is fairly constant at 1 ; 1 up to 12% HNO_3 when it gradually falls off and at the point where the curve meets the side HNO_3-H_2O, the ratio HNO_3/excess H_2O = 82/18.

(c) From these data it would seem that, granting the monohydration of all the sulphuric acid, there remains a series of mixtures in which an-hydrous nitric acid must predominate over hydrated nitric acid, and in all of which the chemical activity towards nitrobenzene is equal. Yet a cursory glance at the vapour pressures of HNO_3 from these acids - drawn from Saposchnikoff data in Fig. XI page 92. is enough to show that the acids vary in vapour pressure over an eight or nine-fold range; in short the chemical activities and the thermodynamic activities do not agree at all.

If we consider all the sulphuric acid of spent acids to be bound up as monohydrate we can recalculate compositions to show how excess water and nitric acid compare.

TABLE V

	50	XV	VII	XIII	V	IX
Mols. H_2SO_4, H_2O	0.00	.1160	.2400	.3747	.5297	.5748
" HNO_3	1.2793	.9015	.8149	.3121	.1141	.0291
" excess H_2O	.2653	.4421	.4336	.2324	.1169	.0221

Ratio of HNO_3 to excess water is as follows:-

Mols. HNO_3	100	100	100	100	100	100
Mols excess H_2O	20.74	49.05	53.21	74.45	102.0	75.95

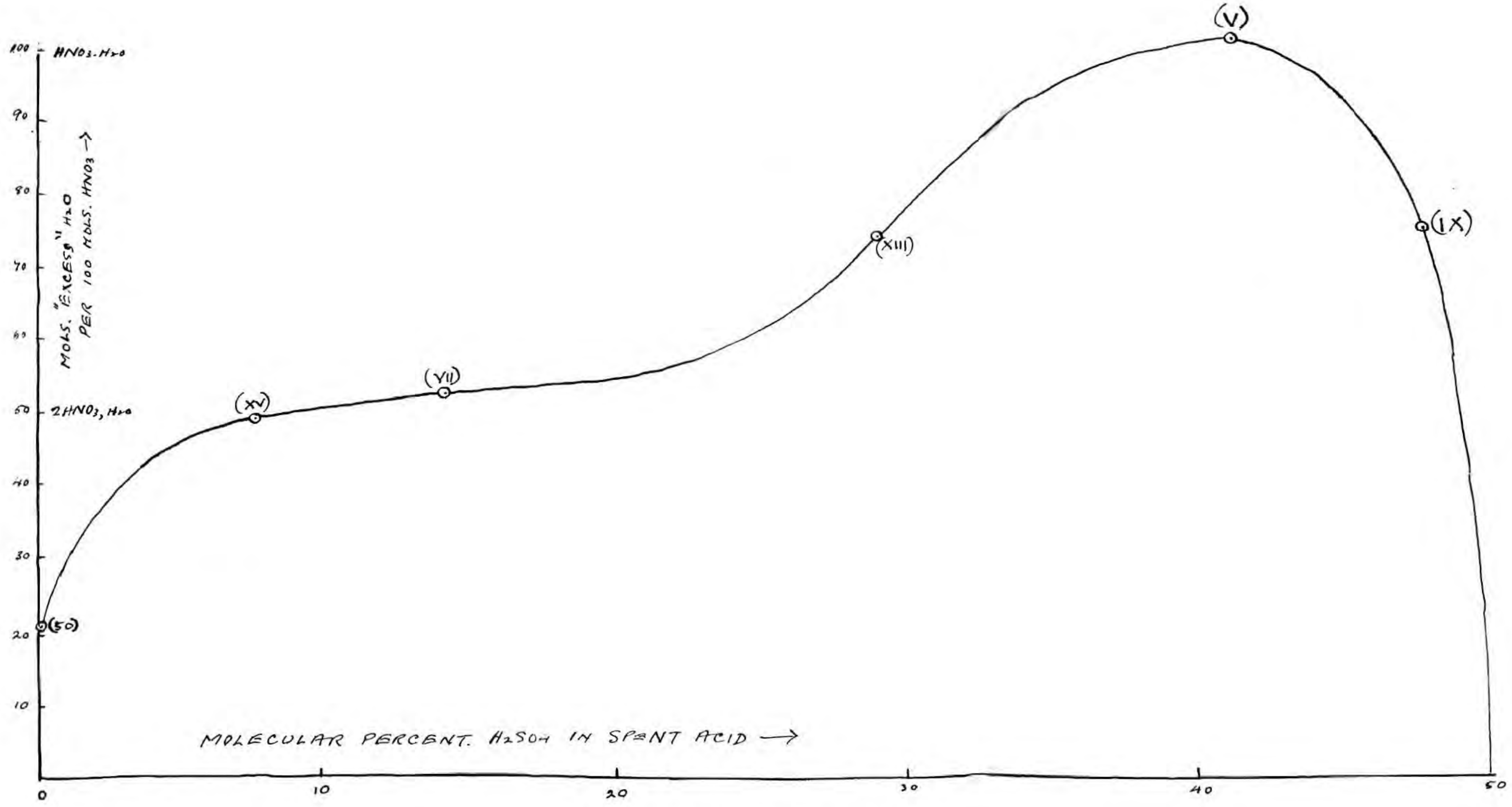
By plotting the ratio of excess water to nitric acid against the sulphuric acid content a curve is obtained showing a sharp maximum at the point where the ratio of molecules of HNO_3 to molecules of H_2O is approximately 1 : 1 and a kink at the point $2(HNO_3),H_2O$ (see Fig.VI page 64). There is a certain amount of significance about the points $HNO_3.H_2O$ and $2(HNO_3).H_2O$ since several workers have supposed definite hydrates to exist at these concentrations (see this thesis, part I), the matter however is highly speculative and whilst not disputing the possibility of this nitric acid hydrate formation in the spent acids it is difficult to se how an acid distributed unevenly between two phases can be considered as a whole in anything but empirical terms.

(d) Kullgren concluded that nitric acid is only capable of nitrating when present as the compound HNO_3 and not as a hydrate; the part played by the sulphuric acid being to set free the vital molecules of anhydrous nitric acid from the hydrate or hydrates present (1907). There is not much doubt that the function of the sulphuric acid is to remove water forming the stable monohydrate $H_2SO_4.H_2O$ but there is no definite reason for concluding that the active constituent formed in the process is the anhydrous molecule of nitric acid for then we would expect fuming nitric acid to have a greater nitrating power than acids with more water present; (the amount of water referred to is excess water over and above that required to $H_2SO_4.H_2O$ formation). Such is not the case. The constitution of nitric acid in its aqueous solutions is not yet definitely settled as a great deal of conflicting results have yet to be explained. It is probable however, from absorption spectrum data that two kinds of molecules exist :- the "pseudo acid" $HO.(NO_2)$ and the true acid HNO_3 which is assumed to be present as oxonium nitrate, $(H.OH_2)(NO_3)$. (when sulphuric acid is added yet a third type of molecule is considered to exist giving rise to nitronium hydrosulphate $\{NO(OH)_2\}(HSO_4)$, and $\{N(OH)_3\}(HSO_4)_2$. Nitronium nitrate, $\{N(OH)_3\}(NO_3)_2$ must therefore exist in anhydrous nitric acid. The absorption spectra of aqueous solutions show that nitronium nitrate is completely hydrolysed by the addition of one molecular proportion of water). W. N. Hartley studied the change in absorption spectrum on adding sulphuric acid to nitric acid and concluded that sulphuric acid displaced the equilibrium between the two types of nitrate spectrum in such a way that by increasing concentration of H_2SO_4 the ester type of molecule is made to predominate over the true acid type. The mechanism must be somewhat as follows:-

$$(H.OH_2)(NO_3) + H_2SO_4 \longrightarrow HO.NO_2 + H_2SO_4.H_2O$$

Any further water above sulphuric acid monohydrate will act in the reverse direction with respect to the nitric acid molecule thus :- $HO.NO_2 + H_2O \longrightarrow (H.OH_2)(NO_3)$

(e) Granting this displacement of equilibrium we must assume that it is the pseudo acid which is instrumental in causing nitration of nitrobenzene, possibly by first of all dissociating into free (HO) and (NO_2) radicals, the (HO) combining with hydrogen ions from ionized true acid



COMPOSITIONS OF ACIDS
WHEN REACTION HAS CEASED

FIG VI

(or its oxonium salt) to form water whilst the free NO_2 group attaches itself to the organic molecule, Whilst not dogmatising on the idea of pseudo acid production it offers at any rate a plausible explanation of how sulphuric acid may perform its work in increasing the nitrating power of acid mixtures.

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§ IIIa VELOCITY OF NITRATION REACTION.

Very few figures can be gathered together from the literature to show any light on the question of reaction velocities in connection with the nitration of mononitrobenzene.

(a) An elaborate investigation into one side of the question, however, appears in a paper by Haavard Martinsen - 1905. He unfortunately confines his attention to a narrow belt of mixed acids lying very near the H_2O - H_2SO_4 side of the triangle, leaving the major part of the triangle unexplored. His object in using such a series of acids was largely to keep the mixtures homogeneous i.e. his mixed acids lay in the area painted red in the previous triangular diagram Fig. IV page 55 . The present work was not planned to investigate reaction velocities directly but since experiments I --- XX can be regarded as an investigation into the time element, approximate curves can be drawn which bring out many important facts.

(b) Seven different mixed acids, distributed across the triangle have been used to nitrate M.N.B. for periods of time ranging, with each acid of the seven, from 2 hours to 24 hours. By estimating the change in nitric acid content, as determined by waste acid analysis, an approximate relation can be established between the nitric acid used up in nitration and the time of reaction. The figures for each experiment have been recalculated so that in each case we consider the initial weight of nitric acid present to be 100 grams.

Table XI shows the recalculated data. By plotting the amount of HNO_3 disappearing against the time of reaction the curves shown in diagram VII page 70 are obtained.

(c) At the outset, it must be pointed out that these curves are not amenable to mass-action treatment since the acid solvent is continually changing in composition and most of the curves refer to heterogeneous nitrations where the velocity of reaction is governed largely by the intimacy of mixing of the two layers.

(d) It has been a matter of no little difficulty to construct these curves since the experimental course was not designed for this purpose. Data is scarce and complications due to heterogeneity etc are particularly troublesome. In their construction the following course was adopted as being the most reasonable :-

(e) All the points I --- XX were marked on the diagram regardless of all conditions except nitric acid content and time. At the side of each point, in brackets, is given the key to the relative quantities used in each experiment. It is obvious that we cannot draw a curve through points obtained by nitrating under different initial conditions, even if the initial mixed acid compositions are identical. For instance, XI and XIII belong to the same mixed acid but XI is more heterogeneous than XIII since the molecular ratio of M.N.B. used to nitric acid present at the start is, for point XI -- 2.4, and for point XIII --- 1.0. But another point, XII, has the same relative molecular quantities ratio as XIII, both being equimolecular nitrations therefore XII and XIII belong to the same system and can be connected by a smooth curve passing through the origin. This curve marked "h" shows how the velocity of nitration varies with the time for the given equimolecular conditions. In the same way the points VI and VII are related and can be joined by a second curve -- e.

(f) Now consider the point XVI which represents the quantity of nitric acid which has disappeared in two hours. Both VI and XVI had the same initial mixed acid but nitration XVI, being the more heterogeneous of the two has not proceeded so quickly as nitration VI; even after nitrating for six hours under these conditions of heterogeneity, the nitric acid consumption is still short of that achieved in the two hours of homogeneous nitration - see points XVII and VI. A curve "d" has been drawn through the points XVI and XVII to represent the change in reaction velocity during the more heterogeneous type of nitration.

(g) For a given mixed acid, therefore, we must draw a bunch of curves to represent the change in reaction velocity, each curve being governed by the initial conditions of relative quantities used. These bunches of curves are contained within the shaded areas on the diagram; FIG VII; the upper limits of these shaded areas, represented by the curves l, j, h, e and c, being true for the least heterogeneous types of nitrations performed in the actual experiments; and the lower limits, represented by the curves k, i, g, d, and b, being true for the conditions of maximum heterogeneity chosen.

(h) Let us now consider, more carefully, these bundles of curves. The first question calling for answer is "Do these bundles taper to a point if a sufficiently long period of time is taken?" If they do, it means that heterogeneity is merely a retarding factor and the final waste acid produced is independant of the relative quantities taken. This question cannot be answered conclusively without a further compilation of a good deal of extra experimental points on the curves --- but the weight of evidence is in favour of a tapering effect. In every case the more heterogeneous curve approaches the more homogeneous one as the time increases and the only point about which there can be any doubt, in this respect, is the point marked XVII. We can safely say that if the relative quantity of mononitrobenzene to mixed acid has any influence on the composition of the final spent acid, this influence is very small.

(i) Next: "Do the curves indicate that the spent acid obtained after a 16 hour nitration is a final acid whose ability to nitrate has been exhausted?". After a period of from 2 to 8 hours the velocity curves become almost straight lines, almost parallel to the time axis. It is evident, therefore, from the shape of the curves and the rapid slowing down of velocity with dilution that for all practical purposes the nitration is complete after sixteen hours. Thus the difference in composition between our sixteen hour waste acids and truly exhausted acids is at the most a very small one and it is very probable that the limiting curve of dinitration constructed from the present work is fairly accurately placed.

