CATALYSIS in the NITRATION of TOLUENE to T.N.T. with APPLICATION of PHYSICAL METHODS to the SEPARATION of the FINAL NITROBODIES.

Thesis for the Degree of
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by

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CHAPTER 1.

HISTORICAL

The production of aliphatic nitrocompounds had been accomplished many years before Mitscherlich isolated nitrocompounds from the action of fuming nitric acid on benzene and toluene. The commercial value of the nitro-aromatics appears to have been appreciated, for the French chemist Collas (Thorpe 1, 576) records the industrial preparation of nitro-benzene (called Essence of Mirbane) for use as a perfume in soaps. It will be recalled that legislation had later to be applied against its use as an almond flavouring in foodstuffs when its poisonous nature was realised. The technical importance of nitrobenzene grew rapidly and during the years 1847 till 1908 patents were granted regarding its manufacture (Chem. Trades. J. 1906. 39. 3859).

Again although the first use of inorganic nitrates in explosives is probably lost in antiquity, it was not until 1845 that the explosive qualities of nitrocompounds were appreciated. In that year Schönbein (Thorpe 4. Vol) and Böttger (ibid) independently found that cellulose on nitration yielded an explosive. It remained for Vieille to gelatinise the material with soluble nitro-cotton and ether-alcohol to give the germ which has grown to the present day propellant industry. To this discovery can be traced the origin of artificial silk and cellulose lacquers etc. (Chardonnet Fr. Pat. 165,345. 1884). The vigour with which Nobel (B.Ps. 2,359. 1863; 1,813. 1864; 1, 345. 1867; 442. 1869; 1,570. 1873) pursued Sobrero's discovery in 1847 of nitroglycerine resulted in the commercial success of Dynamite, Gelignite and finally cordite.

Hausserman isolated picric acid as a product of the reaction of indigo with nitric acid, and Welter (A. chem. phys. 1795. 29. 301) obtained it in the same way from natural silk. Neither of these workers appears to have established the composition of the compound they had prepared and its explosive possibilities were not considered. Even when it was shown that it could easily be produced from phenol (Laurent, A. 1834. 43,

219) no immediate commercial application was found. When Sprengel in 1871 (B.Ps. 921 and 2642; J.C.S. 1873, 796) showed that it could be easily detonated by mercury fulminate its industrial application was assured, and patents were granted for its use as a military explosive (Turpin, B.P. 15,089. 1885; Fr. P. 167,512. 1885; Ger. P. 38,734. 1886). At the outbreak of war in 1914 it was the British service explosive under the name of Lyddite after the town where it was first manufactured; the French and Italians called it Melinite.

T.N.T. was synthesised in 1863 by Wilbrand (Ann. 1863, <u>128</u>, 178) and although its value as an explosive was appreciated at once its production was looked upon with some trepidation because of the difficulty of its synthesis compared with that of picric acid. The contact process for sulphuric acid (Badische Anilin and Sodafabrik, Ber. 1901, <u>34</u>, 4069) made pure concentrated acid and Oleum truly industrial products. The work of Haber (Z. Electrochemie. 1903, <u>9</u>, 381; 1910, <u>16</u>, 244; 1915, <u>21</u>, 191) Frank and Caro (Zeit.angew.Chem. 1906, <u>19</u>, 835; 1909, <u>22</u>, 1178) and Birkeland and Eyde (Met. Chem.Eng. 1912, <u>10</u>, 617; J.Ind.Eng.Chem. 1912, <u>4</u>, 771) on the manufacture of nitric acid from the atmosphere, made available a source of combined nitrogen hitherto thought impossible, and destroyed the last impediment to commercial T.N.T.

The Germans adopted T.N.T. as a shell filler in 1902 (Marshall's Explosives 1, 265) and had used this explosive under service conditions for some time before the outbreak of the "Great War". In 1914 it was being manufactured in Britain on a batch scale. During the war years the use of Lyddite ceased completely. Its disuse was accelerated by its dangerous nature compared with T.N.T. for it was more sensitive to shock, and formed salts in contact with metal shell cases etc. which were very sensitive and resulted in some disastrous explosions (Home Office Papers A.17,412; Annual Reports of H.M.Inspector of Explosives 1890, 48).

The manufacture of T.N.T. on a continuous plant scale was undertaken in October 1917 by Messrs. Chance and Hunt, then managing H.M.Explosive Factory at Oldbury (B.P. 124,461; 125,140). The developments in manufacture of T.N.T. from this point can best be described under technical headings rather than historical.

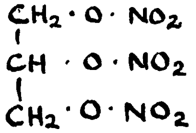
CHAPTER 2.

NITRATING AGENTS

In its simplest form the term "nitration" refers to the production of a carbon-nitro linkage thus:

$$\equiv C - NO_2$$

The product is a nitrocompound. It is perhaps confusing that the expression "nitration" is also applied to the formation of compounds like nitroglycerine, which is in fact glycerol trinitrate:

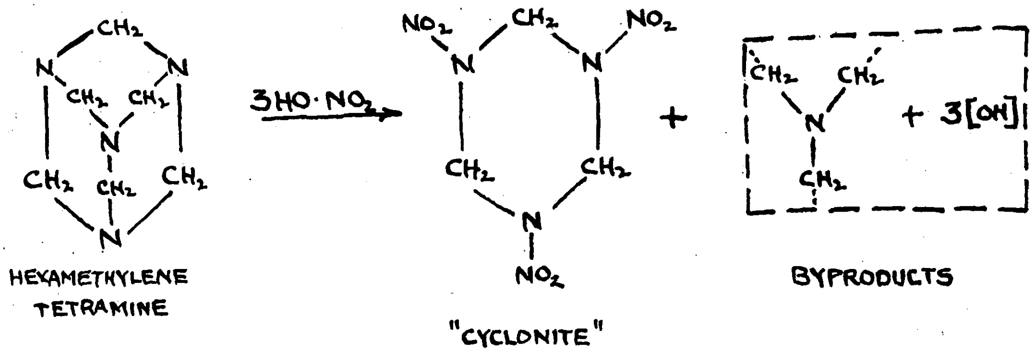


$$\begin{array}{l} CH_2 \cdot O \cdot NO_2 \\ | \\ CH \cdot O \cdot NO_2 \\ | \\ CH_2 \cdot O \cdot NO_2 \end{array}$$

Still more difficult to define is the preparation of compounds with nitrogen-nitro linkages:

$$= N - NO_2$$

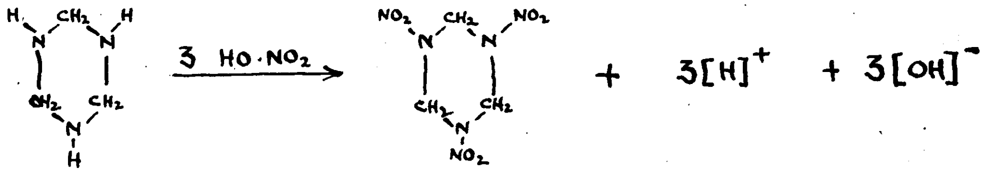
For example the "cyclonite" reaction might be expressed as:



Because of the subsequent reaction of the hydroxyl group:

$$>N-CH_2- \quad + \quad HO\cdot NO_2 \longrightarrow \; >N-NO_2 \quad + \quad -CH_2\cdot OH$$

Professor Linstead (Private Correspondence) has described this as "nitrolysis", emphasising the hydrolysis accompanying nitration. Presumably by this nomenclature the theoretical reaction:



and subsequent combination:

$$3[H]^+ \quad + \quad 3[OH]^- \longrightarrow 3H_2O$$

is nitration, the secondary reaction of the hydroxyl group being the same as that for example in the formation of mono-nitro-toluene:

The method of synthesis is essentially the same, a hydrogen atom of the organic constituent, (or less commonly a substituent group) is replaced by NO_2, the portion split off uniting with the -OH of the nitric acid.

When hydrogen is replaced the reaction can be described by the simple equation:

$$PhH \quad + \quad HO\cdot NO_2 \Longrightarrow PhNO_2 \quad + \quad H_2O$$

It will be obvious from this that the reaction is greatly facilitated by the presence of some agent which absorbs water. Nitrating agents are therefor anhydrous in themselves or are admixed with a dehydrant. The most common reactants are:-

(1) Concentrated nitric acid.

(2) Mixed acids (Nitric acid with sulphuric, acetic, phosphoric acids or anhydrides).

(3) Alkali nitrates with sulphuric or acetic acid.

(4) Organic nitrates, e.g. acetyl nitrate.

(5) Nitrosulphuric acids.

(6) Nitrogen oxides.

In nitrolysis the hydroxyl group of the acid combines with a carbon atom to produce an alcoholic body -

$$-CH_2-OH.$$

Here, the efficacy of dehydration is less obvious. It is nevertheless present. Water is produced by side reactions such as -

$$-CH_2\text{-}OH + HO\cdot NO_2 \longrightarrow -CH_2\cdot O\cdot NO_2 + H_2O$$

and by dilution of the nitric acid its

oxidation potential is increased and its nitrolysing power reduced.

SELECTION OF REAGENT AND ITS DIRECTIVE INFLUENCE

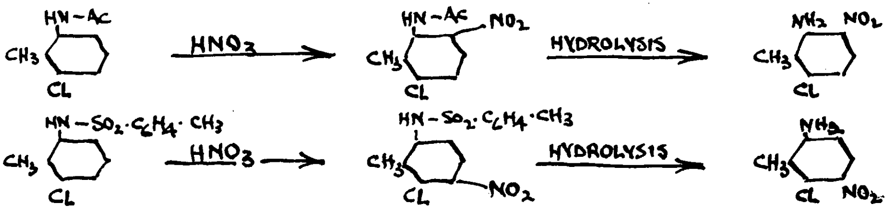
The choice of reagents depends on the organic compound to be nitrated: if for example the latter is easily oxidised a vigorous nitrating agent is excluded. Moreover, if the process is to be a commercial one, the reagent is largely dictated by economic considerations. A third and critical factor in the selection of a nitrating agent, particularly in industry, is its directive influence. Nitration by different reagents may result in isomerically different products, an effect well illustrated by Lauer (J. Prakt. Chem. 1933, 137, 175) in his work on the nitration of amines. A condensed table of his results is shown overleaf. They illustrate moreover, the effect of substituents on orientation.

An interesting case of the effect of substituents on orientation is given by Morgan and Glover (J.Chem.Soc. 1924, 125, 1597) who found that nitration of the acetyl and p-toluenesulphonyl derivatives of 6:chloro-o-toluidine resulted in different products, the reaction being

TABLE 1.

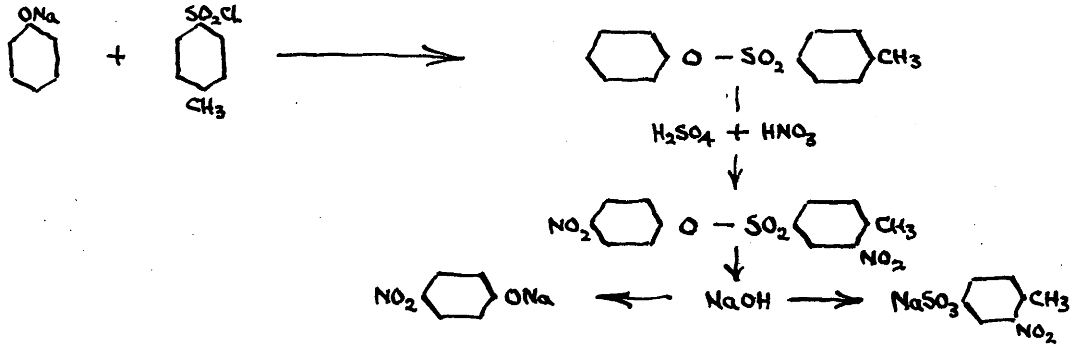
Nitrating Agent	80% HNO$_3$ with glaciel acetic			94% HNO$_3$ with conc sulphuric			HNO$_3$ alone		
	%			%			%		
	ortho	meta	para	ortho	meta	para	ortho	meta	para
Aniline	36	-	64	1	49	50	4	40	56
Acetanilide	30	-	70	8	-	92	42	-	58
Benzanilide	28	-	72	7	-	93	40	-	60
Chloroacetanilide	25	-	75	4	-	96	27	-	73
Toluenesulphanilide	16	-	84	2	-	98	12	-	88

expressed -



Pictet (Ber. 1907, 40, 1165) records that when acetanilide is nitrated in excess of sulphuric acid only 2-5% ortho isomer is formed, the main product being the para compound. With glacial acetic acid and fuming nitric 60% of the product is the ortho substituent, while by acetyl nitrate the product is almost completely ortho-nitro-acetanilide.

The sensitivity to oxidation of phenols and amines often necessitates protection of the active group prior to nitration and the choice of acylating agent is obviously of importance since it may affect the directive effect of the group. An example of ingenious selection of an industrial acylation is given in the German Patent 91,314 (1895) where phenol is protected by forming the p-toluenesulphonyl derivative prior to nitration with nitric and sulphuric acids. The product on hydrolysis yields not only p-nitrophenol, but o-nitrotoluene-p-sulphonate which is valuable as a dye intermediate.



STRUCTURE OF NITRATING AGENTS

Groggins (Unit Processes in Organic Synthesis. McGraw Hill. N.Y. & London 1935) gives the following generalisation with reference to nitrating agents.

(1) They contain the NO_2 group as part of a labile complex.

(2) They are similar in structure to nitric acid esters or acid anhydrides and generally the NO_2 group is held by a shared oxygen atom.

(3) The agents possess pronounced auxiliary valency or free energy for addition, presumably through an oxonium linkage.

(4) On stabilisation after nitration, an acid is split off.

(5) Under certain circumstances, e.g. nitration of amines, the acid split off may participate in a second reaction, o-nitroacetanilide is thus made directly from aniline by reacting with acetyl nitrate or diacetyl-o-nitric acid. The fission in the nitrating complex occurs in the O-NO_2 group.

The first and fourth of these are more the effect of observation than the cause of reaction and the fifth can hardly be described as a generalisation, but 2 and 3 have a considerable bearing on the structure of nitrating agents and their mechanism of reaction.

NITRIC ACIDS AND MIXED ACIDS

Hantzsch (Ber. 1925, 58, 941) from spectrographic studies, and Brunetti and Ollano (Atti.accad. Lincei. 1931, 13, 52) from the Ramam effect, showed that the alkali salts and esters of nitric acid had different absorption spectra in the ultra-violet region.

The concentrated acid was shown to have the same spectrum as that of the esters, while that of the dilute acid was similar to the alkali salts. In solution the salts are electrolytes, while the esters are not hydrolysed. Hantzsch therefore ascribed to nitric acid the structures -

$H^{\cdot}(NO_3)'$

Dilute (true) acid

$\left[N\begin{matrix}O_2\\OH\end{matrix}\right]$

Conc. (pseudo) acid

In solutions of intermediate concentration the mixed spectra showed that both forms could exist together, the conversion of one configuration to the other being gradual (Table 2).

TABLE 2.

HNO_3 normality	pseudo acid %	true acid %
6	2	98
10	50	50
18	72	30

To the pseudo acid Hantzsch also attributed three separate forms -

(1) $HO\cdot NO_2$

(2) $[(HO)_3N][(NO_3)_2]$ nitronium nitrate.

(3) $(NO_3)(H\cdot OH_2)$ hydroxonium nitrate.

by association of the pseudo acid molecule, by itself and with water.

From vapour pressure and conductivity measurements Saposchnikow (Z.phys.chem. 1904, 49, 697; 1905, 51, 609) deduced that a structural change occurred on solution of nitric acid in sulphuric acid. Walden (Z.angew.chem. 1924, 37, 390) and Halbam (Z.phys.chem. 1928, 132, 433) observed the change by absorption spectroscopy. It was attributed by all these workers to the production of anhydride (N_2O_5). Hantzsch claims disproof of the theory from spectroscopic examination of nitric acid anhydride in sulphuric acid.

Hetherington and Masson (J.Chem.Soc. 1933, 105) formulate a mechanism of reaction which depends on the participation of the hydroxonium nitrate described by Hantsch. Schaarschmidt (Z.angew.chem. 1926, 39, 1457) and Klemenc (Z.anorg.allgem.chem. 1924, 141, 231) on the other hand suggest N_2O_5 as the active agent in mixed acids containing powerful dehydrating agents, this reacting with the organic constituent to form an addition complex which breaks down to form the nitrocompound. Again Schaefer (Z.anorg.allgem.chem. 1916, 97, 285; 98, 70) claims that the dehydrating agent removes water of dilution from the nitric acid only to the extent of producing $HO.NO_2$.

NITROSYL SULPHURIC ACID.

This acid may be formed by addition of any of the oxides of nitrogen except N_2O to sulphuric acid, and might therefore be the active agent in mixed acids. It was discovered by Clement and Desormés (Ann.chem. phys. 1806, 59, 329) who suggested from its empirical formula $HSNO_5$ two possible tautomers -

$NO \cdot O \cdot (HSO_3)$	$HO \cdot SO_2 \cdot NO_2$
nitrosyl-sulphuric	nitroxyl-sulphonic

Michaelis and Schumann (Ber. 1874, 7, 1075), from its reaction with phosphorus pentachloride, which they expressed as -

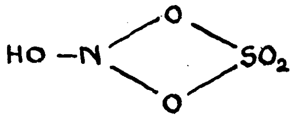
$$NO \cdot O \cdot (HSO_3) + PCl_5 = H(Cl)SO_3 + NOCl + POCl_3.$$

favoured the first formula. Girard and Pabst (Bull.Soc.Chem. 1878, 30, 531) reached the same conclusion from a study of its reaction with sodium halides. Berl (Z.angew.chem. 1910, 23, 2250) on the other hand claims to have formed the nitroxyl sulphonic anhydride by the action of nitric oxides on sulphur trioxide. Biehringer and Borsun (Ber. 1915, 48, 1314; 1916, 49, 1402) assume that the two forms exist in equilibrium in the molten state. They obtained from the nitration of dimethyl-aniline both the p-nitro and p-nitroso compounds, the proportions being shown in Table 3.

TABLE 3.

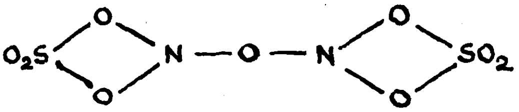
Temperature °C	nitro cpd.%	nitroso cpd.%
10 - 15	8.3	7.5
28 - 30	42.9	39.3

It is interesting to note that the ratios are nearly the same for both temperatures indicating no temperature coefficient of equilibrium. Elliott, Kliest, Wilkins and Webb (J.C.S. 1926, 129, 1219) claim that the p-nitro compound is produced by a secondary oxidation during dilution and is not indicative of the presence of the nitroxyl-sulphonic acid. They suggest a third formula -



and give the following reasons for their assumption:-

(1) Acid with this structure would lose water on heating to give the anhydride -

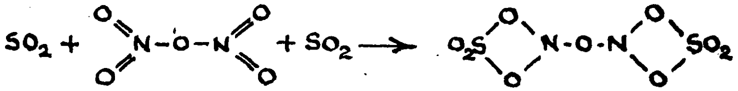


a change parallel to that of the conver-

-sion of nitric acid to its anhydride.

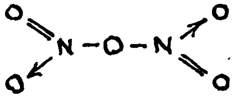
(2) It explains the difficulty of replacing both hydroxyl groups of the acid by nitroso groups.

(3) It explains the Berl method of synthesis of the anhydride from SO_2 and N_2O_5



(4) The structure accounts for the reduction products.

No account appears to have been taken by these workers of the effect on their theory of the possible co-ordinacy of nitrogen pentoxide -



ALKALI NITRATES IN SULPHURIC ACID

The active agent in this case may again be either pseude nitric acid or anhydride. An excess of sulphuric acid and high temperature are necessary to promote the reaction -

$$NaNO_3 + NaHSO_4 \longrightarrow HNO_3 + Na_2SO_4$$

Under these conditions the HNO_3 is dehydrated at least partially to N_2O_5, (Groggins, Unit Processes 15) and the theory of Zchaarschmidt (loc.cit.) may then apply to the reaction.

The use of such agents has largely been obviated by the development of industrial supplies of concentrated acids.

ORGANIC NITRATES

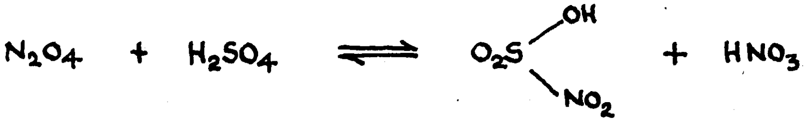
Acetyl and benzoyl nitrates are found to nitrate organic compounds in acetic anhydride solution. Ethyl nitrate under the same conditions is not a nitrating agent, although in presence of stannic or aluminium chloride it does nitrate benzene. Tronov (J.Russ.Phys.Chem.Soc.1930, 61, 2388; 62, 2267) believes the nitrant to be a complex of ethyl nitrate with the metallic salt.

OXIDES OF NITROGEN

Wieland (Ber. 1921, 54, 1776) has shown that nitrogen tetroxide forms additive compounds with a mixture of benzene and petroleum capable of nitrating organic compounds. Phenols and cresols can be nitrated by such reagents. The nitration of cresols by the action of oxides of nitrogen on the sulphonates is well known (Datta and Varma J.Am.Chem.Soc. 1919, 41, 2041). Zchaarschmidt (Zangew.Chem. 1924, 39, 933) effected nitration by metallic complexes of N_2O_4.

In almost every case an auxiliary agent is present in such nitrations and an interesting theory of the complex with sulphuric acid is given by Pink

(J.Am.Chem.Soc. 1927, 49, 2536). He suggests the equilibrium -



$$N_2O_4 + H_2SO_4 \rightleftharpoons O_2S\begin{matrix}OH\\NO_2\end{matrix} + HNO_3$$

According to Pink, equilibrium is almost wholly to the right, since nitric acid is being continually removed in nitrating the organic constituent. Reaction is assisted by the dehydrating action of both sulphuric acid and nitrosulphuric acid. No account appears to have been taken of the effect of liberated water on the reaction. It is suspected that this will have a greater effect than nitric acid in displacing equilibrium to the left.

CHAPTER 3.

MECHANISM OF NITRATION

Theories of nitration can be simply divided into four main classes -

(1) Simple substitution.
(2) Presulphonation.
(3) Cation reaction.
(4) Addition and elimination.

the final class being sub-divided into two subsections involving elimination of (a) nitric acid or (b) nitrogen pentoxide.

SIMPLE SUBSTITUTION

This was probably the earliest view of the nature of the reaction, and is still held by some workers (Othmer, Jacobs, and Levy; Ind.Eng.Chem. 1942, 286)to be the mechanism. It involves the equation-

$$PhH + HO{\cdot}NO_2 \longrightarrow PhNO_2 + H_2O$$

Farmer (J.S.C.I. 1931, <u>50</u>, 75) holds essentially this view of the reaction, the action of the sulphuric acid being the production of nitronium salts which then react with the organic compound directly and not by way of an intermediate sulphonate.

PRESULPHONATION

The nitration of phenol appears to be facilitated by sulphonation. Cross, Bevan, and Jenks (Ber. 1901, 34, 2496) have studied the reaction and concluded that the action of sulphonation in the nitration of phenol makes the organic material soluble in the acid phase. It would be dangerous to base any generalisation on the study of the mechanism of nitration of phenol, for the material is exceptional in acidity, polarity and sensitivity. Sufficient proof of its abnormality is given by the fact that the cresol sulphonates can be nitrated by treatment with "nitrous gases" (Datta and Varma. J.Am.Chem.Soc. 1919, 41, 2041; J.S.C.I. 1927, 4, 321). In spite of the lack of clear specification of the nitrating agent, no evidence is shown by these workers of the formation of nitroso-compounds.

CATION REACTION

The theory postulated by Hetherington and Masson (J.Chem.Soc. 1933, 105) is that of nitration by cations. They were able to observe addition compounds of nitrobenzene with both sulphuric and nitric acids to which they ascribe the formulae -

$$[PhNO_2H]^+[HSO_4]^-$$
$$[PhNO_2H]^+[NO_3]^-$$

They suggest a mechanism to account for the fact that fuming nitric acid does not nitrate benzene, although mixed acid containing sufficient H_2SO_4 to form the monohydrate ($H_2SO_4 \cdot H_2O$) with the water present at the end of reaction, will nitrate till HNO_3 is exhausted. The addition complex with nitric acid breaks down to give the nitrocompound, the whole reaction presumably being represented as -

$$PhH + HO \cdot NO_2 \rightleftharpoons [PhNO_2H]^+ + [OH]^-$$
$$[PhNO_2H]^+ + H_2O \rightleftharpoons PhNO_2 + [H_3O]^+$$
$$[OH]^- + [H_3O]^+ \rightleftharpoons 2H_2O$$

The effect of the addition of sulphuric acid is to liberate pseudo nitric acid from the dissociated hyroxonium nitrate -

$$HNO_3 + H_2O \rightleftharpoons \underset{\text{HYDROXONIUM NITRATE}}{[H_3O]^+[NO_3]^-}$$
$$[H_3O]^+[NO_3]^- + H_2SO_4 \rightleftharpoons [H_3O]^+[HSO_4]^- + \underset{\text{PSEUDO NITRIC ACID}}{HO \cdot NO_2}$$

Usanovich and Cluckov (J.Gen.Chem. U.S.S.R. 194o, 10, (3), 227) agree with the mechanism but include other cations ($N[OH_3]^+$ and $NO[OH]_2^{++}$), and electro-chemical evidence for their existence is given by Usanovich and Suskevich (ibid. 230).

ADDITION AND ELIMINATION OF NITRIC ACID

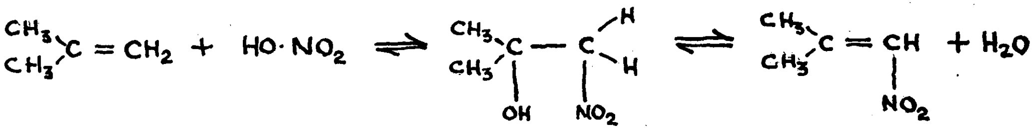
Kekulé (Ber. 1869, 2, 329) obtained in small yield from the treatment of ethylene with anhydrous nitric acid, a nitro-compound to which he attributed the formula -

$$CH_2 = CHNO_2$$

Haitinger (Ann. 1878, 193, 366; Monatsh 1881, 2, 286) extended his work to include isobutylene, isoamylene and tertiary butyl and amyl alcohols. The results were, as in Kekulé's experiments, largely oxidation products but again he was able to isolate compounds of the type -

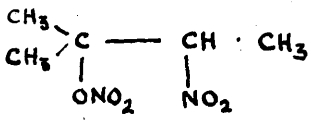
$$(CH_3)_2C=CHNO_2 \qquad \text{and} \qquad (CH_3)_2C=C(NO_2)CH_3$$

The mechanism of the process was considered by Wieland to be represented by -

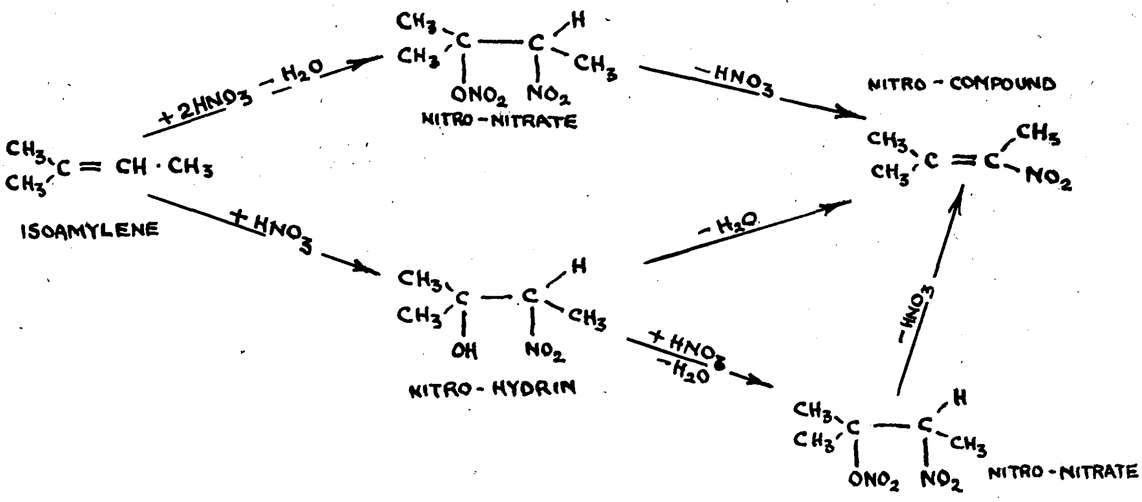


$$(CH_3)_2C=CH_2 + HO\cdot NO_2 \rightleftharpoons (CH_3)_2\underset{OH}{C}-\underset{NO_2}{C}H_2 \rightleftharpoons (CH_3)_2C=\underset{NO_2}{CH} + H_2O$$

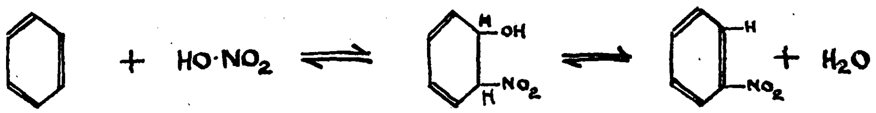
Wieland and co-workers (Ber. 1920, 53, 201; 1921, 54, 1770) used nitric acid in fuming sulphuric acid, and in some cases diluted the organic constituent with carbon tetrachloride. From isoamylene they were able to isolate both the nitrocompound and an intermediate constituent of structure -



The complete reaction is thus expressed as -

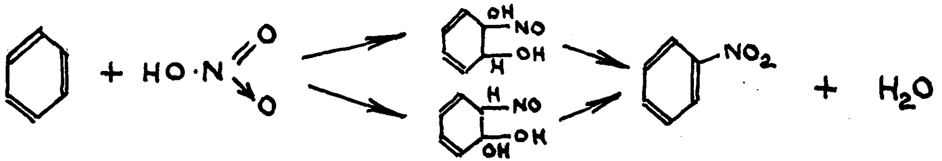


This theory involves the addition of HO and NO_2 to the ethenic carbon atoms and the author suggested the extension of it to aromatic compounds, his postulate being -



Mayer (Ann. 1913, 398, 66) had suggested such a mechanism to account for certain reactions of nitrous acid and phenyl diazonium hydroxide which he considered reacted as HO·NO and $C_6H_5N_2$-OH, and Markownikow (Ber. 1899, 32, 1444) attributed reaction to the addition of a complex HO-SO_2·O·NO .

