INTERACTION OF HYDROCARBONS AND OXIDES OF NITROGEN.

By

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CONTENTS.

Part I - Interaction of Iso-pentane and Nitric Oxide ... ...

EXPERIMENTAL.

A. Static Experiments. ... ...

B. Flow Experiments ... ...

CONTENTS (Continued).

PART II.

Page.

Interaction of Iso-pentane and Nitrogen Dioxide ... ...

EXPERIMENTAL ... ...

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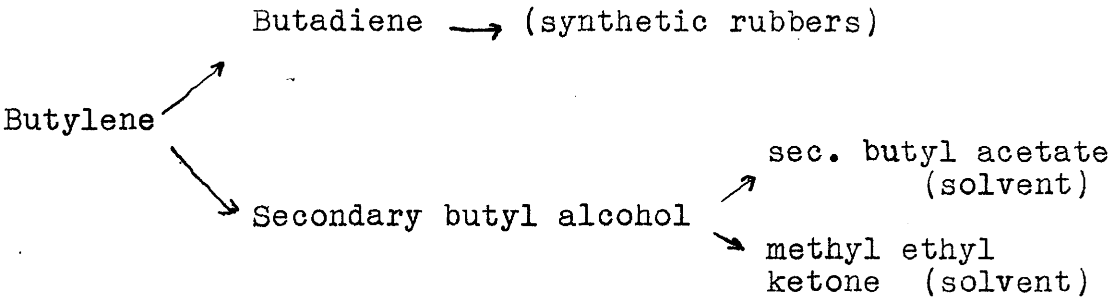
INTRODUCTION.

INTRODUCTION.

During the last few years major developments have taken place in the petroleum chemical industry, though as yet the industry is largely one of a by-product utilisation of the petroleum refining plants. Several factors have contributed to the present state of industry's developments, the more important of which are increased demand for organic chemicals, the considerable improvement in fractional methods making it possible to produce the necessary pure hydrocarbons, and, in particular the installation of a large number of cracking plants required for the production of high quality aviation and motor spirits.

Most of these plants are for catalytic cracking of oil, as a considerable wealth of information has been acquired in the field of catalytic cracking during the last decade. The only advance in thermal cracking made recently is the Polyform process described by Ostergaad and associates[1], though here too there is slight difference from pure thermal cracking, in that the oil is processed in admixture with light hydrocarbons, particularly propane, propylene, butane and butylene either from an outside source or recycled from oil undergoing conversion. The oil is subjected in such an admixture to higher temperatures and conversions per pass, than would be possible under similar conditions in ordinary thermal cracking without excessive coke-formation in the cracking zone. Resulting gasoline yields and octane numbers are stated to be higher than are obtainable by subjecting the same oil to conventional thermal cracking. The fuel gas produced is substantially free of C_4 hydrocarbons and contains small percentages of C_3 hydrocarbons.

In general, the process of cracking an oil converts an appreciable amount of it into gas containing hydrogen, the paraffin hydrocarbons - methane, ethane, propane, butanes and pentanes - and unsaturated hydrocarbons. The unsaturated hydrocarbons are easily isolated in pure form and constitute raw materials from which a large number of derivatives can be made, due to their chemical versatility. Lower unsaturated hydrocarbons are particularly important. Below are listed some of the products, of industrial importance, derived from butylenes, propylene and ethylene.

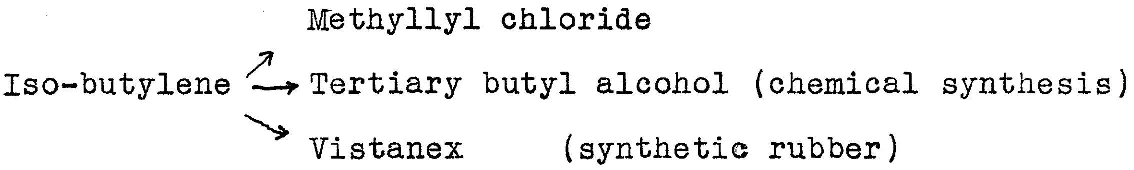


Butylene ↗ Butadiene → (synthetic rubbers)

Butylene ↘ Secondary butyl alcohol

Secondary butyl alcohol ↗ sec. butyl acetate (solvent)

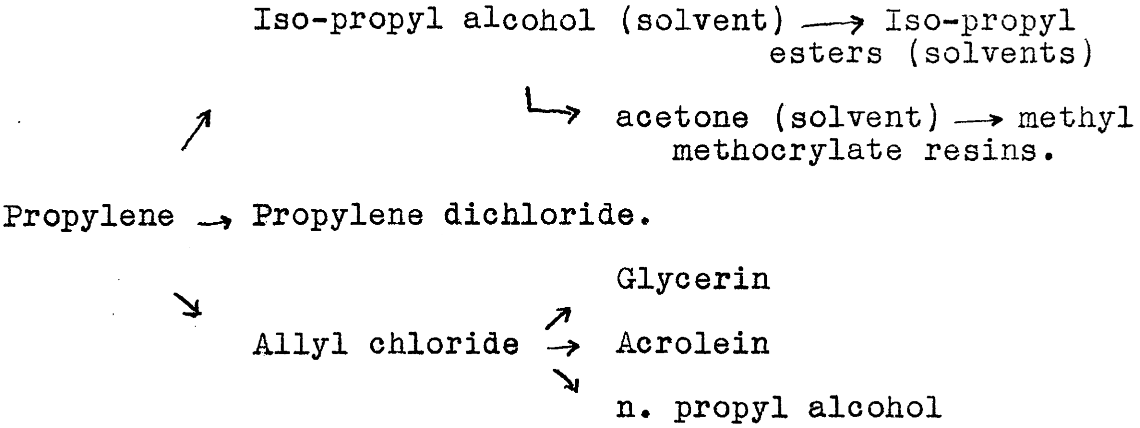
Secondary butyl alcohol ↘ methyl ethyl ketone (solvent)



Iso-butylene ↗ Methyllyl chloride

Iso-butylene → Tertiary butyl alcohol (chemical synthesis)

Iso-butylene ↘ Vistanex (synthetic rubber)



Propylene ↗ Iso-propyl alcohol (solvent) → Iso-propyl esters (solvents)

Iso-propyl alcohol → acetone (solvent) → methyl methocrylate resins.

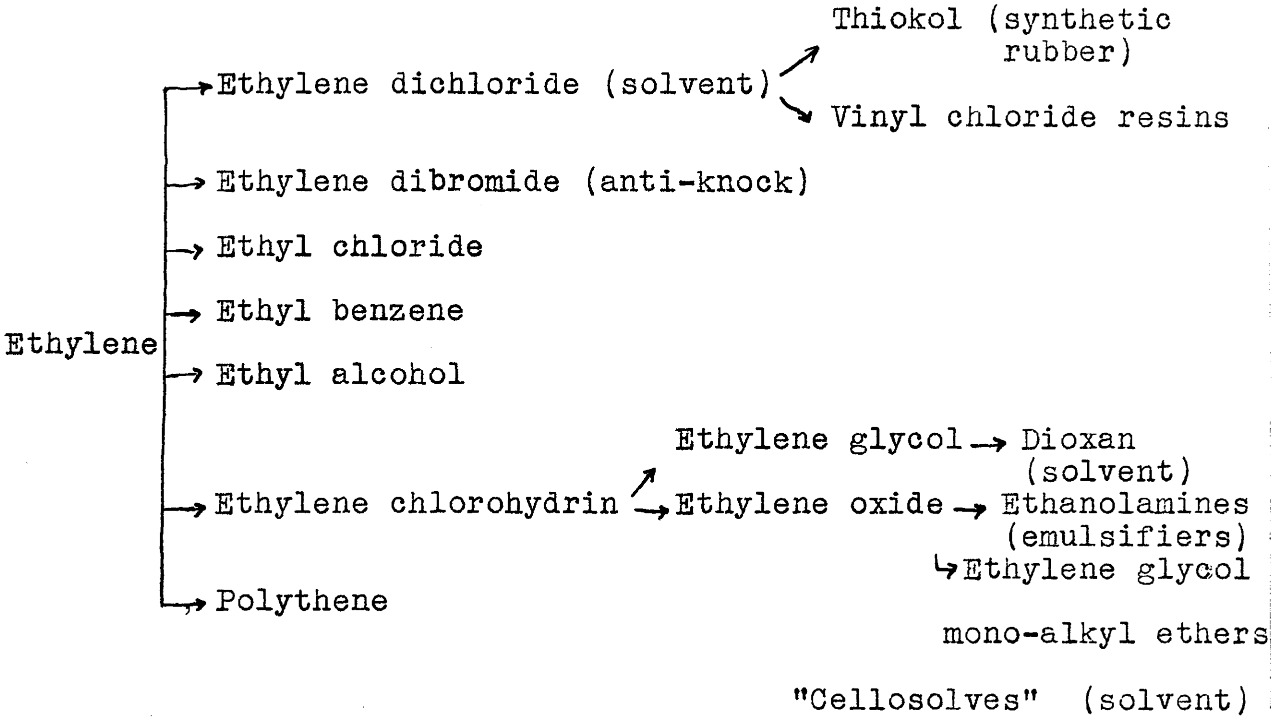
Propylene → Propylene dichloride.

Propylene ↘ Allyl chloride

Allyl chloride ↗ Glycerin

Allyl chloride → Acrolein

Allyl chloride ↘ n. propyl alcohol



Pyrolysis of Paraffin Hydrocarbons.

Saturated paraffin hydrocarbons are more susceptible to thermal than chemical treatment. Pyrolysis of paraffin hydrocarbons has been studied under varied conditions, from a few degrees above room temperature to that of the electric arc and at pressures of few m.m. of mercury to over 14,000 pounds per sq.inch. These studies have been conducted with and without catalytic influences. The pyrolysis of hydrocarbons is of importance from the industrial point of view as well as from that of the pure science. Some of the industries based on the pyrolysis of hydrocarbons are carbon black, motor fuels, lubricating oils, resins, gasoline, organic chemicals, etc. An accurate knowledge of the decomposition reactions is of fundamental importance in the manufacture of such compounds.