(j) It is noteworthy that the velocity of reaction increases rapidly as we increase the percentage of sulphuric acid in the initial mixed acid so that with a mixed acid containing 60 molecular percent of H_2SO_4 nitration is completed in one hour --- see point XX. In connection with this effect of sulphuric acid, important work has been done by Martinsen. Martinsen followed the nitration of nitrobenzene to dinitrobenzene by pipetting samples from the nitration mixture at definite time intervals and either extracting the nitro compound~~s~~ with ether and determining the amount of stannous chloride oxidised by it or estimating the amount of unconsumed nitric acid in a nitrometer. His experiments were carried out with ordinary pure laboratory sulphuric acid or specific gravity 1.839 (gave by titration 95.2% H_2SO_4). Two solutions were employed, a 0.1 normal and a 0.05 normal solution of nitric acid in this solvent. The concentrated nitric acid used had a specific gravity 1.400 at 15°C. = 65.3% HNO_3. 1 cc. of pure nitrobenzene was added to 200 ccs. of M/A and the mixture (either at 25°C or 0°C) shaken to ensure mixing. At the 25°C temperature the extraction method was employed and samples of 10 or 20 ccs. (according to the strength) tested by reducing with a known excess of $SnCl_2$ and estimating the excess before and after reduction with standard 0.05N. iodine solution.

The velocity constants were obtained by expressing

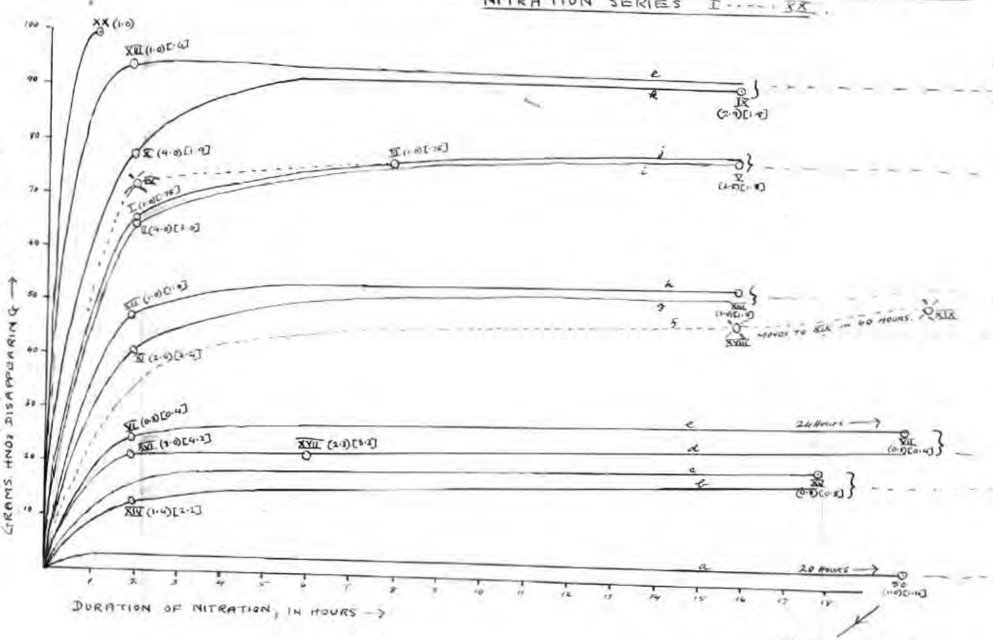
RATE OF DISAPPEARANCE OF HNO_3 IN NITRATIONS.......Series I — XX. TABLE VI.

INDEX OF EXPERIMENT:–	50	XIV	XV	XVI	VI	XVII	VII	XVIII	XIX	XI	XII	XIII	II	I	IV	III	V	X	VIII	IX	XX
COMPOSITION OF MIXED ACID, GIVEN IN MOLS. % :–	0·0S 83·3N 16·7W	7·9S 75·7N 16·4W		14·4S 70·0N 15·6W				24·9S 58·2N 16·9W		29·8S 55·5N 14·7W			40·8S 42·5N 16·7W					47·6S 35·6N 16·8W			62·9S 18·8N 18·3W
GMS. HNO_3 PRESENT AT START	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
" HNO_3 USED IN 2 HOURS	/	12·80	/	13·46	25·10	/	/	/	/	41·84	46·45	/	65·72	68·49	71·06			78·09	74·66	/	/
" " " " 8 "	/	/	/	/	/	22·43	/	/	/	/	/	/	/	/	/	77·04	/	/	/	/	/
" " " " 16 "	/	/	/	/	/	/	/	47·10	/	/	/	55·33	/	/	/	/	79·04	/	/	73·25	/
" " " " n " (n given by small figure in corner)	20) 2·82	/	18) 21·45	/	/	/	24) 29·48	/	70) 52·79	/	/	/	/	/	/	/	/	/	/	/	1) 100

FIG. VII

VELOCITY OF NITRATION.

NITRATION SERIES I ---- XX.



INITIAL ACID Mols. %			FINAL ACID Mols. %		
H_2SO_4	HNO_3	H_2O	H_2SO_4	HNO_3	H_2O
47·6	35·6	16·8	47·9	2·4	49·7
40·8	42·5	16·7	41·1	8·8	50·1
29·8	55·5	14·7	29·0	24·1	46·9
24·9	58·2	16·9	26·5	27·7	46·8
14·4	70·0	15·6	13·9	47·2	39·0
7·9	75·7	16·4	7·4	57·2	35·4
0·0	83·3	16·7	0·0	82·8	17·2

* The figures such as (1·0) mean Mols. M.N.B.(I) taken per Mol. HNO_3 taken. Figures such as [1·4] mean Weight ratio of M.N.B.(I)/M/A

MN.B. used as (a-x) ccs. iodine solution and M.N.B. present at the start as a ccs. of the same iodine solution, then $K_2 = \frac{x}{t(a-x)a}$, t being expressed in minutes.

He found:-

Mean constant for a = 0.1 normal = 1.51
" " " a = 0.05 " = 1.49

The half-life period was found to be proportional to concentration.

for a = 0.1 normal.......... $t_{\frac{1}{2}}$ = 7.6 minutes
" a = 0.05 " .... $t_{\frac{1}{2}}$ = 14.4 minutes

therefore the reaction is bimolecular.

Experiments were also carried out at 0° C with 0.2N, 0.1N and 0.05N solutions of nitric acid and again bimolecular constants were given but the reaction velocity was found to fall away with the period and this is probably because part of the nitrobenzene undergoes sulphonation with the longer time required at 0°. By measuring velocity constants of dilute solutions in sulphuric acid of different strengths he was able to construct a curve showing the relation between reaction velocity and strength of sulphuric acid, a reproduction of which is given in Fig.VIII page 74.

(k) In comparing Martinsen's results with the present work it is necessary to consider the difference in conditions. In his experiments the concentration of sulphuric acid solvent varies over a very small range and nitration is always homogeneous because very little nitric acid is present and the presence of very little nitrobenzene ensures the condition of homogeneity throughout. Thus his reaction velocities represent small distances along curves such as are expressed on our diagram of nitration velocity curves, the distances being so small that the curve may on our scale, be considered as a straight line. Also his acids when considered as mixed acids in the triangular diagram do not overlap with the present mixed acids but are merely a continuation of them to cover the waste acid region lying between $H_2SO_4.H_2O$ and H_2SO_4. Thus his mixed acids are capable of very little nitration since the nitric acid content is so small, whereas in the present work the mixed acids dealt with are able to nitrate large quantities of nitrobenzene.

The formation of corresponding amounts of water continually dilutes the solvent and slows down the reaction velocity.

(1) From the curve expressing Martinsen's results we find an optimum concentration of sulphuric acid where the reaction velocity shows a very pronounced maximum. This occurs at the point where the solvent consists of H_2SO_4, 1 Mol. to H_2O, 0.7 Mol. From this point the curve slopes rapidly down on both sides towards H_2SO_4, H_2O and alsolute H_2SO_4. In order to explain this maximum he supposes the existence of several modifications of the nitric acid molecule, only one of which is active in nitration. As we vary the composition of the ternary mixture he supposes the equilibrium between these modifications to go through a series of changes until at the optimum composition, a maximum amount of the active molecules are present.

(m) It is interesting to notice that Martinsen's figures agree with the present limiting curve of dinitration in that it passes through the point at which sulphuric acid monohydrate represents the spent acid composition. In experiment 2 where his solvent is 1 molecule H_2SO_4 per 1.03 molecules water he gives the following compositions :- " 100ccms.nitration solution, containing 20 ccms. H_2O and 1 ccm. M.N.B.; sulphuric acid of specific gravity 1.839. The specific gravity of diluted acid is 1.782.

H_2SO_4 = 15.16 normal

H_2O = 15.64 normal

and 1 Mol. H_2SO_4 is present to every 1.03 mols. H_2O ---- ----- sufficient nitric acid is present to nitrate all the M.N.B.".

From these figures we can calculate his mixed acid in molecular percentages :-

HNO_3 present = 1.209 grams M.N.B. = .62 grams HNO_3

= .00984 ~~grams~~ molecules of HNO_3.

therefore out of 1 gram molecule of mixed acid we have:-

.00984 gram molecules HNO_3

+ .99016 " " $H_2SO_4 + H_2O$.

and H_2SO_4/H_2O = 100/103, therefore the mixed acid consists of

$$\left\{\begin{matrix} 48.78\%\ H_2SO_4 \\ 0.98\%\ HNO_3 \\ 50.24\%\ H_2O \end{matrix}\right\} \text{ By Molecule.}$$

At 25°c, .62 grams of HNO_3 is present initially. After 370 minutes nitration sufficient nitric acid remains to form 17.2 ccs. of NO in the nitrometer and K_2 the velocity constant is decreasing in value as the period is increased. The velocity of nitration is therefore very slow indicating that this mixed acid lies very near to the limiting curve of dinitration, which agrees with the position of the curve drawn from the results of the present investigation.

(n) It is also noteworthy from Martinsen's results that the temperature coefficient of the reaction velocity is of very high value; K_2 the velocity constant being more than trebled for a rise of 10°c. The fall of reaction velocity when we approach the region near absolute sulphuric acid is quite a general phenomena in nitration. Patart notices it in connection with naphthalene and finds that no nitration takes place in this region. Saposchnikoff whose work on nitrocellulose has already been discussed finds the same true, and accounts for the absence of nitro products in the region by hydrolysis of the nitro esters and consequent sulphonation. In the case of nitrobenzene, nitration does take place with acids containing even free SO_3 but the reaction is very slow.

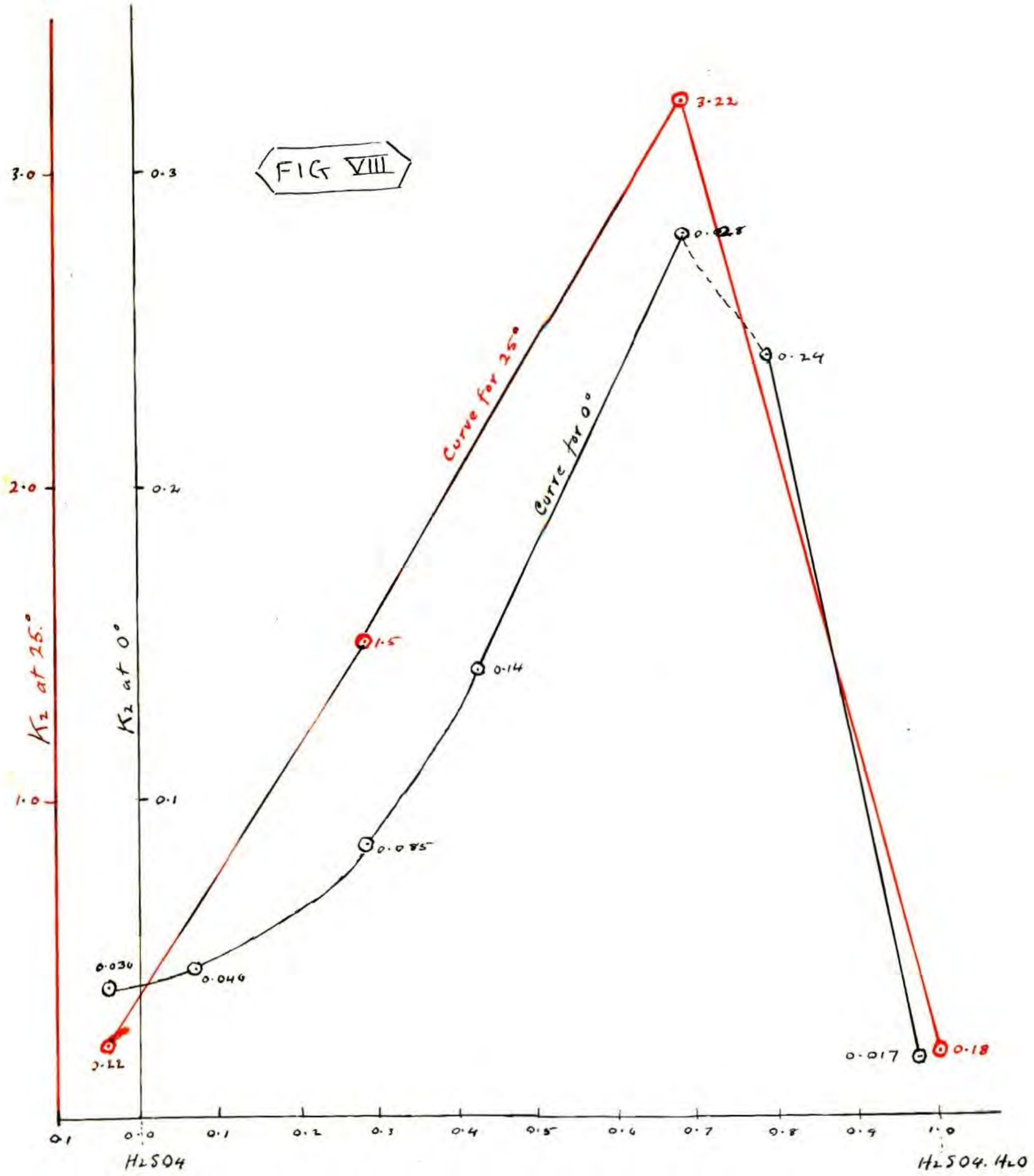


FIG VIII

REPRODUCTION OF MARTINSEN'S VELOCITY CONSTANT CURVE.