Michael and Carlson (J.Am.Chem.Soc. 1935, 2, 1286) although in almost complete agreement with the Wieland theory of ethenic addition in aromatic nitration, claim that the basis of Wieland's deductions was completely erroneous, nitration in all the experiments being due to nitrous acid produced in the oxidising side reactions. From considerations of free energy they showed that addition of nitric acid in a manner similar to that suggested by Wieland is probable however, and postulate a variation of the mechanism sympathetic to the co-ordinated form of pseudo nitric acid and involving simultaneous addition and oxidation -



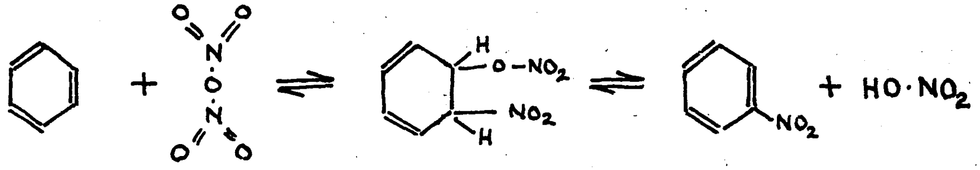
This constitutes one of the more flexible theories of nitration. The development of more highly specialised methods of determining intermediates of reaction might well be directed to a closer study of this mechanism.

ADDITION AND ELIMINATION OF NITROGEN PENTOXIDE

Zchaarschmidt (Z.angew.Chem. 1926, 39, 1457) agrees with Klemenc (Z.anorg.allgem.Chem. 1924, 141, 231) that N_2O_5 produced by the reaction -

$$2\,HNO_3 \underset{H_2O}{\overset{H_2SO_4}{\rightleftharpoons}} N_2O_5 + H_2O$$

is the active agent in mixed acid nitrations, and he favours addition of the pentoxide as a derivative of dihydro-benzene -



The theory is similar to that of Wieland and equally attractive. It is applicable to reaction in benzoyl and acetyl nitrates. This mechanism probably accounts for the non-reactivity of the tetroxide, for it was found that although it is effective in nitrating olefines, a number of loosely bound compounds are also formed, and its reactivity to benzene, chlorbenzene and toluene, is very low. The lack of the nitrate group in the intermediate compound is believed to be responsible. With naphthalene an additive complex is formed with N_2O_4 which does decompose to give the nitro-compound and nitrous acid. Although the reaction is possible in carbon tetrachloride solution, it does not take place in ether, where a stable ether-N_2O_4 complex is formed. Zchaarschmidt further records (Z.angew.Chem. 1924, 39, 933) that in presence of aluminium or stannic chloride N_2O_4 does add to certain aromatics giving complexes which can be hydrolysed to form nitro-compounds and nitrous acid. It is possible moreover to conduct the reaction with N_2O_3, whence hydrolysis gives nitric oxide.

CHAPTER 4.

CATALYSIS

The practical difficulties attending nitration, particularly when mixed acids were not commercially common, led some workers even before 1914 to consider the possibilities of catalysis. When concentrated acids became more readily available, the work was continued in the hope that by its use nitration rate might be increased.

Holleman (Ber. 1906, 39, 1256) studied the catalytic effects of mercury, cobalt, copper and nickel salts on the nitration of toluene, and obtained only negative results. The relative commercial unimportance of nitro-toluenes at this time together with the negative nature of the results apparently deterred other workers from studying the subject, for very little attention seems to have been paid to it till the Great War. In 1913 Wolfstein and Boters (Ber. 1913, 46, 586) found that although mercuric salts have no catalytic effect with mixed acids, they catalyse aromatic nitration in nitric acid alone. In 1914 the nitration of phenol was the immediate concern of the fighting powers and Klemenc (Monatsh 1914, <u>35</u>, 85) records an increase in the rate and ease of reaction of phenol with nitric acid in presence of nitrous acid. He later extended his experiments to toluene with some success (Z.anorg.Chem. 1924, <u>141</u>, 230).

Davis (J.A.C.S. 1921, <u>43</u>, 594) in studying the nitration of benzene in presence of mercuric nitrate found that with high concentrations of nitric acid, picric acid was a product. He postulated the simultaneous entry of the hydroxyl and nitro groups. Zakharov (J.Chem.Ind.Moscow. 1931, <u>8</u>, 30; Am.Chem. Abs. 1931, <u>25</u>, 4864) on the other hand believed the hydroxyl group to be introduced after mononitration of the benzene, the nitrophenol so formed afterwards being converted to the trinitro-compound. Oxidation according to Zakharov is due entirely to the action of dilute HNO_3 and not to the mercuric nitrate.

The effect of hydrogen fluoride on various reactions was studied by Simons and co-workers. He observed an addition compound with sulphuric acid, supposed to be fluorosulphonic acid (Chem.Rev. 1931, 8, 213) and Meyer and Schramm (Z.anorg.allgem.Chem. 1932, 206, 24) showed this to be an effective sulphonating agent. Simons, Passino and Archer (J.Am.Chem. Soc. 1941, 63, 608) extended the investigation to the nitration reaction, and were able to show an increased yield of nitrobenzene at low temperatures. With respect to sulphonation, they observed an apparent orientation effect; depending on the temperature, fluorosulphonic acid with aromatics yielded sulphonic acids or symmetrical sulphones. Patents were granted to Fredenhagen (G.Pat. 529,538. 1930) and Gleich (Russ. Pat. 39,775. 1934) for the use of HF with potassium nitrate for the nitration of benzene and phenol.

Arnall (J.Chem.Soc. 1924, 125, 811) conducted a careful study of the effect of various solvents on the nitration of aromatics, the isomerism of the products forming part of the investigation. Experiments were conducted with various catalysts (mercury, iodine, and copper compounds) and it was concluded that only mercuric nitrate increased the yield of nitro-compounds under standard conditions. A patent (Fr.Pat. 821,767. 1937; Am.Chem.Abs. 1938, 32, 3964) granted to Katalyt-

Chemie A-G. for the use of chrome, tungsten, moli-titanium-nickel, vanadium, gallium and tin in the form of complex acids in the nitration of glycerol, probably represents a development of Arnall's work.

The effect of nitrous acid as a catalyst in nitration has been the subject of much research. Unfortunately most of this concerns the nitration of phenols and amines. Orton (Trans.Chem.Soc. 1902, 81, 806; Ber. 1907, 40, 371) stresses the necessity for the presence of nitrous acid in the nitration of the dialkyl-anilines, assuming the production of intermediate nitroso-compounds. Witt and Utermann (Ber. 1906, 39, 3901) however, obtained good yields of such nitro-compounds in presence of a small quantity of carbamide nitrate, a compound used by Orton for the removal of nitrous acid from nitric acid. The nitration of phenol was investigated by Kartashev (J.Russ.Phys.Chem.Soc. 1930, 62, 2129; Am.Chem.Abs. 1931, 25, 3977), who observed a latent period before nitration commenced, in which the solution (ethyl acetate) turned yellow brown. When reaction began there was a rapid temperature rise accompanying the reddening of the solution. Water and urea were found to influence the latent period. In an atmosphere of carbon dioxide the induction period was reduced whereas oxygen increased it. It was concluded that nitrous acid was produced during the interval, the process being autocatalytic. Estimation of the nitrous acid throughout the experiment showed that it ran parallel to the rate of nitration. Kartashev suggests the following mechanism of nitration -

$$HNO_3 \longrightarrow HNO_2 + [O]^-$$

$$C_6H_5OH + HNO_2 \rightarrow C_6H_4(NO)OH + H_2O$$

$$C_6H_4(NO)OH + HNO_3 \rightarrow C_6H_4(NO_2)OH + HNO_2$$

As evidence of this postulation, attention is drawn to:-

(1) The detection of nitroso-compounds in the early stages of the reaction.

(2) Ease of formation of these compounds and subsequent oxidation of nitroso- to nitro-compounds.

It will be noted that Kartashev observed an increase in the nitrous acid concentration throughout the experiment. This being so, some explanation would appear to be necessary concerning the nascent oxygen shown in this equation.

CHAPTER 5.

KINETICS

Their application to commercial efficiency.

The Gulberg and Waage law of mass action states that the velocity of reaction at any instant is proportional to the existing concentrations of the reacting substances. Considering only irreversible chemical changes, the velocity is represented by -

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x) \ldots\ldots\ldots$$

where x = gm. mols. of substance changed in time t, and a. b. c..... represent the initial concentrations in gm. mols. per litre of the reacting substances.

From this it is obvious that as reaction proceeds its rate decreases so that there is no finite time for completion.

(Fig. 1.) is a typical curve representing degree of nitration against time. It is applicable to the formation of mono-, di-, and trinitro-toluene by mixed

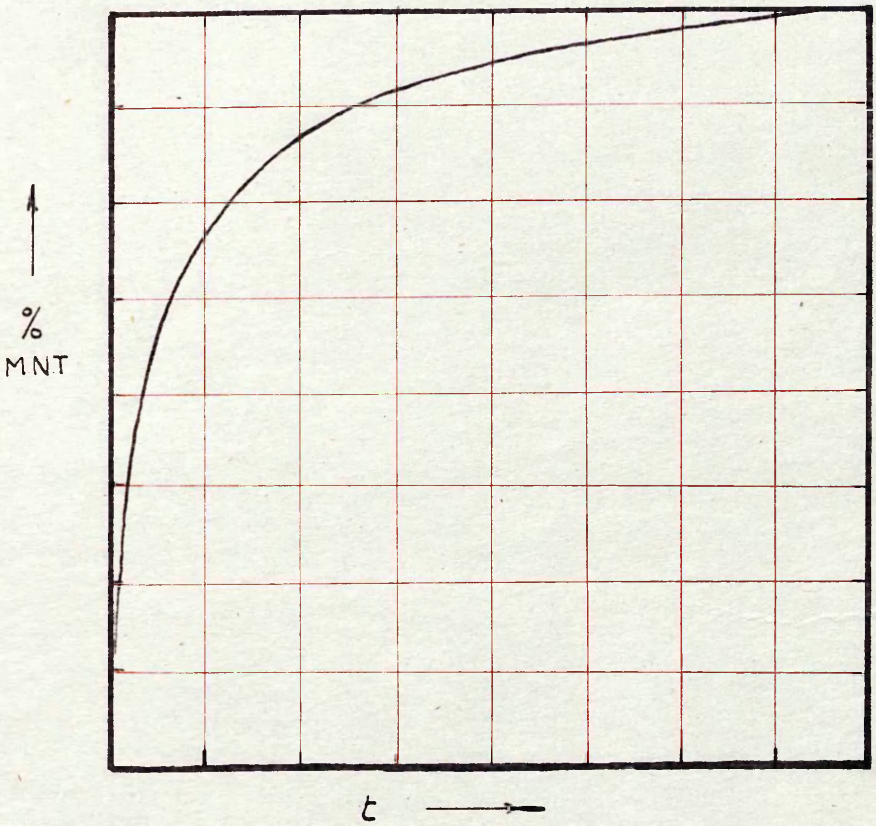


FIG 1

acid, the only difference being in the extent of the time scale, a good average time for virtual completion of the reaction in practice being -

toluene to mononitrotoluene	40 mins.
mononitrotoluene to dinitrotoluene	200 mins.
dinitrotoluene to trinitrotoluene	360 mins.

Owing to the complexity of the nitration reaction (e.g. number of reagents present, frequently separate phases of acid and nitrobody), it is difficult to represent the reaction by the simple mass action law. Plotting for example, extent of reaction on a logarithmic axis, which would with bimolecular reactions result in a straight line, gives a curve.

This does not of necessity indicate high order of reaction. The curve may well result from conflicting diffusion effects between the acid and nitrobody phases, a phenomenon recorded in the nitration of benzene when the acid is swamped with nitrobenzene (Hetherington and Masson, loc.cit.). Indeed Wibaut (Rec.trav.chim. 1915, 34, 241) has shown that under carefully controlled conditions benzene and toluene are converted to the nitro-compounds by a bimolecular reaction.

The abnormal decrease of reaction rate as nitration proceeds has considerable significance in practice. Because of the necessarily long time of reaction, extensive plant must be provided for a relatively small output. Oxidation which accompanies nitration is increased by long time of contact of acid and nitrobody. The oxidation in T.N.T. manufacture is of both side chain and ~~n~~uclear character, the former giving rise to CO and CO_2 and the latter to phenolic compounds and carboxylic acids.

The first difficulty has been largely overcome by continuous contraflow nitration (see next chapter) but the time of contact is necessarily similar to that in batch nitration and oxidation losses are of the same order.

It would be of obvious advantage if the organic mixture could be separated after it had undergone for example 70% conversion to the higher nitro-compound, the un-nitrated material being recycled. In the D.N.T. to T.N.T. stage this degree of conversion is effected in approximately one sixth of the time required for virtual completion of reaction. Such a process would reduce:-

(1) The time of contact with the acid and therefore the extent of oxidation losses.

(2) The amount of nitro-body necessary in circulation in the plant for the production of unit quantity of product, thereby conferring greater safety in operation.

(3) The quantity of acids required for the production of unit yield.

(4) The extent of plant; always assuming that the separation equipment were less extensive than the discarded apparatus.

The separation of such a nitrobody mixture on plant scale is unfortunately not a simple proposition, as exhibited by the difficulties found in removing only a few percent of D.N.T. from T.N.T. (Tech.Rec.Ex. Supply. 1915-18, 2, 20). Here the methods attempted included:-

(1) Washing with boiling water and solutions of salts.

(2) Crystallisation.

(3) Exudation (Pressing and Centrifuging).

Success in all these was only partial. Since that time however two new methods of separation have come to light, and although they have only been utilised commercially to a limited extent they show great promise. These are thermal diffusion and ultra-high vac or so-called molecular distillation.

The first of these, has in the last decade been rapidly developed and Welch (Ann.Rep.Chem.Soc. 1940, 37, 153) describes the separation of isotopes by this technique. The value of molecular distillation need hardly be stressed. This process has attracted considerable interest since its application to the separation of the vitamines, Hickman (Ind.Eng.Chem. 1937, 29, 968; 1938, 30, 796), and prior to the war high grade lubricating oils were being made on a semi-commercial scale in Holland by this method (Proc.Chem. Eng.Gp. 1938, 20, 84).

One of these processes might therefore offer the solution to the separation of nitrobody mixtures at an intermediate stage of nitration to make the recycling system feasible.

CHAPTER 6.

NITRATION PLANT

In the manufacture of nitro-compounds for pharmaceutical, laboratory or dyeing purposes, simple batch nitration is the process normally adopted, since it is easily adapted to the production of a wide variety of compounds. The nitrators for such plant are usually jacketed pans, the interspace of which may be fed with steam or cooling water according to the vigour of the reaction. They are invariably fitted with stirring gear and are sealed to prevent the escape of noxious gases into the workroom. In cases where vigorous reaction is anticipated the pans are fitted with cooling coils. Modern nitrators are of stainless steel although cast iron vessels are still used. If weak nitric acid is present the coils may be of lead, but otherwise these too will be of stainless steel. The Hough patent nitrator illustrated later in this chapter is a large unit of this type.

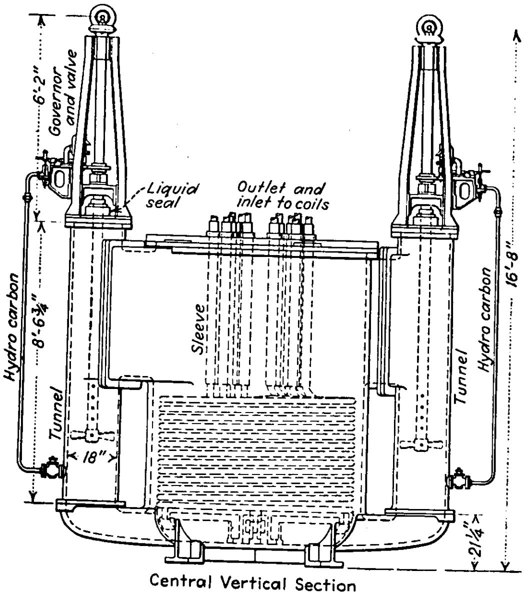
In a plant where production is wholely directed towards the manufacture of a single compound such as tetryl or T.N.T., more specialised equipment may be utilised, for the degree of agitation and cooling required at any stage of the process is known and nitrators can be designed accordingly. During the years 1914-18 under the stimulus of the Great War such unit product nitration developed rapidly.

In 1914 the manufacture of T.N.T. had only commenced in this country and the production of Lyddite was on a 60 lb. batch scale. It became obvious that in spite of the improvements in the manufacture of picric acid, the available supplies of raw materials would not be nearly sufficient to satisfy the needs of the services and the production of T.N.T. became virtually a necessity.

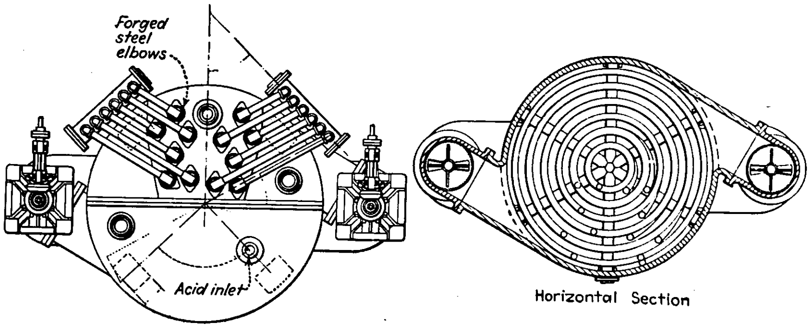
In peace time T.N.T. was made only from the ortho-nitrotoluene; the meta and para isomers were valuable dye intermediates and were separated by distillation and crystallisation. When the need for T.N.T. became critical this separation was abandoned, the whole mono-nitrotoluene being nitrated to T.N.T. The first nitration process was a three stage one the waste acid from the trinitration stage being fortified and used for dinitration, afterwards being used for mononitration. To the efforts of the Woolwich Research Department goes the credit for developing the process to a two stage one. Various modifications were attempted, such as nitration to stages represented by $1\frac{1}{2}$ N.T., $2\frac{1}{2}$ N.T., 3 N.T. (Tech.Rec.Ex.Supply. 2, 5) but the most successful method was to nitrate to the mononitro-compound and then in one operation to convert the product to T.N.T. By this method the use of oleum was obviated, and at the beginning of the war this represented an important economy due to limitations of supply.

Some illustrations of the type of plant used are shown in Technical Records of Explosives Supply 1915-18. volume 2. The American contribution to explosives plant during this period is well illustrated by the nitrator for which patent rights were granted to Hough, in which toluene was nitrated to T.N.T. in one operation. A reproduction of this nitrator is shown in Fig. 2.

The Germans had used T.N.T. as a service explosive before the Great War and by 1914 were direct-



Central Vertical Section



Top Plan

Horizontal Section

·Hough nitrator, cast iron, with external tunnels.

FIG 2

-ing their attention towards continuous plant. (Kubierschky, Ger. Pat. 287,799; J.S.C.I. 1916, 199). The development of such plant in this country was undertaken by Messrs. Chance and Hunt, then managers of H.M. Explosives Factory, Oldbury. Holley and Mott (U.S. Pat. 1,297,170. 1919) describe plant of a similar nature to that used at Oldbury. The success of the process, started in October 1917 (B. Ps. 124,461; 125,140) can be judged from the description and comments concerning it in Technical Records of Explosives Supply. 2, 11., -

"The plant consists of a number of pairs of cast iron pots. One of each pair is agitated and the other acts as settling vessel. From the settling vessel, or separator, the nitrobody goes forward to the next agitator, and the acid travels in the reverse direction to the previous agitator. Thus the nitrobody is continually meeting stronger and stronger acid. The vessels are fitted with coils for temperature control, and the temperature varies in the different pans, having a maximum of 110° C.

The plant has proved to have a remarkable capacity. Although built for a nominal output of 100 tons per week it has proved capable of some 500 tons per week. The consumption of toluene does not differ much from other nitration processes and the advantage lies mainly in the high capacity and consequent saving in labour and capital cost of plant."

Details of such plant have never been fully published for obvious reasons. A complete toluene-T.N.T. plant will incorporate over and above the nitration equipment, purification plant, drying apparatus, certainly acid concentration plant and possibly nitric and sulphuric acid manufacturing equipment. These subsidiary aspects of nitration are too numerous to merit complete discussion here. Reference may be made to Groggins (Unit Processes in Organic Synthesis), Technical Records of Explosives Supply. volumes 1. to 9., and Reports of the Progress of Applied Chemistry (Soc.Chem.Ind. 1919-20-22-24...) for more detailed information.

SECTION 2.

CATALYSIS.

In the nitration of toluene to T.N.T., the least difficult stage is, as would be expected, that from toluene to M.N.T. With even moderately concentrated acids this reaction proceeds with reasonable velocity to virtual completion. On this account catalysis offers relatively little advantage, although its application might permit the use of smaller plant for the same output, or of more dilute acids. There is however, a more important aspect involved, that is the degree of production of meta isomer. This isomer which occurs to the extent of about 4 % in nitration of toluene irrespective of the mode of nitration (Arnall, J.C.S. 1924, 125, 811; Tingle and Blank, J.Am.Chem.Soc. 1908, 30, 1395; Holleman and Sluiter, Rec.trav.chim. 1906, 25, 208; Friswell, J.S.C.I. 1908, 27, 258) is largely responsible for a loss of about 8 % in the manufacture of T.N.T. The gravity of this loss is only equalled by that due to destructive oxidation in the high temperature stage of trinitration.

Will (Ber. 1914, 47, 1718) who prepared all six of the T.N.T. isomers was able to show that at least four of these occur in measurable amounts in crude commercial T.N.T. Of these the β and γ isomers (2:3:4- and 2:4:5-) predominate. Their presence is objectionable for a number of reasons. They reduce the setting point of the product from 80.6 to approximately 78.5° C and markedly affect its stability. As would be expected, they have greater chemical activity than the symmetrical isomer, and accordingly are less suitable for shell filling etc. where shock sensitive metallic salts may be formed. The shock sensitivity of the unsymmetrical isomers themselves is higher than that of the 2:4:6- material, and removal of these is essential for safety in handling both the explosive and filled projectiles.

Prior to the 1914-18 war production of the unsymmetricals was avoided by freeing the M.N.T. of meta-isomer by distillation before further nitration, but the ortho compound distils first (36 %) and this involves great expenditure of heat. Moreover the meta-para cut is not well defined and it is doubtful if the losses of para isomer thus occasioned do indeed offset the losses in purification of T.N.T. made with the whole mononitrotoluene product. The process was therefore early abandoned. It was superseded first by crystallisation but after some devastating explosions which occurred in the recovery of the solvent (Tech.Rec.Ex.Supply. 1915, 2, 20) this too was rejected. To replace it a number of methods were suggested, among these, centrifugal removal of thermally exuded eutectic of D.N.T. with the unsymmetricals, latterly with the addition of phenol to reduce the melting point of the eutectic still further. Water washing proved ineffective and alkali washing was rejected because of the doubtful nature of the products. Washing with sodium sulphite gave better results (Ber. 1914, 47, 709; J.S.C.I. 1914, 23, 376) although the nature of the products of interaction is still controversial.

The reagent is selective, attacking the unsymmetrical isomers in preference to α T.N.T. In spite of this about as much α as β and γ T.N.T. is removed. Accordingly although only 4 % of the T.N.T. is unsymmetrical the loss by sulphiting is more nearly 8 %. Some improvement has resulted from the use of buffers but the overall loss of yield is still high.

The sulphite wash is therefore one of two great sources of loss in the T.N.T. industry and is made necessary entirely by the presence of meta-isomer in mono-nitrotoluene. If catalysis reduced the formation of this isomer it would represent a considerable saving in manufacture.

Catalysis in the di- and tri-nitration stages could not result in reduction of unsymmetricals, but it is here that the greatest concentration of acids is necessary and the time of reaction longest. The use of catalysts to reduce either of these would again be economically advantageous.

The work described in this section has been subdivided into:-

PART 1. Mono-nitration.
PART 2. Di-nitration.
PART 3. Tri-nitration.

In view of the importance and greater effects to be gained by catalysis in mononitration, most of the work has been directed towards this stage. The toluene nitration offers at the same time greater facilities for study since the product is liquid and estimation of degree of nitration simplest.

PART 1.

MONO-NITRATION.

CHAPTER 1.

APPARATUS, METHODS OF ESTIMATION, & EXPRESSION OF RELATIVE ACTIVITIES OF CATALYSTS

APPARATUS.

Fig. 3. is a sketch of the nitration equipment. It consists of a glass vessel A which in the early stages of experiments was set in a water-bath to bring the temperature to 30° C. Cooling is provided when the reaction becomes exothermic by circulation of water in the internal cooling coil B. The stirrer C is of standard "Quickfit" centrifugal type, and capable of giving efficient emulsion of toluene in mixed acid in a few seconds. It was operated at 1000 r.p.m. The nitrator is covered by a loosely fitting lead plate D introduction of toluene being effected by means of a funnel E.

In early experiments the stirrer speed was measured by a tachometer. This was later replaced by a stroboscopic measuring instrument constructed from an electric gramophone motor. A photograph

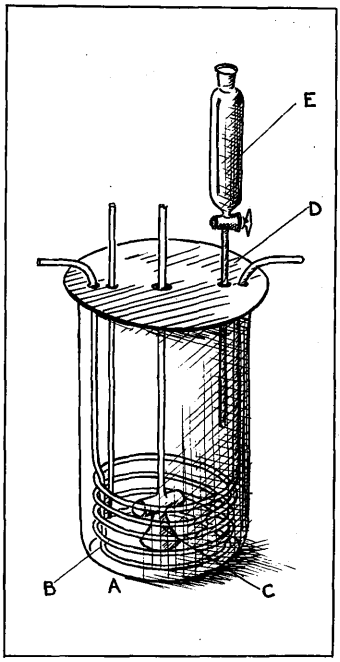


FIG 3

of this machine is shown in Fig. 4. Sector discs (in foreground) with 5, 9, 12, 16, 20, 26, 32, and 40 slots, enable rotational speeds from 300 to 3200 r.p.m. to be obtained. The instrument is shown in use in Fig. 5. The proper sector disc having been selected, the image of the rotating stirrer is rendered stationary by adjustment of the gramophone governor. The speed of the stirrer is then given by -

Gram. revs. x Disc slots.

The calibration of the motor control was extended to cover the range 60-80 r.p.m. and subdivided to give readings to within 0.5 r.p.m. Table 4. shows dial reading against r.p.m. of the observed stirrer and indicates the degree of accuracy. The calibration was checked against readings from a N.P.L. standardised tachometer, simultaneous observations being made of the shaft of a 5 H.P. shunt wound D.C. motor.

Stroboscopic measurement has the special advantage that it imposes no load during the estimation and permits rapid and if necessary, continuous measurement. A single point calibration can readily be obtained from observation of a neon tube on 25 c/s

FIG 4

FIG 5

TABLE 4

— R.P.M. FOR STATIONARY STROBO-IMAGE —

GRAM MOTOR. R.P.M.	NO. OF SLOTS IN SECTOR DISC.								
	5	7	9	12	16	20	26	32	40
60·0	300	420	540	720	960	1200	1560	1920	2400
·5				726	968	1210	1573	1936	2420
61·0	305	427	549	732	976	1220	1586	1952	2440
·5				738	984	1230	1599	1968	2460
62·0	310	434	558	744	992	1240	1612	1984	2480
·5				750	1000	1250	1625	2000	2500
63·0	315	441	567	756	1008	1260	1638	2016	2520
·5				762	1016	1270	1651	2032	2540
64·0	320	448	576	768	1024	1280	1664	2048	2560
·5				774	1032	1290	1677	2064	2580
65·0	325	455	585	780	1040	1300	1690	2080	2600
·5				786	1048	1310	1703	2096	2620
66·0	330	462	594	792	1056	1320	1716	2112	2640
·5				798	1064	1330	1729	2128	2660
67·0	335	469	603	804	1072	1340	1742	2144	2680
·5				810	1080	1350	1755	2160	2700
68·0	340	476	612	816	1088	1360	1768	2176	2720
·5				822	1096	1370	1781	2192	2740
69·0	345	483	621	828	1104	1380	1794	2208	2760
·5				834	1112	1390	1807	2224	2780
70·0	350	490	630	840	1120	1400	1820	2240	2800
·5				846	1128	1410	1833	2256	2820
71·0	355	497	639	852	1136	1420	1846	2272	2840
·5				858	1144	1430	1859	2288	2860
72·0	360	504	648	864	1152	1440	1872	2304	2880
·5				870	1160	1450	1885	2320	2900
73·0	365	511	657	876	1168	1460	1898	2336	2920
·5				882	1176	1470	1911	2352	2940
74·0	370	518	666	888	1184	1480	1924	2368	2960
·5				894	1192	1490	1937	2384	2980
75·0	375	525	675	900	1200	1500	1950	2400	3000 ← N.C.
·5				906	1208	1510	1963	2416	3020
76·0	380	532	684	912	1216	1520	1976	2432	3040
·5				918	1224	1530	1989	2448	3060
77·0	385	539	693	924	1232	1540	2002	2464	3080
·5				930	1240	1550	2015	2480	3100
78·0	390	546	702	936	1248	1560	2028	2496	3120
·5				942	1256	1570	2041	2512	3140
79·0	395	553	711	948	1264	1580	2054	2528	3160
·5				954	1272	1590	2067	2544	3180
80·0	400	560	720	960	1280	1600	2080	2560	3200
ACCURACY	±2·5	±3·5	±4·5	±6·0	±8·0	±10	±13	±16	±20

A.C. mains (3000 light cycles/min.).