The investigation of the pyrolytic reactions is a difficult and complex one both theoretically as well as practically. The reaction products vary in kind and amount during cracking. The production of any one substance at the expense of another will depend on an understanding of the primary and the secondary reactions involved. Attempts have been made to study the primary reactions but the mechanism of decomposition has not definitely been proved for any single hydrocarbon.[2]

A number of theories of pyrolysis have been advanced. According to the theory based on the electron attraction of radicals, iso-pentane on pyrolysis can break up in 3 ways such that a radical possessing greater electron attraction attaches the hydrogen to become paraffin, drawing this hydrogen from the radical with less electron attraction which in turns becomes an olefine. Thus:

$$\text{a).}\quad (CH_3)_2\cdot CH\cdot CH_2\cdot CH_3 \rightarrow CH_3- \;+\; -CH\{(CH_3)\}\cdot Et$$
$$\rightarrow CH_4 \;+\; \text{Butene 1 or 2}$$

$$\text{b).}\quad (CH_3)_2\cdot CH\cdot CH_2\cdot CH_3 \rightarrow (CH_3)_2\,CH- \;+\; -C_2H_5$$
$$\rightarrow C_3H_6 \;+\; C_2H_6$$

$$\text{c).}\quad (CH_3)_2\cdot CH\cdot CH_2\cdot CH_3 \rightarrow (CH_3)_2\,CH\cdot CH_2- \;+\; -CH_3$$
$$\rightarrow (CH_3)_2\,C = CH_2 \;+\; CH_4$$

Callingaert[3] who pyrolysed iso-pentane at 600°C confirms the above theory to be generally true from his experimental data, though it does not explain all the experimental evidence of various other workers.

Kassel[4] has proposed a theory based on fundamental valence considerations to account for the production of more than two molecules per molecule of higher hydrocarbon decomposed. It is assumed that, in the case of n. butane for example, two hydrogen atoms at opposite ends of the carbon chain are brought into close proximity and united to yield a hydrogen molecule. The resulting carbon chain is broken in the center to furnish two molecules of ethylene. In the same way n. pentane may yield methane and two ethylene molecules. This theory which ignores the role of free radicals, does not agree with the experimental behaviour of the two hydrocarbons cited.

Criegee[5] believes that the thermal rupture of carbon chains occurs by removal of hydrogen atoms in the 1 : 4 position, the resulting 1 : 4 - di-radical undergoing stabilisation by cleavage between atoms 2 and 3. The decomposition of n. butane is interpreted in the light of this theory as follows:

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 \longrightarrow H_2 + -CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 -$$

$$\longrightarrow H_2 + 2\ CH_2 = CH_2$$

Rice[6] has proposed an explanation of the thermal decomposition of paraffin hydrocarbons which is more in conformity with the observed facts from the standpoint of view of free radicals. The actual existence of free radicals during the thermal treatment of organic compounds had been demonstrated chemically by Paneth and Hofeditz[7] and spectroscopically by Bonhoeffer and Haber[8]. The method of investigating developed by Paneth and his collaborators consists in dissociating gaseous organic materials at low pressures and then passing the gaseous products over metallic mirrors. In this manner, volatile organometallic compounds are formed which can be subsequently identified. In principle, this procedure consists in allowing the free radicals to combine with various metals before the former have time to combine with themselves or co - existing organic molecules. The experiments have shown that free radicals have an exceedingly short life, their half-periods being generally in the magnitude of 10^{-3} seconds. Rice and his co-workers[6] have applied this procedure to hydrocarbons heated to 700-1100°C at low pressures. As a result of this work Rice proposed his free radical theory according to which when a hydrocarbon decomposes it may be assumed that it dissociates into two free radicals which fly apart. Comparison of the strength of a C-H bond _ 93.3 Kgm. cals. with that of the C - C bond 71.0 Kgm. cals. shows that the dissociation occurs preferentially through a rupture of C - C bond, any breaking of C - H bond is negligible compared with that of C - C bond.

The probability that two radicals collide again is negligible and, therefore, free radicals produced in this way can only decompose or react with surrounding hydrocarbon molecules e.g. a free methyl radical can take a hydrogen atom to form methane and a hydrocarbon radical from the surrounding hydrocarbon. An ethyl group produced in this way can undergo two reactions, the first is similar to the methyl group and produces ethane and a hydrocarbon radical, the second is a dissociation into ethylene and hydrogen atoms. Radicals higher than ethane can decompose in a similar manner into an olefineand either hydrogen or a free radical.

The dissociation of free radicals is possible because in the process a single bond becomes a double bond, this process of internal compensation releases 58.8 Kcals. which can contribute to the minimum activation energy of 71 Kcals. necessary to break a C - C bond.

The decomposition of the paraffin hydrocarbons is represented as a chain type of reaction in which free hydrogen atoms or free radicals combine with one of the hydrogen atoms of the surrounding molecule. The hydrocarbon radical thus decomposes into a compound and either a small free radical or hydrogen atom. Thus a cycle of changes takes place in which certain groups called Carriers are regenerated and start a new cycle and this process may go on for a number of times.

The composition of the products is determined, therefore, almost exclusively by the chain cycle and is practically independent of the primary decomposition of hydrocarbons. It is possible to calculate the composition of the products when a hydrocarbon is allowed to decompose only to a small extent. In such calculations all primary C - H bonds are considered to have the same strength, secondary C - H bonds 1.2 Kcals. less and all tertiary C - H bonds 4 K cals less than a primary C - H bond.

An iso-pentane molecule on pyrolysis will give rise to the following reactions:-

Primary reactions:

a) $(CH_3)_2\,CH\cdot CH_2\cdot CH_3 \longrightarrow (CH_3)_2\,CH\cdot CH_2- \;+\; -CH_3$

b) $(CH_3)_2\,CH\cdot CH_2\cdot CH_3 \longrightarrow CH_3\cdot CH\,(CH_2\,CH_3)- \;+\; -CH_3$

c) $(CH_3)_2\,CH\cdot CH_2\cdot CH_3 \longrightarrow CH_3\cdot CH\,(CH_3)- \;+\; -CH_2\cdot CH_3$

Secondary reactions:

a) $(CH_3)_2\,CH\cdot CH_2- \longrightarrow CH_3\cdot CH = CH_2 \;+\; -CH_3$

b) $CH_3\cdot CH\cdot(CH_2\cdot CH_3)- \longrightarrow CH_3\cdot CH = CH_2 \;+\; -CH_3$

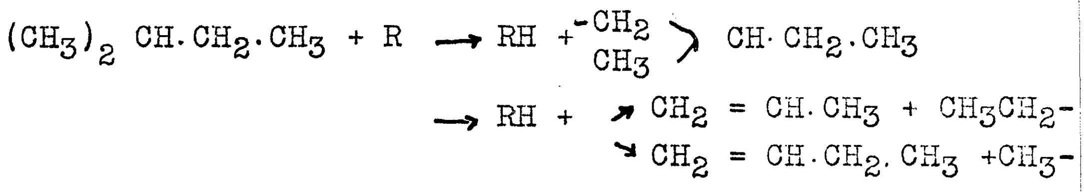
c) $CH_3\cdot CH\,(CH_3)- \longrightarrow CH_3\cdot CH = CH_2 \;+\; -H$

Chain reactions:

a) $(CH_3)_2\,CH\cdot CH_2\cdot CH_3 + R \longrightarrow RH + (CH_3)_2\,CH\cdot CH_2\cdot CH_2-$

$\longrightarrow RH + CH_2 = CH_2 + CH_3\cdot CH = CH_2 + H$

b)



$$(CH_3)_2\,CH\cdot CH_2\cdot CH_3 + R \longrightarrow RH + \begin{matrix}-CH_2\\ CH_3\end{matrix}\Big\rangle\, CH\cdot CH_2\cdot CH_3$$

$$\longrightarrow RH + \begin{cases} \nearrow CH_2 = CH\cdot CH_3 + CH_3CH_2- \\ \searrow CH_2 = CH\cdot CH_2\cdot CH_3 + CH_3- \end{cases}$$

c) $(CH_3)_2\,CH\cdot CH_2\cdot CH_3 + R \longrightarrow RH + (CH_3)_2\,CH\cdot CH(CH_3)-$

$\longrightarrow RH + CH_3\cdot CH = CH\cdot CH_3 + CH_3-$

d) $(CH_3)_2\,CH\cdot CH_2\cdot CH_3 + R \longrightarrow RH + (CH_3)_2\,C(CH_2\cdot CH_3)-$

$\longrightarrow RH + (CH_3)_2\,C = CH_2 + CH_3-$

($R = H$ or CH_3- or $CH_3\cdot CH_2-$)

Thermal decomposition studies of n. heptane by Appleby and co-workers[9] over a temperature range of 550 to 630°C and at pressures of 1.0 and 8.7 atmospheres have indicated that the composition and concentration of the decomposition products are in excellent agreement with Rice's theory. According to them, if the Rice free radical chain theory predicts correctly the products formed in the decomposition of paraffins, then no saturated compounds other than hydrogen, methane, ethane and propane should be found in the pyrolysis at atmospheric pressure of paraffin hydrocarbons. This in turn would imply that the amount of unreacted hydrocarbons remaining after pyrolysis of a liquid paraffin hydrocarbon could be determined from the weight of liquid products remaining after suitable treatment for removing olefines. This hypothesis, that after treatment of the liquid sample to remove olefines, only unchanged charging stock remains, is supported by the refractive index of the treated sample.

The line of reasoning has been tested by Dintses and Frost[10] and Dintses and Zherke[11] who pyrolysed pure n. octane to 20% decomposition in a copper reactor. The liquid and gaseous products showed on most careful analysis no saturated hydrocarbons other than methane, ethane and propane. Further tests were made on fractions of Baku gasoline containing 60% naphthenes that had been treated with concentrated sulphuric acid before pyrolysis. In every case, treatment of the liquid products of reaction with sulphuric acid left a material identical in refractive index and other physical properties with the original stock.