(PART II), § IV. DISTRIBUTION OF COMPONENTS BETWEEN THE TWO LAYERS PRODUCED DURING NITRATION.

(a) Two types of nitration have already been mentioned namely, homogeneous and heterogeneous and these are only particular types dependent on the solubility tendencies in the system - Ternary Mixed Acid - mono.and di - nitrobenzene. In order to investigate the system fully a considerable amount of experimental data would be necessary but for the present purpose, data covering all points in the triangular diagram would be superfluous as we are only directly concerned with the causes at work in arresting the process of nitration; and therefore that particular part of the triangle in which our experiments must be directed is the narrow region lying next to the limiting curve of dinitration.

(b) It was noticed quite early that during a heterogeneous nitration, nitric acid is dissolved by the organic layer in surprisingly large quantities, to such an extent, in fact, that the results of many preliminary nitrations were rendered valueless through inadequate washing and extraction of dissolved waste acid from the organic layer. A set of distribution determinations was therefore carried out, partly to see if any appreciable loss of accuracy is entailed by diluting with water at the end of a nitration, instead of separating the two layers, then washing the organic layer and correcting for its acidity. The advantage of direct dilution is that a clean separation results and only one analysis is necessary. Dilution not only extracts acid from the nitro layer but also throws down any nitro body dissolved by the acid. A second set of experiments was attempted on different lines to show how distribution of components changes along the limiting line of dinitration. It will be understood that a heterogeneous system of four (or five) components is extremely complex; to define the concentration - limits fully, even were chemical actions absent, would require an extensive research along phase-rule lines. What has here been done has therefore been to study the physical equilibria within intentionally restricted ranges.

(1) First Set of Distribution Experiments.

(a) A general stock mixed acid of composition

$$\left\{\begin{array}{llll} 50.4\%\ H_2SO_4; & 36.4\%\ HNO_3; & 13.2\%\ H_2O; & (\%\text{ by weight}) \\ 28.2\%\ \text{"} & 31.7\%\ \text{"} & 40.1\%\ \text{"} & (\%\text{ by molecules}) \end{array}\right\}$$

was made up. This represents the composition of a certain waste acid at the end of two hours' nitration, and therefore can be expressed on the triangle as a point lying just inside the boundary of dinitration. All the starting acids in experiments 1 to 8 (Table VIII) are derived from this stock mixed acid by one of two processes; either by diluting it with water or by mixing it with aqueous 68.4% H_2SO_4 by weight, i.e. 28.2% H_2SO_4 by mol. (which brings the composition along the theoretical line of change during a nitration). Experiments 9 and 10 show the distribitions in binary HNO_3 - H_2O acids.

Practical Details:-

(b) In experiments 1 - 8 acid and organic material were shaken together at the given temperature in a separating funnel for some time. When two layers had settled out the bottom acid layer was run off, weighed and analysed, the top layer being washed well with water and the washings analysed for nitric acid and sulphuric acid in the usual way. Any nitro compound dissolved in the waste acid layer was thrown down with water, taken up in ether, the ether washed, dried and evaporated and the yield of nitro compound weighed. Experiments 9 and 10, with nitric acid along, were performed by dissolving 100 grams of nitrobenzene in 100 grams of 95% HNO_3, then adding water until two layers of suitable size were formed. (It was noticed that after dissolving 100 grams of nitric acid (95.13%) in 100 grams M.N.B. it is necessary to add 31.3 ccs. of water, at 20°, to produce turbidity, i.e., 131.3 grams of nitric acid (72.44%) by weight) will dissolve (42.9% By Mol) 100 grams of M.N.B.)

(2) Discussion of Results.

(a) The results of this first series of experiments are set out in tables VIII and IX pages 96 + 97. The first table VIII shows the principal experimental observations and compositions of initial mixed acid, acid contained in waste acid layer and acid dissolved by the organic layer. The figures for HNO_3 and H_2SO_4 are obtained after correcting for the quantity of water used for washing and dilution after the layers have been separated. The water content of the layer was obtained indirectly by difference from 100%. The second table shows the weights of constituents present in each layer before and after nitration and finally gives the partition coefficient for nitric acid in each case, which is the ratio of weight-concentration of nitric acid in organic layer to that in the acid layer.

(b) A comparison of analytical figures brings out the wide difference in compositions of the two acids obtained from the parent by distribution. In all cases the lower acid layer contains most of the sulphuric acid present whilst the nitro layer takes up chiefly nitric acid, accompanied by small amounts of sulphuric acid and water. It is interesting to consider experiments 3 and 6 which were carried out with the same acid and under the same conditions except that in 6, three times the ordinary quantity of nitrobenzene was used. The weight of acid taken up by the nitro layer was consequently greater (approximately twice the amount) but curiously showed a much higher percentage of both H_2SO_4 and H_2O relatively to HNO_3. Thus in experiment 6 where the weight-ratio M/A/ORG.COMPD. = 1/3, the acid taken up by the nitro layer contains only 68.4% HNO_3 whereas normally we have acids ranging around 90% HNO_3. This is the only example we have of the effect of relative weights on the distribution but it will be remembered that the question of relative weights had an important effect upon the velocity of nitration.

(c) It seems to be quite general to find most of the nitric acid present in the organic layer at end points of nitration and the effect of dilution is rapidly to reduce the solubility until at water concentration of 60 to 70%, (By wt.) considerably less than 1% of acid is retained by the nitrobenzene. In this respect a comparison of the distribution-coefficients of nitric acid (K_{HNO_3}), for different acids is useful thus the concentration of nitric acid in the organic layer (expressed as grams per 100 grams of the layer) with M/AI (lying near the limiting line of dinitration) is 2.1 times as great as its concentration in the acid layer, whilst by direct dilution of this same acid to 50% H_2O the partition coefficient of nitric acid is reduced to 0.18 and at dilutions of about 64% H_2O the relative concentrations are 0.04. It is therefore possible by direct dilution after nitration to do away with the washing process which is often made difficult by emulsification.

(3) Second Set of Distribution Experiments.

(a) In order to enlarge upon these facts another series of experiments was devised so as to ascertain the distribution of components over the whole range of acids lying near the limiting curve of dinitration. Mixed acids capable of nitration were allowed to react at 35° with nitrobenzene for two hours, the composition of both the nitro and acid layer being then determined. The period of two hours is, as was shown in the velocity experiments, enough to bring reaction nearly to a finish. It would have been better to allow a longer time such as twelve hours, but this would have interfered with other parts of the work.

Practical Details.

The improved technique described in § II, (PART II), was used.

(b) In experiments α, β, γ, δ, a time of two hours was allowed for nitration, the temperature being constant at 35°. In experiment λ nearly all the nitric acid was used up and in this case excess of M.N.B. was introduced in order to facilitate separation without raising the temperature above 35°.

Experiments ε and ε′ were carried out with an acid consisted of sulphuric acid and water alone, in the ratio H_2SO_4,H_2O so that actually no nitration takes place. There is definite indication that the limiting curve of dinitration passes through this monohydrate point so that conditions of distribution at this point are directly related to the series of spent acids investigated.

(c) Discussion of Results.(for second set)

The results of the present set of experiments are fully laid out in tables X---XIII pages 98-101. Table XI gives a complete record of the quantities, measured in grams, before and after nitration; table XII and XIII shows the same data presented as *compositions* in molecular percentages.

By plotting these compositions as points on a triangle showing molecular compositions, the organic layer acid, the lower layer waste acid and the aggregate waste acid belonging to a given experiment lie in one straight line; whilst by joining initial acid and aggregate waste acid, we should obtain a "line of change", parallel to the side joining HNO_3 to H_2O, as explained in a previous section on the properties of the triangular diagram. In most cases the figures for sulphuric acid molecular content show less than 1% variation which is quite in line with the expected order of accuracy.

Standardising Conditions :-

(d) The question of relative amounts again arises. The standard conditions chosen for the experiments are equimolecular conditions, i.e., the amount of M.N.B. used in a nitration is the molecular equivalent of the nitric acid present in the initial mixed acid. Thus in all cases we end with a spent acid, dinitrobenzene, and some unused mononitro benzene the latter being equivalent to the unused nitric acid. With so complex a system, embodying four or five components, it is difficult to define the effect of these more or less arbitrary excesses upon distribution, and therefore one must beware of relying too far upon the conclusions drawn from distribution experiments which are standardised in one respect only.

(4) DISCUSSION.

(a) By plotting the molecular percentage compositions of the acids on a triangular diagram one can join corresponding points by three distinct curves (see Fig. IX page 83).

The red line shows compositions of acids contained in the organic layer after two hours nitration, similarly the green line gives the lower layer acid compositions whilst the intermediate black line represents compositions of aggregate waste acids and is therefore a boundary curve terminating the two hour dinitrating zone. The direction of the tie-lines joining corresponding acids is indicated by drawing lines through the three points α , the three points β etc. Considering, for the moment, the black line for aggregate acids we can trace an increasing solubility of acid in organic layer on passing through λ, β , α γ, [illegible] to δ . The following considerations make this quite clear :-

(b) An aggregate spent acid, lying on the black line is made up by adding together the corresponding red line and green line acids in definite proportions. These proportions are represented graphically, by the respective distances of the red line and green line from the black line, these distances being measured along the given tie-line. (The proportions referred to are represented on the diagram in molecular amounts and not in amounts by weight). In this way, a comparison of the distances intercepted on the tie-lines by the aggregate acid composition line (shown in black), gives a measure of the amounts (in molecular quantities), of acid in each layer at the end of two hours nitration.

(c) At a point just above δ (black), two layers are no longer formed during nitration; and since the black line approaches the red line, these two must meet at a point just above δ (black) when the acid dissolved by the organic layer becomes coincident with the total aggregate spent acid. It is a matter for conjecture what happens to the green line beyond γ and δ, but probably it swerves steeply to join the other two at the same point of coincidence.

(d) Experiments ϵ and ϵ' were carried out with practically the same mixed acid but with very different relative quantities; this mixed acid contained no nitric acid at all and was made up to have the composition $H_2SO_4.H_2O$. The results indicate that a small amount of anhydrous, or nearly anhydrous, sulphuric acid is in this case retained by the organic layer, leaving the acid layer slightly diluted. In experiment ϵ equimolecular quantities of H_2SO_4 content and M.N.B. were used, and in ϵ' the ratio M.N.B./H_2SO_4 is about 20; in each case anhydrous sulphuric acid only was dissolved by the organic layer so that waste acid layer ϵ contains 47.95% H_2SO_4 (by mol.) whilst waste acid layer ϵ' (with the greater excess of organic material) has been further reduced to 44% H_2SO_4. This result, about which there is no doubt experimentally, is not what might have been expected; and it suggests, incidentally, that the simple system H_2SO_4 - nitrobenzene may display the formation of a molecular compound.

(e) A distinct bump in the red curve appears near the point α; and here, the nitric acid contained in the organic layer has a maximum value. This might, of course, be only a characteristic of the equimolecular conditions chosen; but it may very well be the reason for the curious

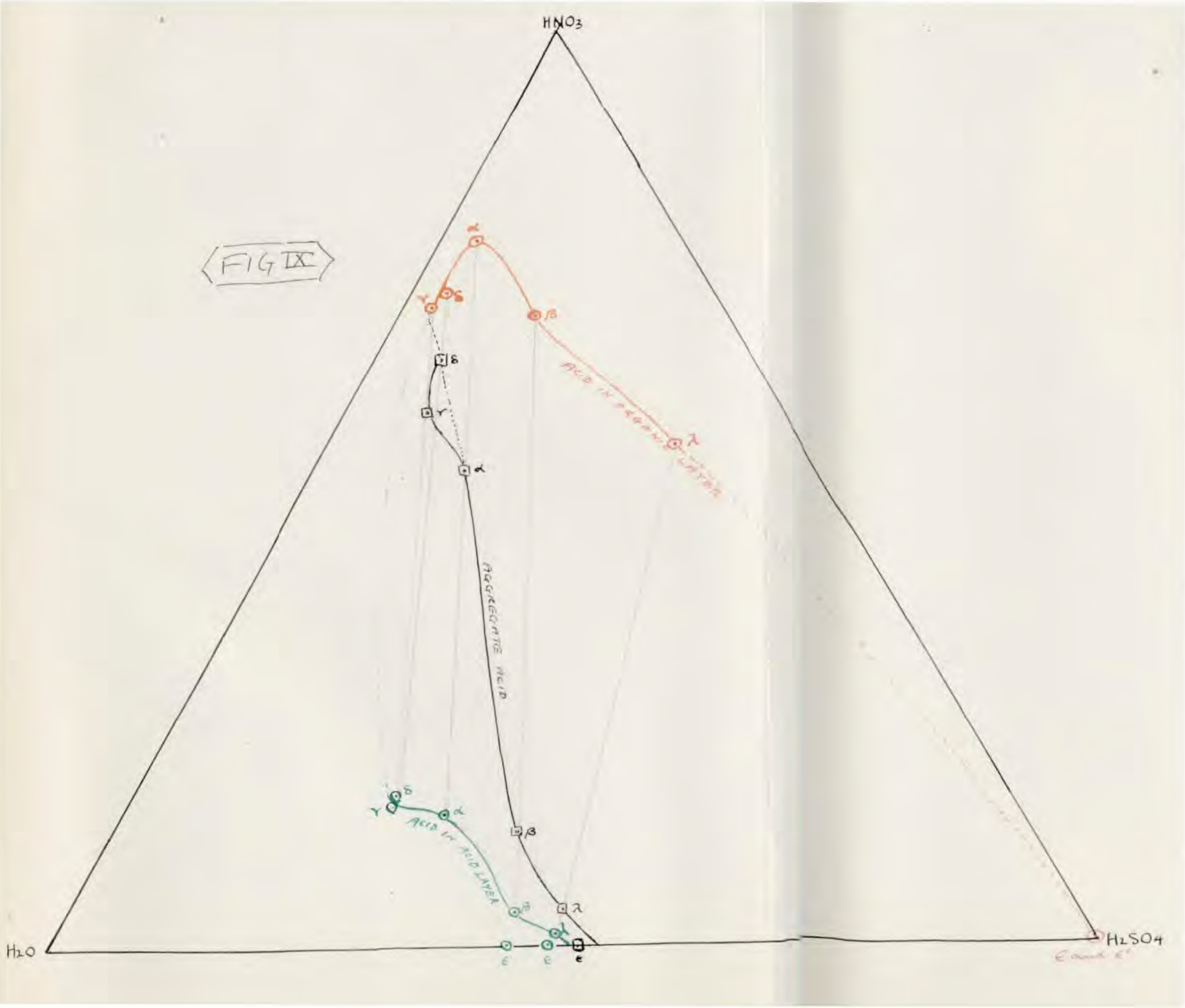


FIG IX

direction change in the black line between the points $\alpha + \delta$, where an increased nitrating velocity is found. This of course is only a suggestion which cannot be supported by the present range of experimental data.