NITRATING ACIDS.

A number of acids were examined in order to find one which gave a suitable reaction rate for measurement. An acid of the following composition was chosen and used in all experiments on mononitration.

HNO_3	5 %
H_2O	25 %
H_2SO_4	70 %

EXPERIMENTAL.

NITRATION.

Nitrations were conducted with 60 gms. of toluene in order that the final yield of M.N.T. would be sufficient to permit a standard set point of T.N.T. to be obtained on continued nitration (see Methods of Estimation). The amount of acid chosen was such as to contain HNO_3 5 % in excess of that required for complete conversion of the toluene to M.N.T.

The acid was first introduced into the nitrator and heated to 30°C by warm water, when the whole batch of toluene was added rapidly. The heating bath was removed, the heat of reaction supplying all the heat necessary to maintain the temperature. The temperature could be controlled within 0.5 C° by circulation of water in the cooling coil.

METHODS OF ESTIMATION.

(1) Degree of Nitration.

At intervals samples of the reaction slurry were removed by pipette without stopping the stirrer. After standing a few seconds the upper layer was separated from the acid, washed twice with water and dried over a small piece of calcium chloride. When no cloudiness was visible in the sample its refractive index was measured with an Abbé refractometer. The relation between refractive index and degree of nitration of toluene is shown in Fig. 6.

(2) Isomeric composition.

Standard Set Point Nitration and Determination.

50 gms. M.N.T. were stirred with 120 gms. 90 % H_2SO_4 and warmed to 50°C. 125 gms. mixed acid (70 % H_2SO_4, 21.5% HNO_3, 8.5 % H_2O) were added and

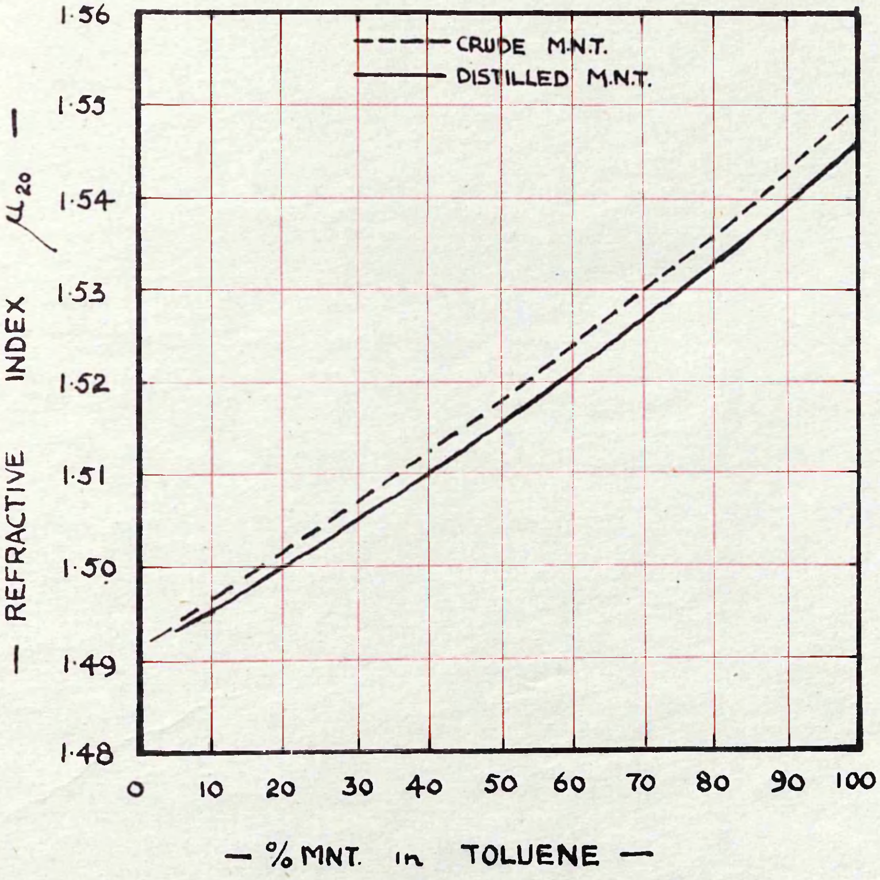

1·56
1·55
1·54
1·53
1·52
1·51
1·50
1·49
1·48
— REFRACTIVE INDEX μ_{20} —
CRUDE M.N.T.
DISTILLED M.N.T.
0
10
20
30
40
50
60
70
80
90
100
— % MNT. in TOLUENE —

FIG 6

the temperature raised to 70°C and maintained for 2 hours. The product was recovered by dilution, washed four times with boiling water and dried for 3 hours at 100°C. This was heated to 100°C with 220 gms. 100 % H_2SO_4 and 125 gms. mixed acid (60 % H_2SO_4, 40 % HNO_3) added slowly. The mixture was maintained at 100°C for 4 hours and the product recovered and washed as before. After drying for 3 hours the set point was determined as follows:-

The molten T.N.T. was poured into a previously heated test tube (6" x 1") to within 1 inch of the top and a heated thermometer and aluminium wire stirrer inserted. The whole was suspended in a larger test tube which was in turn set in a larger air jacket. The set point was taken as the maximum temperature reached after supercooling.

The proportion of meta-isomer present in the original sample of M.N.T. is given by the approximate equation -

$$\% \text{ meta-isomer} \mp 1.94\ (a - T)$$

where $\underline{a}$ = 80.6 and T = set point °C.

Hemimacro Modification.

Where the quantity of M.N.T. available was too small for the above estimation, the following modification was adopted.

5 gms. M.N.T. were treated with 20 mls. 20 % oleum and during 5 minutes 2.5 mls. 97 % HNO_3 added, the temperature being maintained below 40°C. The mixture was heated during 5 minutes to 70°C and maintained for 5 minutes. 4 mls. 97 % HNO_3 were introduced over 5 minutes and the temperature rapidly raised to 120°C. After 20 minutes at this temperature the product was recovered by dilution and washed and dried in the usual way. Its melting point was determined.

The meta-isomer is given by the normal formula except that $\underline{a} = 78$.

RELATIVE ACTIVITIES OF CATALYSTS.

Were the reaction toluene-M.N.T. accurately represented by the equation -

$$H_3C\cdot C_6H_5 + HO\cdot NO_2 \longrightarrow H_3C\cdot C_6H_4\cdot NO_2 + H_2O$$

its rate would be given by the bimolecular expression of the mass action law -

$$\frac{dx}{dt} = k(a-x)(b-x)$$

In the case where the initial molar concentrations of toluene and nitric acid are the same, the equation becomes -

$$\frac{dx}{dt} = k(a-x)^2$$

and integrating -

$$k = \frac{1}{t}\cdot\frac{x}{a(a-x)}$$

This condition is nearly satisfied in the following experiments (HNO_3 only 5 mol. % in excess). Plotting $\frac{x}{a(a-x)}$ against $\frac{1}{t}$ does not however give a straight line. This may be explained by the fact that:-

(1) Reaction mixture is not homogeneous (separate acid and nitrobody phases).

(2) HNO_3 is in solution in H_2SO_4 the concentration of which is being reduced by water of reaction.

(3) As reaction proceeds ionisation of the

nitric acid probably alters due to presence of the water of dilution. With respect to nitration, this is equivalent to abnormal decrease of nitric acid concentration.

It is accordingly incorrect to ascribe under these conditions any significance to the normal equation of mass action, and the order of reaction is quite indeterminate. Because of this, a value of "k" the velocity constant cannot be obtained. For the comparison of catalysts it would be convenient to ascribe to them at least a virtual velocity constant and this has been done throughout the work on the following basis.

The curve representing amount of toluene converted against time has the form shown in Fig. 7. The interrupted line is representative of a catalysed reaction.

As a measure of the catalytic activity the relative areas under the curves could be taken, but because the curves are asymptotic to the line representing complete conversion of toluene, ambiguity arises in deciding what time must be considered in

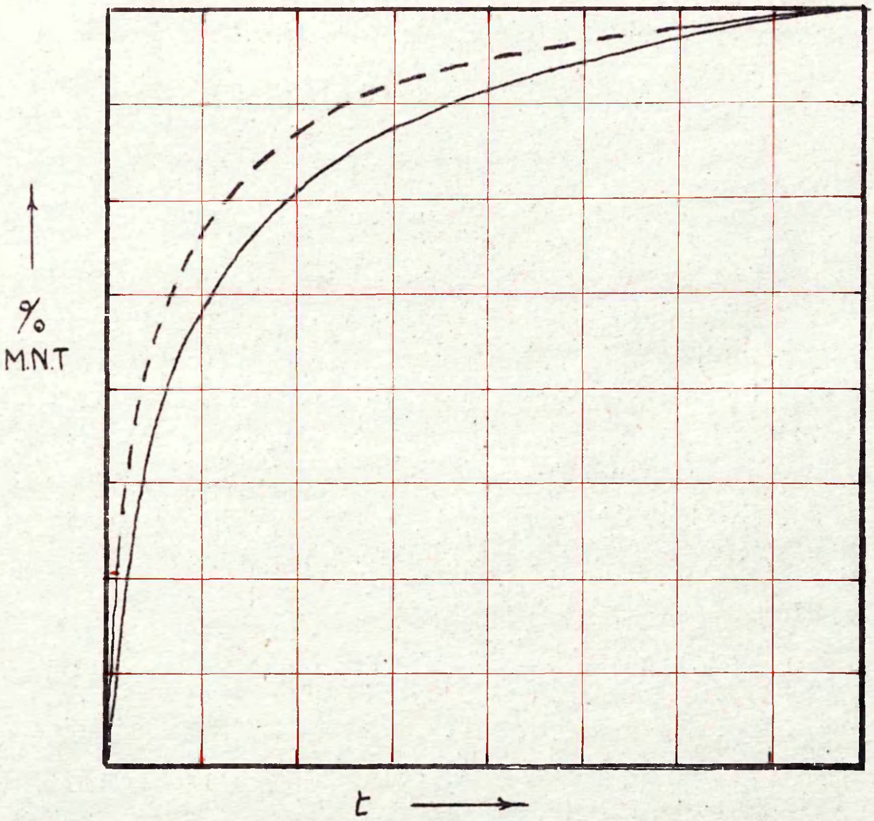


FIG 7

estimating the area under the curve. If on the other hand the area above the curve is taken as a measure of activity, no such uncertainty arises. The time scale may be extended to infinity since the areas so involved are continuously decreasing.

If we now define the activity of a catalyst as the area above the control reaction curve divided by the area above that of the catalysed reaction, we obtain a figure greater than unity for a catalyst and less than unity for an inhibitor. For an ideal catalyst the area above the reaction curve will be zero, that is reaction is completed in zero time, and the activity value will then be infinity.

In some cases the area above the reaction curve is in itself a suitable measure of activity; it is important to note that in this case low area value indicates high catalytic activity.

The value of activity which we will call "A" has no direct relationship to the velocity constant "k", ~~but is a varying power of it.~~

CHAPTER 2.

CATALYSIS BY HALIDES

Primary tests were conducted on the effect of chloride and fluoride ions on the mono-nitration reaction, in which NaCl and KF were used as catalyst sources. These were added (0.1 and 0.5 % ion as a molar proportion of the toluene) to the mixed acid, immediately prior to the introduction of the toluene. The results are shown in Table 5.

TABLE 5.

Catalyst.mol.% on the toluene mass	M.N.T. %.						
	time - minutes.						
	10	20	30	40	50	70	80
0.0 (Control)	33	61	72	80	85		94
0.1 Cl as NaCl	56	76	85	88		92	
0.5 Cl as NaCl	51	76	84	88	92		
0.0 (Control)	36	62	77	86	90		
0.0 (Control)	36	60	73	86	90		
0.1 F as KF	51	67	80	89			
0.5 F as KF	54	68	81	90			
0.5 F as KF	71	86	91	93			
0.5 F as KF	60	77	86	91			

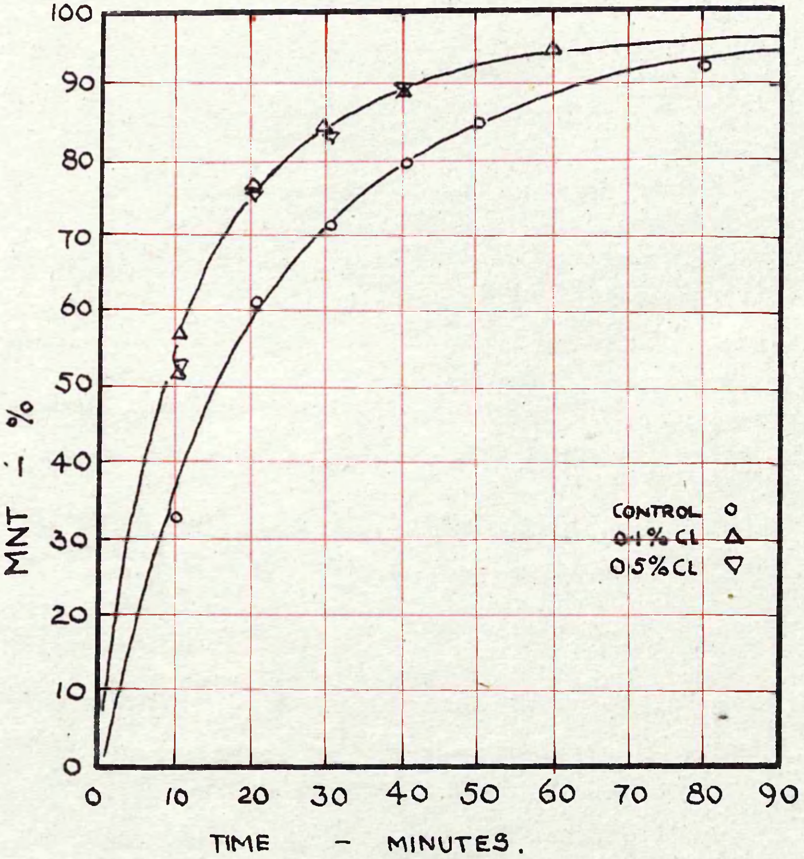

100
90
80
70
60
50
40
30
20
10
0
MNT - %
0
10
20
30
40
50
60
70
80
90
TIME - MINUTES.
CONTROL ○
0·1% CL △
0·5% CL ▽

FIG 8

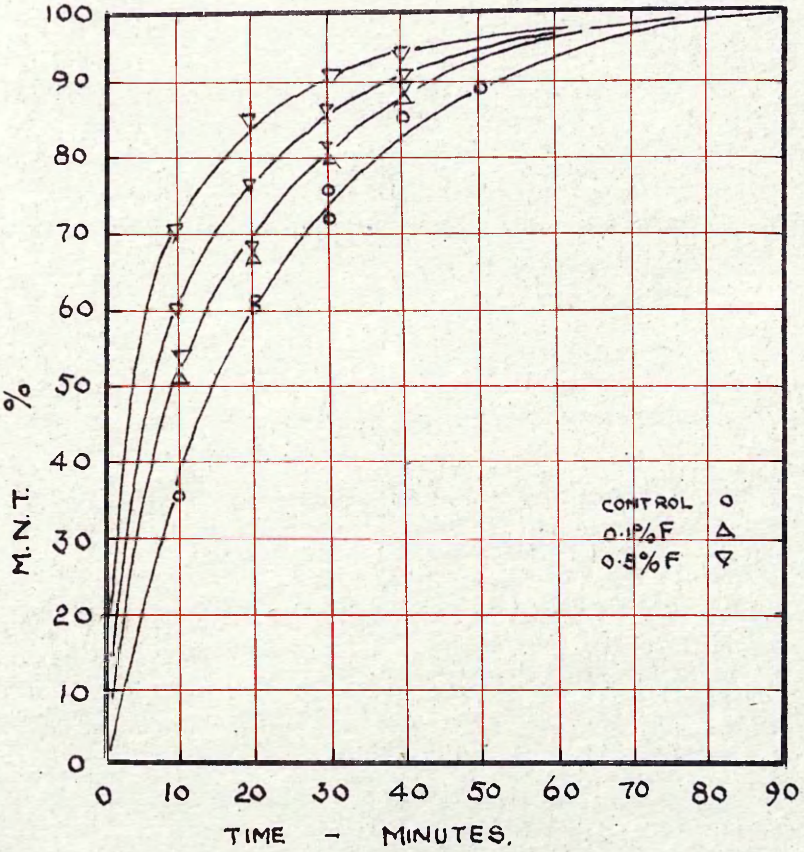

100
90
80
70
60
50
40
30
20
10
0
M.N.T. %
0
10
20
30
40
50
60
70
80
90
TIME - MINUTES.
CONTROL ○
0·1%F △
0·5%F ▽

FIG 9

Figs. 8. and 9. show the reaction curves for these catalysts. The activity figures are -

$A_{.1Cl} = 1.30$
$A_{.5Cl} = 1.30$
$A_{.1F} = 1.41$
$A_{.5F} = 1.54$

They indicate definite catalysis but the results particularly for 0.5 % fluoride are extremely variant, the highest and lowest figures recorded being 1.44 and 1.68.

A digression was made at this point in order to determine the active agent in catalysis by chloride. It was thought that this might be nitrosyl chloride (NOCl), and this was prepared by passing dry chlorine and nitric oxide through a glass tube heated to 300°C, the products being collected in a receiver cooled by solid carbon dioxide. The products were then fractionated to obtain the nitrosyl chloride free from chlorine and nitrogen peroxide. the product was used as catalyst in a nitration similar to those carried out with NaCl. The results are shown in Table 6. and graphically in Fig. 10. (See over).

The activity of nitrosyl chloride is 1.37.

Its similarity to that of chloride suggests that it might be the active component formed by the actionof sodium chloride on mixed acid.

TABLE 6.

Catalyst mol. %.	M.N.T. %. time - mins.				
	10	20	30	40	50
0.0	34	62	72	82	87
0.06	60	78	83		88

The difference in the rate of reaction in the control nitrations of different series indicates distinct variation in the activity of different batches of mixed acids. In order to measure the relative activities of the halide catalysts a large batch of mixed acid was prepared for nitration with the halides of potassium. By utilising salts of the same metal variations due to the positive ion were eliminated. The results of these tests are shown in Table 7.

TABLE 7.

Catalyst mol. %.		M.N.T. %. time - mins.			
		10	20	30	40
0.0		26	52	72	80
0.1	F	47	74	88	
0.1	Cl	53	79	90	
0.1	Br	59	81	90	

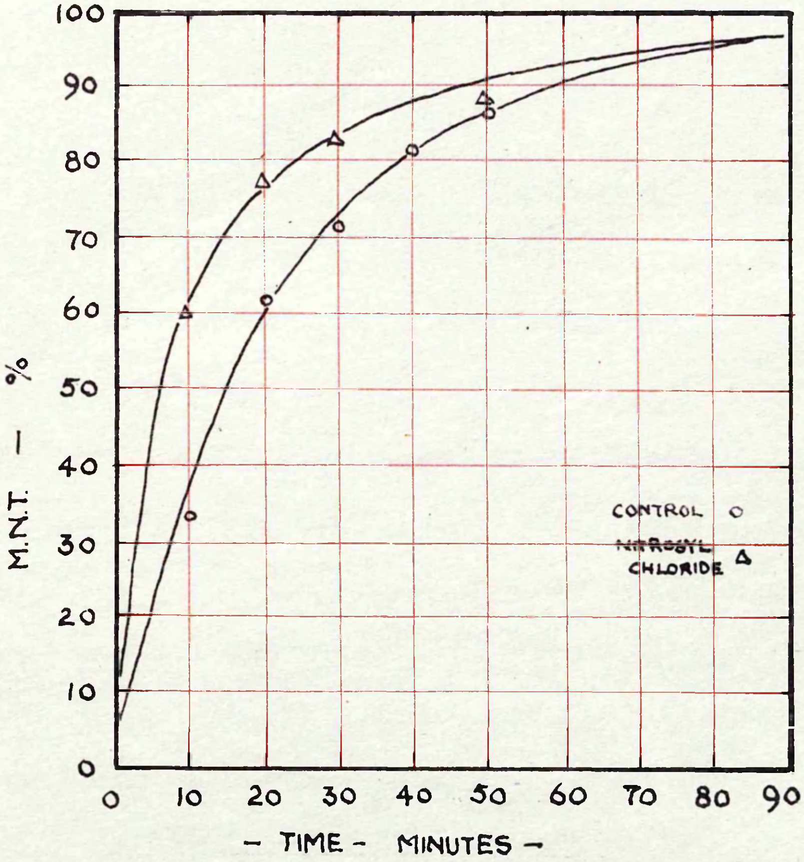

100
90
80
70
60
50
40
30
20
10
0
M.N.T. – %
0
10
20
30
40
50
60
70
80
90
– TIME – MINUTES –
CONTROL ○
NITROSYL CHLORIDE △

FIG 10

Fig. 11. shows the reaction curves. These are much more regularly distributed than the fluoride curves in the previous tests. The activity values are -

$A_F = 1.67$
$A_{Cl} = 1.97$
$A_{Br} = 2.11$
$A_I = 2.33$

Plotting "A" against atomic weight results in a curve. A more linear relationship exists between activity and vertical position in the periodic table. It is only possible to state that activity increases with atomic weight, the actual relationship being indeterminate. For practical purposes the time for completion of reaction is of importance. A special series of experiments were conducted to determine this time in the case of the iodide catalysed reaction. For this purpose the reaction was reckoned complete when 99 % of the toluene had been converted.
Table 8. shows the results obtained and they are plotted against the reciprocal of time in Fig. 12. Plotting against $1/t$ makes the curves more steep at $t = \infty$, and simplifies estimation of time of virtual completion. The 99 % conversion line is shown in

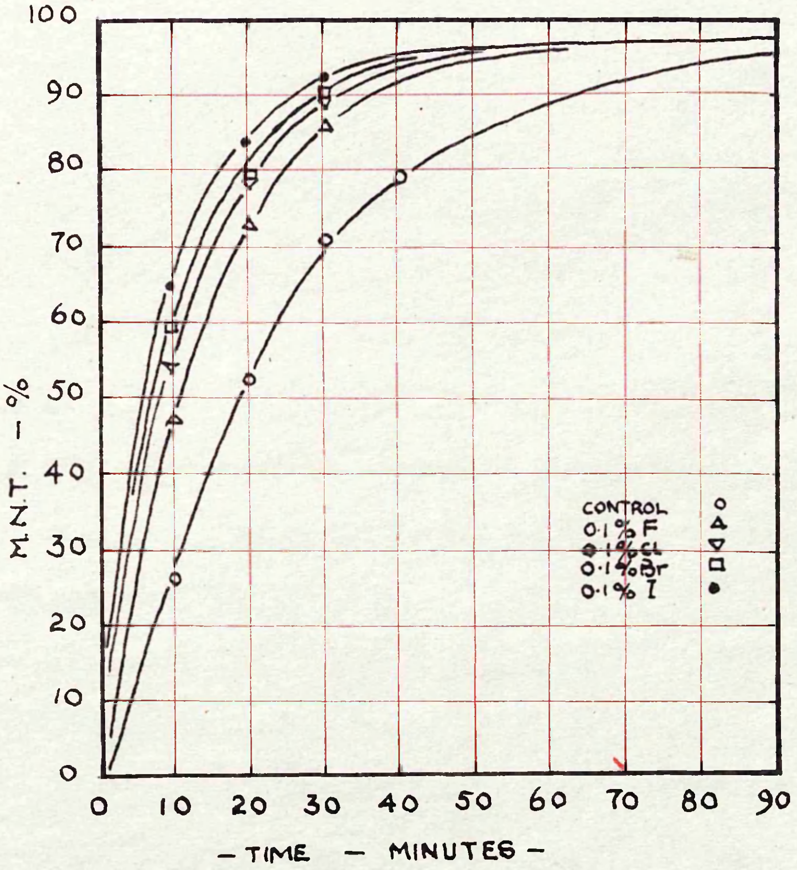

100
90
80
70
60
50
40
30
20
10
0
M.N.T. – %
0
10
20
30
40
50
60
70
80
90
– TIME – MINUTES –
CONTROL ○
0·1% F △
0·1% Cl ▽
0·1% Br □
0·1% I ●

FIG 11

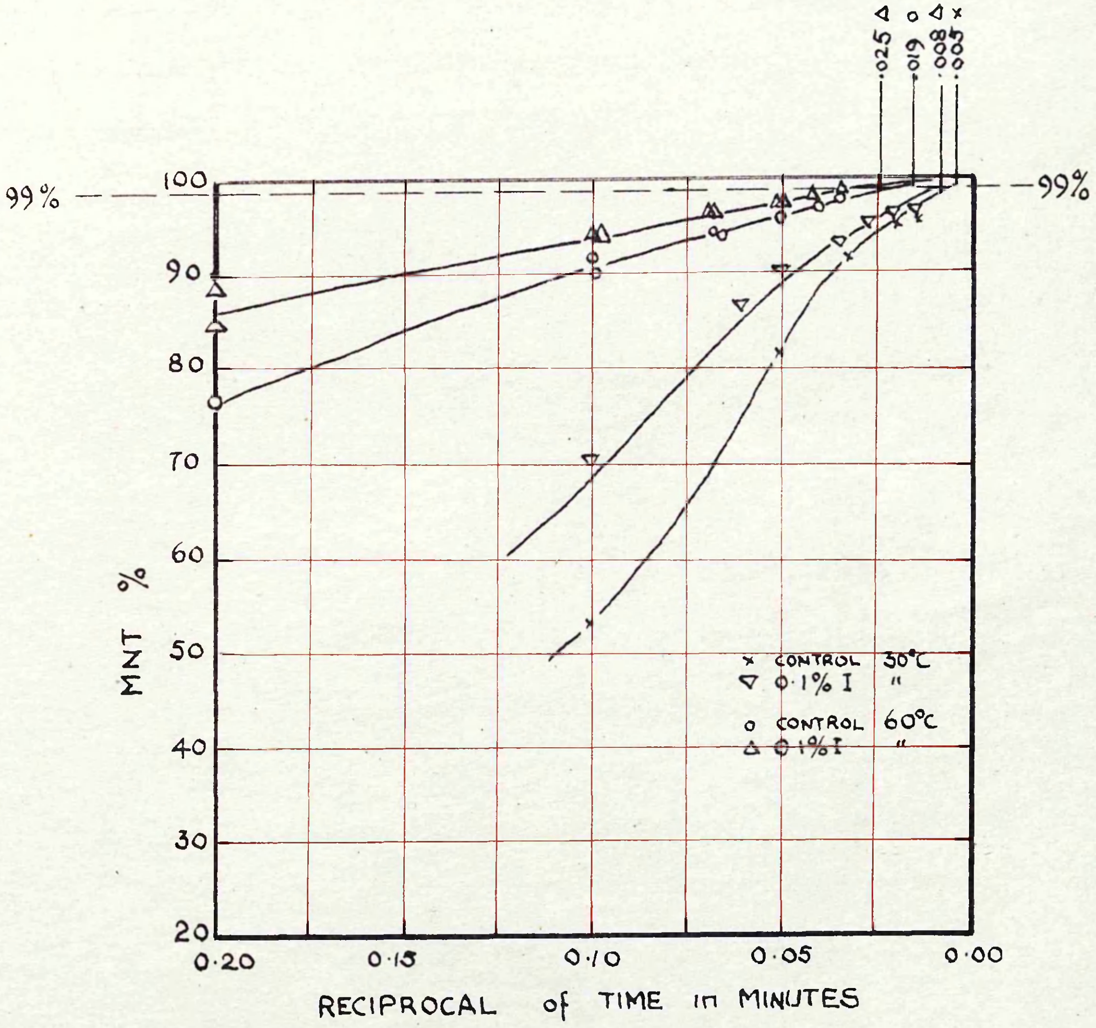
·025 △
·019 o
·008 △
·005 ×
99%
99%
100
90
80
70
60
50
40
30
20
MNT %
0·20
0·15
0·10
0·05
0·00
RECIPROCAL of TIME in MINUTES
× CONTROL 30°C
▽ 0·1% I "
o CONTROL 60°C
△ 0·1% I "

FIG 12

the figure and the intercepts of the reaction curves with this are indicated in the right upper corner of the diagram. The intercepts give the following times for virtual completion of reaction -

	30°C	60°C	
control	200	53	minutes.
0.1 % I.	125	40	

TABLE 8.

Catalyst mol. %.	M.N.T. %.								
	time - minutes.								
	5	10	15	20	25	30	40	50	60
0.0		53		81		93	94	95	95
0.1 I as KI		70		90		93	96	96	96
0.0 *	84	92	96	100	100	100			
0.1 I as KI *	88	93	97	97	98	98			
0.0 *	76	90	93	96	98	98			
0.0 I as KI *	84	94	96	97	97	98			

* reaction conducted at 60°C.

A decrease in overall time of some 35 % is indicated and this might be capable of some industrial application. Against the commercial use of halide as catalyst may be cited the danger of increased corrosion of plant, and the use of such catalysts would be subject to the results of corros-

-ion tests. The considerable increase of the rate of reaction in the early stages of nitration might be made use of in continuous mononitration.

The set points of T.N.T. prepared from M.N.T. catalysed during nitration by fluoride and chloride were 78.3 and 78.4°C. No change in the proportion of isomers is thus indicated.

CHAPTER 3.

CATALYSIS BY THE HEAVY ELEMENTS

The activity of iodine as a catalyst suggested the possibility of catalytic activity by the elements of high atomic weight. It was accordingly decided to measure the catalytic effect of heavy elements from other groups of the periodic table.