From observations employing a molecular beam method, Beeck[12] substantiates the free radical theory. Using a platinum filament covered with unimolecular layer of water at 1550°C, he found that all hydrocarbons except methane are completely decomposed in primary reactions, indicating the formation of free radicals by rupture of carbon bonds. Methane, however, dissociated into free methylene radicals and hydrogen under these conditions. Beeck believes that dehydrogenation of paraffin and olefine hydrocarbons cannot occur unless traces of water or of another non-metallic hydride such as hydrogen sulphide are present and this unimolecular layer on the catalytic surface is the true seat of dehydrogenation.

Bone[13] contends that in the pyrolysis of lower hydrocarbons it is necessary to assume the primary formation of free radicals such as methylene, methenyl ($CH\equiv$) and methyl. The evidence is based on spectrographic data obtained during the combustion of methane, ethane, ethylene and acetylene.

Iso-pentane, nitric oxide and nitrogen dioxide.

During the last few years, the manufacture of chemicals from petroleum hydrocarbons by oxidation has acquired great commercial importance as also the process of nitration of paraffin hydrocarbons with nitric acid in the vapour phase. Nitric oxide and Nitrogen dioxide (inorganic free radicals which are known to aid oxidation and nitration), were selected for studying their action on Iso-pentane which has primary, secondary and tertiary carbon atoms and is comparatively easily available.

PART I.

INTERACTION OF ISO-PENTANE AND NITRIC OXIDE.

INTRODUCTION AND REVIEW OF PREVIOUS WORK.

Nitric Oxide is the simplest known molecule which possesses an odd number of electrons. However, though it is paramagnetic, it is very much less reactive than free atoms, such as hydrogen or even iodine and shows little tendency to dimerize to N_2O_2 except when in the liquid or crystalline state. The stability of nitric oxide is explainable by the fact that it is a resonance structure with the canonical states:

$$:\dot{N} = \ddot{O}: \qquad :\overset{-}{\ddot{N}} = \overset{+}{\dot{O}}: \qquad .\overset{+}{\ddot{N}} - \overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$$

and can, most adequately be represented as having a three- electron bond supplementing a single N - O covalency, as $:N \overset{\cdot\,\cdot\,\cdot}{—} O:$ since it has a very small dipole moment, and the internuclear distance between its two atoms, 1.14A, lies between that calculated for double and triple co-valent links (N = O, 1.18A; N≡ , 1.06A).

The simple gas reactions of nitric oxide with chlorine, bromide and oxygen involve termolecular collisions e.g.,

$$2NO + O_2 \longrightarrow 2NO_2$$

rather than bimolecular reaction chains that are characteristic of molecules containing unpaired electrons. They all proceed at measurable velocity at ordinary temperatures, but are reversible processes at higher temperatures. In high dilution the oxidation of nitric oxide in air leads to the formation of N_2O_3, since the bimolecular reaction, nitric oxide and nitrogen peroxide

$$NO + NO_2 \longrightarrow N_2O_3$$

is faster than its termolecular reaction with oxygen.

The rate controlling stage of the gas reaction between nitric oxide and hydrogen, which proceeds at higher temperatures is again essentially termolecular, though in this case there is some evidence that binary collision complexes of very short life are involved.

Nevertheless the odd electron character of nitric oxide is sufficiently well marked for it to be a valuable diagnostic reagent for other free radicals. Thus it combines instantly in solutions with triphenyl methyl, diphenyl-nitrogen and their analogues. Again, with salts of the transition metals such as iron and cobalt, which possess unpaired d electrons, it forms co-ordination compounds - the nitrosyls - in which electron-pair bonds only are present. It is noteworthy that in all these compounds, the fresh co-valent bond involves the nitrogen atom, as would be expected of the structure.$\ddot{N} = O$: .

Hinshelwood and his co-workers[14] have found that a number of reactions which are suspected to proceed by a free radical chain mechanism are inhibited by the addition of small amounts of nitric oxide. Inhibition of the thermal decomposition of a number of paraffin hydro-carbons by nitric oxide has been studied, principally that of ethane. At present there are conflicting views as to the explanation of this inhibition.

Staveley[15] investigated this reaction at a temperature of 620°C with an ethane initial pressure of 150 m.m. The results of his experiments showed variations in the initial rate of decomposition with the varying proportions of nitric oxide, which were as follows:

	Nitric Oxide	Velocity constant		
a.	0.0 m.m.	58.5	sec^{-1}	$x\ 10^{-5}$
b.	0.65 m.m.	30.6	"	"
c.	1.25 m.m.	19.3	"	"
d.	8.9 m.m.	7.55	"	"
e.	26.0 m.m.	4.25	"	"

He found this reduction of initial rate of decomposition to be a genuine effect and gave an explanation on the theory of formation of free radicals. According to Staveley, the initial rate of thermal decomposition is reduced by the presence of nitric oxide which suppresses the reaction chains by combining with the free radicals or atoms.

Gray, Travers & White[16] confirm the reduction in the rate of decompositions of ethane in presence of nitric oxide but have proposed entirely a different explanation. They found that a rapid reaction took place between ethane and nitric oxide without any apparent increase in volume. The product of ethane-nitric oxide at first increased in concentration in the gas and then diminished. It was not isolated.

The ethane-nitric oxide reaction itself slowed down after an interval, but in doing so, a reaction which appeared to involve ethane and the product of ethane-nitric oxide reaction, developed. One of the products of this reaction was C_2H_4.

The theory of free radicals could not be used to explain the above facts, so Gray and co-workers have suggested that ethane-nitric oxide reactions operated with a lower activation energy than the primary decomposition reaction and removed hot molecules at a faster rate than could be supplied to maintain the Maxwell-Boltzmann equilibrium. The result was that the former process was to a considerable extent substituted for the latter. The ethane-nitric oxide reaction in turn slowed down at a faster rate than could be accounted for by the removal of ethane or nitric oxide. This was associated with the operation of a reaction between ethane and a product of the ethane-nitric oxide reaction at an activation energy still lower than the ethane-nitric oxide reaction itself.

Steacie and Shane[17] attribute the inhibition of decomposition to a radical rearrangement and not to a free radical mechanism. They analysed the products of reaction and found these to be the same as obtained from a purely thermal process.

In spite of all the work done, the mechanism of the decomposition in presence of nitric oxide is still open to question.

Kuhlmann[18] observed the formation of hydrogen cyanide on treating methane with nitric oxide in the presence of heated spongy platinum. This reaction has not been very thoroughly investigated. Huntington[19], however, used this reaction in a process for the production of hydrocyanic acid in which acetylene mixed with nitric oxide was ignited electrically in a cylinder.

Elod and Nedelmann[20] examining the action of nitric oxide on the methane, ethylene and acetylene arrived at the following conclusions:

a. Hydrocyanic acid is produced by the action of nitric oxide on the hydrocarbons at high temperatures. Under similar conditions the yield of hydrocyanic acid is greater from acetylene than from ethylene and at the same time the quantity of polymerized substances and of formaldehyde is larger. The reaction temperature required for methane reaction is 300°C higher than other hydrocarbons for similar yields of hydrocyanic acid.

b. The reaction between nitric oxide and ethylene is catalysed by various materials, of which the best is a mixture of equal parts of quartz and alumina. Addition of steam to the reaction mixture decreases the yield of hydrocyanic acid and increases the production of ammonia. The addition of hydrogen favours the formation of hydrocyanic acid.

c. The production of hydrocyanic acid increases greatly with rising temperature and is large at 1000°C and over. With rising temperature, the ammonia production rises to a maximum and then falls.

According to Elod and Nedelmann, the first stage in the process is the reduction of nitric oxide to ammonia. Part of the ammonia, then reacts with the hydrocarbon to form hydrocyanic acid (probably through intermediary of unsaturated residues such as $= CH_2$ and $\equiv CH$), and the other part undergoes thermal dissociation to yield hydrogen and nitrogen. They considered there was little probability of a reaction of ammonia directly with methane or solid carbon. The production of carbon monoxide may be accounted for by the reaction of ethylene with water vapour formed by reduction of nitric oxide. From these considerations it would appear that the process capable of giving the best results would be the one starting with or favouring the initial formation of ethylene and ammonia. Later results[21] have substantiated this, although the formation of acetylene seems a necessary condition for the production of hydrogen cyanide. Hydrocyanic is probably formed thus:

$$2CO + NH_3 \longrightarrow HCN + CO_2 + H_2$$

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

and by minor reactions involving the formation and decomposition of formaldehyde.

Staveley and Hinshelwood[22] explain that nitric oxide may react with methyl radicals produced as follows:

$$CH_3 + NO \longrightarrow CH_3\ NO \longrightarrow CH_2 = N.OH \longrightarrow HCN + H_2O$$

In the literature of patents there are a few references[23] to nitric oxide being used as vapour phase catalyst for the oxidation of petroleum hydrocarbons.

Platanov and Shaikind[24] have investigated the reaction of nitric oxide on n. heptane, n. hexane and n. pentane in presence of catalysts. At 450° - $500^{\circ}C$, with Kaolin mixed with the oxides of aluminium, cerium and thorium as catalysts, the products consisted of ammonia, nitric oxide, nitrogen, carbon monoxide, methane and unsaturated hydrocarbons. At 250° - $300^{\circ}C$, in the presence of vanadium pentoxide and platinum black as catalysts, water, carbon monoxide, nitrogen and unchanged hydrocarbons were found.

No experimental data on the reaction between nitric oxide and iso-pentane being available, it was considered to be of interest to examine this reaction in view of the fact that the hydrocarbon contains primary, secondary and tertiary carbon atoms. Two sets of experimental conditions have been studied, using in the first case, static conditions and in the other streaming conditions.

EXPERIMENTAL.

A. STATIC EXPERIMENTS.

i, PREPARATION OF REACTANTS, ANALYTICAL METHOD AND APPARATUS.

PREPARATION OF REACTANTS.

ISO-PENTANE.

Iso-pentane boiling between 26° to 31°C was treated with a little sulphuric acid to remove any unsaturated hydrocarbons, then washed thoroughly with water to remove the acid. The residue was fractionated in a Fenske fractionating column and a fraction boiling between 27.7° to 28.1°C collected. This fraction has been used for all the experiments described below. Pure iso-pentane boils at 27.9°C.

NITRIC OXIDE.