Nothing much can be gathered from the organic nitro-body dissolved by the acid layer. It is certainly noticeable that more nitrobenzene is contained in waste acids near the H_2SO_4-H_2O side of the triangle but these acids are of greater bulk since they are dissolved to a much less extent by the organic layer. There is a tendency however, to extract dinitrobenzene rather than mononitrobenzene on account of the relative solubilities of these two nitro compounds in sulphuric acid.

* * *

(II) §V SEAT OF NITRATION IN A HETEROGENEOUS NITRATION.

We have seen in the previous account of distribution in two phase nitrations how the acid splits up into two fractions: a fraction rich in nitric acid, dissolved by the organic layer, and a second fraction containing nearly all the sulphuric acid and water, together with remaining nitric acid. In the majority of cases separation into two layers occurs while the nitration is still going on; thus one or perhaps both of these acid fractions must be capable of performing nitration. It was in order to find out in which layer the subsequent nitration takes place that the following experiments were devised.

(1) Practical Details.

(a) An average mixed acid containing by weight 55.85% H_2SO_4, 39.41% HNO_3 and 4.74% H_2O was employed in only partial nitration until two layers formed; then the reaction was deliberately interrupted, before nitration had gone to its limit, by separating these two layers; 248.29 grams of acid (which contained the molecular equivalent of 191.1 grams M.N.B.) required 45 ccs. of M.N.B. to first produce two layers, nitration being fairly rapid and addition taking 40 minutes. A further 10 ccs. of M.N.B. was added and allowed to react. The mixture was next poured into a separating funnel and separated at the given temperature (35°c). A fairly sharp separation was obtained, but both fractions on cooling became milky through decreased solubilities. The layers were weighed and samples taken for analysis, acid being extracted by diluting with water and analysis in the usual way whilst the dinitrobenzene content was obtained by isolating and weighing it.

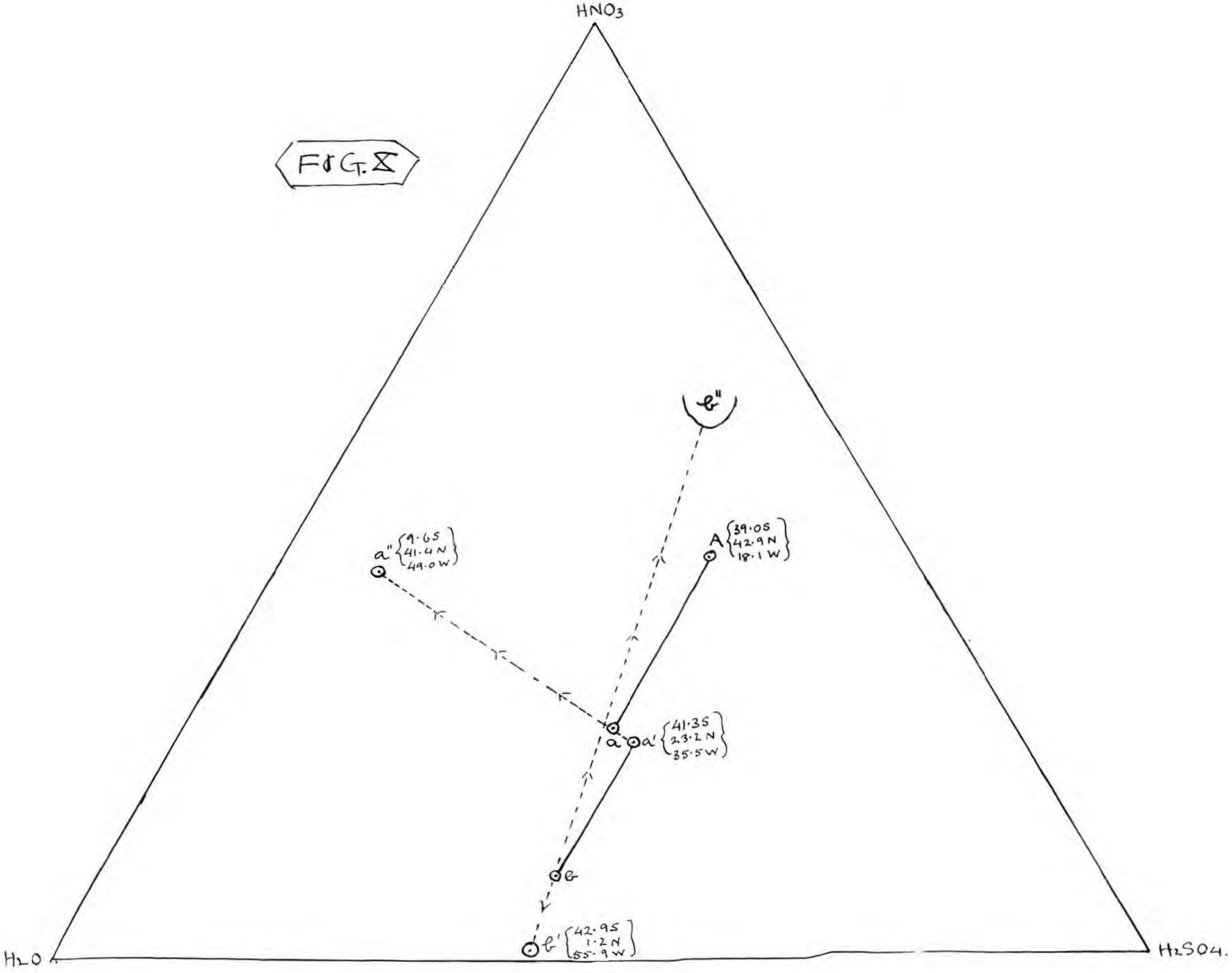
(b) The remainder of the organic layer (of known composition) was then treated with a further quantity of mononitrobenzene two layers being produced. A very small rise of temperature (only 5°c) suggesting that very little, if any, further nitration was taking place; further M.N.B. was added, however, and the mixture shaken at 35° for an hour and a half. The two layers were then separated in the usual way. On washing the organic layer, a particularly stable emulsion formed, the consequent error in separation greatly reducing the accuracy of analytical figures for composition.

(c) The remainder of the acid layer from the initial stoppage was then treated with nitrobenzene, additions of 5 ccs. at a time. Two phases were always present and a considerable amount of nitration took place. After 40 ccs. of M.N.B. had been added solid D.N.B. was deposited and the whole mixture became very buttery and difficult to shake. More M.N.B. was added and shaking continued at 35° for a further hour. The contents of the flask were then cooled, poured into a separating funnel and allowed to stand for three days, the two layers separated and analysed in the usual way; again trouble was experienced through emulsions forming on washing the organic phase.

It is quite evident from the results that the ability to nitrate lies in the acid layer, after the solubility limit has been reached. The fraction of acid dissolved by the organic phase, although it contains much nitric acid, is perhaps too weak in sulphuric, for nitration to be performed. The course of the experiments is best represented in a triangular diagram of molecular percentages (see Fig. X page 88). The initial mixed acid, A, is allowed to perform a certain amount of nitration until its composition has reached the point "a". At "a" two layers are present and the acid in the organic layer has the molecular composition represented by a'' whilst the acid layer consists of a'. The acid layer is much heavier than the nitro layer and consists of 199.75 grams of acid a' together with 41.2 grams of dissolved dinitrobenzene whilst the organic layer has a total weight of 65.8 grams, consisting of 27.4 grams of acid and 38.4 grams of D.N.B. The acid a'', in the organic layer, when separated off and treated with more mononitrobenzene is unable to perform further nitration. This is now seen to be what might be expected, since a'' does not lie within the dinitrating zone, whereas the acid a' is well within the boundary and can accordingly nitrate <u>more</u> nitrobenzene, which it does until it reaches the point b, when the nitration process ceases. At b, two layers are again present, the larger acid layer being represented by b' while the acid dissolved in the nitro layer is b''. The composition of the acid b'' is not very definite since the analysis was made very inaccurate by formation of a stable emulsion. It is noteworthy that the tie-lines (marked in dotted line) change direction rapidly as nitration proceeds. Thus at first, when two layers form and about half the nitration has taken place, the acid layer lies inside the dinitrating zone and contains a good deal of dissolved nitro compound. The acid fraction contained in the organic layer contains most of the nitric acid but evidently takes no immediate part in the process. As nitration proceeds, a gradual change takes place in these fractions and at the end, the conditions are reversed so that the acid in the organic layer is represented by b'', well within the nitration zone whilst the acid layer analysis shows ~~14~~ b' to now lie outside the zone. It was shown in the previous set of distribution determinations that this end condition (with organic layer acid well within the dinitration zone), is quite general for acids lying near the limiting curve of dinitration; and the tie-lines obtained by the previous second set of distribution experiments lie in the same general direction as the tie-line b'bb''.

Since the acid fractions dissolved by the organic layer when nitration ceases, lie well within the dinitration area we would expect them to continue nitrating. It is easy enough to understand the inability of the organic-layer-acid a'' to perform nitration but WHY SHOULD AN ACID FRACTION, WHOSE COMPOSITION IS SIMILAR TO THAT OF AN INITIAL MIXED ACID HAVE LOST THIS POWER ?

FIG. X



]

Evidently there must be some essential difference between an organic layer acid fraction in "equilibrium" (from the point of view of distribution) with an acid layer acid, and an acid of similar composition which is not in "equilibrium" with a second layer. It may be, that in the organic layer acid fractions, the H_2SO_4 has been satisfied with M.N.B. instead of water.

If we denote M.N.B. by the symbol B, then in view of data for extraction of anhydrous sulphuric acid by B from sulphuric acid monohydrate, one might conceive reaction-equilibrium :-

$$H_2SO_4.H_2O + B \rightleftharpoons H_2SO_4.B + H_2O.$$

In "acid layer" this naturally mostly goes to the left hand side. But in the "organic layer" it would be pushed towards the right hand side, much more. Also, if there is any additional H_2SO_4 over and above the quantity equivalent to total H_2O, that additional H_2SO_4 will not be "anhydrous" but will form more $H_2SO_4.B$. Thus in the organic layer the H_2SO_4 would, ~~only~~ owing to its being a good deal used up to form $H_2SO_4.B$, not be available as a dehydrator; and the water present in the organic layer would be "free", or at least would be free to hydrate HNO_3 or whatever it does. This can account for Distribution Experiment 6, where a large excess of M.N.B. lowered the HNO_3/H_2SO_4 ratio in the organic layer. It probably did so by setting free water that had been hydrating H_2SO_4, (c.f. ϵ and ϵ'), and leaving it free to hydrate HNO_3, and hydrated HNO3 would naturally be less soluble in the organic layer than anhydrous HNO_3 would. Also in the nitrations, the "red line" acid very likely has its water at least as little united with H_2SO_4 molecules as in the "black-line" acids, if the H_2SO_4 is being more or less occupied in forming $H_2SO_4.B$.

These considerations are reasonably suggested by the experimental facts. To <u>prove</u> them will require a separate and detailed study of the system :-

H_2SO_4 - H_2O - M.N.B.

§ VI NITRATION OF MONONITROTOLUENE.

Using the method of nitration and analysis described in the work on nitrobenzene a few test nitrations were carried out using O - mononitrotoluene instead of mononitrobenzene. The duration of each nitration was two hours.

The velocity of nitration of O - nitrotoluene to 2 : 4 dinitrotoluene is greater than the corresponding change, M.N.B.⟶D.N.B., so that in 2 hours the waste acid produced is slightly more dilute than the corresponding 16 hour waste acid of the nitrobenzene system.
The following table shows the compositions of initial mixed acids and waste acids produced, after 2 hours :-
(In Molecular Percentages.)

TABLE VII

	Compn of Mixed Acid			Compn of Waste Acid.		
	H_2SO_4	HNO_3	H_2O	H_2SO_4	HNO_3	H_2O
1	13.96	69.39	16.65	14.18	43.37	42.45
2	0.00	80.91	19.09	0.00	72.66	27.34
3	21.63	59.48	18.89	21.64	33.59	44.77
4	46.82	31.49	21.69	47.10	0.25	52.65

The compositions of waste acids 1, 2, 3 and 4 have been plotted on triangular diagram, Fig. XI page 92, and the two hour limiting curve of dinitration for toluene marked, together with the limiting line of dinitration (16 - 24 hours) as determined for benzene. The curves marked in red are Saposchnikoff's isobars of pressure for the vapour pressure of ternary mixed acids(which are referred to in this thesis).