The periodic classification is shown in Fig. 13. Elements examined are circled. Whenever they were available the sulphates or nitrates of the elements were employed so as to avoid interference by effects of acid radicals. Estimation of activity was carried out in exactly the same manner as with the halides in the previous chapter. The amount of catalyst added was 0.1 %, a molecular percentage of the element based on the mass of toluene. The product of all nitrations was converted to T.N.T. by the hemi-macro method described on Page 61. Samples which showed high melting point in this test were

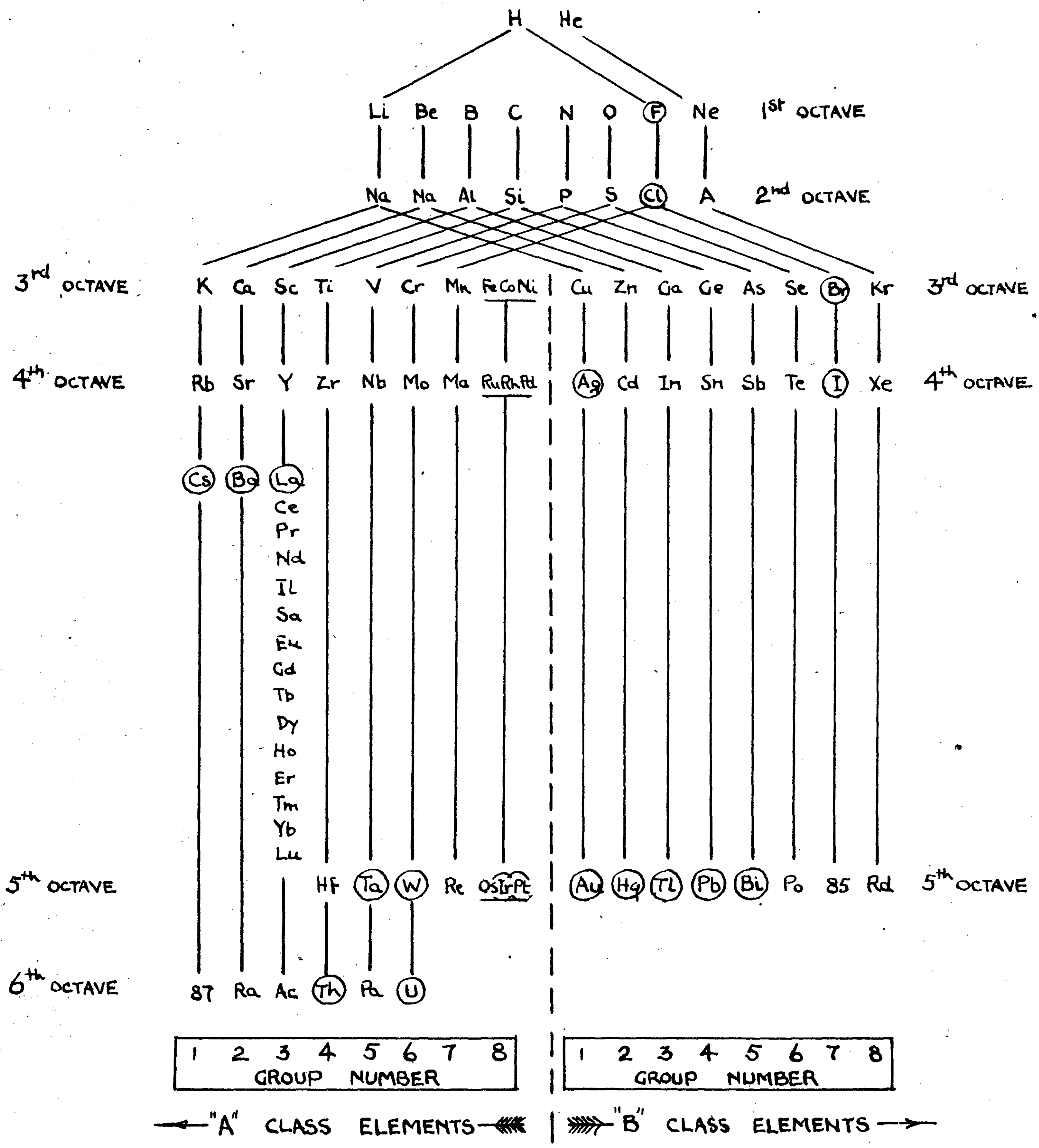

H He
Li Be B C N O F Ne
1st OCTAVE
Na Na Al Si P S Cl A
2nd OCTAVE
3rd OCTAVE
K Ca Sc Ti V Cr Mn FeCoNi
Cu Zn Ga Ge As Se Br Kr
3rd OCTAVE
4th OCTAVE
Rb Sr Y Zr Nb Mo Ma RuRhPd
Ag Cd In Sn Sb Te I Xe
4th OCTAVE
Cs Ba La
Ce
Pr
Nd
Il
Sa
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
5th OCTAVE
Hf Ta W Re OsIrPt
Au Hg Tl Pb Bi Po 85 Rd
5th OCTAVE
6th OCTAVE
87 Ra Ac Th Pa U
1 2 3 4 5 6 7 8
GROUP NUMBER
1 2 3 4 5 6 7 8
GROUP NUMBER
"A" CLASS ELEMENTS
"B" CLASS ELEMENTS

FIG 13

subjected to the more accurate Dry Set Point test. The results are shown in full in Table 9.

The column of the table headed "Activity Area" contains values of the area above the reaction curves measured on the dimensions of M.N.T. % and minutes. The reaction curves have not been plotted because their number and close proximity to one another result in a very confused diagram. Fig. 14. shows the activity area plotted against periodic group number. The activity area of the control reaction is shown as a dotted line across the graph. It will be noted that elements exhibiting high activity have a low activity area, that of the ideal catalyst being zero. Points below the dotted line represent positive catalysts and above the line negative catalysts or inhibitors.

A remarkable co-relation exists in the form of the two curves. Considering first only the elements of the fifth double octave, metals of the left hand or "A" octave all lie on the upper line (low catalytic activity) and those of the "B" octave on the lower line (high activity). In periodic groups 1, 2, and 3, there is a progressive slight increase in activity,

TABLE 9.

Catalyst.	M.N.T. %. Time-mins.			M.Pt. of T.N.T. °C	Dry Set Point °C	Activity Area min. %.
	10	20	30			
Control	53	68	82	76.5	78.52	1660
Silver	68	81	91	74.9		1225
Caesium	53	73	82	77.1	78.60	1670
Gold	58	81	91	76.5		1315
Barium	52	70	83	76.1		1685
Mercury	66	81	88	76.6		1298
Lanthanum	58	74	85	74.8		1600
	56	74	84			
Thallium	63	85	91	76.5		1188
Lead	55	75	85	76.5		1610
Thorium	48	70	80	76.8		1950
	48	69	87			
Tantalum	48	67	77	76.7		2030
Bismuth	53	75	87	76.8		1558
Tungsten	55	74	84	77.1	78.50	1630
Uranium	48	69	81	77.1	78.60	1765
Iodine	70	82	90	77.1	78.60	1200
Iridium	56	81	90	76.6		1410
Platinum	55	81	91	76.5		1375

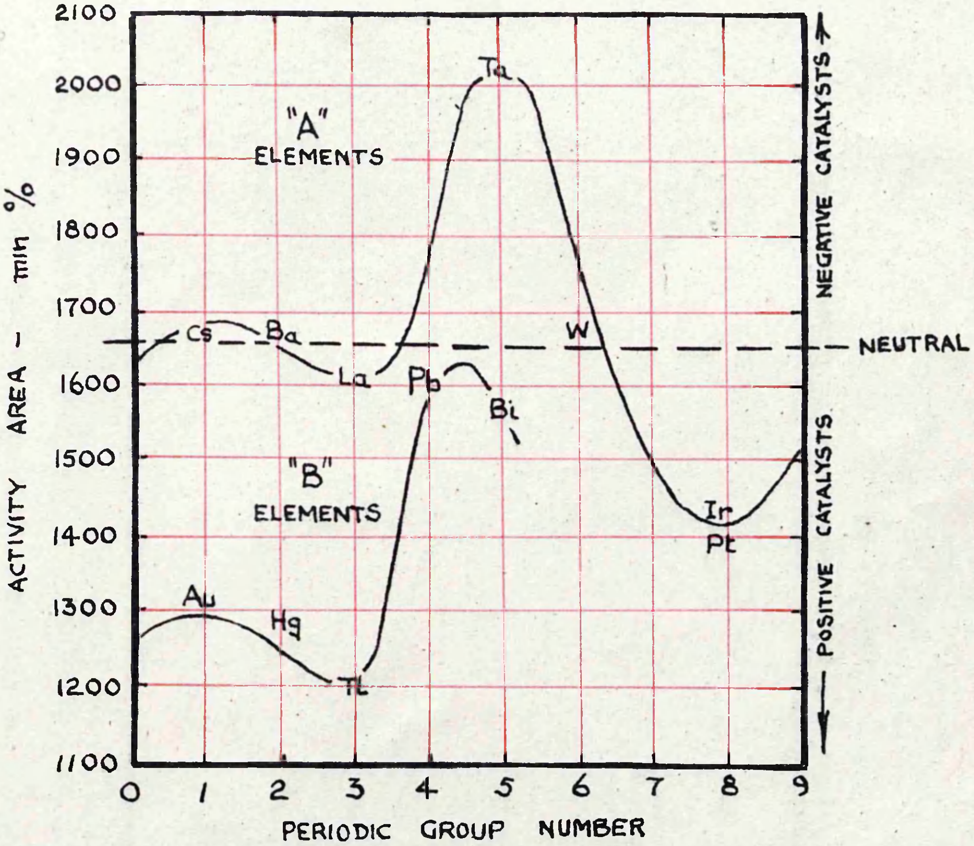

2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
ACTIVITY AREA - min %
0
1
2
3
4
5
6
7
8
9
PERIODIC GROUP NUMBER
"A" ELEMENTS
"B" ELEMENTS
Ta
Cs
Ba
La
Pb
Bi
W
Ir
Pt
Au
Hg
Tl
NEUTRAL
NEGATIVE CATALYSTS
POSITIVE CATALYSTS

FIG 14

but while the "A" group elements are almost neutral those of the "B" class are highly active. In groups 4. and 5. the activity falls sharply, so distinctly in fact that tantalum (group 4A) is a definite inhibitor. In the "B" group this fall in activity renders lead and bismuth nearly neutral. Through groups 6, 7 and 8 activity again increases sharply so that iodine (7B) and iridium and platinum (8A) are all active catalysts.

Fig. 15. has been constructed to show graphically not only the fifth double octave, but the whole periodic classification in panorama. On this, points representing all the elements in Table 9. have been plotted. The activity areas for the halogens, have been deduced from the results of estimations in the previous chapter and are also shown in the figure. Making the speculative assumption that curves of "group activity" of the previous figure apply throughout the whole periodic classification we may then construct a graph representative of the activity of all the elements.

It will be observed that in octave 4B iodine has an activity area of 1200 units while bromine (3B) has the value 1270. This gives the "B" octave curve a slight upward inclination as we proceed from right to left on the graph, the curve passing successively through the points -

I	Group	7	Octave 4B	1200
Br	"	7	Octave 3B	1270
Cl	"	7	Octave 2B	1320
F	"	7	Octave 1	1440

The relative activity areas of uranium (octave 6A) and tungsten (5A) give the mean gradient of the "A" octave curve. This curve will gradually approach that of the "B" octave elements so that when we reach the area on the left of the graph representing the elements in the first two single octaves of the periodic table, the curves are superimposed.

The activity areas of all the elements would then be supposed to be the appropriate points on the curves as shown. The points referring to the elements the activity areas of which were measured, have again been circled.

Silver is the only element the activity of which could not be reconciled to the curve embracing the other elements and this we must assume to have been due to some experimental error.

The set point determinations indicate that M.N.T. prepared in presence of these catalysts contains the normal quantity of meta-isomer.

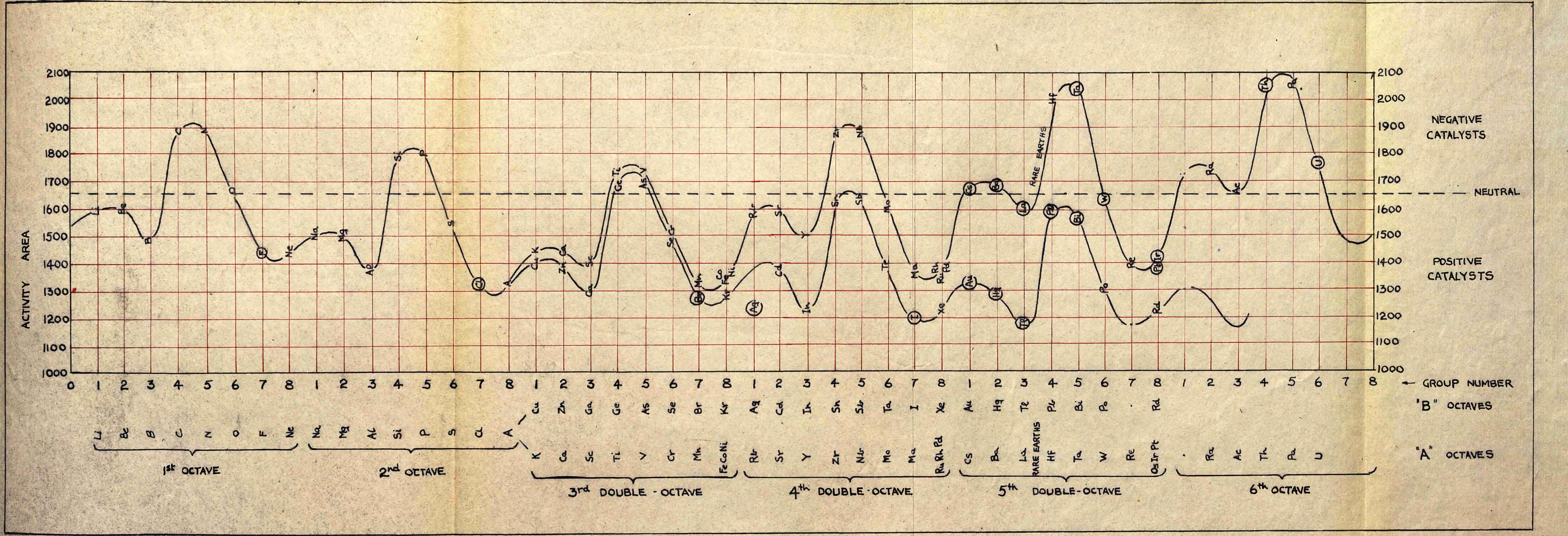

ACTIVITY AREA
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
NEGATIVE CATALYSTS
NEUTRAL
POSITIVE CATALYSTS
← GROUP NUMBER
"B" OCTAVES
"A" OCTAVES
Li Be B C N O F Ne
1st OCTAVE
Na Mg Al Si P S Cl A
2nd OCTAVE
Cu Zn Ga Ge As Se Br Kr
K Ca Sc Ti V Cr Mn Fe Co Ni
3rd DOUBLE - OCTAVE
Ag Cd In Sn Sb Te I Xe
Rb Sr Y Zr Nb Mo Ma Ru Rh Pd
4th DOUBLE-OCTAVE
Au Hg Tl Pb Bi Po · Rd
Cs Ba La RARE EARTHS Hf Ta W Re Os Ir Pt
5th DOUBLE-OCTAVE
· Ra Ac Th Pa U
6th OCTAVE
RARE EARTHS

FIG 15

CHAPTER 4.

NATURALLY OCCURRING CATALYSIS

In an earlier series of experiments it was found that nitration toluene reacted with mixed acid much faster than the same material freshly distilled at atmospheric pressure, the total time of nitration under identical conditions being nearly two hours for the latter and only thirty minutes for the former. The effect was attributed to the presence of chloride or thiophenes in the toluene, but the subject was felt worthy of more complete investigation and the following series of experiments was conducted to elucidate the point.

High gravity toluene (S.G. 0.868) was fractionated in a Young's column in batches of 1500 mls. This volume was separated into three equal fractions, the corresponding fractions of a second batch similarly treated being combined (see Fig. 16). In this way three samples of 1000 mls. were obtained.

These were individually distilled, three fractions of 300 mls. being drawn and the final 100 mls. residues being combined. 200 mls. of this residue were distilled and rejected. The remaining 100 mls. was removed from the still as final residue of the original 3000 mls. of toluene.

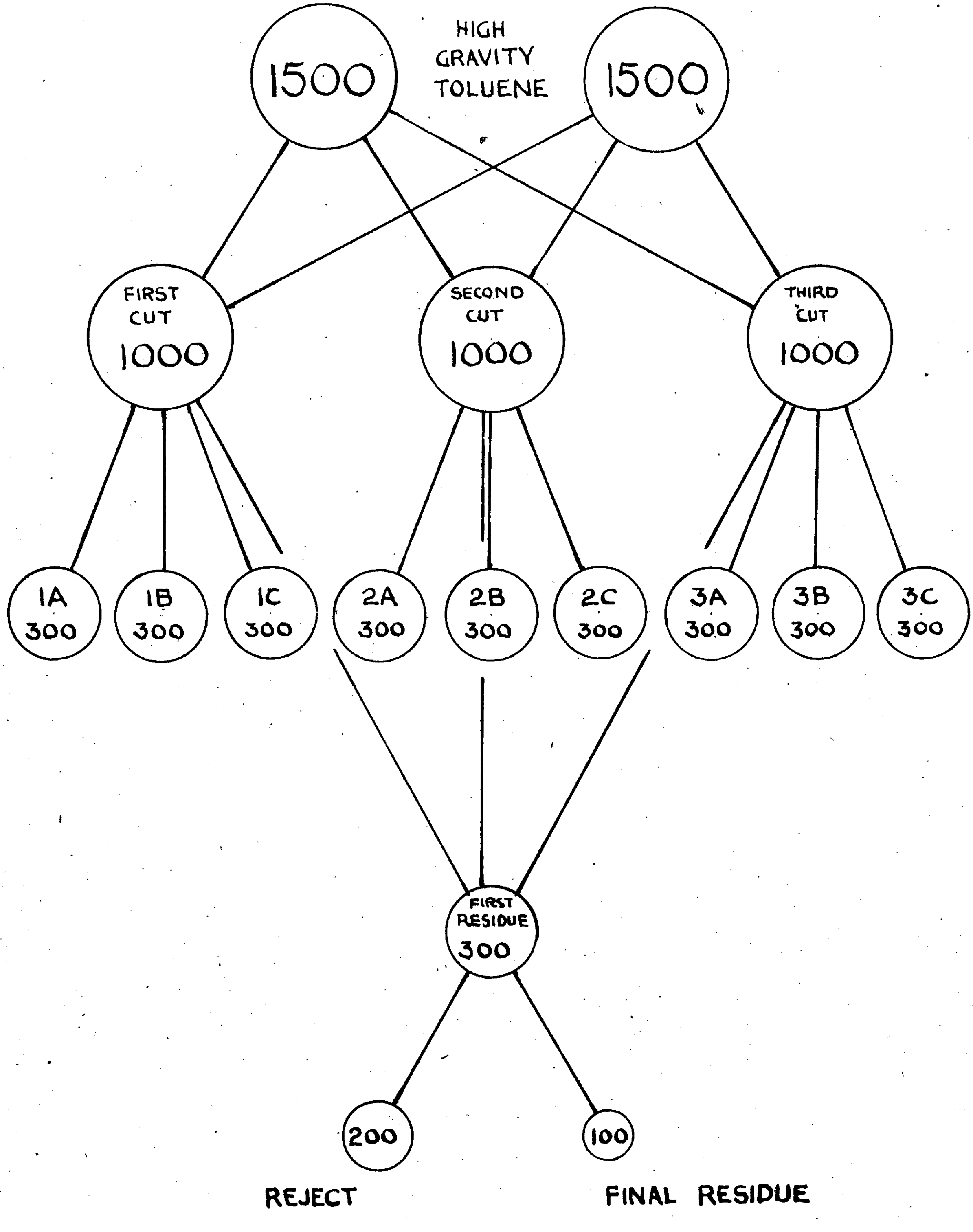
The process was repeated, corresponding fractions again being combined till a good supply of each fraction was available. The distillation temperature of the fractions is shown graphically in Fig. 17.

ESTIMATION OF CHLORIDES.

An attempt was made to estimate chloride in each of the samples by precipitation with silver nitrate solution. No turbidity could be detected in any of the samples even with the aid of a sensitive turbidimeter.

ESTIMATION OF THIOPHENES.

Each fraction was treated with a solution of 1 % isatin in pure concentrated sulphuric acid. On prolonged standing all fractions gave a blue



TOLUENE FRACTIONATION SCHEME

FIG 16

colour indicating the presence of thiophenes. Thiophenes were estimated as thiophene using Denigés reagent prepared as follows:-

10 gms. mercuric oxide was finely ground and dissolved in a solution of 40 mls. conc. sulphuric acid in 220 mls. distilled water. The solution was filtered and preserved in a well stoppered bottle.

To conduct the estimation 50 mls. toluene were placed in a stout boiling tube and 20 mls. of the reagent added. The tube was closed by a tightly fitting cork and mechanically shaken for three hours. The solution was filtered through a tared sinter crucible and the precipitate $(HgO.HgSO_4)_2C_4H_4S$ dried in an air oven at 50°C for 6 hours.

Such estimations were carried out in triplicate on each of the fractions. The average results are shown in Table 10. and graphically in Fig. 17.

The rates of nitration of the separate fractions were then determined in exactly the same manner as for the halide catalysts. The results are shown in Table 11.

The values of the activity area for the nitration of each distillation fraction is plotted in

TABLE 10.

Sample No. (see Fig.17.)	Thiophene %
1A	0.0134
1B	0.0143
1C	0.0198
2A	0.0190
2B	0.0127
2C	0.0232
3A	0.0175
3B	0.0206
3C	0.0258
R	0.0205

TABLE 11.

Fraction No.	M.N.T. %.							Activity area. min. %.
	time - minutes.							
	5	10	15	20	25	30	35	
1A	11.4	24.0	38.4	54.6	68.0	80.4	87.3	2050
1B	18.8	46.2	58.0	72.8	87.6	94.2	98.0	1445
1C	24.2	40.4	58.0	71.5	85.6	90.2	94.5	1505
2A	17.9	24.2	48.0	66.0	84.0	90.0	94.1	1410
2B	26.4	54.2	72.0	82.6	88.8	93.8	97.6	1217
2C	20.8	43.5	64.0	78.2	87.5	92.2	96.2	1400
3A	25.1	35.0	52.0	67.7	78.8	88.0		1560
3B	17.9	46.2	50.0	65.8	80.3	90.3	96.2	1485
3C	24.2	43.5	48.4	68.0	80.5	87.8		1620
R	64.4	80.3	90.2	94.5	95.8	97.8	99.2	610

Fig. 17. along with the curves representing proportion of thiophenes and temperature of distillation. Comparison of the graphs shows that the activity of the residue cannot be attributed to the thiophene content alone, but accompanies an increase in the boiling point of the toluene. In the first fraction (1A) where the boiling point is low the activity is also low (high activity area).

That catalysis is not due to thiophene was conclusively proved by nitrating a pure sample of toluene to which 0.1 % of thiophene was added. The reaction rate was normal indicating complete inactivity of thiophene and the dry set point of T.N.T. made from the M.N.T. product so obtained was 78.7°C.

It was thought that catalysis in the residue might be due to the presence of mono- and di-cyclopentadienes. Claxton and Hoffert (Coke Oven Manager's Year Book 1941, 146) describe the estimation of these in commercial benzole. The test employed by these workers consists of shaking 5 mls. of toluene with an equal quantity of 0.5 % sodium hydroxide in methanol, and 0.4 mls. 1 % hydroquinone in methanol. After shaking for 15 seconds and

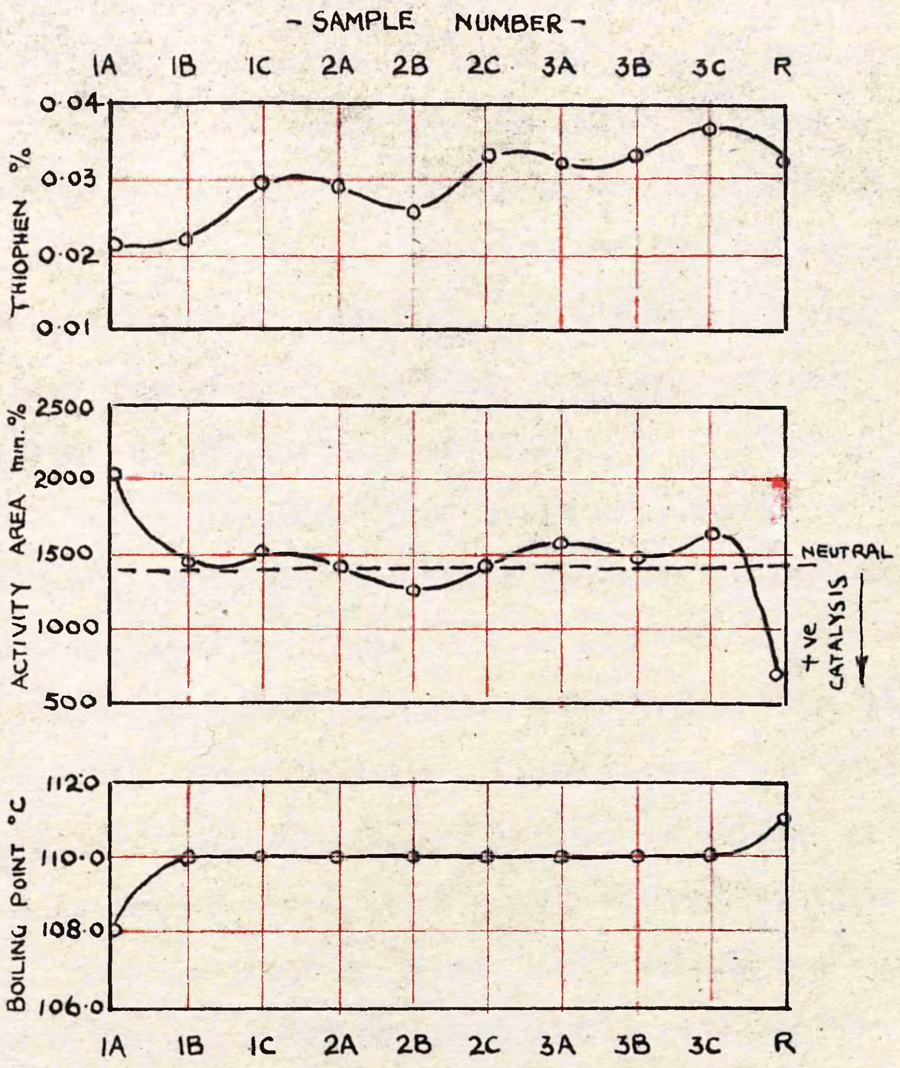

- SAMPLE NUMBER -
1A
1B
1C
2A
2B
2C
3A
3B
3C
R
THIOPHEN %
0·04
0·03
0·02
0·01
ACTIVITY AREA min.%
2500
2000
1500
1000
500
NEUTRAL
+ve CATALYSIS
BOILING POINT °C
112·0
110·0
108·0
106·0
1A
1B
1C
2A
2B
2C
3A
3B
3C
R

FIG 17

standing 10 seconds, a green colour is produced in presence of mono-cyclopentadiene. The test showed that all the toluene fractions were free of the compound. Since the tests were conducted on freshly distilled toluene, depolymerisation of the dimer, if present, would have occurred, and the monomer would therefore have been detected. The fact that none was found was taken as evidence that none of the polymers was originally present.

It was concluded that residual toluene contained some catalyst other than chloride, thiophene or cyclopentadiene. That the catalyst is not produced by hydrocarbon cracking at the temperature of atmospheric distillation was shown by the fact that the residue from vacuum distillation of toluene had the same reactivity as that from normal distillation.

In an attempt to obtain some information concerning the nature of the catalyst present in the toluene residue the reactivity of the material after various acidic and alkaline washes was studied. Table 12. shows the results of this series of experiments.

TABLE 12.

Material	Method of distillation	Washing medium.	M.N.T. %.			
			time - minutes.			
			5	10	15	20
Toluene	Atmospheric	Water	27.0	50.0	66.3	76.0
"	"	---	51.5	72.0	86.6	94.1
Residue	"	Water	50.5	75.0	85.9	91.0
"	Vacuum	---	51.5	72.8	79.1	86.6
"	"	Water	49.0	69.8	74.4	86.6
"	Atmospheric	5N H_2SO_4	48.2	69.6	77.5	83.7
"	"	5N $NaHCO_3$	48.2	68.0	82.2	88.1
"	"	5N NaOH	35.0	56.5	69.6	77.5

The only washing medium which materially reduced the subsequent reaction rate was sodium hydroxide. The catalyst would therefore appear to be acidic in nature. Moreover the ineffectiveness of sodium bicarbonate in extracting the catalyst suggests phenolic form rather than a carboxylic acid. Acidification of the sodium hydroxide washings and extraction with ether did not yield any product.

One of the greatest difficulties was that of obtaining a good supply of distillation residue, in view of the fact that only 100 mls. could be produced from long distillations of 3000 mls. of toluene. Glasgow Corporation (Provan Chemical Works) were able to supply some gallons of tailings from distillation on the plant of low gravity toluene from gas works benzole. It was thought that this product might be richer in catalyst than normal nitration toluene thereby rendering isolation of the catalyst more simple. This toluene in fact showed great lack of reactivity compared with high gravity material (Table 13.). On distillation, the residue showed no increased reactivity compared with the middle cut of the product. No catalyst could be isolated from the residue, nor did washing with sodium hydroxide reduce the activity of the residue.

TABLE 13.

Description of sample.	S.G.	M.N.T. %.			
		time - minutes.			
		5	10	15	20
1.gall. sample from final 5.galls. toluene distillation (Provan Chemical Works).	0.860	17.0	37.0	53.0	61.4
100 mls. residue from lab. distillation of 3000 mls. of previous sample.	0.862	17.0	40.0	55.0	61.4
1.gall. sample penultimate 5.galls. toluene distillation (Provan Chemical Works).	0.857	17.0	37.0	53.0	61.4
100 mls. residue from lab. distillation of 3000 mls. of previous sample.	0.860	15.0	37.0	53.0	61.4
High Gravity nitration toluene.	0.868	27.0	50.0	66.3	76.0

In view of the difficulty of isolating any catalyst from the residual toluene a new approach was made to the subject, in which phenolic compounds were added to the toluene prior to nitration, to determine if they did indeed exert a catalytic effect. The results of the experiments are shown in Table 14. As in the previous tests the amount added was 0.1 mol. % on the weight of the toluene.