This was prepared by the action of sulphuric acid on sodium nitrite. Concentrated sulphuric acid was dropped on to sodium nitrite (A.R.) covered with 2 to 3 times its weight of water. The nitrogen dioxide so produced was absorbed in sodium hydroxide solution and the nitric oxide collected over water.

METHOD OF ANALYSIS.

Macfarlane's gas analysis unit was used for the analysis of the gaseous products of the reaction. The estimation of various gases was carried out as follows:-

a. Nitric oxide was absorbed in a cold saturated solution of ferrous sulphate.

b. Carbon dioxide was absorbed in a 30% aqueous solution of caustic potash.

c. Unsaturated hydrocarbons (CnHm) were absorbed in a bromine solution having 10% potassium bromide.

d. Carbon monoxide was absorbed in an ammonical cupurous chloride solution.

e. Saturated hydrocarbons (CnH2n+2) were determined by explosion with a suitable excess of oxygen and then noting the diminution in volume as well as the contraction after absorption in caustic potash.

APPARATUS.

As shown in Fig 1. (page 26) the apparatus consisted of the reaction bulb of pyrex glass (about 2" x 4") having a long narrow capillary to which was attached a full length mercury manometer. The capillary was provided with a number of stop-cocks. At the stop-cock C

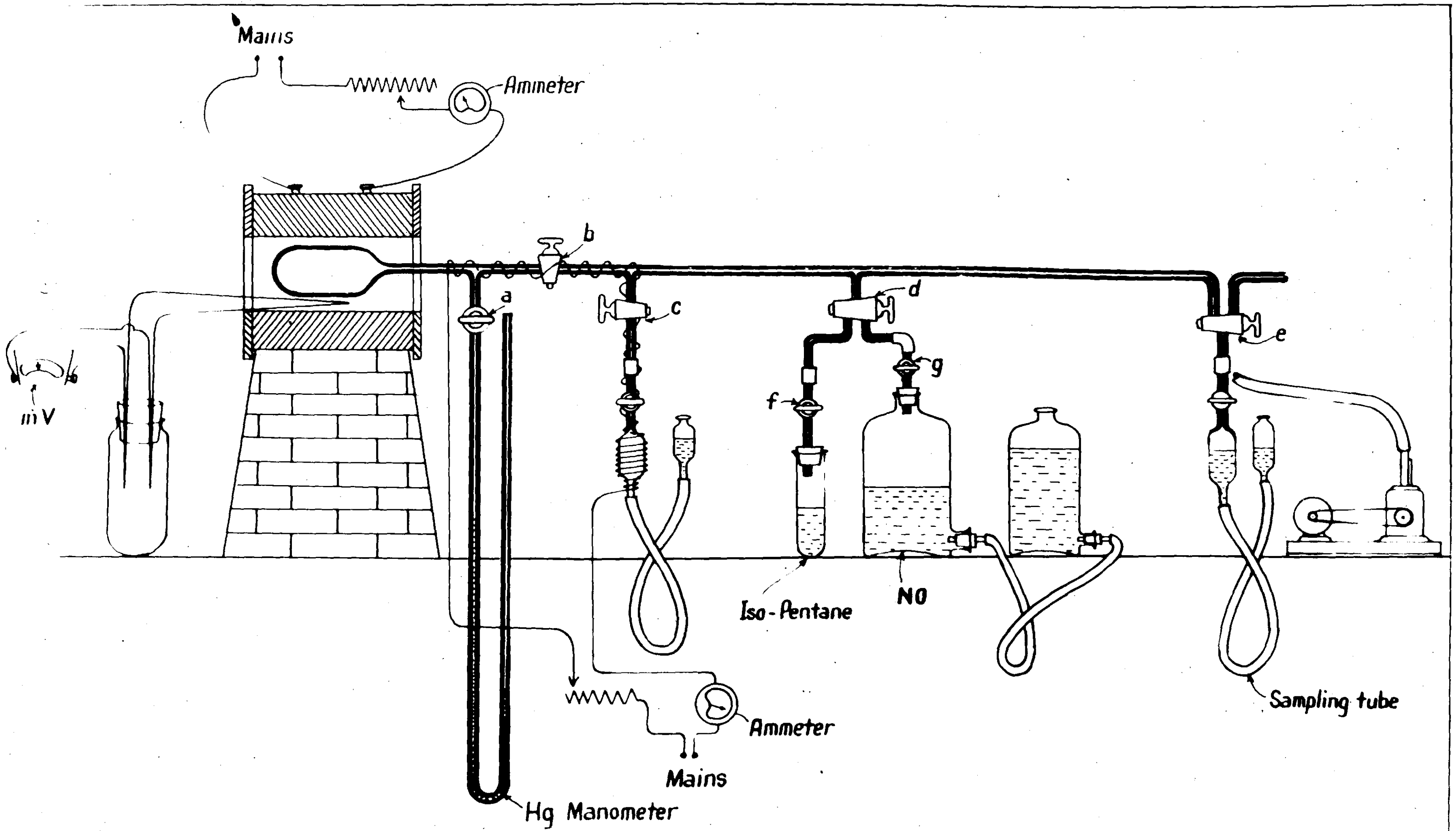

Mains
Ammeter
b
a
c
d
e
g
f
mV
Iso-Pentane
NO
Sampling tube
Ammeter
Mains
Hg Manometer

Fig. 1.

was attached a sampling tube of about 60 C.C. capacity filled with mercury. Nichrome wire was wound round it to enable the sampling tube to be warmed when required. Iso-pentane and nitric oxide were introduced in the bulb through the three-way stop-cock d. Through the second three-way stop-cock e, the apparatus was evacuated when necessary and also the sample of the gas after reaction was taken out by removing the connection with the vacuum pump and connecting to a sampling tube charged with mercury.

The bulb was placed in an electric furnace which had been standardised and found to give a uniform temperature zone of about eight inches. The temperature of the furnace was recorded by means of a Chromel-Alumel thermocouple whose cold junction was maintained in ice.

PROCEDURE.

The method adopted for carrying out an experiment was as follows:

The bulb after being heated at a known temperature for some time was evacuated by connecting the vacuum pump through the stop-cock e and opening the stop-cocks a and c. After the apparatus had been evacuated, the stop-cock e was closed and the level of the mercury in the manometer was observed, to test the apparatus for leaks. When the apparatus had been confirmed to be air-tight, the stop-cock f and d were opened to introduce a little iso-pentane into the bulb, after which these were closed and the bulb re-evacuated. This process was repeated to insure the complete absence of oxygen. The manometer reading was taken and then the required amount of iso-pentane introduced and the manometer reading again recorded. After that the nitric oxide was introduced in the bulb by opening stop-cocks g and d. The manometer reading was again taken. The total initial pressure of iso-pentane and nitric oxide was kept practically the same in all the experiments about 520 m.m.

During the winter months when the room temperatures were appreciably low, it was found necessary to warm the capillary tube as otherwise, the iso-pentane condensed. To avoid this, the sampling tube connected through the stop-cock c was used. Nichrome wire was wound round it, as also along the capillary tube from stop-cock b on to the point where the capillary entered the furnace and by passing a current through this wire, the system was kept warm enough to prevent condensation. To start with this sampling tube was completely filled with mercury, iso-pentane gas was introduced into it by lowering the levelling tube after closing stop-cocks b and e, and opening the stop-cocks c, d, and f. No condensation occurred under these conditions. The required amount of iso-pentance gas was then transferred into the bulb from the sampling tube.

ii, REACTIONS - GENERAL DISCUSSION.

The reaction bulb was heated to a temperature of 250°C; the first temperature to be investigated. It was maintained at that temperature for some time; known volumes of iso-pentane and nitric oxide were introduced in the bulb following the procedure described earlier. The bulb was kept at that temperature for half an hour. No change in pressure was noticed. The temperature was raised to 300°C, the bulb maintained at that temperature for half an hour but as before no change was noticed. Temperatures of 350°C, 400°C, 450°C, 500°C, 525°C and 550°C were tried. At 350°C and 400°C, no pressure change could be detected. At the temperature of 450°C, a slight but definite change in pressure was seen. This change in pressure was fairly appreciable at 500°C and at higher temperatures.

At 525°C, a few experiments were made with various proportions of iso-pentane and nitric oxide to see the changes in pressure with time (Table I). Curves were drawn showing the increase in pressure with time (page34). From these it is seen that in the case of pure iso-pentane, a steady stage was not reached even after 320 minutes whereas in the case of 50% iso-pentane and 40% nitric oxide a steady stage was reached after about 200 minutes and in the case of 12.5% iso-pentane with 70% nitric oxide, a steady stage was reached in about 90 minutes.

A detailed study of the reaction was made at this temperature of 525°C. Iso-pentane 71.7% and nitric oxide 27.5% were heated (out of contact with air), in the bulb for a period of 180 minutes at 525°C. Sample of the gaseous products of reaction on analysis showed those to contain unreacted nitric oxide, carbon dioxide, unsaturated hydrocarbons, carbon monoxide and saturated hydrocarbons. In the case of the saturated hydrocarbons ($C_n \ H_{2n+2}$), the value of n, i.e., the number of carbon atoms were determined by standard gas analysis methods. This value was used in calculating the amount of the saturated hydrocarbons present.

Besides the gaseous products, a trace of a liquid product along with a solid which appeared to be mostly carbon was seen in the bulb.

The various variables on which this reaction of iso-pentane and nitric oxide is dependent are:

1. Proportions of iso-pentane and nitric oxide.
2. Temperature.
3. Time of contact.

An attempt was now made to study the influence of each of these variables on the reaction.

TABLE I.

CHANGES IN PRESSURE WITH TIME.