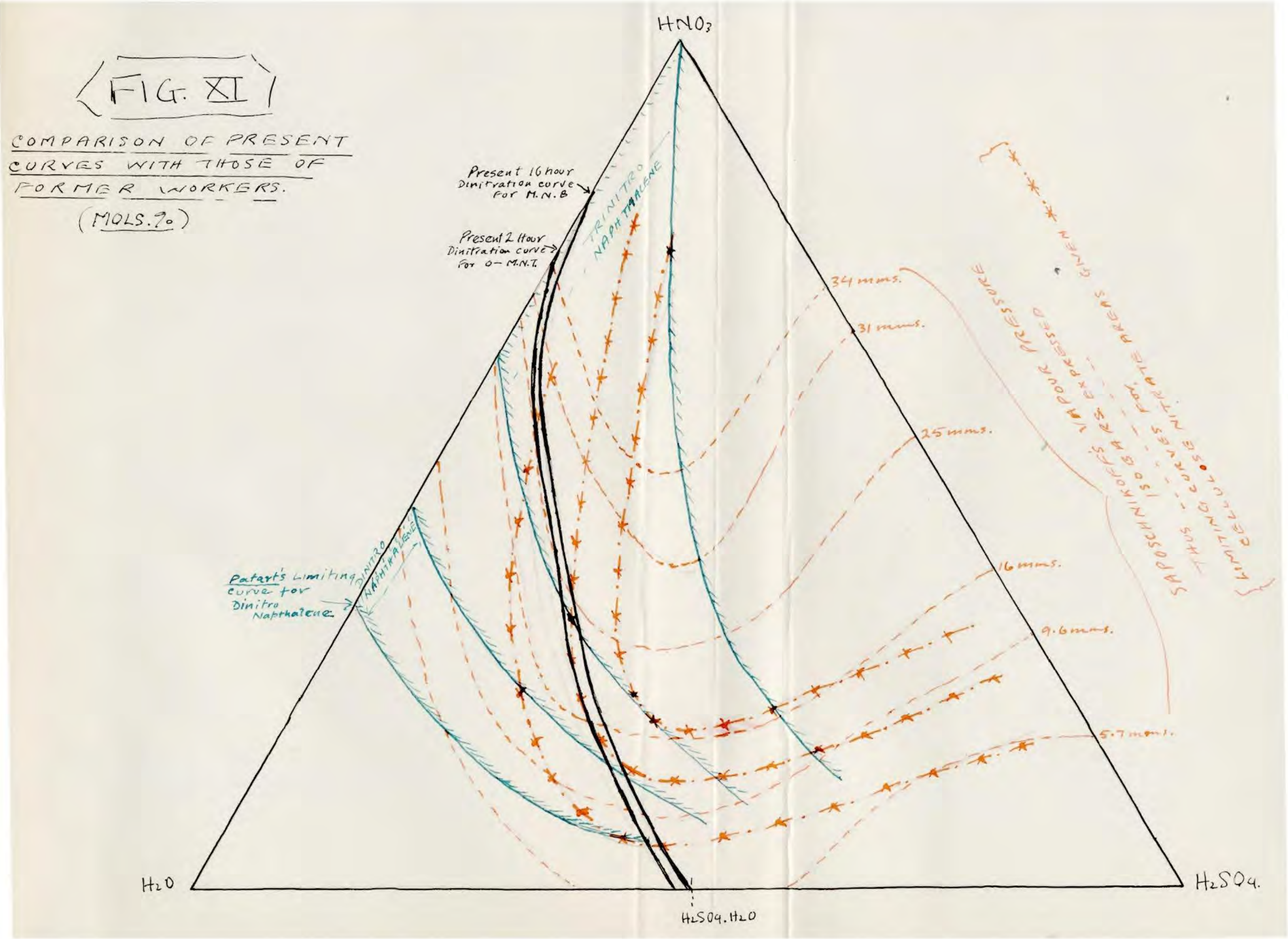
The general direction of the nitrotoluene curve is similar to that for nitrobenzene and there is again evidence that the curve cuts the base of the triangle at, or near, the point representing the composition of <u>sulphuric acid monohydrate</u>.

The two curves are shown in the triangular diagram Fig.XI page 92, and in the same diagram are marked A. A. Saposchnikoff's vapour pressure isobars for ternary acid mixtures, to which frequent reference has been made in the text.

FIG. XI

COMPARISON OF PRESENT CURVES WITH THOSE OF FORMER WORKERS.

(MOLS.%)



CONCLUSIONS.

The present work has been designed as an introduction into a systematic investigation of the process of nitration.

Much of the ground work has been cleared up and many important lines of investigation have been opened out for future study.

The chief factors affecting the process of nitration are :-

(a) Composition of nitrating acid; the effect of sulphuric acid in increasing the ability to nitrate and the effect of water in decreasing this ability, also the formation of sulphuric acid monohydrate in the nitrating acid.

(b) The relative quantities used. This effect is chiefly concerned with heterogeneity and the retarding of reaction velocity due to incomplete mixing.

(c) Distribution effects:- which are occasioned by the nitrating acid dividing into two fractions when two layers are produced during nitration.

A summary of the present work is given at the beginning of this thesis.

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DISTRIBUTION EXPERIMENTS. FIRST SET.

EXPERIMENTAL OBSERVATIONS. TABLE VIII

Experiment.		8	1	4	2	6	3	5	7	9	10
COMPN. OF INITIAL ACID in Wgts. %	H_2SO_4	50.67	50.42	50.42	53.92	63.31	63.31	28.45	18.44	0.0	0.0
	HNO_3	35.30	36.40	36.40	28.85	10.07	10.07	20.71	17.59	66.99	57.65
	H_2O	14.03	13.28	13.18	17.23	26.62	26.62	50.84	64.07	33.01	42.35
Grams of Acid Used.		100	100	100	100	100	100	89.5	100	142	165
Grams of Nitro Compd.		100	100	100 (MIXTURE)	100	300	100	89.5	100 (MIXTURE)	100	100
Temperature.		45°	20°	20°	20°	16°	20°	16°	16°	20°	20°
ACID LAYER. Wgt. of Acid Layer.		71.00	70.0	70.72	77.98	88.68	93.80	86.15	99.36	107.23	152.56
COMPN. OF ACID in Wgts. %	H_2SO_4	68.64	69.10	68.41	67.36	68.60	67.11	29.50	18.61	0.0	0
	HNO_3	9.56	9.77	10.26	9.35	1.69	4.00	18.14	16.95	59.6	54.05
	H_2O	21.80	21.13	21.33	23.25	29.71	28.89	52.36	64.44	40.4	45.95
Gms. of dissolved Org. Matter		0.8 D.N.B.	-	0.5	-	-	-	-	-	5.0	3.0
ORGANIC NITRO LAYER. Wgt. of Org. Layer.		128.43	130.0	129.13	121.60	310.71	105.80	91.97	100.74	134.35	112.00
Wgt. of Washing Water.		200	200	200	200	200	100	100	-	200	100
Yield of Washings.		229.65	229.56	230.0	222.7	211.18	106.4	103.21	-	240.57	115.27
Yield of Washed Nitro Compd.		99.90	100.08	98.04	99.0	299.46	99.7	88.76	-	94.92	96.55
Analysis of washings in weights %	H_2SO_4	0.86	0.79	0.83	0.61	1.29	0.30	.05	-	0.0	0.0
	HNO_3	11.44	11.40	11.70	9.25	3.62	5.58	3.20	-	12.84	10.67
	H_2O	87.70	87.81	87.47	90.14	95.09	94.12	96.75	-	87.16	89.33
Wgt. of Acids + Aq. dissolved in Organic Layer.		29.65	29.56	30.0	22.7	11.18	6.40	3.21	-	40.57	15.27
COMPN. OF DISSOLVED ACID in Wgts. %	H_2SO_4	6.66	6.13	6.36	5.99	24.38	4.99	1.50	-	0.0	0.0
	HNO_3	88.63	90.60	89.70	90.77	68.40	92.77	97.55	-	76.14	80.20
	H_2O	4.71	3.27	3.94	4.34	7.22	2.34	0.95	-	23.86	19.80

DISTRIBUTION EXPERIMENTS. FIRST SET.

COMPOSITIONS OF LAYERS BY WEIGHT. TABLE IX

Experiment.	8	1	4	2	6	3	5	7	9	10
PRESENT AT START.										
Gms. H_2SO_4	50.67	50.42	50.42	53.92	63.31	63.31	28.45	18.44	0.0	0.0
Gms. HNO_3	35.30	36.40	36.40	28.85	10.07	10.07	20.71	17.59	95.13	97.35
Grms. H_2O	14.03	13.18	13.18	17.23	26.62	26.62	50.84	64.07	46.85	67.65
Gms. Nitro Compd.	100	100	100	100	300	100	100	100	100	100
Total Initial Weight.	200	200	200	200	400	200	200	200	241.98	265
ACID LAYER (after distribution)										
Gms. H_2SO_4	48.74	48.38	48.39	52.52	60.97	62.95	28.40	18.60	0	0
Gms. HNO_3	6.79	6.84	7.25	7.32	1.50	3.75	17.46	16.85	63.90	82.45
Gms. H_2O	15.47	14.78	14.04	18.14	26.41	27.20	50.81	62.96	33.33	67.11
Gms. Nitro Compd.	0.8	0.0	1.04	-	-	-	-	-	5.0	3.0
Total weight of Acid Layer.	71.0	70	70.72	77.98	88.88	93.8	96.67	99.36	107.23	152.56
ORGANIC LAYER (after distribution)										
Gms. H_2SO_4	1.98	1.83	1.91	1.36	2.72	0.32	.05	0	0	0
Gms. HNO_3	26.28	26.17	26.91	20.60	7.65	5.94	3.20	1.59	30.90	12.30
Gms. H_2O	1.44	1.60	1.18	0.74	0.81	0.14	.03	0	8.53	3.15
Gms. Nitro Compd.	99.90	100.08	98.96	99.0	299.46	99.7	100.0	99.15	94.92	96.55
Total weight of Organic Layer.	128.43	130	129.13	121.60	310.71	105.8	103.28	100.74	134.35	112.0
PARTITION COEFF:-										
$K_{HNO_3} = [HNO_3]_{ORG} / (HNO_3)_{ACID}$	2.14	2.06	2.03	1.81	1.46	1.41	0.18	0.04	0.39	0.20

EXPERIMENTAL RESULTS.

DISTRIBUTION EXPERIMENTS. SECOND SET. TABLE X

Experiment.		α	β	γ	δ	ε	ε'	λ
COMPOSITION OF M/A in weights %	H_2SO_4	26.22	57.77	14.40	11.82	84.05	84.57	64.40
	HNO_3	68.35	37.15	80.00	82.48	0.00	0.00	31.32
	H_2O	5.43	5.08	5.60	5.70	15.95	15.43	4.28
Weight of M/A used.		110.12	161.90	72.17	131.25	116.00	12.38	127.64
Weight of M.N.B. used	I	146.62	117.30	112.30	211.23	130.58	Mixture 258.72	171.42
Extra M.N.B. added.	II	-	(329.31)	-	-	-	-	144.34
Aggregate initial weight.		256.74	608.51	184.47	342.48	246.58	271.10	443.40
SEPARATION.								
Weight of [illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Weight of Org. Layer.		217.61	485.30	170.86	328.78	125.58	260.06	342.36
Aggregate weight after separation.		255.64	607.50	183.82	342.48	246.58	271.10	443.40
Loss of weight.		1.10	1.01	0.65	0	0	0	0
ACID DILUTION AND ANALYSIS.								
Weight of Diluting Water		69.25	116.93	0.0	0.0	340.50	191.92	211.52
		Chiefly DNB.	D.N.B.			M.N.B.		D.N.B.
ACID CONSISTS OF:-	M.N.B. + D.N.B.	1.46	6.45	0	0	7.59	0.62	5.00
	Waste Acid.	36.77	115.75	12.96	13.70	113.41	10.42	96.04
	Water.	69.25	116.93	0.00	0.00	340.50	191.92	211.52
ANALYSIS OF ACID IN WGTS %	H_2SO_4	21.40	38.81	55.49	54.37	20.83	4.176	25.77
	HNO_3	6.34	2.092	21.26	22.99	0.00	0.000	0.486
	H_2O	72.26	59.098	23.25	22.64	79.17	95.824	73.744
	HNO_2 (Reckoned in HNO_3 figure	-	-	-	-	0	0	0.28

Two Stage Washings.

ORGANIC LAYER. FIRST WASHING ETC.		α	β	γ	δ	ε	ε'	λ
Weight of Wash Water.		131.46	151.30	132.44	212.27	74.64	166.11	240.74
Weight of Once Washed Nitro Compd.		155.46	470.70	116.20	215.05 +2.6	121.99	258.70	334.49
Weight of Washings.		192.53	165.62	186.40	325.32 -2.6	77.20	166.95	247.73
Aggregate Weight.		347.99	636.32	302.60	540.37	199.19	425.65	582.22
Loss in weight on separation for first wash		1.08	0.24	0.70	0.68	1.03	0.52	0.88
Washings consist of:-	Acid. by difference	61.07	14.32	53.96	2.6 gms DNB +110.45	2.56	0.84	6.99
	Water	188.36	151.30	132.44	212.27	74.64	166.11	240.74
Analysis of Washings in weights %	H_2SO_4	1.57	1.823	1.67	2.23	3.57	1.12	1.375
	HNO_3	21.43	6.48	24.81	29.08	0.00	0.00	1.435
	H_2O	77.00	91.697	73.52	68.69	96.43	98.88	99.190
	HNO_2 (Reckoned in HNO_3 figure)	-	-	0.13	0.146	0.0	0.0	-

ORGANIC LAYER. SECOND WASHIN ETC.		α	β	γ	δ	ε	ε'	λ
Weight of Wash Water.		56.90	153.07	47.96				
Weight of twice washed Nitro Compd.		155.35	469.51	114.74				
Weight of Washings		56.75	155.28	48.89				
Aggregate weight.		212.10	624.79	163.63				
Loss in weight on separtion.		0.26	-0.02	0.50				
Washings consist of :-	Acid.		155.28	0.97				
	Water.			47.96				
Analysis of Second Wshings weights %	H_2SO_4		0.078	0.01				
	HNO_3		0.075	1.14				
	H_2O		Rest	Rest				
	HNO_2 (Reckoned in HNO_3 figure)		-	-				
DENSITY OF NITRO PRODUCTS AT 15°c.		1.264	1.258	1.242	1.2355	1.209	1.258	1.2660

NITRATION M.N.B. → D.N.B.