TABLE 14.

Sample.	M.N.T. %.							Dry set point	Activity Area
	TIME - MINUTES.								
	5	10	15	20	25	30	35		
Toluene	20.8	43.5	70.0	80.0	87.9	93.5	97.2	78.7	1270
"xylene	21.0	32.0	57.5	69.6	80.7	88.1	93.5	78.3	1450
"phenol	42.6	69.6	80.7	91.1	93.0	94.1	95.6	78.5	955
"o-cresol	37.0	58.1	76.4	88.1	92.6	94.1	96.5	78.4	1050
"m-cresol	37.0	59.8	79.2	90.0	93.0	94.1	96.5	78.6	975
"Residue"	64.4	80.3	90.2	94.5	95.8	97.8	99.2	78.3	610

The results indicate positive activity of phenols and cresols. It will be observed that xylene exerts no influence on the reaction rate from which it would appear that the activity of the catalyst is closely associated with the polarity of the substituents in the benzene nucleas.

The M.N.T. produced in these nitrations was con-

-verted to T.N.T. by the standard method and the dry set point determined. The results are shown in the Table 14. beside the activity areas. All the samples show a slightly low set point probably due to the presence of the nitrated phenolic bodies.

Extraction of the M.N.T. with 5N sodium carbonate gave a deep red solution which deposited red crystals on standing for a few hours. These crystals were filtered off and recrystallised from water. Finally the solution of the crystals was acidified and the yellow precipitate obtained recrystallised from alcohol. The product had M.Pt. 81°C and was thought to be a mixture of 3:5-dinitro-ortho- and para-cresols. (Nolting and Ferol, Ber. 1885, 18, 2670).

As an aid in the investigation dinitro-cresols were prepared from ortho- and para-cresols by a simplification of the method of Datta and Varma (J.Am.Chem.Soc. 1919, 41, 2041). The method described consists of sulphonating and then steam distilling to remove unchanged cresol, after which nitration is conducted at low temperature, by oxides of nitrogen. The sulphonate of cresol is easily hydrolysable and it was found that no matter how long steam distillation was conducted free cresol always occurred in the product. Moreover low temperature nitration gives poor yield.

An adaption of the method was made, the preparation being modified as follows:-

The sulphonic acids were prepared by heating the cresols with 100 % H_2SO_4, diluting with an equal mass of water and heating to 90°C, when concentrated nitric acid (70 %) was added slowly till reaction subsided. The solution was stirred while cooling and granulated dinitro-cresol so formed filtered off and recrystallised from alcohol. No tar was produced and the yield was always over 90 % of the theoretical.

3:5-dinitro-ortho-cresol	M.Pt. 86.5°C
3:5-dinitro-para-cresol	M.Pt. 81.5°C

A mixed melting point conducted with the material isolated from M.N.T. and each of the above substances in turn showed no depression with the para- compound.

Acetyl derivatives of both nitrocresols, prepared by refluxing with acetic anhydride containing a few drops of syrupy phosphoric acid, gave M.Pt. para- 154°C and ortho- 96°C. That of the compound isolated from mono-nitrotoluene gave M.Pt. 154°C and was therefore the derivative of the 3:5-dinitro-para-cresol.

The solubility of the dinitro-ortho-cresol in sodium carbonate was found to be much higher than that of the para compound and this probably accounts for the failure to isolate the former salt by crystallisation. Nolting (loc. cit.) suggests that the nitrocresols are formed during the nitration by oxidation of the toluene by mixed acid or oxides of nitrogen, or by oxidation of 3:4:5- or 2:3:5- trinitrotoluene presumed to be formed in the reaction.

Although D.N.T. is sometimes produced during vigorous mononitration it is thought unlikely that any T.N.T. can be formed under the conditions here, but the first hypothesis of Nolting made the subject worthy of investigation, particularly in view of its possible bearing on oxidation losses in T.N.T. manufacture.

1500 mls. of toluene were fractionated in a four pear column, the first 100 mls. being drawn as first cut and the final 100 mls. as residue. The middle cut was then fractionated in the same manner the first and last 100 mls. being collected separately and mixed with the corresponding cuts of the first distillation. This process was repeated till the first cut was 600 mls. the middle 300 mls. and the residue 600 mls.

Samples of each fraction were extracted with sodium hydroxide solution and the extract steam distilled to remove toluene. Acidification and extraction with ether gave only a very small residue of tar the character of which could not be determined. An attempt to form a picrate of any cresol present in the toluene by direct refluxing with picric acid was unsuccessful.

150 mls. of residual toluene were refluxed for 90 minutes with solid sodium hydroxide. The toluene was poured off and a little water added to dissolve the sodium hydroxide. By coupling with diazotised para-nitraniline and with benzidine, red and brown dyes were obtained.

A 70 ml. sample of each of the cuts was nitrated and the nitrocresols extracted from the M.N.T. with 40 mls. 5N sodium carbonate, and the solution of the sodium salts set aside to crystallise. A sample of undistilled toluene was similarly treated. The sodium salts were then filtered in tared sinter crucibles and dried in a vacuum dessicator before weighing. The results of the estimations are shown in Table 15.

TABLE 15.

Source of M.N.T.	Nitrocresols in M.N.T. %	Cresol in toluene. %. (theoretical)
Undistilled toluene	0.42	0.34
1st. cut.	0.18	0.15
Middle cut.	0.09	0.07
Residue.	0.78	0.63

In view of the method of estimation these results must be regarded as very approximate. The differences are nevertheless so marked as to be significant. It is reasonable to conclude that the residual toluene gives a much larger yield of nitrocresols on nitration than any other fraction. This may be construed in one of two ways. Either -

(a) The cresol is originally present in the toluene to the extent of approximately

0.3 %.

or (b) The catalyst which occurs in the residual toluene must promote the oxidation of toluene to cresol, or of M.N.T. to nitrocresols.

In support of the first assumption may be cited the fact that dyes may be produced by coupling the sodium hydroxide extract with para-nitraniline or benzidine. The small quantity of tar obtained by acidification and extraction of the sodium hydroxide extract indicates the possible presence of some foreign substance in the toluene, though it gives no indication of its nature. Adoption of this theory involves the assumption that the cresol present is not removed by normal sodium hydroxide washing and subsequent distillation of the toluene during manufacture. The result of the test is therefore somewhat inconclusive. At this point the origin of the cresylic bodies was left so that a study of the catalytic properties of phenols might be more fully pursued.

Nitrations were conducted in which 0. 5 % phenolic compounds were added as catalysts, to determine which of these produced the greatest acceleration in the rate of reaction. The results are shown in Table 16.

TABLE 16.

Catalyst	M.N.T. %.				Activity Area. min. %.
	time - minutes.				
	5	10	25	20	
Control	34.0	53.2	68.0	76.0	1670
Phenol	38.9	57.0	69.6	77.6	1550
Benzyl alcohol	38.9	64.1	72.8	80.7	1420
o-cresol	37.0	57.5	71.2	83.7	1340
m-cresol	44.5	64.7	79.1	86.6	1170
p-cresol	40.7	59.8	72.8	80.7	1290
Catechol	40.8	63.2	75.0	84.0	1240
Resorcinol	40.8	63.2	75.0	84.0	1240
Quinol	42.6	63.2	77.5	85.2	1200
Pyrogallol	46.3	64.7	76.0	80.7	1260
3:5 DN-p-cresol	44.5	63.2	74.3	82.2	1320

Plotting the activity area against the number of polar groups indicates a slight increase in activity as polarity increases. The m-cresol result can only be attributed to experimental error. This is bo~~u~~rne out by the fact that when ortho- and meta-cresols were previously tested (Table 14.), they showed the same activity. It is interesting to note that benzyl alcohol shows a slightly higher activity than phenol.

CHAPTER 5.

CATALYSIS BY THE ALCOHOLS

The high catalytic activity of the phenols as compared to that of xylene (Table 14.) coupled with the fact that poly-hydroxycompounds exhibit higher activity than the monohydric members of the same series suggests that catalysis and polarity are associated. It therefore appeared possible that the alcohols might be catalytically active and a number of these were examined. Their application in plant would not be limited by their effect on the metals of the nitrators as are ionised halides. Moreover the study of catalysis by alcohols might give further evidence to justify the assumption that the phenolic compounds are active in consequence of their high polarity.

As before the catalysts were added to the reaction mixture to the extent of 0.5 % on the mass of toluene, and nitrating conditions were exactly the same as before. Three separate batches of mixed acid were used in the tests, and although they were all composed as accurately as could be ascertained -

5 %	HNO_3
25 %	H_2O
70 %	H_2SO_4

variations in their activities were apparent. Results are thus recorded under headings of Batch "A" etc., and a comparison blank is given for each batch of acid. (Table 17.)

In Fig. 18. the activity areas are plotted against the number of carbon atoms for each member. An interesting effect is that of branching in the carbon chain. With the primary alcohols no definite catalysis is evident and in fact these sometimes show a slight inhibiting effect. Secondary and tertiary alcohols on the other hand exhibit distinct activity. It would appear that maximum activity is exhibited by alcohols in which branching is a maximum (isopropyl and tert-butyl). For a time activity increases with molecular weight, but this rapidly passes through a maximum between propyl and butyl alcohols, after which increase in molecular weight results in lower activity.

TABLE 17.

Catalyst.	Acid batch "A"					Acid batch "B"				
	M.N.T. %. time - minutes				Activity area min.%.	M.N.T. %. time - minutes				Activity area min.%.
	5	10	15	20		5	10	15	20	
Control	43.0	63.2	76.0	85.1	1130	34.0	53.2	68.0	77.5	1340
Methanol	42.6	63.2	75.0	83.7	1138	34.0	54.8	69.6	77.5	1350
Ethanol	37.0	58.1	72.8	83.7	1210	33.0	54.8	71.2	83.7	1260
N-propanol	35.0	59.0	74.4	83.7	1210	32.0	53.1	68.0	77.5	1340
Iso-propanol	58.0	80.7	87.0	97.4	750	49.9	71.2	83.7	91.1	1005
N-butanol	38.0	58.1	72.8	82.2	1200	33.0	51.5	66.3	74.4	1368
Iso-butanol	42.6	64.0	76.0	85.1	1130	34.0	54.0	68.0	77.5	1330
Sec-butanol	47.1	73.0	84.1	92.0	910	48.2	72.0	83.7	91.1	1010
Glycol						36.0	56.5	71.2	83.7	1194
Glycerol	49.9	72.8	82.2	89.6	870	43.0	63.2	77.5	86.6	1020

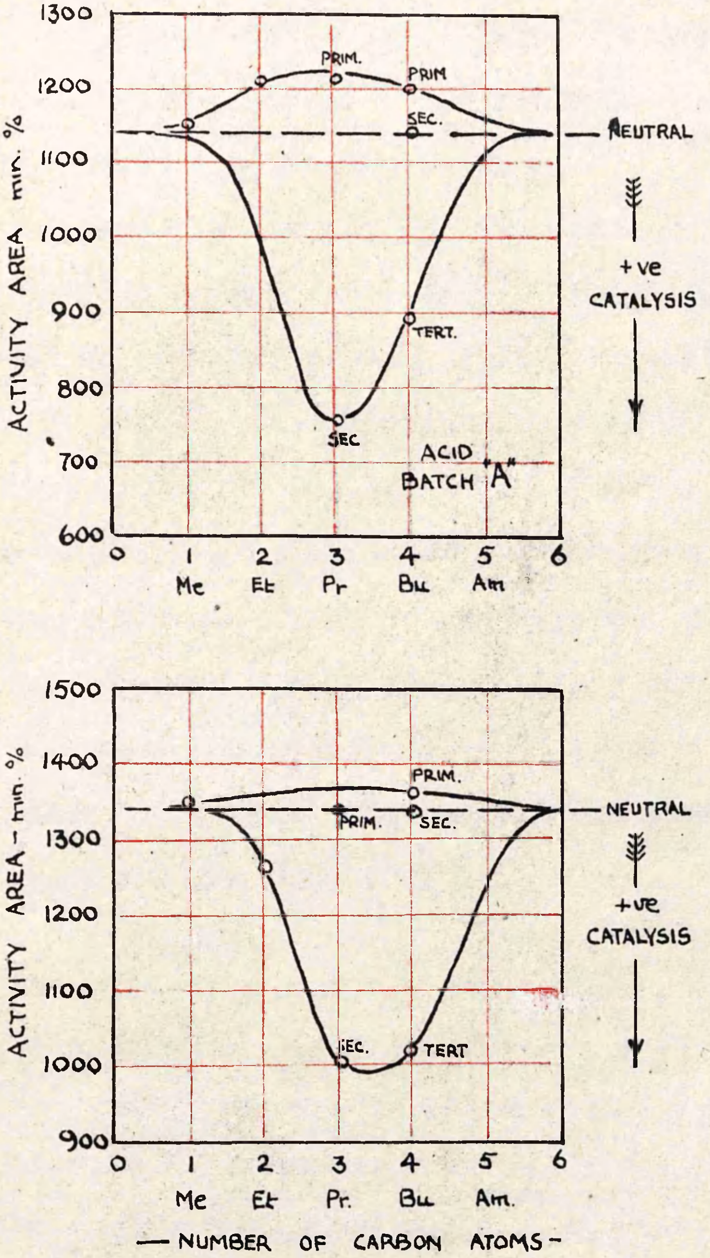

1300
1200
1100
1000
900
800
700
600
ACTIVITY AREA min. %
PRIM.
PRIM
SEC.
TERT.
SEC
NEUTRAL
+ve CATALYSIS
ACID BATCH "A"
0
1
2
3
4
5
6
Me
Et
Pr
Bu
Am
1500
1400
1300
1200
1100
1000
900
ACTIVITY AREA - min. %
PRIM.
PRIM.
SEC.
SEC.
TERT
NEUTRAL
+ve CATALYSIS
0
1
2
3
4
5
6
Me
Et
Pr.
Bu
Am.
— NUMBER OF CARBON ATOMS —

FIG 18

Consideration of the series methyl alcohol, glycol and glycerol, indicates that activity increases with the number of polar groups. This series was not continued far enough to observe any maximum.

Experiments were now extended to aldehydes, ketones and carboxylic acids (Table 18.). Again they have been plotted as activity area against number of carbon atoms (Fig. 19.). For this purpose carbon atoms in the polar groups are discounted. Thus methyl-ethyl ketone is taken as a molecule of three carbon atoms and one polar group. Experiments were not very comprehensive but it would appear that activity increases as we pass from carboxylic acids through ketones to aldehydes, maximums being observed with propionic acid, methyl-ethyl ketone and acetaldehyde.

It is to be clearly understood that by catalytic activity of alcohols and other organic substances is intended only the effect of such addition on the rate of reaction. Catalysis in these cases is undoubtedly brought about not by the compounds themselves, but by their products of reaction with the nitrating medium. The nomenclature has been adopted purely for simplicity.

TABLE 18.

Catalyst. 0.5 mol.%.	M.N.T. %. time - minutes.				Activity Area min. %.	Dry Set Point
	5	10	15	20		
Control	39.0	58.4	75.2	86.6	1090	78.8
Acetaldehyde	51.5	76.0	88.1	96.5	694	
	53.2	76.0	88.1	96.5		
Propionaldehyde	48.3	69.6	79.1	89.6	912	78.7
	46.3	68.0	79.1	89.6		
Dimethyl-ketone	43.0	63.2	77.5	86.6	1017	
	44.5	61.4	77.5	86.6		
Methyl-ethyl-ketone	49.0	68.0	82.2	89.6	915	78.7
	47.0	66.3	79.1	86.6		
Formic Acid	40.7	58.1	72.1	83.7	1090	
Acetic Acid	44.5	63.1	77.5	86.6	1020	
Propionic Acid	44.5	64.7	76.0	85.1	1020	78.7

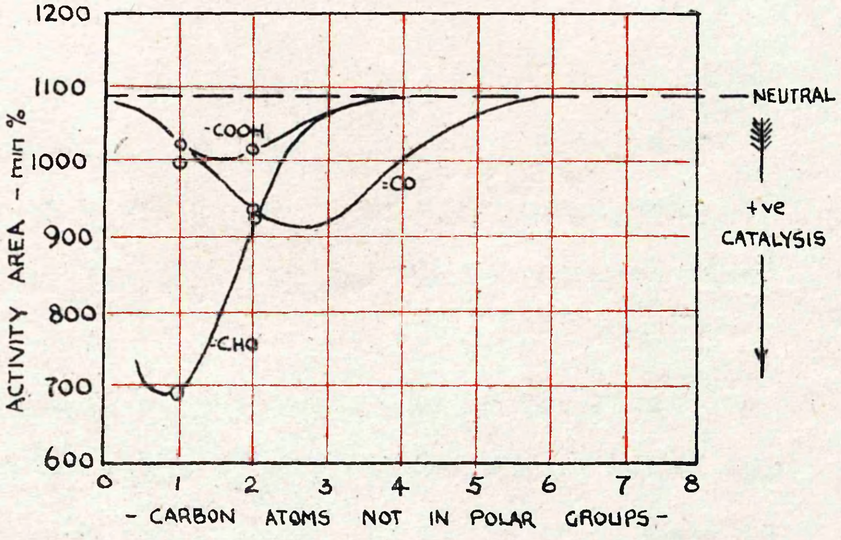

1200
1100
1000
900
800
700
600
ACTIVITY AREA - min %
0
1
2
3
4
5
6
7
8
- CARBON ATOMS NOT IN POLAR GROUPS -
-COOH
=CO
-CHO
NEUTRAL
+ve
CATALYSIS

FIG 19

CHAPTER 6.

THE EFFECT OF INTERFACIAL TENSION

It was early apparent that the increased rate of reaction observed in presence of the catalysts described in chapters 2. to 5. might be explained by their effect on the interfacial tension between mixed acid and toluene.

Experiments were carried out in the first instance on the particle size in emulsions of mixed acid and toluene, with and without the addition of catalyst. These experiments in which attempts were made to obtain photomicrographs of the suspension under standard conditions of agitation, had to be abandoned on account of the too rapid movement of the particles. Measurement by turbidimeter was likewise unsuccessful because the degree of turbidity is not a linear function of the size of particles. It was decided to measure the interfacial tension between mixed acid and toluene, since this is a primary factor governing the size of toluene particles under standard conditions of agitation.

The measurement was made by the drop weight method, and readings are expressed as drop weights, since the actual interfacial tension was not of primary interest. The toluene employed was a distilled high gravity material and the following mixed acids were used.

Series 1.		Series 2.		Series 3.	
H_2SO_4	70%	H_2SO_4	60%	H_2SO_4	50%
H_2O	30%	H_2O	35%	H_2O	45%
HNO_3	-	HNO_3	5%	HNO_3	5%

These were chosen so as not to react with toluene at room temperature, but to emulate the approximate surface tension of the normal mixed acid used in the previous experiments.

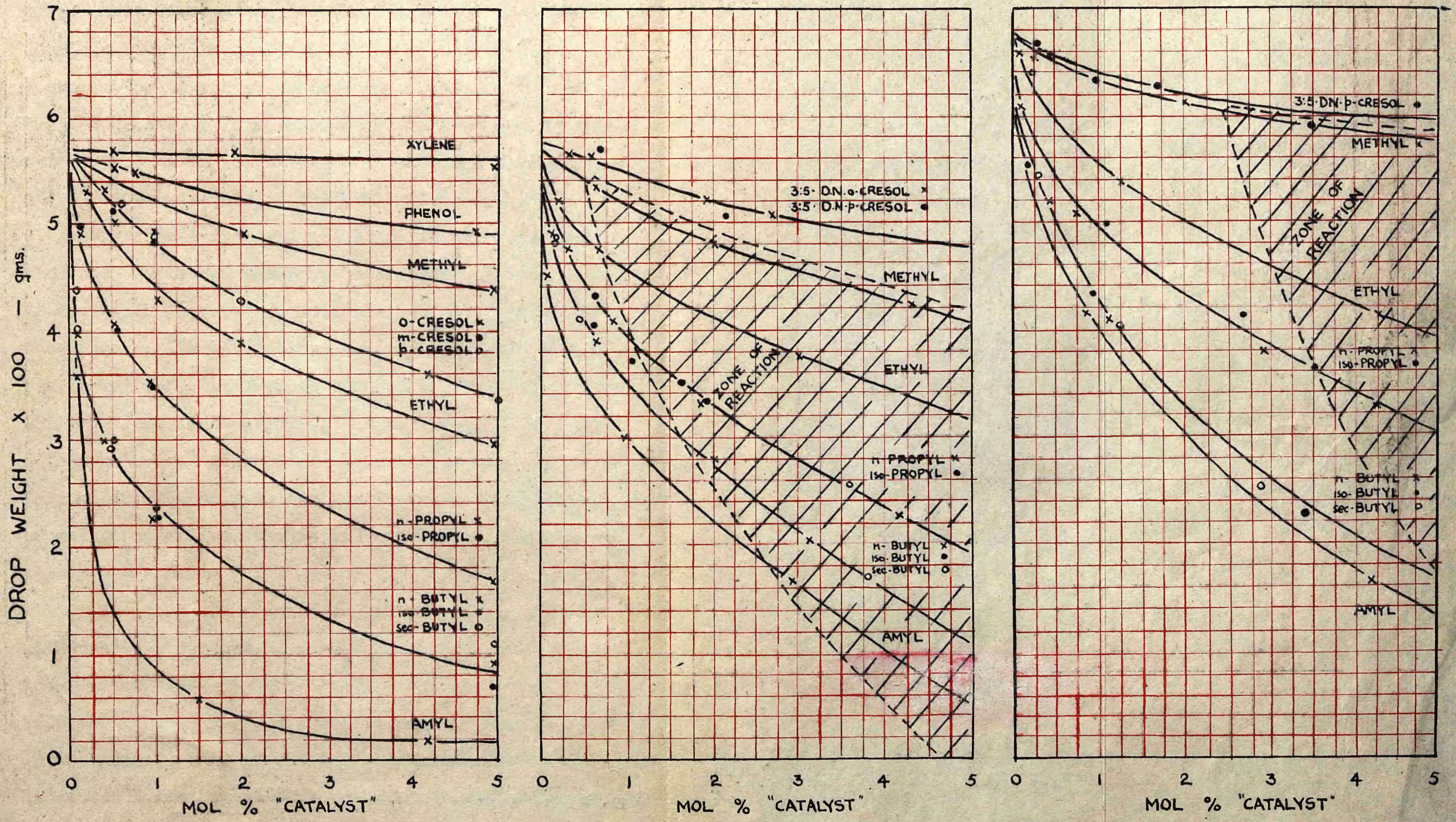
The acids were dropped into weighed amount of toluene contained in a narrow necked flask, the stopper of which was removed only when the dropping tip was immersed. A blank experiment was carried out to determine loss by evaporation and this proved to be negligible. The temperature throughout the experiments was 18°C.

The flask containing the toluene was weighed and 25 drops of mixed acid introduced before reweighing. Catalyst was then added and the flask reweighed, the difference giving the mass of catalyst for the following test. The former difference in weight multiplied by four (i.e. mass of 100 drops) is plotted against the proportion of catalyst in the graphs which follow (Fig. 20.).

When cresols are added to mixed acids containing nitric acid, reaction may occur. Accordingly nitrocresols were used in tests with acids 2 and 3. It was noted that with certain concentrations of alcohols, reaction did occur, as evidenced by a slow evolution of gas. This zone of reaction is shaded in the accompanying graphs.

The results show that there is a marked decrease in the interfacial tension of toluene and mixed acid by the addition of hydroxycompounds, except in the case of phenols. The effect increases with increase in the molecular weight and with the higher alcohols is marked even in presence of small proportions of the catalyst.

The increased reactivity of toluene on addition



SERIES 1

SERIES 2

SERIES 3

FIG 20

of alcohols might be explained by the fact that the alcohols reduce the interfacial tension and thereby increase the degree of dispersion of the toluene in the mixed acid. This theory however does not explain the difference in reactivity with primary, secondary and tertiary alcohols of the same molecular formula, since these show the same reduction in the interfacial tension. Moreover although interfacial tension decreases with increase in molecular weight throughout the whole series methanol to amanol, catalytic effect passes through a maximum at propanol. The two effects are therefore incompatible. It may be said then that although the reduction in interfacial tension is possibly partly responsible for the increase in the rate of reaction between toluene and mixed acid, it is certainly not wholely so.

The case with regard to the cresols is clear. Although they produce no marked depression of the interfacial tension, they catalyse the nitration of toluene. They must therefore be regarded as catalysts in the normal sense of the word. ~~Their role in the nitration may be that of an antioxidant, the alcohols behaving similarly.~~

PART II.

DI-NITRATION.

CHAPTER 7.

THE EFFECT OF CHLORIDE ON THE RATE OF DI-NITRATION.

After the detection of catalytic effect of halides in mononitration it was decided to study the effect of chloride on dinitration.

The product near the end of reaction being solid at room temperatures it was necessary to adopt a method of estimation other than refractive index. Specific gravity was found to be a suitable criterion. In order that large samples would not have to be removed from the reaction mixture special pyknometers were made with a capacity of 0.05 to 0.40 mls. One of these is shown on stand beside a sinter crucible to illustrate comparative size, in Fig. 21. A pyknometer of capacity 0.15 mls. gives approximately 1 % accuracy when weighed to 0.2 mg.

To carry out the estimation, a sample of 2 mls. of reaction slurry were removed from the nitrator and drowned in 10 mls. of water. The nitrobody was

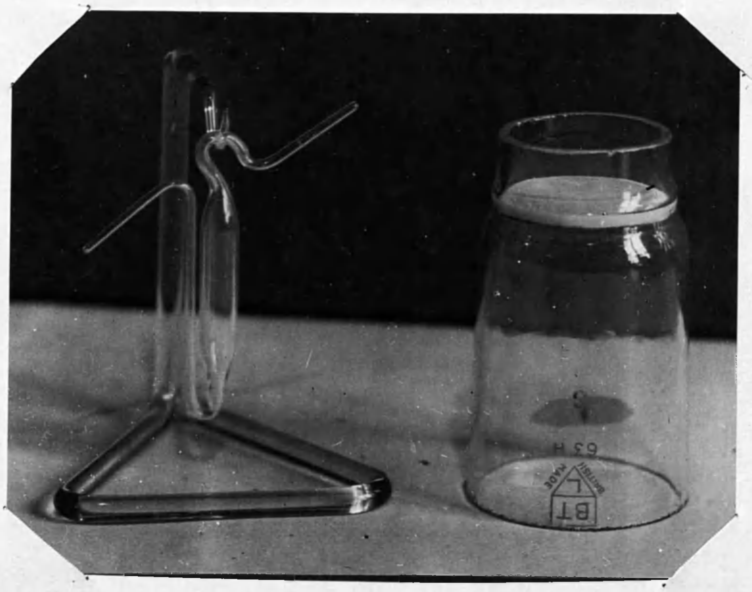


FIG 21

separated in a hand centrifuge and washed twice with water. After drying at 90°C till it showed no turbidity, its specific gravity was determined at the same temperature.

The nitrating acid had composition -

HNO_3	5 %
H_2SO_4	75 %
H_2O	20 %

Again it was found that activity varied with different batches of acid and a large batch of acid was made for use throughout the tests.

The M.N.T. used was a commercial sample containing traces of acids used in its manufacture. Two experiments were conducted on a vacuum distilled product. The results of all the tests are shown in Table 19. The apparatus used was the same as that for mononitration and the temperature was maintained at 20°C throughout.

In general only very slight activity is exhibited by chloride under these conditions. Bearing in mind the increased corrosion which would attend the use of sodium chloride under plant conditions, its adoption would not appear to be justified.

TABLE 19.

Catalyst Mol. %.	D.N.T. %. time - minutes.					Activity area min. %.
	10	20	30	60	100	
Control	35	58	73	91	99	2640
Control	37	60	74	91	98	2580
0.1 % Cl.	47	73	82	91	100	2300
1.0 % Cl.	50	75	83	91	100	2240
1.0 % Cl.	37	61	75	90	99	2520
Control	12	25	36	66	98	5440
Control	12	25	36	66	98	5440
0.5 % Cl.	13	26	37	67	98	5400
0.5 % Cl.	13	26	37	69	99	5200
Control *	19	36	52	80	100	4060
0.5 % Cl.*	21	42	58	84	100	3620

* Distilled M.N.T.

PART III.

TRI-NITRATION.

CHAPTER 8.

EFFECT OF HALIDES, CRESOLS, AND ALCOHOLS ON THE RATE OF TRI-NITRATION.

The mononitration apparatus was adapted for trinitration by allowing for continuous heating of the external water-bath. As the nitrations were carried out in a large excess of sulphuric acid and were thus single phase reactions, stirring conditions were not critical.

The progress of reaction was followed by measurement of the specific gravity of the nitrobody. At intervals samples of the slurry were removed from the nitrator and drowned in water. The nitrobody was separated by centrifuging, washed with boiling water, dried in a steam oven for three hours and its specific gravity at 95°C measured using one of the small pyknometers. Experiments on the optimum size of pyknometer showed that one of about 0.3 mls. capacity gave reliable results without necessitating the removal of unduly large samples from the nitrator.

The method of nitration consisted of heating the nitrobody and sulphuric acid to the desired temperature of nitration and adding the calculated quantity of nitric acid to the solution. 50 gms. D.N.T. were heated in the nitrator with 380 gms. 100 % H_2SO_4 to 100°C. 180 gms. of a mixture of 20 % HNO_3 and 80 % H_2SO_4 were added cold when it was desired to start the reaction. The latter dry acid was made from 5 % oleum and 95 % HNO_3. By the addition of an anhydrous acid, heat of dilution on addition was avoided. The addition of this acid reduced the temperature in the nitrator to 95-97°C. Immediately afterwards the temperature rose to 104-107°C by the heat of reaction, and cooling was applied via the coils to maintain the temperature at 100°C. Later, cooling was unnecessary the water-bath at 100°C maintaining the proper temperature.