Iso-pentane only		Iso-pentane 90% Nitric Oxide 8%		Iso-pentane 50% Nitric Oxide 40%		Iso-pentane 12.5% Nitric Oxide 70%	
Time Minutes	Change in pressure mm.	Time Minutes	Change in pressure mm.	Time Minutes	Change in pressure mm.	Time Minutes	Change in pressure mm.
2	11	2	2	2	2	2	1
4	23	4	4	4	8	4	2
6	32	6	7	6	14	6	3
8	40	8	11	8	19	15	4
16	64	10	15	10	25	20	5
20	78	12	19	12	29	25	6
25	92	14	24	16	39	30	8
30	106	16	29	20	52	40	10
40	129	20	39	30	74	60	11
50	151	24	48	38	93	70	11
60	190	30	60	48	113	92	12
80	216	35	79	60	138	108	12
92	242	40	92	65	144	120	12
102	264	45	103	70	150	140	12
112	278	50	116	80	162	160	12
120	288	60	141	90	171	200	12
132	306	72	156	100	180		
152	324	80	168	110	187		
177	342	96	186	130	190		
187	347	112	200	148	192		
207	365	136	222	160	196		
217	369	168	250	172	197		
237	383	184	260	185	198		
247	391	200	270	200	198		
257	395	220	282				
287	407	240	288				
307	418						
317	420						

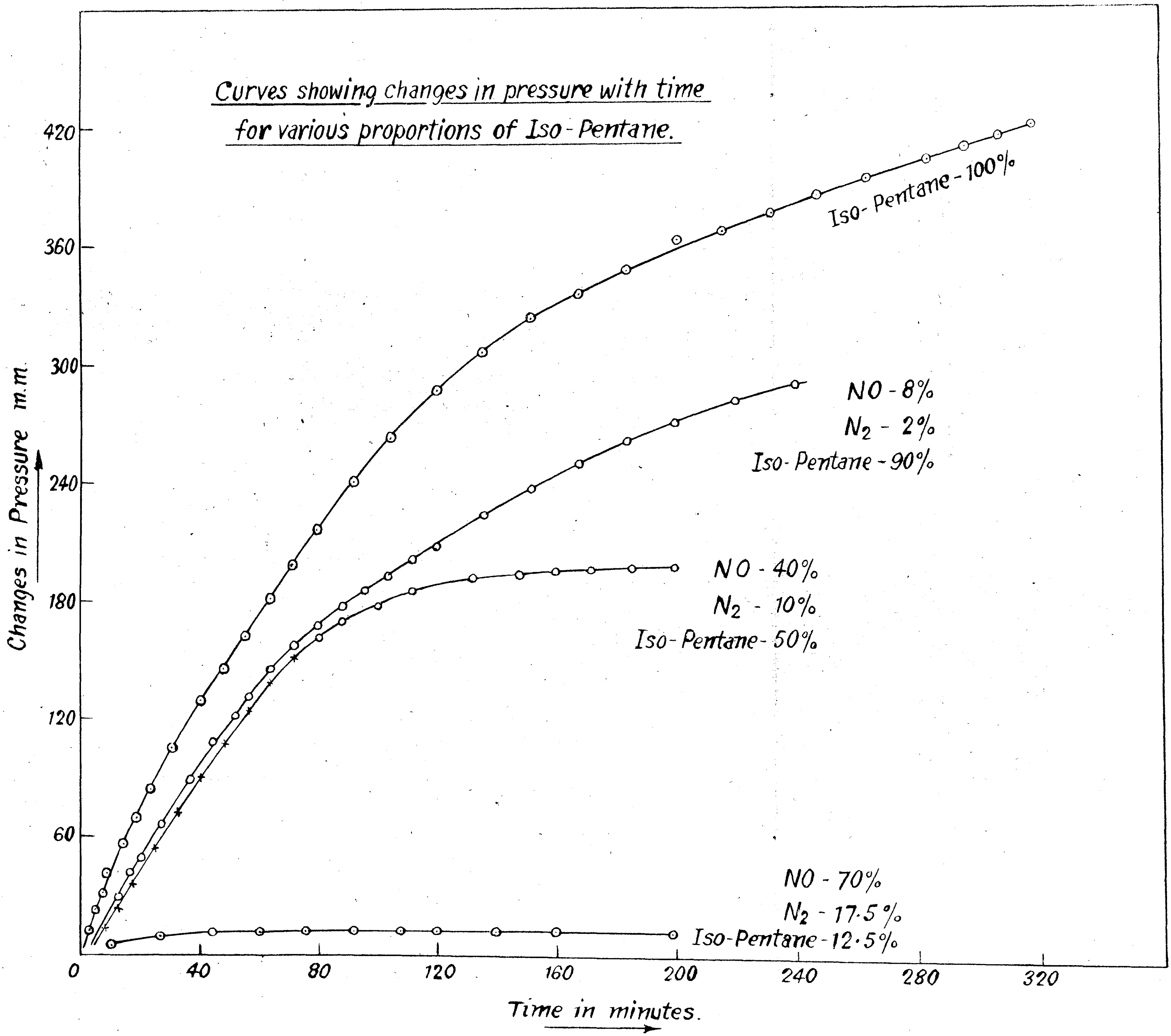

Curves showing changes in pressure with time for various proportions of Iso-Pentane.
Changes in Pressure m.m.
420
360
300
240
180
120
60
0
40
80
120
160
200
240
280
320
Time in minutes.
Iso-Pentane - 100%
NO - 8%
N_2 - 2%
Iso-Pentane - 90%
NO - 40%
N_2 - 10%
Iso-Pentane - 50%
NO - 70%
N_2 - 17·5%
Iso-Pentane - 12·5%

Fig. 2.

iii, Effect of varying the proportions of Iso-pentane and Nitric Oxide.

At 525°C, a number of experiments was made with varying proportions of iso-pentane and nitric oxide. The gaseous products of the reaction were analysed in each case. The results of these experiments are given on the pages 37- 38.

Curves were plotted showing the formation per 100 volumes of iso-pentane, of carbon dioxide, carbon monoxide, unsaturated hydrocarbon and saturated hydrocarbons. A curve showing the ratio of nitric oxide used to total nitric oxide present was also drawn; these are given on page 39.

These curves show:

a) an increase in the formation of carbon dioxide and carbon monoxide with increase in the proportion of nitric oxide in the reaction mixture,

b) the formation of unsaturated hydrocarbons reaches a maximum and then decreases with decreasing proportion of iso-pentane,

c) the formation of saturated hydrocarbons increases with decrease in the proportion of iso-pentane,

d) the ratio of nitric oxide used to the total nitric oxide present increases, reaches a maximum and then decreases, with increasing amounts of nitric oxide in the reaction mixture.

An experiment was made (expt. No.1, page 37) in which iso-pentane alone was heated in the bulb for 180 minutes. Analysis of the gaseous products showed those to contain unsaturated and saturated hydrocarbons. The yields of these per 100 volumes of iso-pentane were greater than in the case of experiments in which nitric oxide had been used. The value of n, was found to be 1.7 whereas it varied from 1.4 to 1.1, in the case of experiments made with nitric oxide and iso-pentane.

Iso-pentane and nitric oxide.

TABLE 11.

TEMPERATURE 525°C.

	Experiment No.	1.	2.	3.	4.
1.	Percentage Composition of Reactants.				
	a) Iso-pentane - %	100	71.7	61.0	50.0
	b) NO - %	-	27.5	37.6	47.0
	c) N_2 - %	-	1.8	2.4	3.0
2.	Time of Contact. - minutes	180	180	180	180
3.	NO used - %	-	19.3	22.4	36.9
4.	Ratio of NO used to total present.	-	0.7	0.6	0.79
5.	CO_2 formed - %	-	0.55	1.7	1.2
6.	CO_2 formation per 100 vols. of Iso-Pentane.	-	0.8	2.8	2.4
7.	Cn Hm formation - %	21.6	6.6	10.0	8.8
8.	Cn Hm formation per 100 vols. of Iso-Pentane.	21.6	9.4	16.5	17.6
9.	CO formation - %	-	8.8	7.3	11.1
10.	CO formation per 100 vols. of Iso-Pentane	-	11.6	12.0	22.2
11.	C_nH_{2n+2} formation - %	84	75	64.5	54.0
12.	C_nH_{2n+2} formation per 100 vols. of Iso-pentane.	84	105	106	108
13.	Contraction / Absorption	1.4	1.65	1.65	1.7
14.	Value of n in C_nH_{2n+2}	1.7	1.4	1.3	1.2

Iso-pentane and Nitric Oxide.

TEMPERATURE 525°C.

	Experiment No.	5.	6.	7.	8.
1.	Percentage Composition of the Reactants.				
	a) Iso-Pentane - %	45.7	43.8	30.2	23.5
	b) NO - %	51.0	52.8	65.6	71.9
	c) N_2 - %	3.3	3.4	4.2	4.6
2.	Time of contact - minutes	180	180	180	180
3.	NO used - %	42.5	43.6	44.7	42.6
4.	Ratio of NO used to total present.	0.83	0.83	0.73	0.58
5.	CO_2 formed - %	2.4	1.6	1.8	1.7
6.	CO_2 formation per 100 vols. of Iso-Pentane	5.2	3.7	5.8	7.0
7.	C_nH_m formation - %	11.6	9.9	5.9	4.0
8.	C_nH_m formation per 100 vols. of Iso-Pentane.	25.5	22.9	16.4	17.0
9.	CO formation - %	9.9	9.2	13.2	13.0
10.	CO formation per 100 vols. of Iso-Pentane.	21.6	21.8	44	55.3
11.	C_nH_{2n+2} formation - %	49	49	38	34.4
12.	C_nH_{2n+2} formation per 100 vols. of Iso-Pentane	109	112	126	146
13.	Contraction / Absorption	1.78	1.74	1.86	1.9
14.	Value of n in C_nH_{2n+2}	1.2	1.2	1.1	1.1