QUANTITIES IN LAYERS (In Grams).

DISTRIBUTION EXPERIMENTS. SECOND SET. TABLE XI

Experiment.	α	β	γ	δ	ε	ε'	λ
TOTAL AMOUNTS USED.							
M/A used.	110.12	161.90	72.17	131.25	116.00	12.38	127.64
M.N.B. used.	146.62	$\left\{\begin{matrix}117.30\\+329.31\end{matrix}\right\}$	112.30	211.23	130.58	MIXT 258.72	$\left\{\begin{matrix}171.42\\+144.34\end{matrix}\right\}$
H_2SO_4 present at start.	28.86	93.53	10.40	15.52	97.53	10.47	82.20
HNO_3 " " "	75.27	60.15	57.74	108.20	0.00	0.00	39.97
H_2O " " "	5.99	8.22	4.03	7.53	18.47	1.91	5.47
Aggregate.	256.74	608.51	184.47	342.48	246.58	271.10	443.40
UPPER LAYERS.							
D.N.B. (by denisity)	39.76	109.70	18.48	28.06	0.0	60.30	86.10
M.N.B. (byvdifference)	115.59	361.00	96.26	189.59	121.99	198.40	248.39
H_2SO4 present.	3.92	3.15	3.12	7.86	2.793	1.863	3.36
HNO_3 "	53.46	10.87	46.98	94.05	0.0	0.0	3.51
H_2O present (by diff)	3.69	0.82	5.12	9.22	0	0.0	0.77
Total Acids + Aqua	61.07	14.84	55.22	111.13	2.79	1.86	7.87
M.N.B. + D.N.B.	155.35	470.70	114.74	217.65	121.99	258.70	334.49
Aggregate.	216.42	485.54	169.96	328.78	124.78	260.56	342.36
LOWER LAYER.		Chiefly DNB.			M.N.B.		D.N.B.
M.N.B. + D.N.B. present.	1.46	6.45	0	0	7.59	0.62	5.00
H_2SO_4 present	22.69	90.31	7.19	7.45	94.57	8.45	79.25
HNO_3 "	6.72	4.87	2.76	3.15	0.00	0.00	1.49
H_2O " (by diff)	7.36	20.57	3.01	3.10	18.84	1.97	15.30
Acids + Aq.	36.77	115.75	12.96	13.70	113.41	10.42	96.04
Aggregate.	38.23	122.20	12.96	13.70	121.00	11.04	101.04
Partition Coeff. $K_{HNO} = \frac{[HNO_3] org}{[HNO_3 acid}$	1.405	1.701	1.298	1.244	No Nitric present		1.21
TOTAL AGGREGATE AT END.	254.74	607.74	182.92	342.48	245.78	271.60	443.40
LOSS OF WEIGHT ON EXPERIMENT.	2.00	0.77	1.55	0.0	0.80	-0.50	0.0

NITRATION M.N.B. → D.N.B.

MOLECULAR QUANTITIES IN THE LAYERS.

DISTRIBUTION EXPERIMENTS. SECOND SET. TABLE XII

[illegible]	α	β	γ	δ	ε	ε′	λ
BEFORE NITRATION.							
Mols. M/A used.	1.8220	2.3650	1.2465	2.2944	2.0203	0.2128	1.7766
Mols. M.N.B. used.	1.1920	.9535	.9127	1.7180	1.0610	1.9728	1.3930
Mols H_2SO_4 at start.	.2943	.9535	.1060	.1582	.9943	.1067	.8382
Mols. HNO_3 " "	1.1950	.9550	.9167	1.7180	0.0000	0.0000	.6346
Mols. H_2O " "	.3327	.4565	.2238	.4182	1.0260	.1061	.3038
INITIAL AGGREGATE.	3.0140	3.3185	2.1592	4.0124	3.0813	2.1854	3.1696
AFTER NITRATION.							
Upper Layer.							
Mols. D. N. B.	.2366	.6530	.1100	.1670	0	.3588	.5124
Mols M. N. B.	.9397	.2576	.6509	1.5410	.9917	1.6140	.8455
Mols. H_2SO_4	.0400	.0321	.0318	.0801	.0285	.0190	.0343
" HNO_3	.8485	.1726	.7456	1.4930	0.0000	0.0000	.0557
" H_2O	.2049	.0455	.2844	.5120	0.0	0.0	.0122
Total Mols., Acid + Aq.	1.0934	0.2502	1.0618	2.0851	0.0285	0.0190	.1022
" " M.N.B. + D.N.B.	1.1763	.9106	.7609	1.7080	.9917	1.9728	1.3579
UPPER LAYER AGGREGATE.	2.2697	1.1608	1.8227	3.7931	1.0202	1.9918	1.4601
LOWER LAYER.							
Mols. Org. Compd.	.0087	.0384	0	0	.0452	-	.0298
" H_2SO_4	.2313	.9207	.0733	.0760	.9640	.0862	.8080
" HNO_3	.1067	.0073	.0438	.0500	0.0000	0.0000	0.0237
" H_2O	.4087	1.1430	.1672	.1722	1.0465	.1094	.8497
Mols Acid + Aq.	.7467	2.1410	.2843	.2982	2.0105	.1956	1.6814
LOWER LAYER AGGREGATE.	.7554	2.1794	.2843	.2982	2.0557	.1956	1.7112
TOTAL MOLS. AT END.	3.0251	3.3402	2.1070	4.0913	3.0759	2.1874	3.1713
NO. OF MOLS. LOST IN EXP.	-.0111	-.0217	.0522	-.0789	.0054	-.0020	-.0007

M.N.B. to D.N.B.

MOLECULAR COMPOSITIONS OF ACIDS IN BOTH LAYERS.
(at equilibrium)

DISTRIBUTION EXPERIMENTS. SECOND SET. TABLE XIII

Experiment.		α	β	γ	δ	ε	ε′	λ
UPPER LAYER								
Organic Layer. Mols.%	H_2SO_4	3.66	12.84	3.00	3.84	100	100	33.57
	HNO_3	77.60	69.00	70.25	71.60	0	0	54.51
	H_2O	18.74	18.16	26.75	24.56	0	0	11.92
LOWER LAYER.								
Acid Layer. Mols. %	H_2SO_4	30.98	43.00	25.78	25.49	47.95	44.07	48.06
	HNO_3	14.30	3.61	15.41	16.77	0.0	0.0	1.41
	H_2O	54.72	53.39	58.81	57.74	52.05	55.93	50.53
AGGREGATE W/A.								
(both layers together) Mols. %	H_2SO_4	14.71	38.94	7.81	6.55	48.68	49.02	47.23
	HNO_3	51.91	12.86	58.65	64.73	0.00	0.00	4.45
	H_2O	33.38	48.20	33.54	28.72	51.32	50.98	48.32

NITRATION OF M.N.B. to D.N.B.

EXPERIMENTAL READINGS.

FOR NITRATIONS (10 ------25) TABLE XIV

INDEX OF EXPERIMENT.		XX	23	10	22	19	21	18	X'	TEST (a)	TEST (b)	TEST (c)	25A	25B	24A	24B	20
COMPN of M/A in Wgts. per cent.	H_2SO_4	0.00	8.27	20.15	23.0	33.~~100~~ .88	34.22	48.31	53.92	54.41	54.41	54.41	61.34	61.34	66.69	66.69	69.98
	HNO_3	95.13	87.23	75.43	72.0	62.09	62.07	47.56	28.85	42.42	42.42	42.42	35.79	35.79	30.31	30.31	27.26
	H_2O	4.87	4.50	4.42	5.0	4.03	3.71	4.13	17.23	3.17	3.17	3.17	2.87	2.87	3.00	3.00	2.76
WGT. OF M/A used.		100.0	110.57	88.80	105.09	68.34	105.08	61.09	138.52	66.76	200.18	608.35	128.10	154.00	166.79	151.43	113.67
WGT. of MN.B used.		150.0	158.01	131.09	155.49 +74.28	120.06	160.37	121.80	143.58	138.55	417.18	1600.0	156.80 +286.71	506.90	456.65 +123.16	498.37	268.39
ccs. of M.N.B. required to be added to produce two layers.		only one phase	Only one phase.	45	50	23	30		Less than 10.	15.	45	145	22		27	24	16
Total Water added to Dilute the W/A		400.0	104.36	100.60	73.15	50.03	50.29	40.38	120.75	51.26	154.53	463.0	123.72	147.05	136.76	135.99	80.04
WGT. of ORGic. LAYER.		148.33	168.66	138.33	250.80	132.89	188.04	134.46	145.68	152.32	459.20	1739.0	471.80	533.43	489.90 +123.16	530.00	288.68
WGT. of ACID LAYER (+Diluting Water)		500.63	203.32	177.29	156.10	104.42	126.58	87.38	256.10	103.10	310.70	931.4	222.90	272.40	266.87	254.00	172.10
COMPOSITION OF DILUTE W/A. in grams.	ACID	100.63	98.96	76.69	82.95	54.39	76.29	47.00	135.35	51.84	156.37	468.0	99.18	125.3	130.11	118.0	92.06
	EXTRA WATER	400.00	104.36	100.60	73.15	50.03	50.29	40.38	120.75	51.26	154.33	463.0	123.72	147.1	136.76	136.0	80.04
COMPOSITION OF DIL. W/A. in Wgts. per cent.	H_2SO_4	0.00	4.31	9.63	14.19	22.24	28.28	33.39	29.02	34.87	34.83	35.12	35.21	34.47	41.36	39.73	45.86
	HNO_3	18.79	40.32	29.89	34.45	25.19	25.59	13.08	14.37	8.73	8.66	8.11	2.85	6.43	1.18	0.46	0.337
	H_2O	81.21	55.37	60.48	51.36	52.57	46.13	53.53	56.61	56.40	56.51	56.77	61.94	59.10	57.56	59.81	53.803
% HNO_2 by Wgt., in the diluted W/A		---	0.35	0.12	0.1	very small	< 0.3	very small	< 0.4	0.48	0.48	0.52	0.4	0.4	0.50	0.64	0.5
DENSITY $\triangle_{15^\circ}$ OF NITRO PRODUCT		1.2104	1.2383	1.2564	1.2390	1.2696	1.2444	1.2770 ~~1.2106~~	1.2106	1.275	1.2749	1.264	1.2543	1.2435	1.251	1.256	1.2449
COMPN of NITRO PRODUCT	D.N.B. (By density)	1.5	24.03	31.27	36.80	37.70	58.60	42.47	< 1.0	47.54	143.4	452.7	102.6	89.64	124.2	119.1	81.47
	M.N.B. (By differences)	146.83	144.63	107.06	214.00	95.19	129.44	91.99	> 144.7	104.78	315.8	1286.3	369.2	443.79	488.86	410.9	207.21
TOTAL WGT. BEFORE NITRATION.		650.0	372.94	320.49	408.01	238.43	315.74	223.27	402.85	256.57	772.89	2671.4	695.33	808.0	883.36	785.79	462.10
TOTAL WGT. AFTER NITRATION.		648.96	371.98	315.62	406.90	237.31	314.62	221.84	401.78	255.42	769.90	2670.4	694.70	805.8	879.93	784.00	460.78

NITRATION OF M.N.B. TO D.N.B.

ACTUAL WEIGHTS OF COMPONENTS

BEFORE AND AFTER NITRATION

(10 --------- 25) TABLE XV

INDEX OF EXPERIMENT.	XX	23	10	22	19	21	18	X'	TEST (a)	TEST (b)	TEST (c)	25A
BEFORE NITRATION												
Gms. H_2SO_4	0.00	9.15	17.89	24.17	23.15	35.96	29.51	74.72	36.32	108.90	331.10	78.58
Gms. HNO_3	95.13	96.43	66.99	75.67	42.43	65.23	29.05	39.97	28.32	84.91	258.10	45.84
Gms. H_2O	4.87	4.98	3.92	5.26	2.75	3.90	2.52	23.87	2.12	6.35	19.29	3.68
Gms. M.N.B.	150.00	158.01	131.09	229.77	120.06	160.37	121.80	143.58	138.55	417.18	1600.00	443.51
Aggregate Wgt. Before Nitration.	250.00	268.57	219.89	334.87	188.39	265.36	182.88	282.14	205.31	617.34	2208.49	571.61
AFTER NITRATION.												
Gms. H_2SO_4	0.00	8.76	17.08	22.15	23.22	35.79	29.18	74.32	35.95	108.30	327.10	78.48
Gms. HNO_3	94.07	81.96	52.99	53.78	26.30	32.39	11.40	36.63	9.00	26.91	75.54	6.35
Gms. H_2O	6.56	8.24	6.62	7.02	4.83	8.11	6.42	24.40	6.81	21.16	65.36	14.35
Gms. M.N.B.	146.83	144.63	107.06	214.00	95.19	129.44	91.99	144.70	104.78	315.80	1286.30	369.20
Gms. D.N.B	1.50	24.03	31.27	36.80	37.70	58.60	42.47	1.00	47.54	143.40	452.70	102.60
Aggregate Wgt. after Nitration.	248.96	267.62	215.02	333.75	187.24	264.33	181.46	281.05	204.08	615.57	2207.00	570.98
Change in weight of $H_2SO_4 + HNO_3 + H_2O$	+ 0.63	-11.60	-12.11	-22.14	-13.99	-28.79	-14.09	-3.17	-15.00	-43.81	-140.35	-28.92
Change in weight of organic substance.	-1.67	+10.65	+7.24	+ 21.03	+12.83	+27.67	+12.66	+2.12	+13.77	+42.02	+139.00	+28.29
Aggregate change in weight.	-1.04	-0.95	-4.87	-1.11	-1.16	-1.12	-1.43	-1.05	-1.23	-1.79	-1.35	-0.63

NITRATION OF M.N.B. to D.N.B.