Catalysts were added to the sulphuric acid-D.N.T. mixture just prior to the addition of the nitric acid. In every case the amount was 0.5 % as a molecular percentage of the D.N.T. The results are shown in Table 20.

TABLE 20.

Catalyst.	T.N.T. %.								Activity Area min. %.
	time-minutes.								
	10	20	40	60	80	120	160	200	
	Acid Batch "A"								
Control	48	62	78	83	86	90	93	95	3920
Control	48	62	79	83	86	91	94	96	3800
Cl as KCl.	48	66	82	90	93	96	98	99	2840
Cl as KCl.	54	72	84	90	93	96	98	98	2840
I as KI.	50	72	85	90	93	95	97	98	2840
	Acid Batch "B"								
Control	59	75	83	86	89	91	93	95	3360
3:5 DN-p-cresol	61	81	91	93	95	97	98	99	1830
3:5 DN-p-cresol	62	82	91	94	96	98	98	99	1780
	Acid Batch "C"								
Control	53	73	86	93	96	98	99	100	1980
Control	56	74	86	92	95	97	98	99	2050
Control	52	72	87	92	94	96	98	99	2160
3:5 DN-p-cresol	59	74	86	92	95	97	99	99	2050
3:5 DN-p-cresol	56	75	87	93	96	98	99	100	1960
Amyl alcohol	52	71	87	91	94	96	98	99	2240
I as KI.	55	73	90	93	95	98	99	100	1920

SECTION 3.

SEPARATION OF NITROBODIES.

The objects in catalysis in nitration of toluene may be simply stated as:-

(1) In mono-nitration, alteration of isomeric composition.

(2) In all nitration, mono-, di-, and tri-, increase in rate of reaction.

The first object has as yet proved as incapable of solution by catalysis as by any other variation of the nitration process. In the second object some success has attended the experiments, the most marked increase being observed in catalytic mono-nitration. It is however the di- and tri-nitration that the greatest time of contact between the reagents is necessary. It would appear therefore that if a purification method were available which would remove D.N.T. from T.N.T. it would render possible the reduction of time of nitration simply by discharging the final nitrobody from the tri-nitrator before completion of reaction, thus attaining the same object as catalysis in tri-nitration.

During the first World War attempts were made to evolve a commercial method of purifying T.N.T. from D.N.T. by both chemical and physical methods. Success was limited but it was considered that the problem might be capable of solution in the light of more modern developments, and the following section is devoted to a study of the separation of the higher nitrobodies.

Moreover it is possible that if large proportions (e.g. 30 %) of D.N.T. could be removed from T.N.T. it might be made the basis of a more economical manufacturing process, since the conversion of D.N.T. to a nitrobody mixture containing 70 % T.N.T. can be effected in approximately one sixth of the time required for complete conversion. The di-nitrobody, provided it was removed by physical means and was not chemically combined in any way, would be available for recycling. As far as can be ascertained no consideration has been given to the technical separation of mixtures like this, but as has been mentioned the removal of small quantities (up to 1 %) of D.N.T. has been studied. Technical Records of Explosive Supply 1915-18, 2, 20, describe the following processes:-

(1) Purification by Organic Solvents.

Crystallisation from alcohol and benzene-alcohol mixtures on the plant gave good results but was abandoned after some disastrous explosions. These apparently occurred in recovering the solvent by distillation and some modification here might yet made the process practicable.

(2) Crystallisation from sulphuric, nitric or mixed acids.

The main difficulties were -

(a) Large amounts of H_2SO_4 required.

(b) Accumulation of unsymmetrical T.N.T.'s in mother liquor rendering it unsuitable for nitration purposes.

(c) Difficulties of filtering and handling strongly acid mother liquors.

Crystallisation being a cumbersome process under plant conditions, it is doubtful if either of these methods represents ideal industrial practice.

(3) Purification by Hot Water Washing.

This method was quite unsuccessful.

(4) Centrifugal Methods.

D.N.T. and T.N.T. gave low melting eutectics, removed by washing with hot water in a basket centrifuge. This method gave very promising results and aroused a great deal of interest at the time of its application. It was further improved by the addition of phenol to the mixture to give a lower melting eutectic of the D.N.T. rendering washing more simple.

(5) Pressure Methods.

These were based on the same principle as that of the centrifugal methods, but the eutectic was removed by pressing the nitrobody. Separation was found to be less complete.

(6) Purification by Aqueous Solution Washing.

This method is very well-known, the final development resulting in the modern sulphite process.

Some of these processes have been examined here with a view to their extension to mixtures containing large amounts of D.N.T. In particular, efforts have been directed towards the use of two recent methods of separation, namely thermal diffusion and high vacuum distillation.

Welch (Ann.Rep.Chem.Soc. 1940, 37, 153) describes the separation of gaseous isotopes by thermal diffusion, and Kendal (Nature 1942, 150, 136) refers to the separation of liquids of different molecular weights by the same process. The method appears to give critical separation but is liable to be slow in certain cases.

The separation of mixtures by so called molecular distillation which involves the reduction of pressure over the materials to such an extent that permanent gas molecules become so sparse as not to interfere with the free flight of the vapour molecules, is one that merits particular note. References to the use of this valuable technique are innumerable. Its discovery followed the invention by Gaede (Ann.d. Phys. 1915, 46, 357) of the mercury diffusion pump and its subsequent improvement by Langmuir (Phys.Rev. 1916, 8, 48) enabling the attainment of previously impossible low pressures. Its application to the separation of vitamines (Hickman U.S.P. 1,925,559. 1930; Carr and Jewell B.P. 415,088. 1933; Nature 1933, 131, 92; Waterman and Van Dijck Dutch P. 37,435. 1933) is now well-known, some of these being produced for commercial distribution by this method.

Of particular interest with respect to plant application is the description by Burch and Van Dijck (Proc.Chem.Eng.Gp. 1938, 20, 81) of a pilot plant for the production of high grade lubricating oils, in yields of four to eight tons distillate per day.

Patents have been obtained for improvements in both pumping equipment and stills, chiefly concerning the use of oil instead of mercury in diffusion pumps and schemes for combining the still and pump in one unit. Latest designs of oil diffusion pump incorporate automatic fractionation of the oil and presentation of best oil to the inlet end of the pump.

High vacuum distillation appeared to offer great possibilities of the separation of nitrobody mixtures and had certainly not been one considered as a commercial separation. Attention was nevertheless directed towards the other methods discussed previously.

CHAPTER 1.

EXTENSION OF APPLICATION OF EARLY METHODS

Of the six methods described in Technical Records of Explosive Supply only three appeared to merit further examination, namely crystallisation from solvents, and from acids, and the eutectic principle. Obviously separation by water washing would be ineffective because of the low solubility of D.N.T. in water, and the sulphite method is inapplicable because the nitrobody removed by this means is not recoverable.

For crystallisation the starting material prepared was 30 % D.N.T. 70 % T.N.T. No attempts were made to emulate plant conditions, the material being crystallised in batch from a number of solvents in order to determine only the efficiency of separation. The composition of the products were estimated here as in all separation experiments by density determination at 95°C. The results are summarised in

Table 21.

TABLE 21.

Process	T.N.T. in product %
Crystallisation from alcohol	96.5
Crystallisation from alcohol	97.5
Crystallisation from 93 % H_2SO_4	79.0
Crystallisation from benzene-alcohol	100.0
Washing with hot alcohol	69.5
Washing with hot alcohol	69.0

Alcohol appears to give a suitable efficiency in crystallisation and a mixture of benzene and alcohol combines good separation with a high product-solvent ratio. The danger of explosion mentioned earlier would seem to be the only difficulty, but this might be sufficient to prohibit its industrial application. Alcohol washing, as opposed to crystallisation, is quite ineffective.

Sulphuric acid crystallisation effects partial separation but the bulk of acid necessary is high and would be cumbersome in plant.

For the purpose of testing the efficiency of the eutectic method of separation, a six inch basket centrifuge was used. Granules of 30 % D.N.T. in T.N.T. were prepared for the tests by pouring the liquid nitrobody into rapidly stirred cold water. This material was centrifuged and washed with water at 60°C. There was no change in composition. The experiment was repeated at 70°C with the same result except that a great deal of the nitrobody was washed through the basket. A similar experiment was conducted on a granular mixture consisting of 25 % D.N.T. 70 % T.N.T. and 5 % Phenol. By centrifugal washing at 60°C the product contained 76 % T.N.T. but again a great deal of nitrobody was carried away in the wash liquor.

The results indicate that a high degree of control would be necessary to effect only partial separation and the process was pursued no further. The separation of a liquid from granules of nearly the same melting point must inevitably result in a wasteful if not inefficient process.

CHAPTER 2.

SEPARATION OF NITROBODY MIXTURES BY THERMAL DIFFUSION

The principle of thermal diffusion can most simply be illustrated with the apparatus shown in Fig. 22. If the tube is filled with coal gas and the central wire heated to redness, the gas mixture circulates up the wire and down the walls of the tube as indicated by the arrows. The hydrogen because of its lower density travels up the wire more rapidly than the carbon monoxide, whereas at the walls of the tube on the downward path the reverse holds true. Hydrogen therefore concentrates at the top of the tube and carbon monoxide at the bottom. The process may be made continuous by injecting the coal gas at the middle of the tube and withdrawing hydrogen and carbon monoxide at each end.

The separation has proved so effective and economical that it has been suggested to replace the expensive solvent separation at present in use in the

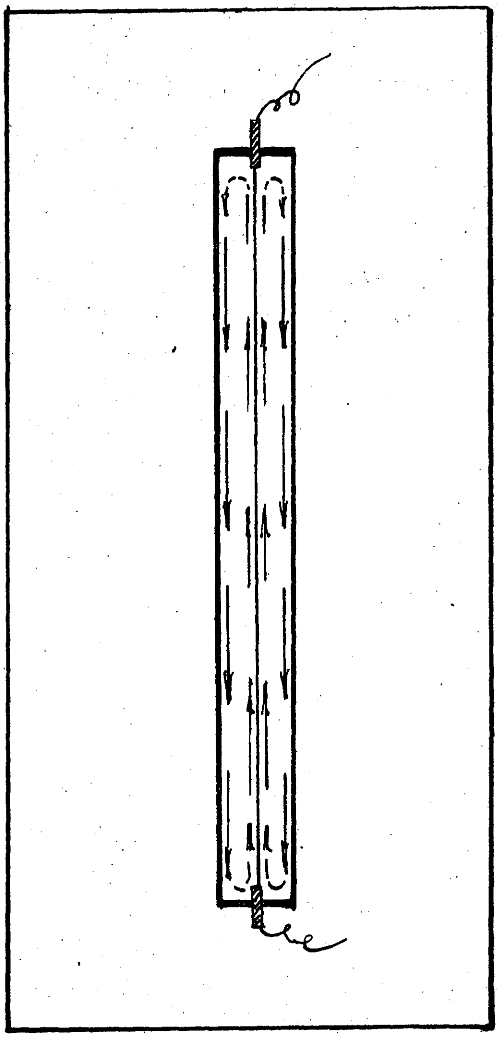


FIG 22

Solvay ammonia fixation process.

In the separation of liquids or of gases of closely associated molecular weights the essential condition is that the temperature gradient through the material should be as steep as possible. This is secured by reducing the gap between the heated and cooled surfaces to a minimum and operating at maximum possible temperature difference.

For the separation of D.N.T. - T.N.T. mixtures the first apparatus was constructed of glass. It is shown with essential dimensions in Fig. 23. The outer tube is heated by steam while the inner tube is maintained at 60°C by circulation of water in the jacket. A mixture of 50 % D.N.T. in T.N.T. was used in the experiments as this is liquid at lower temperatures than the 30 % D.N.T. mixture, and therefore permitted the utilisation of a greater temperature difference.

The method of operation was as follows:-
The tube was filled with molten eutectic by injection at the lower drain tube. After running for some time the lower cock was opened to permit the egress of a few grams of liquid. The composition of this

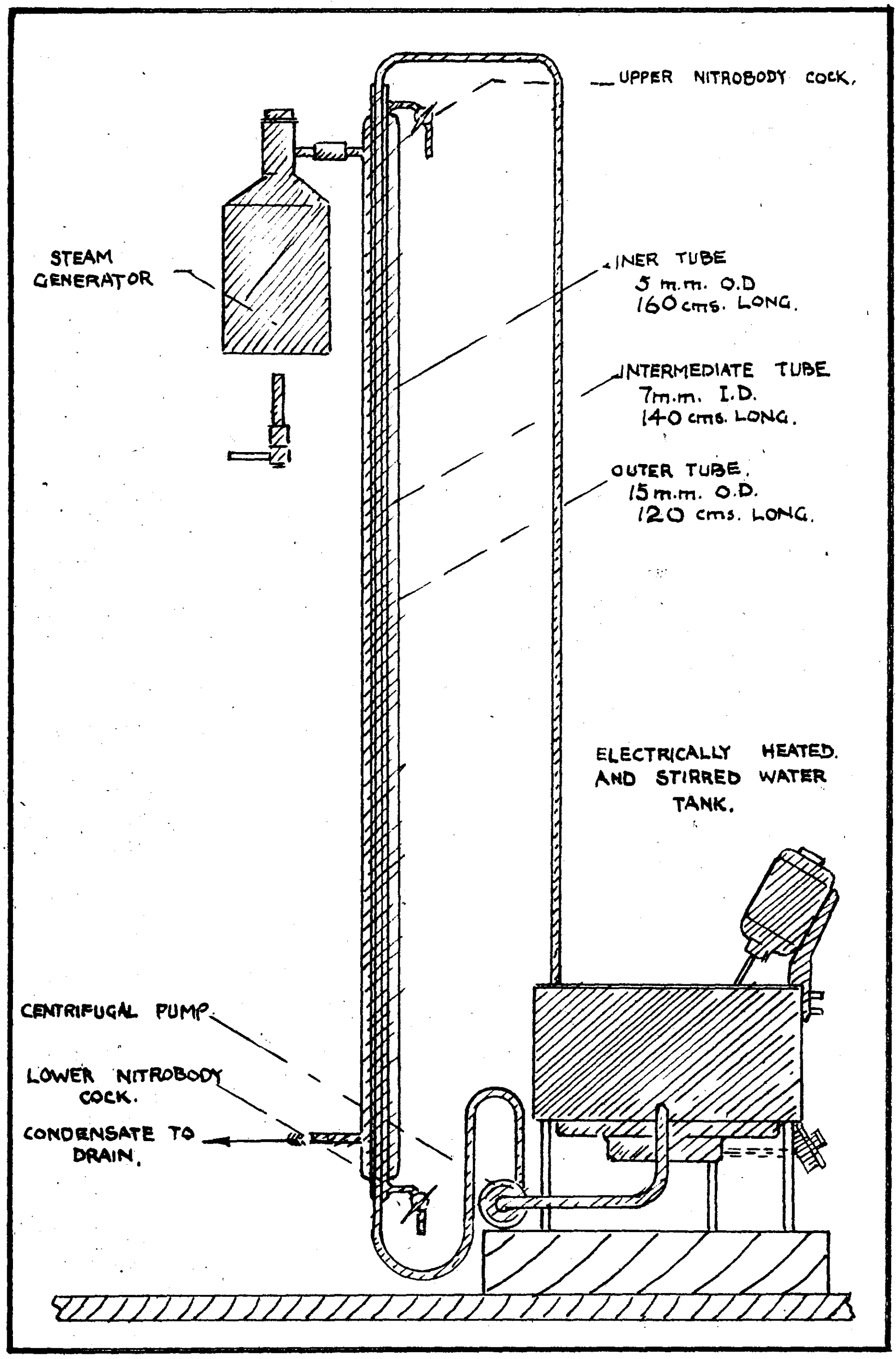

UPPER NITROBODY COCK.
STEAM GENERATOR
INER TUBE
5 m.m. O.D
160 cms. LONG.
INTERMEDIATE TUBE
7m.m. I.D.
140 cms. LONG.
OUTER TUBE.
15 m.m. O.D.
120 cms. LONG.
ELECTRICALLY HEATED. AND STIRRED WATER TANK.
CENTRIFUGAL PUMP.
LOWER NITROBODY COCK.
CONDENSATE TO DRAIN.

FIG 23

was estimated by measurement of its specific gravity.

Runs were conducted in which the material was subjected to thermal diffusion for 2, 3, and 4 hours. Although the products exhibited slight increase in melting point they did not differ in specific gravity. Separation was therefore negligible.

It was thought that the lack of separation might be attributed to the low heat transfer coefficient of glass resulting in poor thermal gradient in the nitrobody and a metal diffusion unit was built. To ensure the maximum effect, the heating was made electrical so that the heated wall temperature could be increased beyond 100°C. The length of the apparatus was also increased and central feed was adopted so that samples could be drawn at both ends of the tube and continuous sampling was possible. The apparatus is shown diagramatically in Fig. 24. It was convenient to make the heated tube the outer one. Water at 60-80°C was circulated in the inner tube by a high speed centrifugal pump.

The method of operation here is obvious. With hot water circulating in the central tube and

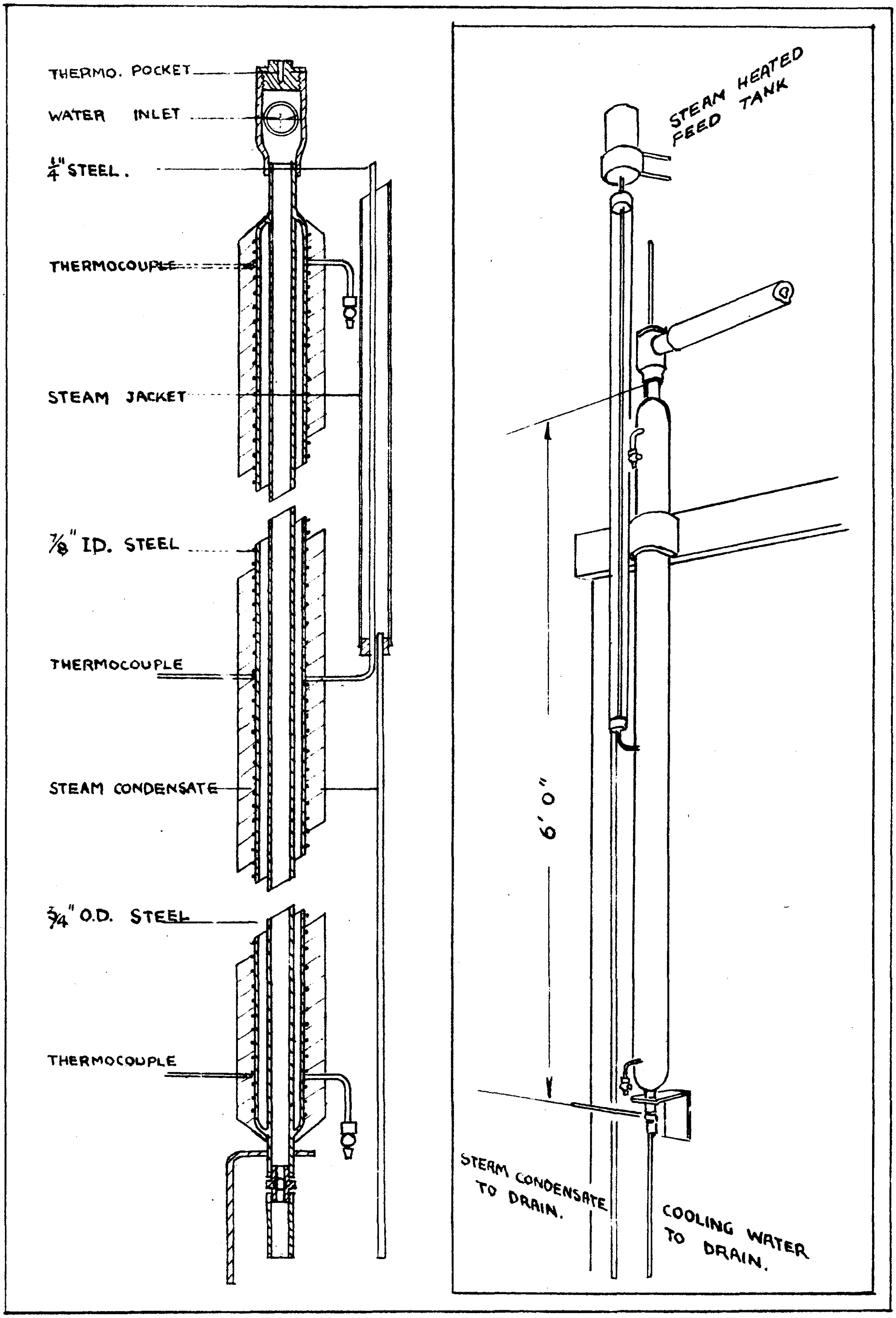

THERMO. POCKET
WATER INLET
$\frac{1}{4}$" STEEL.
THERMOCOUPLE
STEAM JACKET
$\frac{7}{8}$" I.D. STEEL
THERMOCOUPLE
STEAM CONDENSATE
$\frac{3}{4}$" O.D. STEEL
THERMOCOUPLE
STEAM HEATED FEED TANK
6' 0"
STEAM CONDENSATE TO DRAIN.
COOLING WATER TO DRAIN.

FIG 24

steam applied to the feed tank, the charge was introduced and the sample cocks at top and bottom of the apparatus opened till nitrobody flowed freely from them. Current was then applied and the jacket temperature raised to the desired value and samples were drawn at intervals and their composition estimated.

Runs were conducted in which the samples were taken every hour, every two hours, and continuously. Again no separation could be detected and the method was abandoned. Apparently the low temperature gradient compatible with safe operation (120-80°C) coupled with the high viscosity of nitrobody mixtures renders diffusion ineffective.

CHAPTER 3.

SEPARATION BY STEAM DISTILLATION

Steam distillation appeared to offer possibilities of separation of D.N.T. and T.N.T. and although the yields were known to be low the problem was pursued. A simple steam distillation of D.N.T. shows that the yield is nearly 3.5 parts of nitrobody per thousand of steam. It was thought that by the use of superheated steam the yield might be increased to permit its economical application on plant. The following experiments were therefore conducted.

The apparatus is shown diagramatically in Fig. 25. Superheated steam formed by passage through the coil immersed in the heated sulphuric acid bath, bubbled through the nitrobody and thence to the condenser. The nitrobody separated from the condensed water in the receiver and could be filtered off, dried in vacuum and weighed. Tests were con-

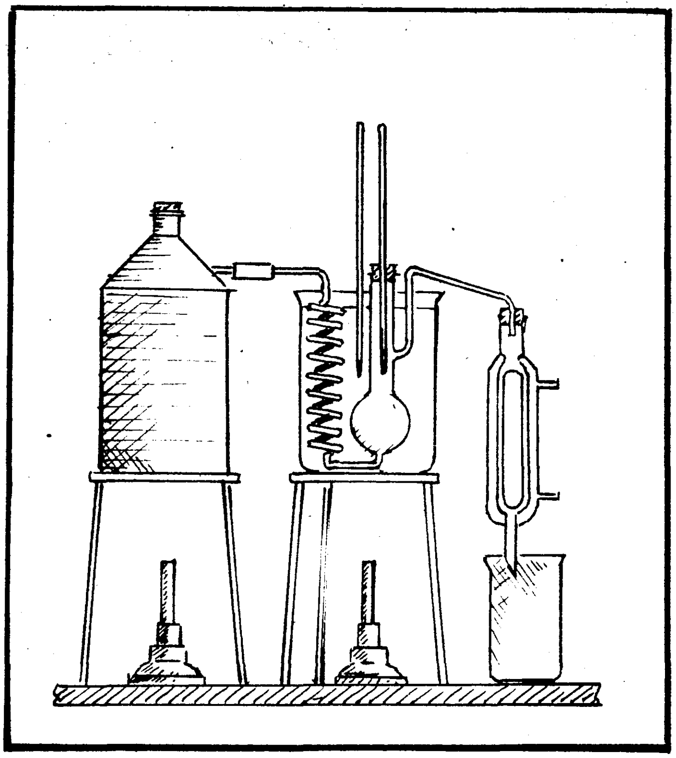


FIG 25

-ducted at temperatures up to 160°C and the results are shown in Table 22.

TABLE 22.

	D.N.T.			T.N.T.			DNT/TNT
$10^3/T$ cent.	parts per 1000	V.P. p cms.	$\log_{10} p$ cms.	parts per 1000	V.P. p cms.	$\log_{10} p$ cms.	mass ratio.
2.68	0.35	0.021	-1.674				
2.48	1.45 1.69 2.20	0.300	-0.523	0.326 0.321	0.055	-1.259	5.4
2.36	4.25 4.65 5.20	1.325	0.122	1.12 1.03 0.90 0.90	0.280	-0.553	4.8
2.30	9.20 8.30 10.10	3.260	0.513	1.88 1.81	0.655	-0.183	5.0
	Average Mass Ratio.						5.0

The table also shows calculated values of the vapour pressures of the nitro-bodies, assuming the validity of the equation -

$$P_n = \frac{m_n \times M_w}{m_w \times M_n} \times P_w .$$

where P is the pressure in cms. of mercury, M the molecular weight in grams, and m is the mass distilled, the suffixes referring to water and nitrobody.

On distilling a mixture of 30 % D.N.T. in T.N.T. slight improvement was observed in the product but the process was very slow and would certainly be uneconomical industrially.

The values of vapour pressure obtained from the steam distillation are of some interest. Plotting $\log_{10}p$ against $10^3/T$ (Fig. 26.) they form reasonably straight lines, and can therefore be expressed in the form $e^{B - \frac{L}{RT}}$. They are however not in agree-with the results of Menzies (J.A.C.S. 1920, 42, 2218). Probably the high results obtained by steam distillation may be partly explained by entrainment, but the divergence of results is extremely marked. Furthermore an example of the original paper by Menzies showed that in order to prevent distillation of nitrobody into the McLeod gauge used in his measurements, part of the apparatus was purposely cooled below the temperature of estimation. It therefore appeared possible that his results were low. In view of the importance of a knowledge of vapour pressure in high

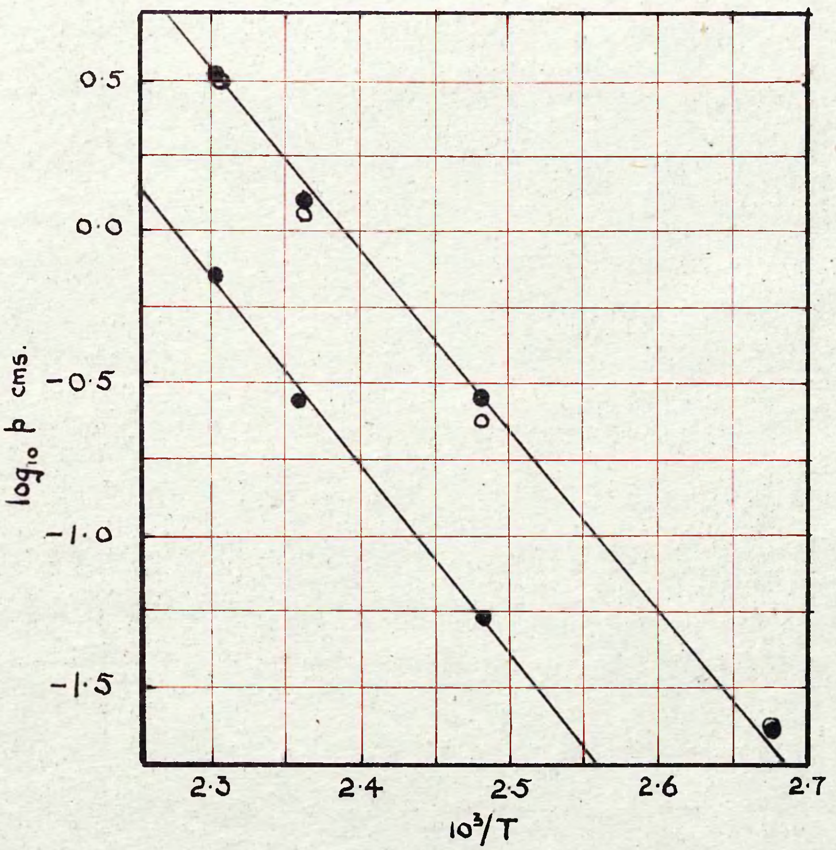


FIG 26

vacuum distillation it was decided to carry the investigation further and the following chapter is devoted to a description of the experiments.

CHAPTER 4.

THE VAPOUR PRESSURE OF NITROBODIES

The vapour pressure of T.N.T. being low it was at first thought that a dynamic method of estimation would have to be employed in order to get reliable results. Apparatus for dynamic estimation, quite apart from its complexity of construction involves a considerable expenditure of time in acquiring the necessary technique of operation. A static method was therefore first attempted to obtain an approximation of the value. Correlation with other results indicated that the degree of accuracy was higher than was originally anticipated and it was not necessary to revert to other methods.