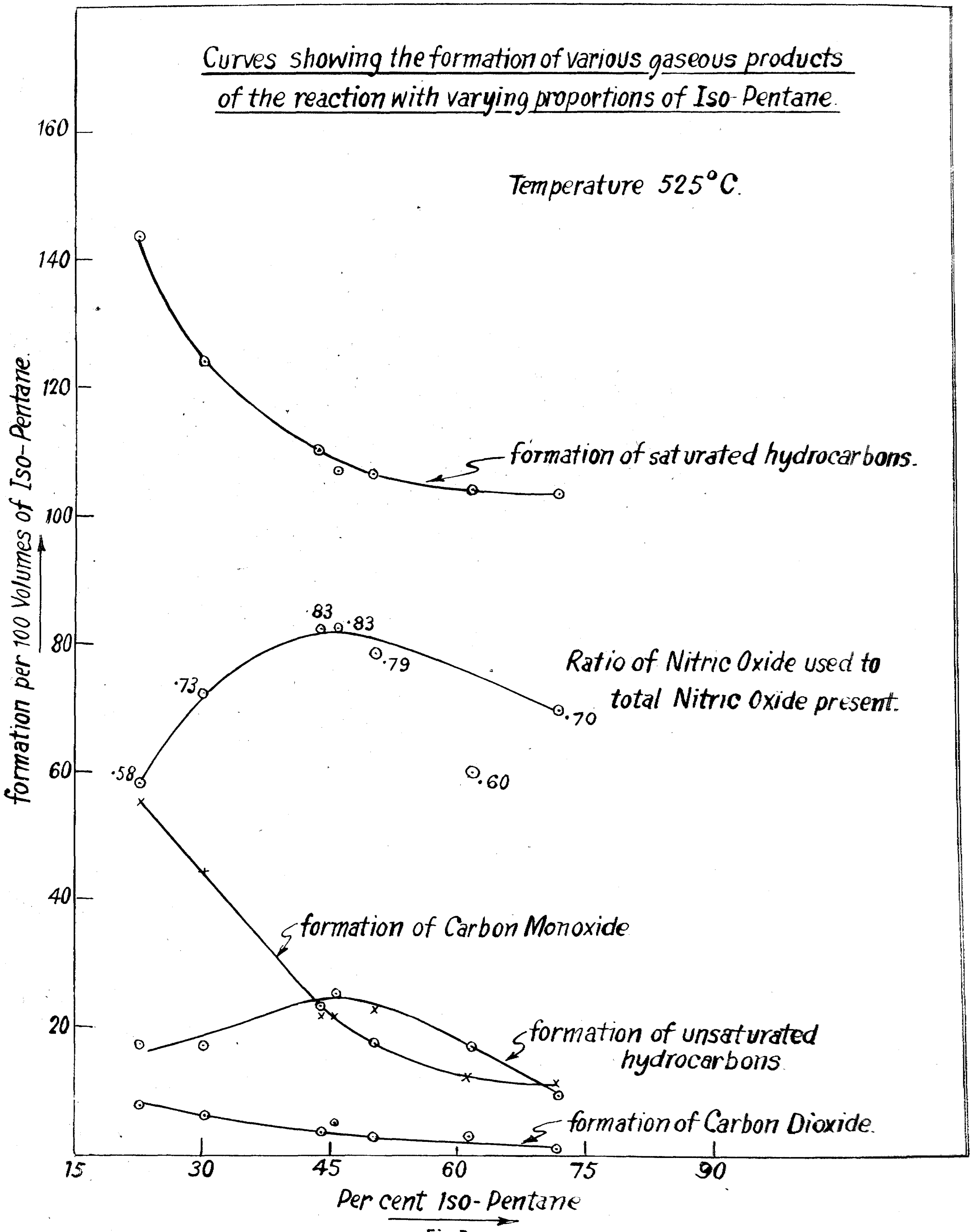

Curves showing the formation of various gaseous products of the reaction with varying proportions of Iso-Pentane.
Temperature 525°C.
formation of saturated hydrocarbons.
Ratio of Nitric Oxide used to total Nitric Oxide present.
·83
·83
·79
·73
·70
·58
·60
formation of Carbon Monoxide
formation of unsaturated hydrocarbons
formation of Carbon Dioxide.
formation per 100 Volumes of Iso-Pentane.
160
140
120
100
80
60
40
20
15
30
45
60
75
90
Per cent Iso-Pentane

Fig. 3.

iv, INFLUENCE OF TEMPERATURE.

To study the influence of temperature, sets of experiments with varying proportions of iso-pentane and nitric oxide, similar to that of 525°C, were made at the temperature of 550°C, 500°C and 450°C. The results of these are tabulated on pages 47-52. From the table of the results of analysis of gaseous products it is seen that at 450°C, the value of contraction by absorption i.e. c/A varies from 0.8 to 0.93 and consequently the value of 'n' varies from 3.9 to 3.4; for a reaction time of 180 minutes. In one case (Expt. No.78, temperature 450°C) when the reaction time was increased to 1170 minutes, the value of n was found to be 1.75. In this case there was increased formation of carbon dioxide, carbon monoxide, saturated hydrocarbons and a decrease in the formation of unsaturated hydrocarbons.

The ratio of nitric oxide used to total present was also higher.

The value of 'n' at 500°C varied from 1.7 to 1.25; at 525°C, it varied from 1.4 to 1.1 and at 550°C from 1.2 to 1.0. This shows as might be expected that the average number of carbon atoms in the saturated hydrocarbons in the gaseous products decreased on increasing the temperature or increasing the reaction time.

Curves for these temperatures, similar to one drawn for the 525°C were plotted and are given on pages 53-55. These curves show the variations in the formation of gaseous products for varying proportions of iso-pentane and nitric oxide. The general shape of these curves for the various sets of experiments is same except those for 450°C. In particular the curve showing the formation of unsaturated hydrocarbons at that temperature shows a steady increase with increase in the proportion of iso-pentane. In all other cases the formation of unsaturated hydrocarbon increases, reaches a maximum and then falls with decrease in the proportion of iso-pentane in the reaction mixture.

The ratio of nitric oxide used to total nitric oxide present increases, reaches a maximum, and then falls with decrease in proportion of iso-pentane.

The formation of carbon dioxide, carbon monoxide and saturated hydrocarbons increases with decrease in the proportion of iso-pentane though the increase in formation of carbon monoxide and saturated hydrocarbons is very much more as compared to increase in the formation of carbon dioxide.

Curves showing the variations in formation of carbon dioxide, carbon monoxide, unsaturated hydrocarbons and saturated hydrocarbons with increase in temperature were drawn (pages 56- 59) for 21% iso-pentane, 30% iso-pentane, 45% iso-pentane, 60% iso-pentane and 70% iso-pentane in the reaction mixture.

FORMATION OF CARBON DIOXIDE.

In general there is an increase in the formation of carbon dioxide though it is of a small order, with increase in temperature. In case of 21% iso-pentane and 30% iso-pentane, it is more noticeable (page 56).

FORMATION OF THE UNSATURATED HYDROCARBONS.

In the case of unsaturated hydrocarbons (page 57), there is a steady decrease in their formation for the reactants having iso-pentane concentration of 60% and 70% but for the reactants having iso-pentane proportion of 21%, 30% and 45%, there is at first an increase in the formation upto a temperature of 475° to 500°C, further increase in temperature, results in decreased yields.

FORMATION OF CARBON MONOXIDE.

The formation of carbon monoxide increases rapidly with increase in temperature though in this case, similar to the formation of carbon dioxide, the increase is much less rapid in cases of reactants having 60% iso-pentane and 70% iso-pentane as compared with reactants having less (page 58).

FORMATION OF SATURATED HYDROCARBONS.

With the increase in temperature there is an increase in formation of these for all the varying proportions of iso-pentane (page 59). The variations in the average value of 'n' of these hydrocarbons have already been discussed.

PRODUCTS OF THE REACTION OTHER THAN GASES.

Besides the gaseous products in all these experiments, as already mentioned a liquid along with some solid which appeared to be mostly carbon was seen in the capillary tube when the bulb was evacuated after completion of an experiment. To get an idea of its compositions, as the amount was far too small for analysis, the weight balance of carbon, hydrogen nitrogen and oxygen was made. The amounts of carbon, hydrogen, nitrogen and oxygen introduced were calculated from the amounts of iso-pentane and nitric oxide taken for the reaction. The amounts of these i.e. carbon, hydrogen, nitrogen and oxygen in the gaseous products were calculated from the value of nitric oxide left unreacted, formation of carbon dioxide, carbon monoxide, unsaturated and saturated hydrocarbons. The unsaturated hydrocarbons were assumed to be C_3H_6 and for the saturated hydrocarbon, the value of 'n' as determined by the gas analysis was used. The difference between these two calculations gave the amounts of carbon, hydrogen, nitrogen and oxygen in the residue.

Value of carbon, hydrogen, oxygen and nitrogen in the residue for an experiment from each set of readings are given below:

TABLE 111.

	1	2	3	4
Temperature:	550°C	525°C	500°C	450°C
Percentage composition of reactants:				
(Iso-pentane - percent.	63.3	61.0	60.0	60.0
(Nitric oxide - percent.	34.5	37.6	34.6	37.6
Residue:				
Carbon - percent.	0.1107 gm	0.1010 gm	0.0911 gm	0.0338 gm
Hydrogen - percent.	0.0186	0.0172	0.0156	0.0069
Oxygen - percent.	0.0177	0.0154	0.0141	0.0040
Nitrogen - percent.	0.0182	0.0180	0.0170	0.0060

The empirical formula for carbon and hydrogen calculated from the above given weights of carbon and hydrogen comes out to be as follows:

No.1	CH_2
No.2	CH_2
No.3	CH_2
No.4	$C_2 H_5$

A reaction bulb in which a number of experiments had been made was cut open to examine the residue more fully. The residue was scraped from the bulb, the amount so collected was extremely small even for a proper micro-analysis for carbon and hydrogen to be made. The ether extract of this residue showed fluorescence.

From all the results of the analysis of the gaseous products of the reaction as well as carbon, hydrogen, nitrogen and oxygen content of the residue as calculated, it is seen that there is a definite difference in set of readings at 450°C and sets of readings at other temperatures. The temperature of 500°C or above is more favourable for the reaction of iso-pentane and nitric oxide.

Iso-Pentane and Nitric Oxide.

TABLE 1V.

TEMPERATURE 550°C.