TABLE SHOWING GRAM - MOLECULES PRESENT BEFORE AND AFTER NITRATION

(10 ---------25) TABLE XVI

INDEX OF EXPERIMENT.	XX	23	10	22	19	21	18	X'	TEST (a)	TEST (b)	TEST (c)	25A	25B	24A	24B	20
BEFORE NITRATION.																
Mols. H_2SO_4	0.0	0.09329	0.18240	0.24640	0.23600	0.36660	0.30085	0.76170	0.37030	1.11050	3.37550	0.80120	0.96330	1.13450	1.03000	0.81110
" HNO_3	1.51000	1.53100	1.06350	1.20100	0.67360	1.03550	0.46110	0.63460	0.44960	1.34800	4.09700	0.72790	0.87500	.80240	0.72850	0.49180
" H_2O	0.27020	0.27630	0.21750	0.29220	0.15260	0.21640	0.13980	1.32500	0.11760	0.35240	1.07000	0.20420	0.24520	.27530	6.25245	0.17425
" M.N.B.	1.21900	1.28400	1.06500	1.86700	0.97570	1.30300	0.98970	1.16700	1.12600	3.39000	13.00400	3.60400	4.12000	4.71200	4.05000	2.18100
AGGREGATE...............	2.99920	3.18459	2.52840	3.60660	2.03790	2.92150	1.89145	3.88300	2.06350	6.20090	21.54650	5.33730	6.20350	6.92420	6.06095	3.65815
AFTER NITRATION.																
Mols. H_2SO_4	0.0	0.08930	0.17414	0.22585	0.23675	0.36490	0.29750	0.75770	0.36650	1.10400	3.33500	0.80000	0.95750	1.12550	1.02850	0.80460
" HNO_3	1.49300	1.30100	0.84120	0.85380	0.41760	0.51410	0.18100	0.58160	0.14290	0.42730	1.19900	0.10085	0.27810	0.05000	0.01857	0.00921
" H_2O	0.36400	0.45720	0.36730.	0.38950	0.26800	0.45000	0.35625	1.35400	0.37790	1.17400	3.62700	0.79640	0.77040	0.91900	0.88390	0.69700
" M.N.B.	1.19350	1.17500	0.87000	1.73940	0.77360	1.05200	0.74750	1.17600	0.85140	2.56650	10.45500	3.00000	3.60700	3.97300	3.33900	1.68400
" D.N.B.	0.00892	0.14300	0.18610	0.21900	0.22430	0.34860	0.25270	0.00595	0.28290	0.85320	2.69300	0.61040	0.53340	0.73900	0.70870	0.48480
AGGREGATE.............	3.05942	3.16550	2.43874	3.42755	1.92025	2.72960	1.83495	3.87525	2.02160	6.12500	21.30900	5.30765	6.14640	6.80650	5.97867	3.67961
MOLS.																
Initial-final H_2SO_4	--	-.004	-.008	-.020	± 0	-.002	-.003	)-.004	-.004	±0	-.040	-.001	-.006	-.009	-.001	-.006
Loss of HNO_3	0.017	.230	.222	.347	.256	.521	.280	.053	.307	.921	2.898	.627	.597	.752	.710	.483
Gain of H_2O (gain)	.094	.181	+.150	.097	.115	.234	.216	.029	.260	.822	2.557	.592	.525	.644	.631	.523
Loss of MNB	.026	.109	.195	.128	.201	.251	.242	+.009	.375	.824	2.549	.604	.513	.739	.711	.497
Gain of DNB (gain)	+.009	+.143	+.186	.219	.224	.349	.253	.006	.283	.853	2.693	.610	.533	.739	.709	.485
Excess MNB, un-nitrated, added.	1.20	1.14	.88	1.64	.75	0.95	.74	1.16	.84	2.54	10.3	3.0	3.7	4.0	3.3	1.7
Approx.mols. MNB added before 2nd layer came.	>all(1.22)	>all(1.28)	.45	.5	.23	.30		<.1	.15	.45	1.45	.22		.27	.24	.16
∴ excess mols.MNB put in after 2nd layer came	--	~~99~~	.61	1.37	.74	1.0	.98	1.1	0.97	5.75	11.65	3.38		4.44	3.81	2.02

about here, nitration begins to be a 2-layer process. Hitherto the second layer has been the essentially superfluous, un-nitratable, MNB added.

NITRATION OF M.N.B. TO D.N.B.

PERCENTAGE (MOLECULAR) COMPOSITION OF ACIDS.
BEFORE AND AFTER NITRATION (10 ......25)

TABLE XVII

INDEX OF EXPERIMENTS.	XX	23	10	22	19	21	18	X'	TEST (a)	TEST (b)	TEST (c)	25A	25B	24A	24B	20
BEFORE NITRATION																
Total Mols. of Acid present.	1.78020	1.90059	1.46340	1.73960	1.06220	1.61850	0.90175	2.72130	0.93750	2.81090	8.54250	1.73330	2.08350	2.21220	2.01095	1.47715
COMP^{N} of M/A IN MOLECULAR %s.																
H_2SO_4	--	4.91	12.46	14.17	22.22	22.65	33.37	27.99	39.51	39.51	39.51	46.22	46.23	51.28	51.21	54.90
HNO_3	84.82	80.56	72.67	69.05	63.41	63.97	51.14	23.32	47.95	47.95	47.95	41.99	41.99	36.28	36.24	33.29
H_2O	15.18	14.53	14.86	16.78	14.36	13.37	15.50	48.69	12.54	12.54	12.54	11.78	11.77	12.44	12.55	11.80
AFTER NITRATION																
Total Mols. of Acid Present.	1.85700	1.84750	1.38264	1.46915	0.92235	1.32900	0.83475	2.69330	0.88730	2.70530	8.16100	1.69725	2.00600	2.09450	1.93097	1.51081
COMP^{N} of W/A IN MOLECULAR %s																
H_2SO_4	0	4.83	12.59	15.37	25.67	27.45	35.64	28.13	41.30	40.80	40.87	47.12	47.72	53.62	53.25	53.24
HNO_3	80.40	70.40	60.84	58.10	45.28	38.67	21.68	21.59	16.10	15.79	14.69	5.94	13.86	2.39	0.96	0.61
H_2O	19.6	24.77	26.57	26.53	29.05	33.85	42.68	50.27	42.60	43.39	44.44	46.91	38.40	43.99	45.79	46.12
	One layer only. →|															
Mols. M.N.B.+D.N.B per 100 mols.W/A.	64.75	71.34	76.39	133.30	107.1	105.4	119.8_2	43.90	127.8_4	126.4_2	161.1_3	212.75	206.4	225.0	209.6_5	143.5_2
Ratio $\frac{HNO_3}{H_2O}$ after deducting $1H_2O$ per $1H_2SO_4$	4.1_0	3.5_3	4.35	5.20	13.39	6.04	3.08	0.98	12.38	6.10	4.11	--	--	--	--	--
Change in H_2SO_4% by analysis [Theory = 0]	--	--.08	+.13	+1.20	+3.45	+4.80	+2.27	+ 0.14	+1.79	+1.29	+1.36	+0.90	+1.49	+2.34	+2.04	-1.66

M.N.B. → D.N.B.

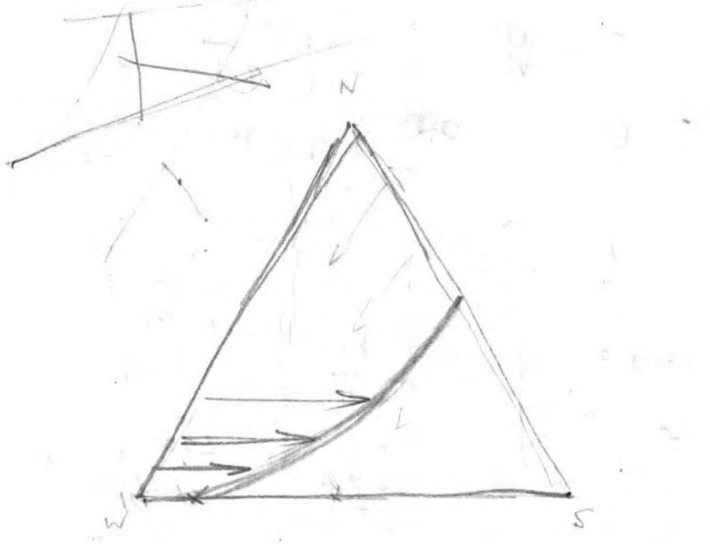
EXPERIMENTAL RESULTS FROM SERIES OF TEST NITRATIONS (I---XX) TABLE XVIII

Experiment		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XII	XIV	XV	XVI	XVII	XVIII	XIX	XX	50
Compn. of M/A Wgt. %	H_2SO_4	57.44	57.44	57.44	57.44	57.44	23.20	23.20	64.70	64.70	64.70	43.74	43.74	43.74	13.27	13.27	23.20	23.20	38.00	38.00	80.3	0.00
	HNO_3	38.31	38.31	38.31	38.31	38.31	72.21	72.21	31.12	31.12	31.12	52.30	52.30	52.30	81.68	81.68	72.21	72.21	57.24	57.24	15.4	95.30
	H_2O	4.25	4.25	4.25	4.25	4.25	4.59	4.59	4.18	4.18	4.18	3.96	3.96	3.96	5.05	5.05	4.59	4.59	4.76	4.76	4.3	4.70
Wgt. of M/A used.		154.63	81.04	115.43	118.78	89.76	103.71	100.84	90.29	87.08	87.90	68.75	67.77	84.22	56.16	88.50	61.38	103.23	120.58	120.54	115.13	87.03
Wgt. of M.N.B. used. (I)		115.57	242.43	86.25	88.99	164.45	46.13	41.10	54.91	155.14	168.40	168.16	69.14	86.04	122.15	46.82	259.69	336.64	135.15	136.26	34.62	157.39
" " " " (II)		135.74	0.00	114.26	186.47	50.54	127.99	115.27	213.80	56.47	45.33	=	90.66	148.51	-	167.89	-	-	252.20	395.44	-	-
Wgt. of Diluting Water.		448.50	382.37	421.93	334.54	417.87	424.26	450.49	365.54	468.82	383.59	389.24	377.32	462.91	375.98	480.38	435.53	405.01	490.77	489.75	-	392.29
Aggregate.		854.44	705.84	737.87	728.78	722.62	702.09	707.70	724.54	767.51	685.22	626.15	604.89	781.68	554.29	783.59	756.60	844.88	998.70	1141.99	-	636.71
No. of ccs. M.N.B. added to produce 2 layers.		30	16	20	ALWAYS TWO LAYERS.	—	40	37	16	16	15	18	16	18	45	ONE LAYER.	27	43	30.5	30.5	22.84 grams	ALWAYS ONE LAYER
SEPARTION.																						
Wgt. of Org. Layer.		279.63	256.36	224.40	297.89	233.69	186.04	169.92	287.84	229.26	229.60	177.95	170.78	251.02	125.16	224.30	266.14	346.69	408.73	555.34	-	156.80
Wgt. of Acid Layer.		574.49	449.02	513.20	430.47	488.67	516.31	537.51	436.51	537.79	455.41	447.84	433.66	530.27	428.80	558.60	490.16	497.99	589.17	584.80	-	479.45
Aggregate.		854.12	705.38	737.60	728.36	722.36	702.35	707.43	724.35	767.03	685.01	625.79	604.44	781.29	553.96	782.90	756.30	844.68	997.90	1140.14	-	636.25
Loss of Wgt. on experiment.		0.32	0.46	0.27	0.42	0.22	- 0.26	0.27	0.19	0.48	0.21	0.36	0.45	0.39	0.33	0.69	0.30	0.20	0.80	1.85	-	0.46
Compn. of Dil. W/A in Wgt. %	H_2SO_4	15.52	10.42	12.975	15.90	10.634	4.63	4.38	13.420	10.485	12.493	6.75	6.841	6.931	1.666	2.036	2.879	4.75	7.94	8.00	-	0.00
	HNO_3	3.25	2.37	1.927	3.06	1.471	10.86	9.55	0.344	0.341	1.076	4.67	4.379	3.710	9.330	10.160	7.118	11.61	6.20	5.57	0.0	16.81
	H_2O	81.23	87.21	85.098	81.04	87.895	84.51	86.07	86.236	89.174	86.431	88.58	88.780	89.359	89.004	87.804	90.003	83.64	85.86	86.43	-	83.19
Density of Nitro Product at 15°c.		1.2920	1.2534	1.2967	1.2700	1.2735	1.2646	1.2773	1.2605	1.2704	1.2635	1.2550	1.2626	1.2634	1.2340	1.2472	1.2260	1.2330	1.2527	1.2440	Solid D.N.B.	1.2145
REMARKS.		2 Hrs.	2 Hrs.	8 Hrs.	2 Hrs. —3 Hrs. Reverse addition:- M/A to M.N.B.	16 Hrs.	2 Hrs.	23 Hrs	2 Hrs.	16 Hrs.	2 Hrs	/	/	/	–	/	–	6 Hrs	16 Hrs.	"70" Hrs.	1 hour	19 Hrs.