As manometric liquid, Apiezon Oil B. was used. The vapour pressure of this oil at room temperature is 0.0001 micron and the specific gravity approximately 0.870 . Oil B. is non-viscous and therefore ideal for application in fine manometers. Before use its specific gravity at various temperatures was measured by pyknometer. Fig. 27. shows the line obtained by plotting the results. From this -

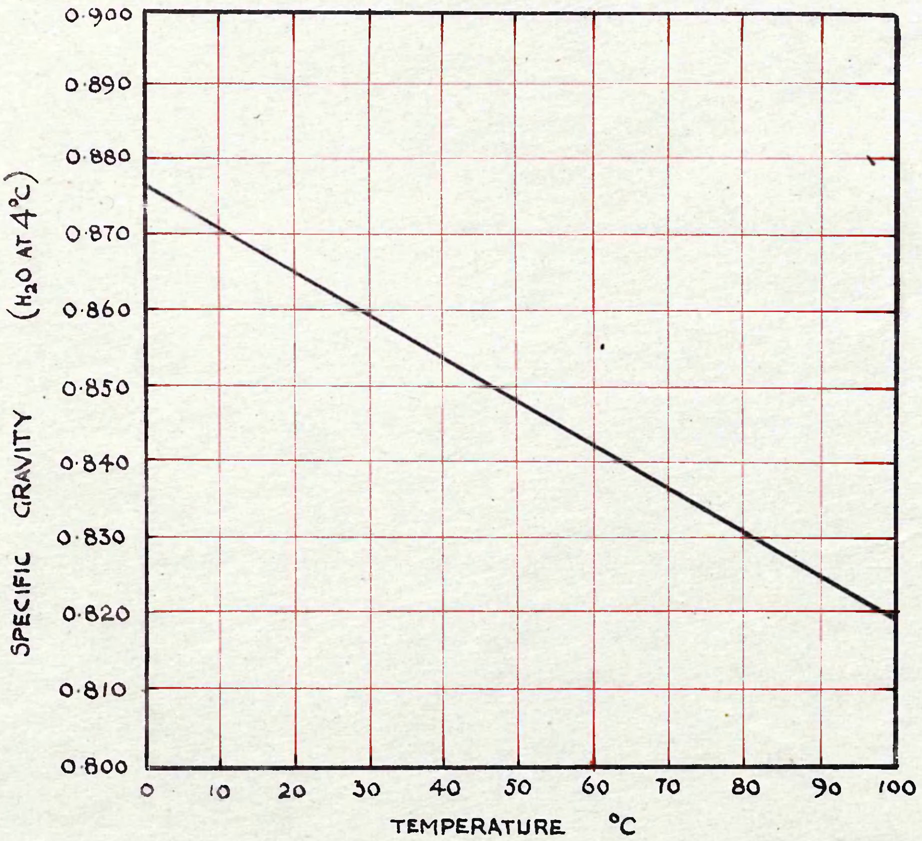
$$D_0 = 0.877 \quad \text{and} \quad \alpha = 0.000573$$

for the equation -

$$D_t = D_0 \ (1 - \alpha t).$$

The apparatus used for the vapour pressure determinations is shown in Fig. 28., the principle being that of balancing via a manometer the pressure of the nitrobody at a known temperature against that of the nitrobody at absolute zero. Because of the very low gradient of the vapour pressure against temperature over the range 0°C to -273°C it was only necessary to cool the standard bulb to -70°C to obtain accurate readings. Solid carbon dioxide therefore satisfied the cooling requirements and this was conveniently obtainable.

To facilitate charging and discharging, the nitrobody bulbs were fixed to the manometer by ground glass joints. Pyrex "B 19" fittings were first used and later German Standard "A 15" fine ground soda joints. This system was abandoned because of the



— APIEZON OIL "B" —

FIG 27

difficulty of obtaining a high vac grease which would not evolve gas at temperatures above 40°C. In later experiments the nitrobody was placed in the bulbs before they were sealed to the manometer.

Evacuation was by mercury pump backed by a rotary oil pump and the residual pressure was measured with a McLeod gauge prior to sealing. A number of tubes were rendered useless by the presence of residual gases occasioned by insufficient baking. In all 14 tubes were constructed and sealed and the results quoted are the lowest obtained.

Procedure.

The bulbs containing the nitrobody having been fused on to the manometer and the latter filled with oil, the tube was clamped in an inclined position so that the oil ran into the reservoir "A". The limb extending from this bulb was coupled to the pumping system and a constriction made in the glass before vacuum was applied. When the pressure had fallen to 5×10^{-3} m.m. the tube was baked for 15 minutes by application of the soft flame from a bunsen burner. The apparatus was allowed to cool and a further baking

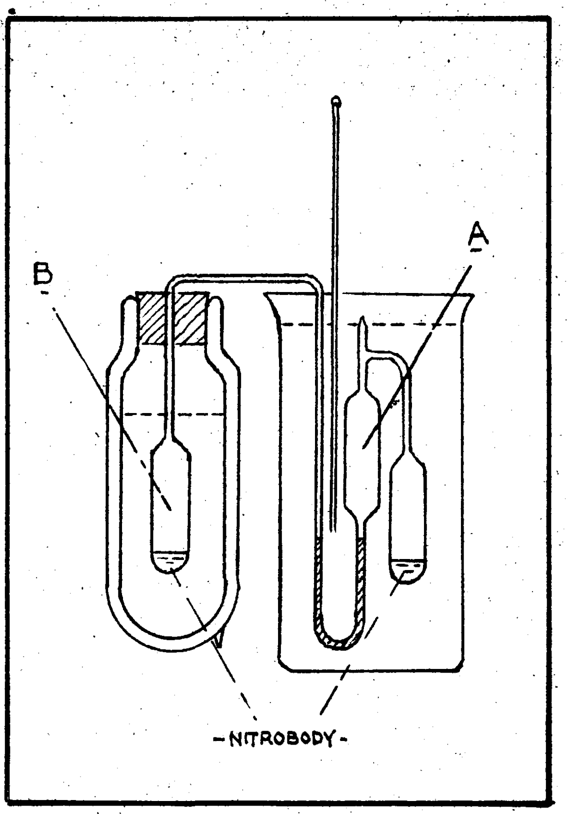


FIG 28

carried out after an hour. The seal was made without permitting the apparatus to cool, and the tube was then rotated into a vertical position and clamped.

The whole apparatus was suspended in water at room temperature and after an hour the difference in pressure in the limbs was measured to provide a zero correction. Measurement of relative heights of liquid in the manometer limbs was made by means of a carefully levelled travelling microscope.

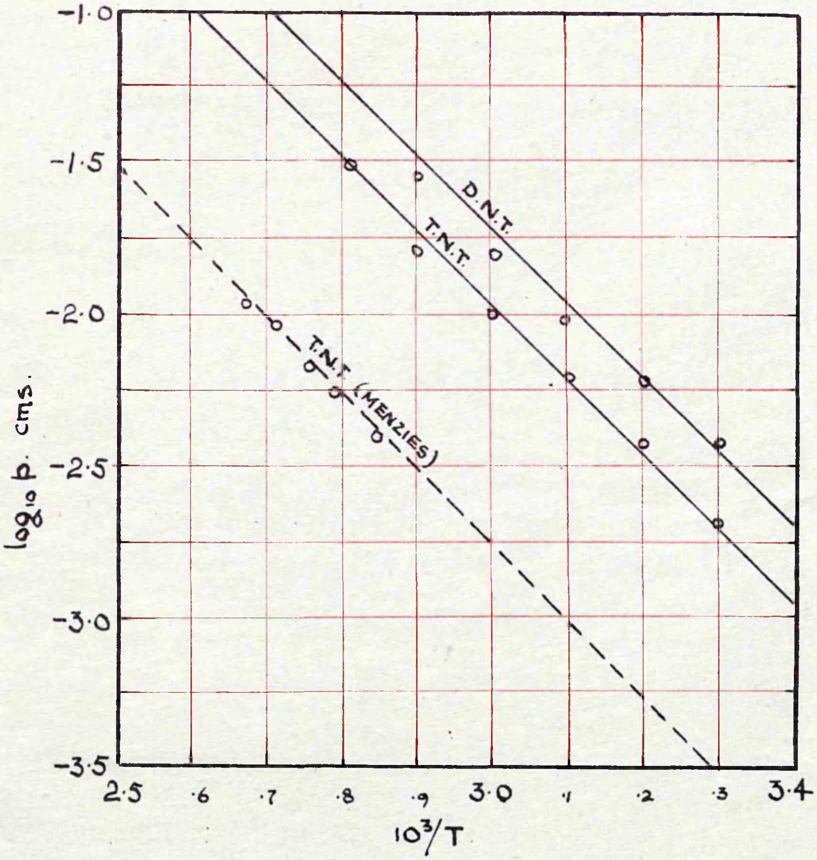
The bulb "B" was cooled in solid carbon dioxide and after an hour another reading was taken. This reading referred to the vapour pressure of the nitro-body at room temperature. The water-bath was then very slowly heated till the temperature had risen 5 to 10°C and maintained there for half an hour before a new reading was made. After this the levels were noted every 5 minutes till they were constant before the temperature was again increased. By continuing this procedure readings within the range 10 to 80°C were obtained in about 12 hours. When measurement had been started, the apparatus was not allowed to cool till the last value had been obtained. The tube was afterwards immersed in water and allowed to stand overnight when a further zero correction reading was made to ensure that gassing had not occurred during the experiment. Results were obtained for T.N.T. (set point 80.3), 2:4-D.N.T. and tetranitromethane (T.N.M.). These are shown in Table 23. and graphically in Figs. 29. and 30. Dotted lines in the graphs represent the corresponding values by Menzies.

TABLE 23.

Temp. °C	Vapour Pressure Cms. Hg. at °0 C		
	D.N.T.	T.N.T.	T.N.M.
20	0.00267	0.00114	- -
30	0.00386	0.00225	- -
40	0.00626	0.00401	2.65 (2.66)
50	0.00975	0.00623	4.33 (4.42)
60	0.01550	0.0100	6.80 (7.06)
70	0.0276	0.0160	10.8 (10.9)
80	- -	0.0324 (.0042)	16.4 (16.4)
90	- -	(0.0067)	23.9 (23.9)
100	- -	(0.0106)	33.9 (33.9)

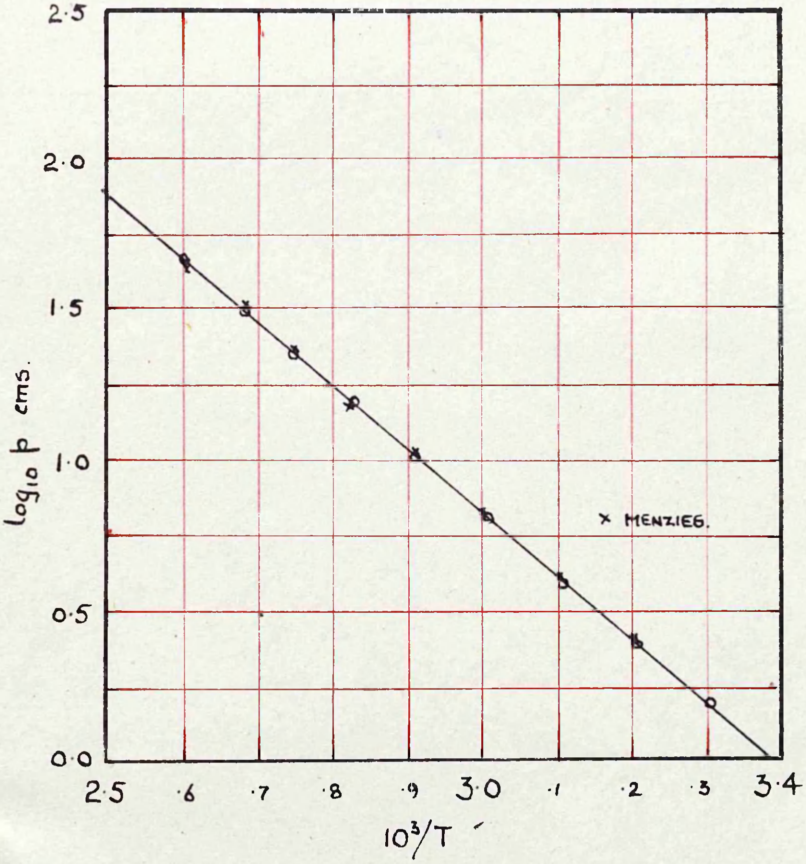
Values by Menzies bracketed.

The equations for the lines shown in Figs. 29. and 30. are -



- V.P. of NITROBODIES -

FIG 29



V.P. of T.N.M.

FIG 30

are -

$$\log_{10} p = \frac{-2{\cdot}63 \times 10^3}{T} + 6{\cdot}12 \qquad \text{(D.N.T.)} \;\ldots\;\ldots\; 1.$$

$$\log_{10} p = \frac{-2{\cdot}63 \times 10^3}{T} + 5{\cdot}92 \qquad \text{(T.N.T.)} \;\ldots\;\ldots\; 2.$$

$$\log_{10} p = \frac{-2{\cdot}13 \times 10^3}{T} + 7{\cdot}23 \quad \text{Tetra-nitro-methane} \;\ldots\;\ldots\; 3.$$

These give latent heats of sublimation calculated from the Arrhenius equation -

D.N.T.	12	K.cals./gm.mol.
T.N.T.	12	K.cals./gm.mol.

and latent heat of volatilisation -

T.N.M.	9.7	K.cals./gm.mol.

A recent unpublished figure gives the vapour pressure of T.N.T. over the liquid at 80.3°C as 0.257 m.m. Equation 2. above gives 0.295 m.m. which represents fair agreement in view of the fact that entirely different methods of estimation were employed. The value by Menzies is 0.0295 m.m., ten times lower than the above results. The cooling applied by Menzies to reduce distillation to the McLeod gauge would explain such low results. Complete agreement is reached with Menzies in the case of tetra-nitromethane where no mention is made of the necessity to cool the leads to the McLeod gauge. It is interesting to note that Menzies checked his T.N.T. measurements by determination of the loss in weight on passage of air through the nitrobody and obtained results in agreement to within 2 %.

The values of vapour pressure of D.N.T. and T.N.T. obtained by distillation of nitrobody in steam (previous chapter) may be expressed as -

$$\log_{10} p = \frac{-5{\cdot}87 \times 10^3}{T} + 14{\cdot}01$$

and $$\log_{10} p = \frac{-5{\cdot}87 \times 10^3}{T} + 13{\cdot}32$$

These equations are not in agreement in any way with the values recorded above. The error is most likely due to entrainment of nitrobody droplets in the steam and generally to insufficient time of contact and therefore poor equilibrium.

CHAPTER 5.

SEPARATION OF NITROBODIES BY ULTRA-HIGHVAC DISTILLATION

Patent literature describes innumerable stills of this kind but they can nearly all be included in the following classifications:-

(A) INTERMITTENT OR BATCH STILLS.

Single heater surface and condenser situated one to five centimetres apart and capable of being dismantled for recovery of the product and residue. Such a unit is illustrated on Page 93. Proceedings Chemical Engineering Group 1938, 20.

(B) CONTINUOUS STILLS.

(1) Multi-heater and condenser stills generally embodying alternate horizontal heaters and condensers and permitting cycling of product from the first condenser to the second heater etc., by means of small magnetic pumps. By adjustment of the temperature of the various stages an equivalent of fractionation can be obtained.

(2) Vertical cylindrical types modelled on the design by Burrows shown on Page 94. of the Proceedings of Chemical Engineering Group 1938, 20.

(3) Stills after the pattern by Hickman (B.P. 512,583; 545,781. 1938) which might be described as an adaption of the cylindrical type, but introducing the use of a conical condenser and heater, the latter being rotated so that distilland travels up the wall centrifugally instead of downwards by gravity. Projections on the central condenser force the product of fall back on the heater and be recycled. The Hickman still, to which further reference will be made, constitutes to date the nearest approach to a fractionating system as we understand the term applied to normal pressure distillation.

Liquid vapour equilibrium is a condition non-existent in ultra-high-vacuum distillation, a fact which on first glance appears to be a serious handicap. Its place is in fact taken by a critical separation condition involving adjustment of the mean free path of the flying molecules so that only one constituent may reach the condenser as product. Very high efficiency is therefore possible. It is important to observe that the vapour pressure of the constituents need not be the criterion of separation, thus rendering possible the distillation into two constituents of a mixture the separation of which is not practicable by normal distillation.

For first experiments on the separation of nitrobody mixtures a still was constructed on the lines of the Burrows continuous type (Fig. 32.), the only essential modification being the application of heat to the lower end block to prevent the solidification of the explosive during extraction from the unit. This was simply effected by steam circulation. Vacuum was obtained by a mercury vapour diffusion pump backed by a rotary oil pump. The central column was heated electrically. In early runs the nitrobody was found to distribute itself unevenly on the heater due to its high surface tension and it was to rectify this that the wire spiral was wound on the heater.

Only a few runs were satisfactory enough to merit attention. The results of two of these are shown in Table 24.

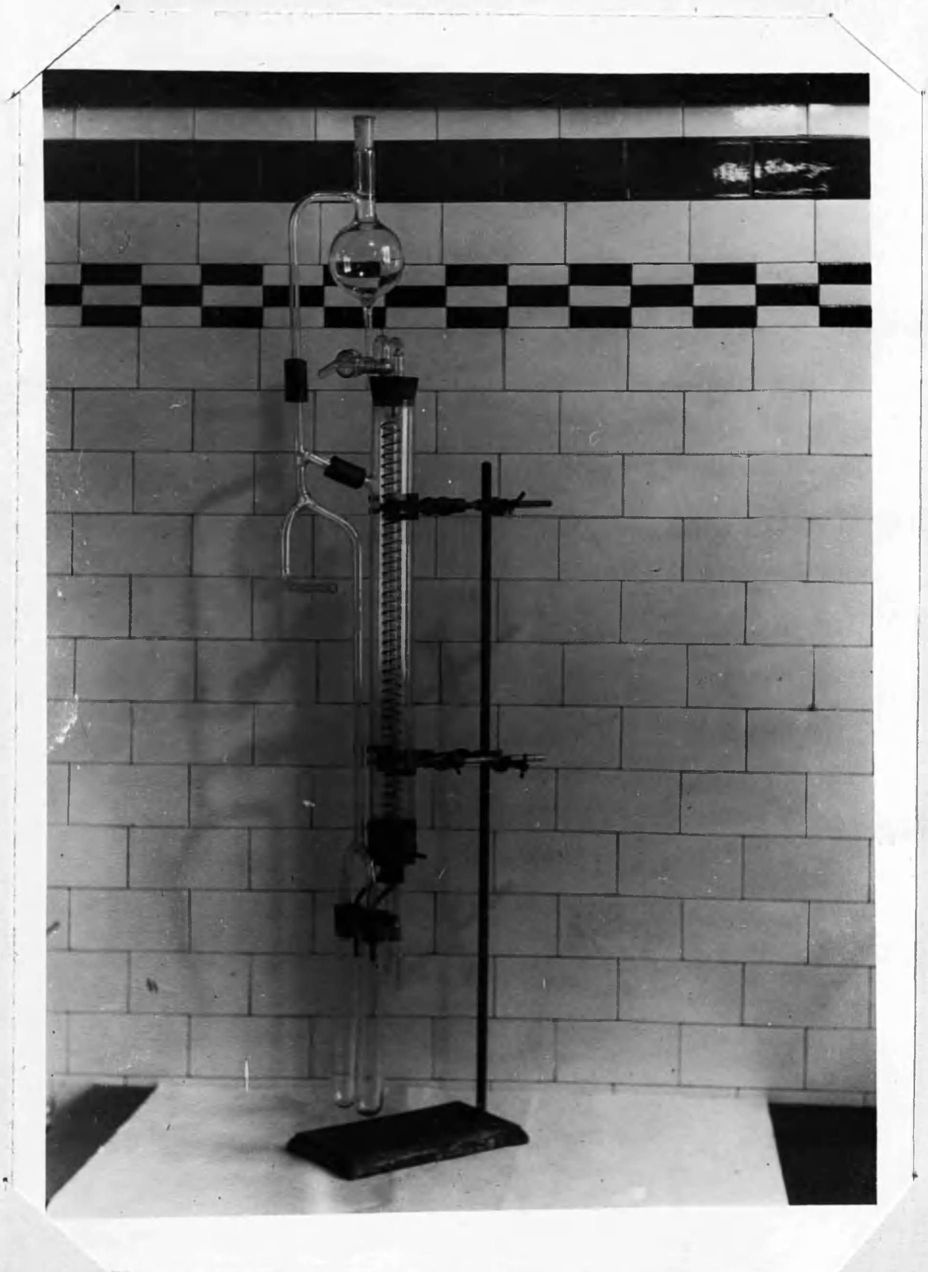


FIG 32

TABLE 24.

Distillation of Nitrobodies.

Temp. °C	Feed		Product		Residue	
	Rate. ml/hr.	Comp. % T.N.T.	Rate. ml/hr.	Comp. % T.N.T.	Rate. ml/hr.	Comp. % T.N.T.
115	50	50	20	37.5	30	56
114	50	50	20	34	30	56

The degree of separation is low and it was thought that the heater - condenser distance was short in comparison to the mean free path of T.N.T. at 115°C. It was desirable to maintain this temperature of distillation because of the high yield it makes possible and it was decided to measure the mean free path of the nitrobodies at this temperature, the results being useful in the design of future stills and providing information necessary for the calculation of the theoretical efficiency of the process.

To obtain some idea of the magnitude of the migrational path of T.N.T. over the nitrobody, an attempt was made to use the simple apparatus shown in Fig. 33. The strip of paper standing in the nitrobody was impregnated with a fluorescent indicator and the

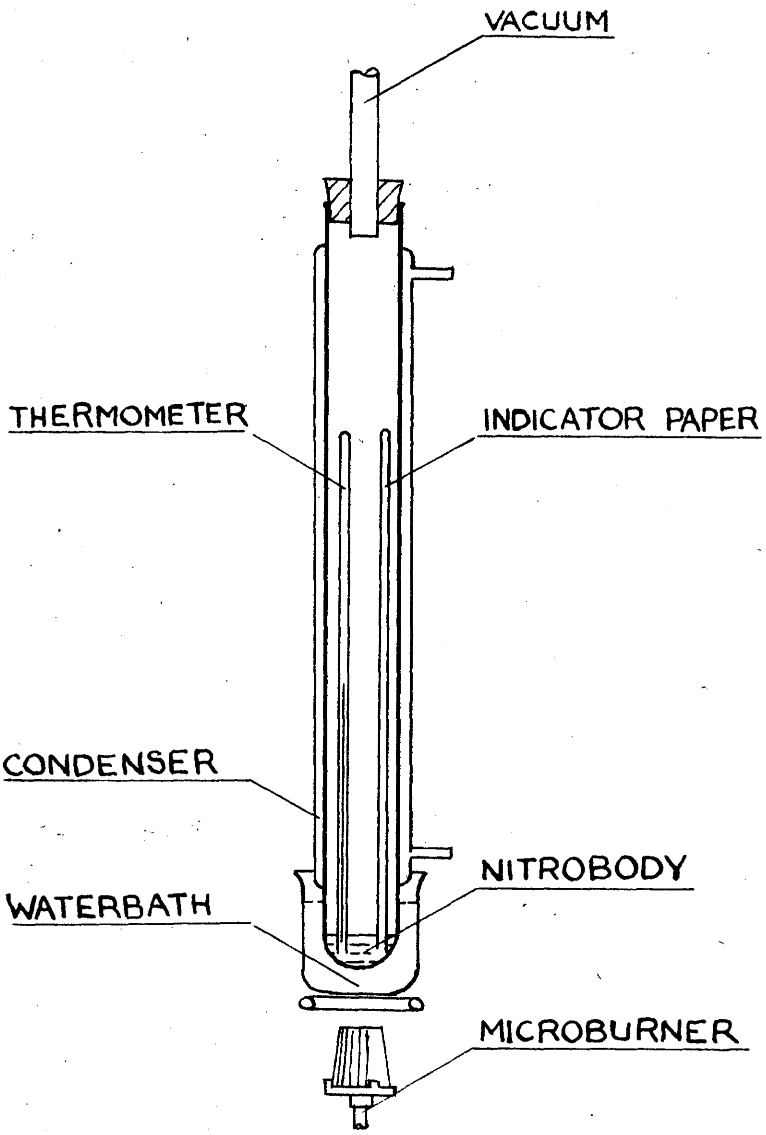

VACUUM
THERMOMETER
INDICATOR PAPER
CONDENSER
NITROBODY
WATERBATH
MICROBURNER

FIG 33

apparatus was illuminated by ultra-violet light. It was thought that the nitrobody vapour would quench the fluorescence for a distance equal to its migrational path. Although quenching occurred, no clear line of demarkation was obtained.

Apparatus was then constructed which enabled the actual yield of nitrobody at various heater - condenser distances to be measured quantitatively. This is shown in Fig. 34.

The unit consists essentially of a vertical heater over which the nitrobody is continuously circulated, a movable condenser being provided to collect the product, and the whole encased in a chamber capable of evacuation. From Fig. 34. it will be seen that the nitrobody circulator pump shaft passes through a double gland, the interspace of which is filled with the nitrobody under test, the level here being maintained by a header tank. The pump is fed with nitrobody by gravitational flow from the shallow pan inside the unit and circulates it over the face of the heater. The end plate and gland feed box are heated by steam circulated in the $\frac{1}{4}$" copper tubes

FIG 34

U.H.V. DISTILLATION UNIT.

seen in the figure. The cover can bears on a rubber ring recessed into the end plate and on the application of vacuum the apparatus is sealed by virtue of the pressure of the atmosphere on the ends. The cover is provided with a window and electric light so that distribution conditions on the heater etc. can be studied during running. The water cooled condenser is covered by a copper plate during evacuation of the unit, to prevent the condenser being coated with nitrobody before conditions are steady. This plate is thrown off by energisation of the solenoid mounted behind it.

Figs. 35. 36. 37. and 38. are photographs of the apparatus. The first two show the distillation unit with and without the cover can. In the third the apparatus has been dismantled to show the double gland, pump and condenser parts; they are arranged as far as possible in the order of assembly. The last illustration is one of the complete apparatus. On the left are the McLeod gauge, rotary oil pump and mercury diffusion pump. Behind the still is the switchboard with the solenoid switch on the right.