	Experiment No.	1.	2.	3.	4.
1.	Percentage Composition of the Reactants.				
	a) Iso-Pentane - %	83.6	81.3	67.8	63.3
	b) Nitric Oxide - %	15.4	17.5	30.2	34.5
	c) N_2 - %	1.0	1.2	2.0	2.2
2.	Time of Contact - mins.	180	180	180	180
3.	NO used - %	11.1	11.8	24.7	28.1
4.	Ratio of NO used to total present.	0.72	0.69	0.82	0.84
5.	CO_2 formed - %	0.8	1.0	2.8	1.1
6.	CO_2 formation per 100 vols. of Iso-Pentane.	1.0	1.2	4.4	1.6
7.	Cn Hm formation - %	9.4	9.4	7.7	8.6
8.	Cn Hm formation per 100 vols. of Iso-Pentane.	11.2	11.6	11.4	13.6
9.	CO formation - %	6.0	4.7	7.7	7.5
10.	CO formation per 100 vols. of Iso-Pentane	7.0	5.6	11.4	11.8
11.	Cn H_{2n+2} formation - %	76.0	77	56	70.4
12.	Cn H_{2n+2} formation per 100 vols. of Iso-Pentane.	90	93	83	111
13.	Contraction / Absorption	1.87	1.8	2	1.94
14.	Value of n in Cn $H_{2n} + 2$	1.1	1.2	1	1

Iso-Pentane and Nitric Oxide.

TEMPERATURE 550°C.

	Experiment No.	5.	6.	7.	8.
1.	Percentage Composition of Reactants.				
	a) Iso-Pentane - %	47.8	41.0	30.8	17.5
	b) Nitric Oxide - %	49.0	55	65.0	77.5
	c) N_2 - %	3.2	3.5	4.2	5.0
2.	Time of Contact - minutes.	180	180	180	180
3.	NO used - %	40.9	44.5	40.5	46.5
4.	Ratio of NO used to total NO present.	0.83	0.8	0.64	0.6
5.	CO_2 formed - %	1.6	2.9	3.1	2.1
6.	CO_2 formation per 100 vols. of Iso-Pentane.	3.4	7.3	10.0	11.7
7.	Cn Hm formation - %	6.0	4.4	2.8	1.1
8.	Cn Hm formation per 100 vols. of Iso-Pentane.	12.4	10.8	9.1	6.3
9.	CO formation - %	11.5	12.5	13.2	12.2
10.	CO formation per 100 vols. of Iso-Pentane.	23.5	32.0	42.8	69.0
11.	Cn H_{2n+2} formation - %	59.0	50.5	43.1	15.6
12.	Cn H_{2n+2} formation per 100 vols. of Iso-Pentane.	120	124	136	145
13.	Contraction / Absorption.	2	1.8	2.0	2.0
14.	Value of n in Cn $H_{2n + 2}$	1.0	1.1	1.0	1.0

Iso-Pentane and Nitric Oxide.

TABLE V.

TEMPERATURE 500°C.

	Experiment No.	1.	2.	3.	4.
1.	Percentage Composition of Reactants.				
	a) Iso-Pentane - %	82.0	64.1	62.9	60
	b) Nitric Oxide - %	15.5	31.2	32.1	34.6
	c) N_2 - %	2.5	4.7	5.0	5.4
2.	Time of Contact - minutes.	180	180	180	180
3.	NO used - %	11.0	24.4	27.7	28.1
4.	Ratio of NO used to total present	0.71	0.78	0.8	0.81
5.	CO_2 formed - %	1.5	1.8	0.5	1.8
6.	Formation of CO_2 per 100 vols. of Iso-Pentane.	1.8	2.8	0.8	3
7.	Formation of Cn Hm - %	20.4	16.4	14.7	12.6
8.	Cn Hm formation per 100 vols. of Iso-Pentane	25.0	25.6	23.4	21.0
9.	CO formation - %	2.5	4.5	5	4.95
10.	CO formation per 100 vols. of Iso-Pentane	3.0	7.0	8	8.3
11.	C_nH_{2n+2} formation - %	61.6	60.9	61.6	61.5
12.	C_nH_{2n+2} formation per 100 vols. of Iso-Pentane	85.0	95	98	101.2
13.	Contraction / Absorption	1.4	1.6	1.6	1.67
14.	Value of n in C_nH_{2n+2}	1.7	1.4	1.4	1.4

Iso-Pentane and Nitric Oxide.

TEMPERATURE 500°C.

	Experiment No.	5.	6.	7.	8.
1.	Percentage Composition of Reactants.				
	a) Iso-Pentane - %	54.9	41.8	30.0	18.6
	b) NO - %	39.0	50.3	60.6	70.4
	c) N_2 - %	6.1	7.9	9.4	11.0
2.	Time of Contact - minutes	180	180	180	180
3.	NO used - %	31.2	38.1	36.2	37.6
4.	Ratio of NO used to total present.	0.8	0.75	0.6	0.53
5.	CO_2 formation - %	2.5	1.5	1.5	2.3
6.	CO_2 formation per 100 vols. of Iso-Pentane.	4.6	3.5	5.0	12.3
7.	$C_n H_m$ formation - %	15.6	13.2	8.1	4.8
8.	$C_n H_m$ formation per 100 vols. of Iso-Pentane.	28.4	30.5	27	25
9.	CO formation - %	6.7	6.0	9.6	10.5
10.	CO formation per 100 vols. of Iso-Pentane.	12.2	14.5	32	56
11.	$C_n H_{2n+2}$ formation - %	52.6	47	33.6	21
12.	$C_n H_{2n+2}$ formation per 100 vols. of Iso-Pentane.	98	112	112	125
13.	Contraction / Absorption.	1.8	1.6	1.7	1.7
14.	Value of n in $C_n H_{2n+2}$	1.4	1.4	1.3	1.25

Iso-Pentane and Nitric Oxide.

TABLE VI.

TEMPERATURE 450°C.

	Experiment No.	1.	2.	3.	4.
1.	Percentage Composition of Reactants.				
	a) Iso-Pentane - %	85.5	80.0	70.0	47.1
	b) NO - %	13.8	18.8	28.2	49.7
	c) N_2 - %	0.9	1.2	1.8	3.2
2.	Time of Contact - minutes	180	180	180	180
3.	NO used - %	20.0	4.3	11.9	16.1
4.	Ratio of NO used to total present	0.14	0.22	0.42	0.33
5.	CO_2 formation - %	1.1	1.4	1.5	1.6
6.	CO_2 per 100 vols. of Iso-Pentane	1.3	1.8	2.1	3.3
7.	Cn Hm formation - %	28.6	32	23	9.6
8.	Cn Hm formation per 100 of Iso-Pentane	34.0	40	32.8	20.5
9.	CO formation - %	1.2	2.8	2.5	2.4
10.	CO formation per 100 vols of Iso-Pentane	1.6	3.5	3.5	5.1
11.	$C_n H_{2n+2}$ formation - %	50.8	47	56	40
12.	$C_n H_{2n+2}$ formation per 100 vols. of Iso-Pentane	59.8	60	80	85
13.	Contraction / Absorption	0.93	0.93	0.9	0.93
14.	Value of n in $C_n H_{2n+2}$	3.4	3.4	3.7	3.4

Iso-Pentane and Nitric Oxide.

TEMPERATURE 450°C.

	Experiment No.	5.	6.	7.	8.
1.	Percentage Composition of Reactants.				
	a) Iso-Pentane - %	60.0	61.3	32.1	20.0
	b) NO - %	37.6	36.4	63.8	75.2
	c) N_2 - %	2.3	2.3	4.1	4.8
2.	Time of Contact - minutes.	180	1170	180	180
3.	NO used - %	9.6	30.7	15.8	9.9
4.	Ratio of NO used to total NO present	0.23	0.84	0.25	0.13
5.	CO_2 formation - %	1.3	3.4	1.1	1
6.	CO_2 formation per 100 vols. of Iso-Pentane.	2.2	5.5	3.4	5
7.	$C_n H_m$ formation - %	19.3	12.4	8.3	2.5
8.	$C_n H_m$ formation per 100 vols. of Iso-Pentane.	32.8	20.4	25.2	12.5
9.	CO formation - %	0.8	5.5	2.2	1.5
10.	CO formation per 100 vols. of Iso-Pentane	1.3	8.1	6.8	7.5
11.	$C_n H_{2n+2}$ formation	46	62.5	34	20.5
12.	$C_n H_{2n+2}$ formation per 100 vols. of Iso-Pentane.	76	102	106	103
13.	Contraction / Absorption.	0.8	1.36	0.91	0.9
14.	Value of n in $C_n H_{2n+2}$	3.9	1.75	3.6	3.8