WEIGHTS OF CONSTITUENTS IN SERIES OF TEST NITRATIONS (I --- XX) TABLE XIX

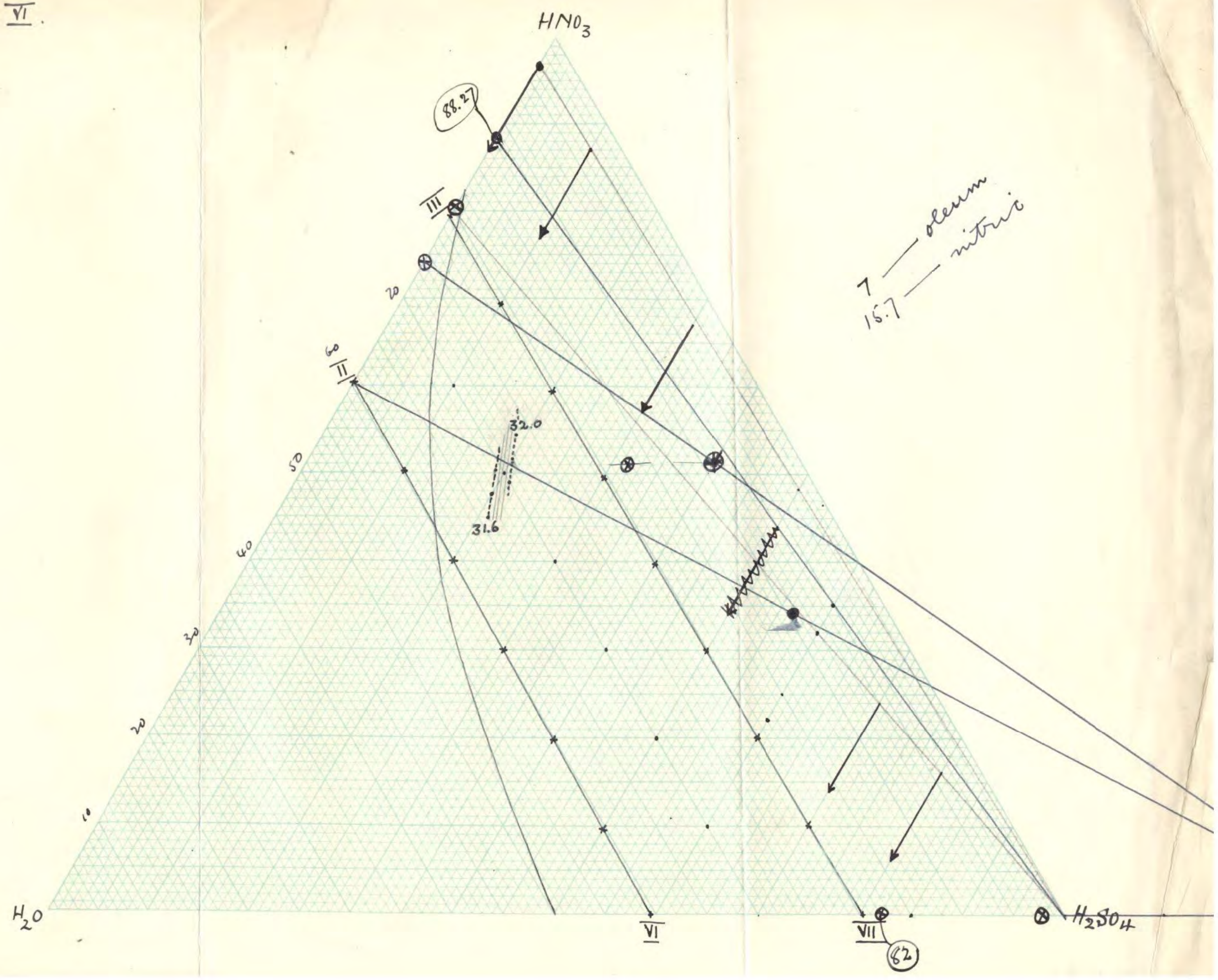
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	50
AT START.																					
Gms. H_2SO_4	88.73	46.54	66.32	68.23	51.56	24.05	23.39	58.42	56.34	56.88	30.08	29.65	36.84	7.457	11.74	14.24	23.95	45.82	45.82	-	0.00
Gms. HNO_3	59.24	31.04	44.23	45.51	34.39	74.86	72.80	28.10	27.10	27.36	35.96	35.45	44.04	45.870	72.28	44.33	74.54	69.04	69.04	-	82.91
Gms. H_2O (in M/A)	6.66	3.46	4.88	5.04	3.81	4.80	4.65	3.77	3.64	3.66	2.71	2.67	3.34	2.833	4.48	2.81	4.74	5.72	5.72	-	4.12
" M.N.B. (I)	115.57	242.43	86.25	88.99	164.45	46.13	41.10	54.91	(155.14	213.73	168.16	69.14	86.04	122.15	46.82	259.69	336.64	135.15	136.26	-	157.39
(" M.N.B. (II))	135.74	0.00	114.26	186.47	50.54	127.99	115.27	213.80	56.47)	-	-	90.66	148.51	-	167.89	-	-	252.20	395.44	-	-
(" H_2O (for dilution))	448.50	382.37	421.93	334.54	417.87	424.26	450.49	365.54	468.82	388.59	389.24	377.32	462.91	375.98	480.38	435.53	405.01	490.77	489.75	-	392.29
Aggregate Wgt.	854.44	705.84	737.87	728.78	722.62	702.09	707.70	724.54	767.51	685.22	625.15	604.89	781.68	554.29	783.59	756.70	844.88	998.70	1141.99	-	636.71
AT END.																					
Gms. H_2SO_4	89.16	46.77	66.60	68.44	51.96	23.91	23.54	58.57	56.38	56.89	30.23	29.65	36.75	7.144	11.38	14.15	23.66	46.77	46.79	-	0.00
Gms. HNO_3	18.67	10.64	9.89	13.17	7.19	56.08	51.34	1.503	1.834	4.90	20.92	18.99	19.67	40.000	56.78	34.99	57.83	36.52	32.58	-	80.60
Gms. H_2O (in W/A)	18.16	9.24	14.78	14.32	11.65	12.06	12.14	10.887	10.756	10.03	7.35	7.70	10.94	5.676	10.06	5.49	11.49	15.11	15.68	-	4.78
" H_2O (additional)	448.50	382.37	421.93	334.54	417.87	424.26	450.49	365.54	468.82	388.59	389.24	377.32	462.91	375.98	480.38	435.53	405.01	490.77	489.75	-	392.29
Gms. M.N.B.	173.73	201.85	135.2	212.79	163.18	137.19	116.06	217.60	163.28	170.32	138.69	127.45	186.49	109.98	182.96	244.16	306.26	322.86	67.20 +Rest	-	153.03
Gms. D.N.B.	105.90	54.51	89.20	85.10	70.51	48.85	53.86	70.25	65.98	59.28	39.26	43.33	64.53	15.18	41.34	21.98	40.43	85.87	92.70	-	5.80
Aggregate Wgt.	854.12	705.38	737.60	728.36	722.36	702.35	707.43	724.35	767.03	685.01	625.79	604.44	781.29	553.96	782.90	756.40	844.68	997.90	1140.14	-	636.50

EXPERIMENT	I	2	III	IV	V	VI	VII	VIII												
AT START. Mols. H_2SO_4	.9045	.4746	.6762	.6956	.5256	.2451	.2385	.5956	.5744	.5798	.3066	.3023	.3756	.0760	.1197	.1452	.2441	.4672	.4672		0.00
" HNO_3	.9404	.4928	.7021	.7225	.5457	1.1885	1.1555	.4461	.4302	.4343	.5708	.5628	.6992	.7284	1.1475	.7037	1.1830	1.0955	1.0955		1.3165
" H_2O	.3696	.1920	.2708	.2796	.2114	.2663	.2581	.2092	.2020	.2031	.1504	.1481	.1853	..1572	.2486	.1555	.2630	.3177	.3177		.2286
Aggregate Mols. Acid.	2.2145	1.1594	1.6491	1.6977	1.2827	1.6999	1.6521	1.2509	1.2066	1.2172	1.0278	1.0132	1.2601	0.9616	1.5158	1.0044	1.6901	1.8804	1.8804		1.5451
Mols. M.N.B. (I)	.9395	1.9700	.7012	.7233	1.3365	.3750	.3341	.4464	1.2610	1.7377	1.3670	.5620	.6994	.9930	.3805	2.1110	2.7360	1.0980	1.1080		1.2793
" M.N.B. (II)	1.1030	0.0000	.9288	1.5158	.4108	1.0405	.9370	1.7380	.4590	-	-	.7368	1.2075	-	1.3650	-	-	2.0500	3.2140	(1 MOL M.N.B taken, per MOL. HNO_3 in M/A. No HNO_3 present in W/A at end of one hour. W/A. Compn calculated on 0.0% HNO_3.)	-
Aggregate Mols. at start.	4.2570	3.1294	3.2791	3.9368	3.0300	3.1151	2.9232	3.4353	2.9266	2.9549	2.3948	2.3120	3.1670	1.9546	3.2613	3.1154	4.4261	5.0284	6.2024		2.8244
Time. Hours -------	2	2	8	2	16	2	23	2	16	2	2	2	16	2	18	2	6	16	70		19
AT END. Mols. H_2SO_4	.9090	.4769	.6790	.6979	.5297	.2438	.2400	.5971	.5748	.5800	.3081	.3023	.3747	.0728	.1160	.1443	.2412	.4769	.4770		0.0000
" HNO_3	.2964	.1689	.1570	.2091	.1141	.8903	.8149	.0239	.0291	.0778	.3320	.3015	.3123	.6350	0.9015	.5554	.9180	.5798	.5171		1.2793
" H_2O.	1.0080	.5127	.8202	.7944	.6466	.6692	.6736	.6041	.5969	.5564	.4078	.4273	.6071	.3150	.5581	.3047	.6376	.8391	.8708		.2653
Aggregate Mols. Acid.	2.2134	1.1585	1.6562	1.7014	1.2904	1.8033	1.7285	1.2251	1.2008	1.2142	1.0479	1.0311	1.2941	1.0228	1.5756	1.0044	1.7968	1.8958	1.8649		1.5446
Mols. M.N.B.	1.4100	1.6410	1.0980	1.7300	1.3265	1.1150	.9435	1.7670	1.3273	1.3850	1.1280	1.0370	1.5160	.8942	1.4870	1.9840	2.4890	2.6250	3.7600		1.2440
" D.N.B.	0.6305	.3245	.5308	.5064	.4197	.2907	.3206	.4180	.3926	.3528	.2336	.2579	.3841	.0903	.2460	.1308	.2406	.5111	.5516		.0345
Aggregate Mols. at end.	4.2539	3.1235	3.2840	3.9378	3.0366	3.2090	2.9926	3.4101	2.9207	2.9520	2.4095	2.3260	3.1942	2.0073	3.3086	2.1192	4.5264	5.0319	6.1765		2.8231
Total Mols. lost in experiment.	+.0031	+.0059	-.0049	-.0010	-.0066	-.0939	-.0694	+.0252	+.0059	+.0029	-.0147	-.0140	-.0272	-.0527	-.0473	-.0082	-.1003	-.0035	+.0259		+.0013
COMPN. OF M/A in Mols. % H_2SO_4	40.84	40.84	40.84	40.84	40.84	14.44	14.44	47.61	47.61	47.61	29.81	29.81	29.81	7.90	7.90	14.44	14.44	24.83	24.83	62.9	0.00
HNO_3	42.46	42.46	42.46	42.46	42.46	69.95	59.95	35.57	35.57	35.57	55.49	55.49	55.49	75.74	75.74	69.95	69.95	58.24	58.24	18.8	83.27
H_2O	16.70	16.70	16.70	16.70	16.70	15.61	15.61	16.82	16.82	16.82	14.70	14.70	14.70	16.36	16.36	15.61	15.61	16.93	16.93	18.3	16.73
COMPN. OF W/A in Mols. % H_2SO_4	41.07	41.17	41.00	41.03	41.06	13.52	13.88	48.76	47.87	47.77	29.90	29.84	28.95	7.12	7.36	14.37	13.42	25.14	25.57	62.9	0,00
HNO_3	13.39	14.58	9.48	12.29	8.84	49.38	47.16	1.95	2.42	6.41	32.27	29.76	24.14	62,08	57.20	55.30	51.07	30.55	27.73	0.0	82.84
H_2O	45.54	44.25	49.52	46.68	50.10	37.10	38.96	49.29	49.71	45.82	37.83	40.40	46.91	30.80	35.44	30.33	35.51	44.31	46.70	37.1	17.16
Mols. M.N.B required to produce 2 layers.	.2947	.1572	.1964	TWO LAYERS	.1530	.3930	.3635	.1572	.1572	.1475	.1768	.1572	.1768	.4421	ONE LAYER	.2653	.4225	.2928	.2928	.1857	ONE LAYER
Mols. M.N.B. disappearing in nitration.	.6325	.3290	.5320	.5091	.4208	.3005	.3276	.4074	.3927	.3527	.2390	.2618	.3909	.0988	.2585	.1270	.2471	.5230	.5620	.2814	.0353
Mols. M.N.B. (I) taken, per Mol. HNO_3	.999	4.00	.999	1.001	2.450	0.3155	0.2892	1.000	2.932	4.002	2.395	0.999	1.000	1.364	0.3316	3.000	2.313	1.0003	1.0100	1.000	0.972
Mols. M.N.B. for 2 layers, per 100 orig. Mols. HNO_3	31.4	31.9	28.0	-	28.1	33.0	31.4	35.2	36.5	34.0	31.0	28.0	25.3	60.7	∞	37.7	35.7	26.77	26.77	66.0	∞



limiting line of denitration dividing the triangular diagram ~~[illegible] of the~~ the ternary acid mixtures into 2 zones such that all acids within a limited specified area are capable of denitration whereas acids represented by points outside the area cannot denitrate mononitro

Fig. VI.



7 — oleum
15.7 — nitric