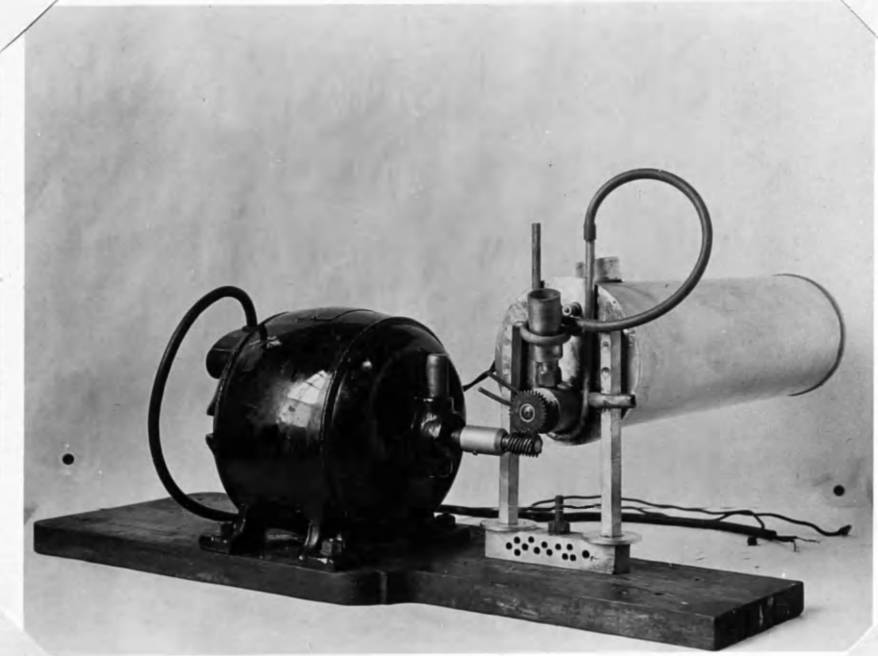


FIG 35

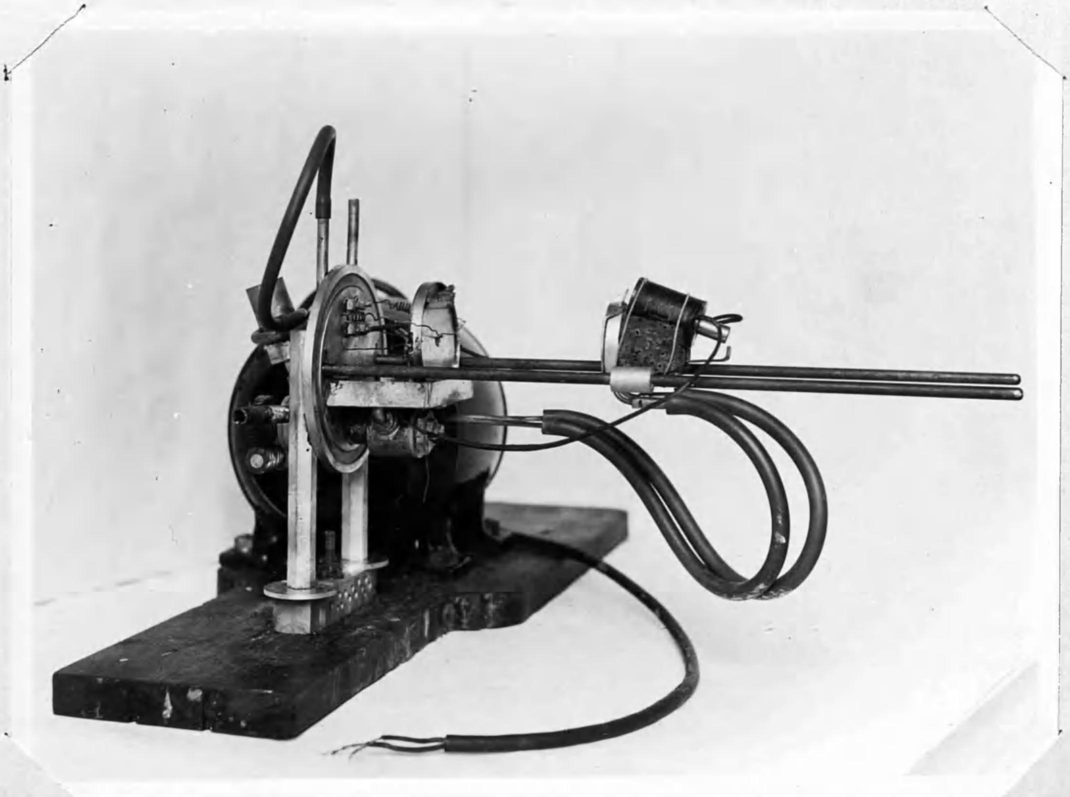


FIG 36

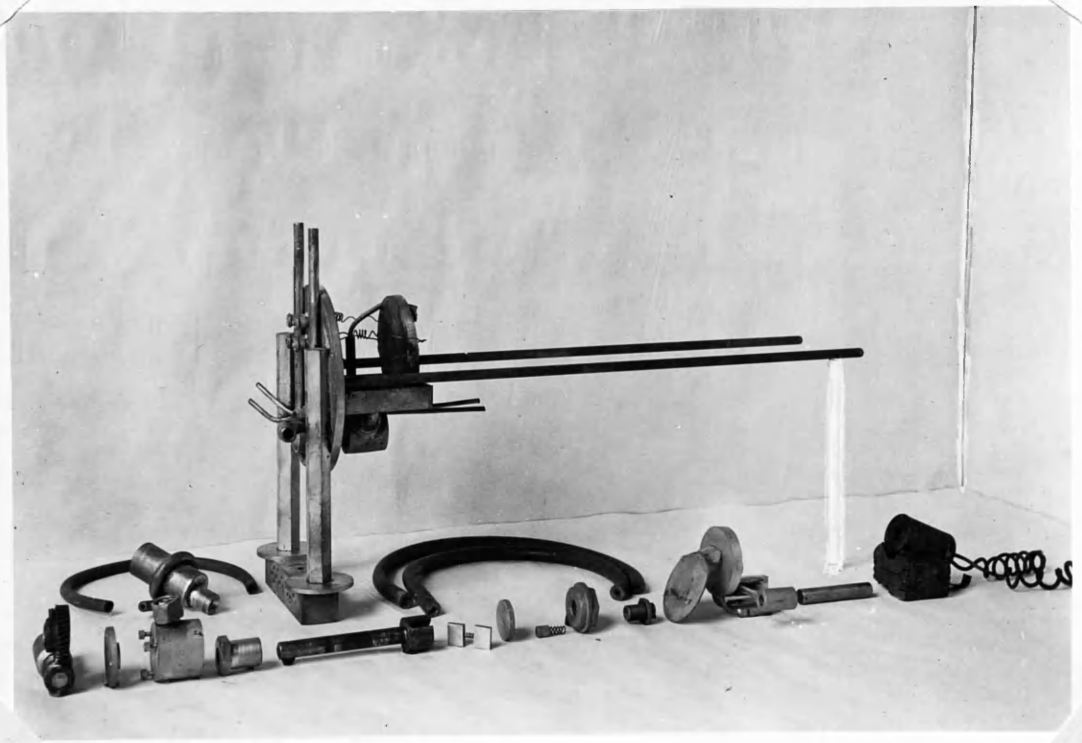


FIG 37

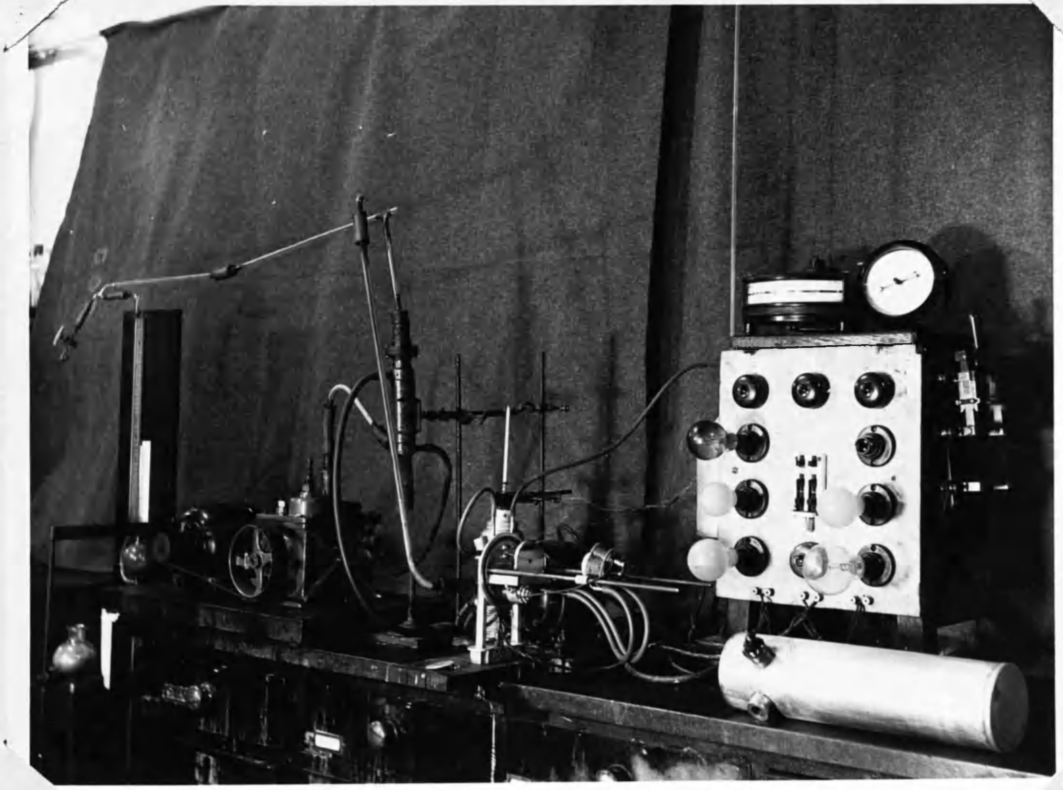


FIG 38

In order to reduce the number of terminal holes in the end plate and therefore minimise the danger of leak, and earth return circuit was operated. This necessitated a special circuit layout to enable the solenoid to be operated and this is shown in Fig. 39.

During the evacuation, the double-throw-double-pole switch is in the position "A". The heater is thus supplied with current. The solenoid is coupled to the earth end of the heater and is inoperative. When conditions are steady and the condenser is to be exposed, the switch is thrown momentarily into the position "B". With the switch in this position the solenoid and heater are in series and the earth side of the mains coupled to the casing. The solenoid is energised and the rod flies through the coil to detach the cover plate, which falls into the bottom of the can. At this instant the stop watch is started and product is being collected. Distillation is stopped by opening the air valve and breaking the vacuum.

The method of operation will be obvious from the description. The results obtained with D.N.T.

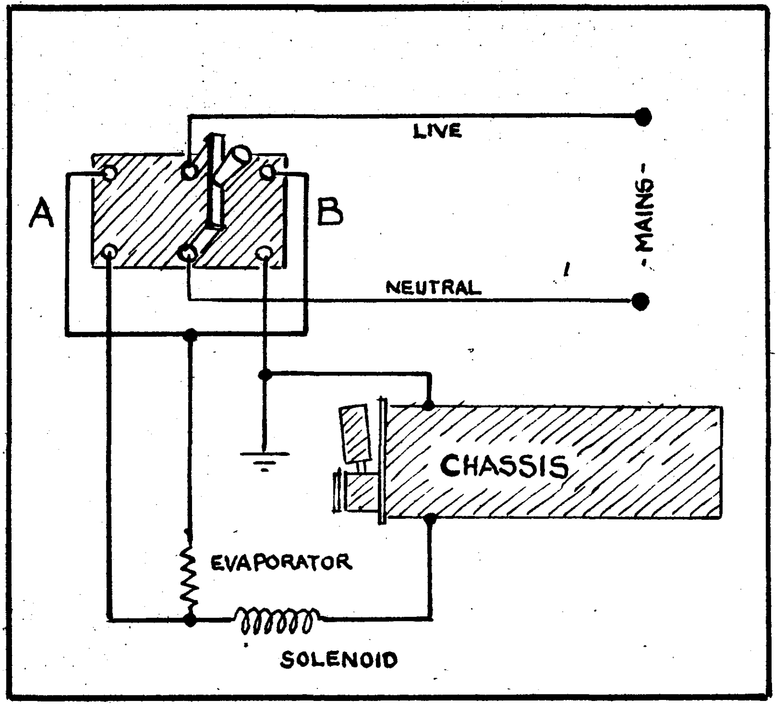


FIG 39

and T.N.T. are shown in Tables 25. and 26.

TABLE 25.

Distillation of D.N.T.

No.	Still pressure mm. Hg.	Duration mins.	Heater-condenser gap. cms.	Mass collected gms.	Rate of product, Kg/sq.m/hr.	$10^2/d^2$. reciprocal cms.
1	4×10^{-3}	6	12.1	0.043	0.345	0.68
2	2×10^{-3}	8	9.8	0.143	0.860	1.40
3	5×10^{-3}	8	9.8	0.214	1.290	1.40
4	5×10^{-3}	3	7.5	0.118	1.730	1.79
5	6×10^{-3}	6	6.0	0.376	2.990	2.78
6	5×10^{-3}	6	6.0	0.306	2.440	2.78
7	6×10^{-3}	6	6.0	0.393	3.130	2.78
8	5×10^{-3}	6	3.9	0.973	7.750	6.58
9	5×10^{-3}	4	3.9	0.674	8.050	6.58
10	3×10^{-3}	3	3.9	0.555	8.882	6.58

TABLE 26.

Distillation of T.N.T.

No.	Still pressure mm. Hg.	Duration mins.	Heater-condenser gap. cms.	Mass collected gms.	Rate of product Kg/sq.m/Hr.	$10^2/d^2$. reciprocal cms.
1	3×10^{-3}	10	14.5	0.017	0.081	0.48
2	3×10^{-3}	7	10.0	0.070	0.472	1.00
3	6×10^{-3}	7	10.0	0.059	0.400	1.00
4	5×10^{-3}	7	10.0	0.061	0.410	1.00
5	6×10^{-3}	7	8.0	0.162	1.100	1.56
6	6×10^{-3}	7	8.0	0.124	0.845	1.56
7	4×10^{-3}	5	5.9	0.181	1.725	2.86
8	4×10^{-3}	5	5.9	0.144	1.372	2.86
9	5×10^{-3}	7	5.9	0.249	1.700	2.86
10	5×10^{-3}	5	3.9	0.364	3.480	6.58
11	4×10^{-3}	5	3.9	0.295	2.820	6.58
12	6×10^{-3}	5	3.9	0.445	4.250	6.58
13	3×10^{-3}	5	2.6	1.496	14.200	14.80

The curves in Fig. 40. show the relation between the mass of nitrobody collected against the heater - condenser distance.

Fig. 41. shows the mass plotted against $10^2/d^2$. The lines are essentially straight up to a certain point, when a distinct inflexion occurs. This deviation from the law of reciprocal squares, when the yield increases disproportionately, is believed to occur when the condenser is less than the mean free path distance from the heater.

The yield of nitrobodies within this distance should theoretically be infinity, assuming an infinite supply of heat and infinite heat transfer coefficient, and the broken lines (d = 4.6) and (d = 3.2) represent approximately these infinity values for D.N.T. and T.N.T. respectively.

The equations for the straight inclined portions of the curves are -

$$m_D d^2 = 95{\cdot}4 \quad \cdots\cdots\cdots \quad (1)$$

$$m_T d^2 = 54{\cdot}8 \quad \cdots\cdots\cdots \quad (2)$$

where - m_D = mass of D.N.T. (Kg./sq.m./hr.)
m_T = " " T.N.T. (" " .)

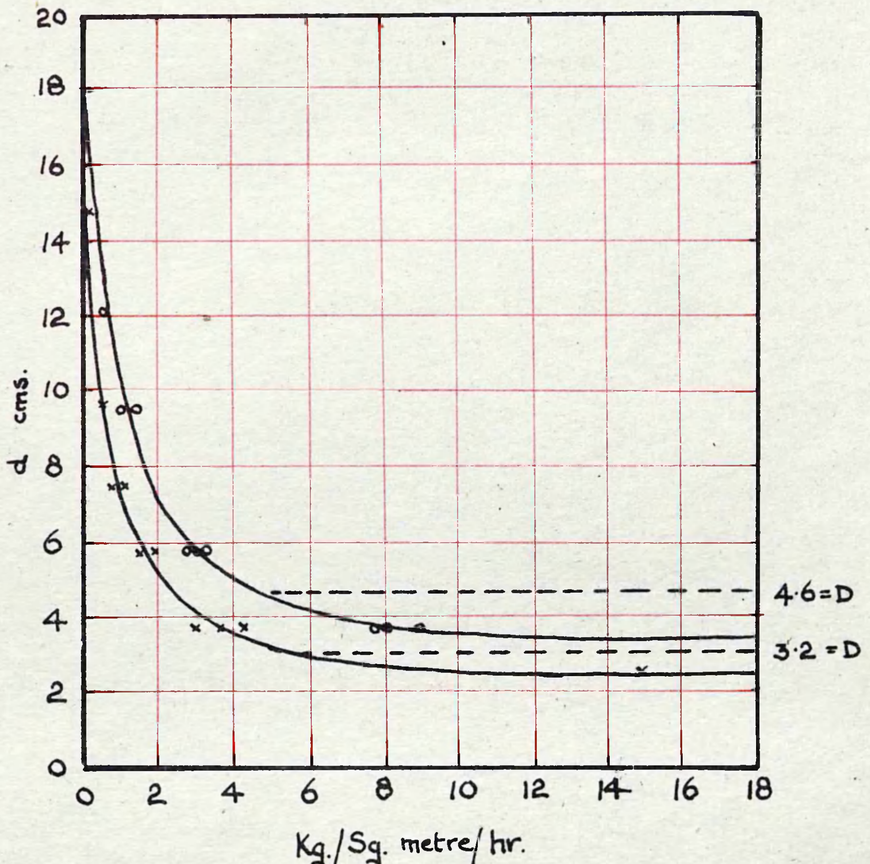

20
18
16
14
12
10
8
6
4
2
0
d cms.
0
2
4
6
8
10
12
14
16
18
Kg./Sq. metre/hr.
4·6=D
3·2=D

FIG 40

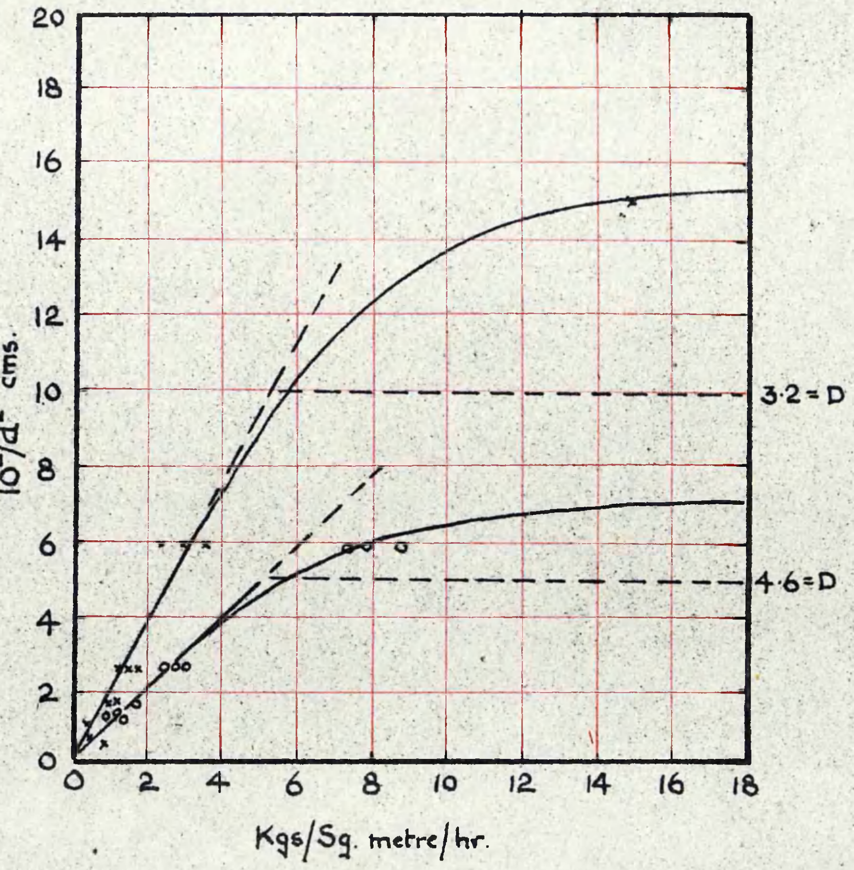

20
18
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
16
18
10²/d² cms.
Kgs/Sq. metre/hr.
3·2 = D
4·6 = D

FIG 41

and d = heater-condenser distance in cms.

then $m_D / m_T = 1{\cdot}79$ . . . . (3)

Equations 1. 2. and 3. are tenable so long as d is greater than 4.6. For values of d less than 4.6 but greater than 3.2 equation 2. is tenable but equation 1. becomes inoperative as m_D/d^2 increases disproportionately theoretically becoming infinity. This renders equation 3. equal to infinity. When d is less than 3.2 both m_D/d^2 and m_T/d^2 increase disproportionately and the ratio m_D/m_T is indeterminate.

In the distillation of a mixture of these nitrobodies at 115°C, spacing the condenser between 3.2 and 4.6 cms. from the heater will result in the yield of D.N.T. being much greater than that of the T.N.T. Theoretically the yield of D.N.T. will be infinite. In practice this will be controlled by the rate at which heat can be supplied to the nitrobody. Furthermore if the film of nitrobody on the heater can be made very thin the overall heat transfer will be determined by the film coefficient of the input side. Using steam or electricity it should be possible to obtain a heat transfer coefficient of 200 - 300 B.Th.U's./Hr./

B.Th.U's/Hr./°F/sq.ft. enabling rapid separation to be conducted.

The ratio of the yields of D.N.T. and T.N.T. is independent of the composition of the feed provided the film of mixture on the heater is only one molecule thick, since the law of partial pressures does not influence the product of molecular distillation.

By placing the condenser less than 3.2 centimetres from the heater, the ratio of D.N.T. to T.N.T. in the product will be entirely controlled by the ratio in the feed and the latent heat of evaporation of the constituents. Only very slight fractionation if any will occur. In the first design of still the heater-condenser distance was only 1.5 cms. and fractionation at 115°C could only be very inefficient.

Langmuir (Phys.Rev. 329, <u>2</u>, 1913 and 149; <u>8</u>, 1916) in his work on loss of tungsten from electrically heated filaments in vacuum, derived the equation for rate of distillation -

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p(1-r)$$

where -

m = gms/sec/cm^2.
M = gm.mol.wt.
T = absolute temperature.
R = gas constant (83.158×10^6 ergs/°C.)
p = pressure in dynes/cm^2.
r = proportion of molecules reflected.

It was further shown by Langmuir that the proportion of molecules reflected from the condenser is small and for most purposes r can be neglected.

The equation is almost universally applicable and has been expressed in many different forms. E.W.M. Fawcett (Proc.Chem.Eng.Gp. 1938, 20, 85) gives a practical adaption of the Langmuir equation as -

$$N = 5{\cdot}83 \times 10^{-2}\, p \Big/ \sqrt{\frac{M}{T}} \text{ gms./sec/cm}^2 \quad . \ . \ . \quad (2)$$

No units are stated and in an effort to determine these it was observed that in this equation the M and T have been inverted with respect to the original Langmuir expression. A study of the derivation shows that an error has occurred in the transcription. The derivation is as follows -

$$m = p\sqrt{\frac{M}{2\pi RT}}.$$

Taking R = 83.158×10^6 (Knudsen).

$$m = \frac{43.75}{10^6} p \sqrt{\frac{M}{T}}$$

Here p is in dynes/cm². (Langmuir p in m.m. of mercury $= \frac{p}{10} \times 13.6 \times 981$

$= 1334.2$ dynes/cm².

then $$m = \frac{43.75}{10^6} \times 1334.2\, p \sqrt{\frac{M}{T}}$$

$$= 5.837 \times 10^{-2}\, p \sqrt{\frac{M}{T}} \quad \ldots\ldots\ldots\ldots \text{(a)}$$

p being expressed in m.m. mercury.

It has been the experience of many workers in this field that under good conditions 95 % of this theoretical yield can be obtained in practice.

From the equation for the vapour pressure of T.N.T.

$$\log_{10} p = \frac{-2.63 \times 10^3}{T} + 5.86$$

p = 1.202 m.m. at 115°C., whence the theoretical rate of distillation is -

$$m = \frac{5.83}{10^2} \times 1.202 \sqrt{\frac{228}{388}} \text{ gms/sec/cm}^2.$$

$$= \frac{5.83}{10^2} \times \frac{1.202}{10^3} \times 3600 \times 0.766 \text{ Kq/Sq.m/hr.}$$

$$= 1960 \text{ Kq/Sq.m./hr.}$$

The greatest yield recorded in the experiments with the movable condenser unit was 14 Kg/sq.m./hr. This very low yield may be accounted for by the fact that the condenser was smaller than the heater and film conditions on the heater poor.

CHAPTER 6.

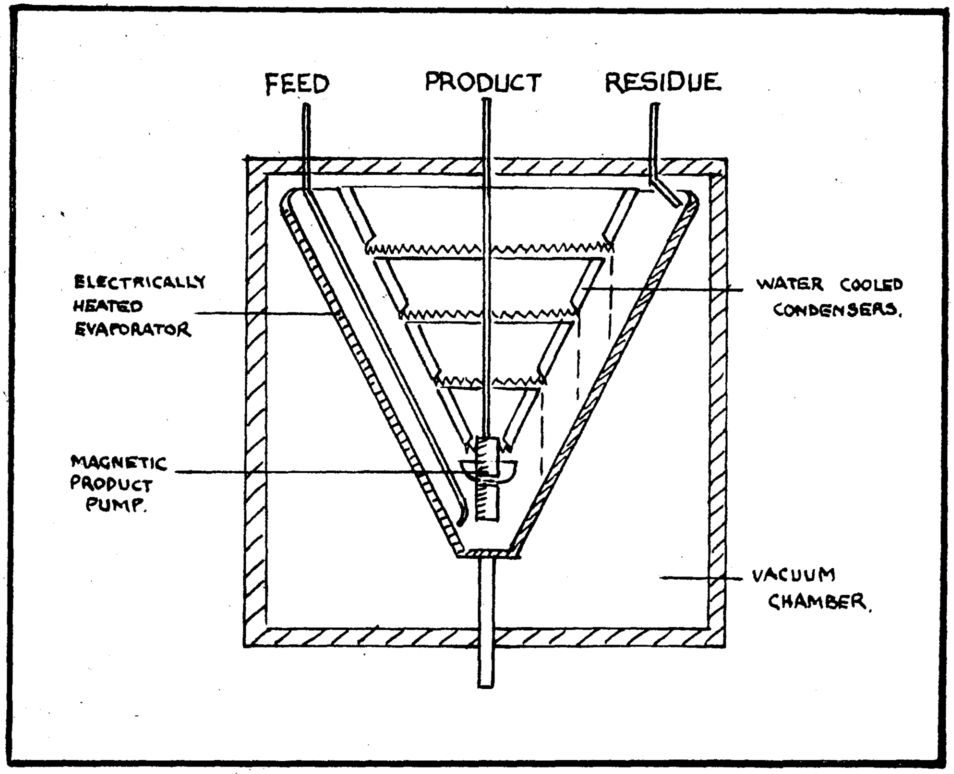
A PRACTICAL HIGH-VAC STILL WITH RECYCLE FRACTIONATION

As a basis for the design of a practicable fractionating still the Hickman patent (loc. cit.) is worthy of note.

Fig. 42. is a diagramatic sketch of the still from the patent specification. The advantages attending such a design may be readily appreciated from the drawing.

(1) By centrifugal elevation of the feed on evaporator, a very thin film will be produced and this is an essential for rapid effective separation.

(2) The use of centrifugal force to elevate the feed over the heater makes possible gravitational return of product to the heater, to constitute refractionation. As far as is known this is the first



— THE HICKMAN STILL —

FIG 42

attempt to employ the reflux system in high-vac distillation.

There appears to be only one theoretical defect, that is of a central condenser surrounded by the evaporator, as opposed to the more normal system of condenser round evaporator. In the latter state tangential impact of molecules on the condenser is impossible. Hickman's design may lend itself to somewhat higher rebound characteristics and the term (1 - r) in the Langmuir equation will probably be sensibly less than unity. It is nevertheless almost certain that the advantages will considerably outweigh this defect, and the principle is to be commended.

Unfortunately the sketch in the Patent Specification is very diagramatic and an attempt to produce a workable design from the original brings to light a number of difficulties.

(1) The cones are shown supported at one end only. Unless perfect dynamic balance could be assured it would be necessary to support the evaporator at both ends.

(2) The driving shaft entering at the bottom of the vessel would necessitate a somewhat cumbersome sealing gland.

(3) Cones are difficult to machine to dimensions of dynamical accuracy and conically wound electric heaters are always liable to loosen easily.

It is not easy to obtain all the advantages of the Hickman still while avoiding these defects but the design (Fig. 43.) is suggested as embodying the essential conditions of recirculation without the use of cones. Recycling is effected by the inclined rings on the condenser.

The still may be conveniently described as follows:-

<u>The Main Drive Motor</u> on the extreme left of the elevation is coupled to the shaft of the still by a spline so that the latter may move longitudinally with reference to the motor.

<u>The Thrust Box</u> incorporating an Acme screwed half-nut by which a section of the drive shaft may be advanced towards the feed box.

The Feed Box. Feed is effected through a central hole in the drive shaft. Control is by the cone seated valve, the male member of which is the thrust shaft referred to previously. In order that the level in the feed tank may be maintained, a sight glass is provided in the side of the feed block. The feed enters this chamber through a final splash degasser and its rate of entry is again controlled by a needle valve (on the degasser head). A diffusion pump is mounted beside the degassing tube for its evacuation.

Commutator. Electrical connections to the interior of the still are effected in a slip-ring commutator. The evaporator has a simple earth return circuit so that only one heater lead is necessary. The other two slip-rings on the commutator are for earth return thermocouples. It will be noted that in the rotor there are two conductor channels (elevation). Current is distributed in two conductors so that the evaporator shall be dynamically balanced and free from vibration when running.

The Evaporator. This issealed by an oil filled gland.

The vacuum port is in the opposite end plate and concentric with the hollow cylindrical condenser. This is planned to ensure that no distillate reaches the pumping system. The diffusion pump is built directly on the end plate and like the degassing vapour pump, fitted with a Pirani gauge.

<u>The Extraction Pumps</u>. The distillate and residue extraction pumps are on the extreme right of the elevation. They are sealed by virtue of the fact that the exit liquid flows round the ram in a gland box before delivery to atmosphere.

Provision has been made for preheating the feed by incorporating totally enclosed electric heaters in the feed box, commutator, and seal gland.

The still could be fairly simply adapted to the separation of D.N.T. and T.N.T. In this case it would be most simple to provide steam preheaters. It would be advisable to heat the exit tubes and extraction pumps with steam and a water supply at 80°C would be required for the condenser.

No lagging has been shown in the drawing. In normal practice heat would, of course, be con-

-served by covering the hot sections with magnesia or asbestos wool.

ELEVATION — HALF SECTION

PLAN
HALF SECTION XOY

SECTION ASB

END VIEW

— CONTINUOUS RECYCLING HIGH-VAC. STILL —

SCALE 1/2

ROYAL TECH. COLL. JAN 1945

DRAWN : G. Edwards.

MAXIMUM THROUGHPUT (50% PRODUCT)	100 L/HR.
EVAPORATING SURFACE	1·5 SQ. FT.
CONDENSING SURFACE	0·9 SQ. FT.

EXTRACTION PUMPS.

BORE 0·5" } EFFICIENCY 70%
STROKE 1·0" } 50 LITRES/HR. MAX.

BOLTS STUDS SETSCREWS ETC.

KEY	NO. OFF.	DESCRIPTION	KEY	NO. OFF	DESCRIPTION.
1	4	HOLD DOWN BOLTS 6" x 5/8" WHIT.	15	3	SET SCREWS 3/4" x 1/4 B.S.F.
2	6	SET SCREWS 1" x 3/8" B.S.F.	16	3	STUDS. 3 1/4" x 5/16" B.S.F.
3	14	SET SCREWS 3/4" x 3/8" B.S.F.	17	3	SET SCREWS. 1" x 1/4" B.S.F.
4	5	BOLTS. 1 1/4" x 5/16" B.S.F.	18	12	BOLTS. 3/4" x 7/16" B.S.F.
5	6	SET SCREWS 5/8" x 5/16" B.S.F.	19	5	BOLTS. 1/2" x 1/4" B.S.F.
6	6	SCREWS. 1/2" x No. 0. BA.	20	10	BOLTS. 1" x 1/2" B.S.F.
7	6	STUDS. 1 1/2" x 5/16" B.S.F.	21	12	BOLTS. 3/4" x 7/16" B.S.F.
8	6	SET SCREWS. 1" x 7/32 B.S.F.	22	8	SCREWS 3/8" x No. 0. BA.
9	6	SET SCREWS. 1" x 3/8" " *	23	6	SET SCREWS. 3/8" x 7/32" B.S.F.
10	6	SET SCREWS. 5/8" x 5/16 B.S.F.	24	12	SCREWS. 5/8" x No 2. B.A.
11	6	BOLTS. 1" x 3/8" B.S.F.	25	6	SET SCREWS. 3/4" x 3/16" B.S.F.
12	1	SET SCREWS. 1/2" x 1/8" B.S.F.	26	6	SET SCREWS. 1" x 7/32" B.S.F.
13	6	BOLTS. 3/4" x 5/16" B.S.F.	27	12	SET SCREWS. 5/8" x 5/32 B.S.F.
14	6	BOLTS. 3" x 1/4" B.S.F.	*		"TOMMY BAR" TYPE.

PREFABRICATED. MATERIALS —

MOTORS

1 OFF D.C. 250V 1 HP. 600-1450 R.P.M. SHUNT WOUND. - SPLINE SHAFT.

2 OFF. D.C. 250V 1/8 HP. 1000-2000 R.P.M. SHUNT WOUND.

PUMPS.

1 OFF. MERCURY DIFFUSION. 2"

1 OFF. MERCURY DIFFUSION 1 1/2"

2 OFF. ROTARY OIL PUMPS. 25 L/MIN.

GEARS.

2. OFF. 20:1 WORM REDUCTION GEAR BOXES (OPPERMAN.)

FEED PREHEATERS

TOTALLY ENCLOSED ELECTRIC HEATERS — "HOT POINT" TORRIBAR TYPE.