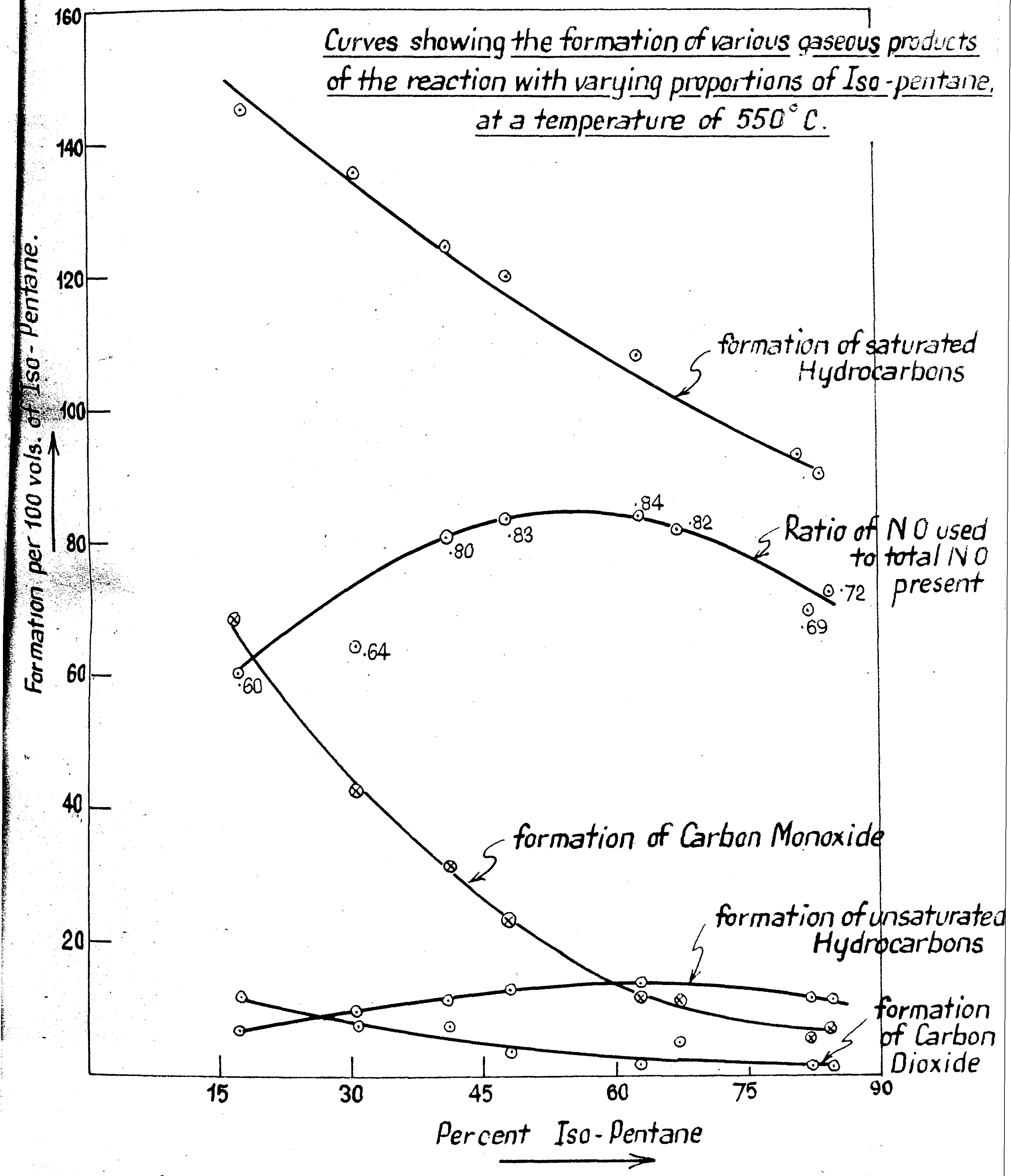

Curves showing the formation of various gaseous products of the reaction with varying proportions of Iso-pentane, at a temperature of 550° C.

Fig. 4.

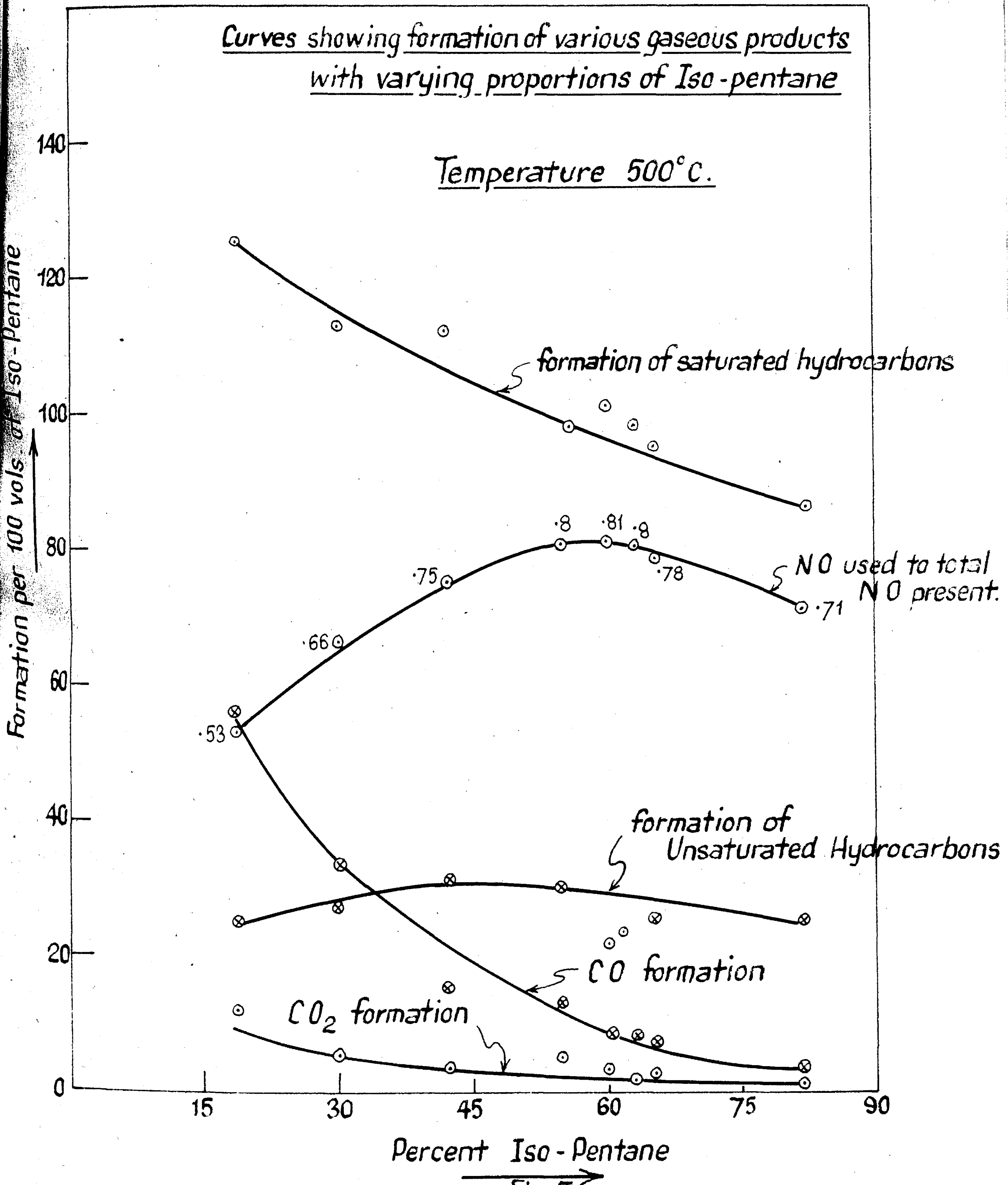
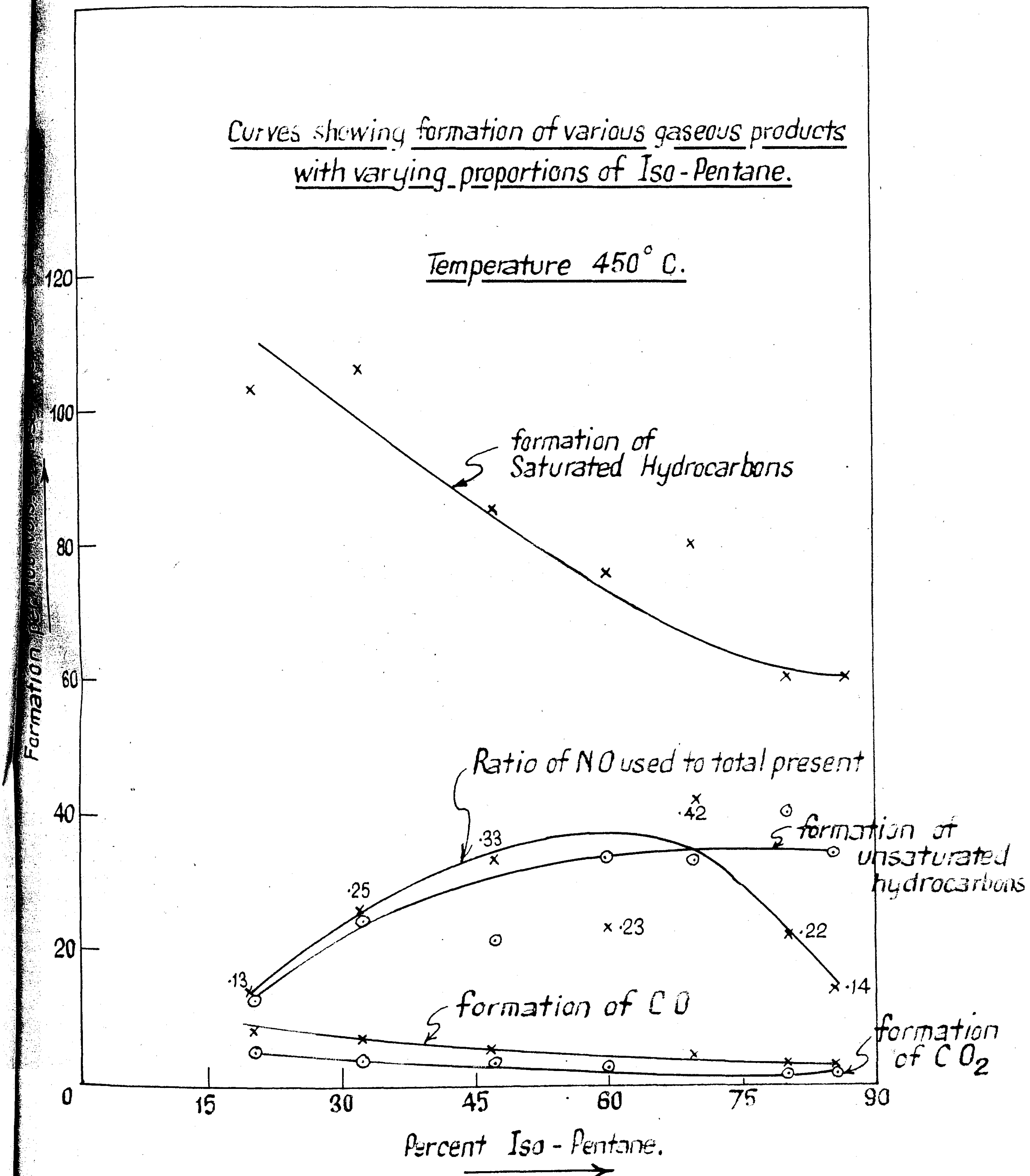

Curves showing formation of various gaseous products with varying proportions of Iso-pentane
Temperature 500°C.
Formation per 100 vols of Iso-Pentane
Percent Iso-Pentane
0
20
40
60
80
100
120
140
15
30
45
60
75
90
formation of saturated hydrocarbons
N O used to total N O present.
·53
·66
·75
·8
·81
·8
·78
·71
formation of Unsaturated Hydrocarbons
C O formation
C O2 formation

Fig. 5.



Curves showing formation of various gaseous products with varying proportions of Iso-Pentane.

Temperature 450° C.

Fig. 6.

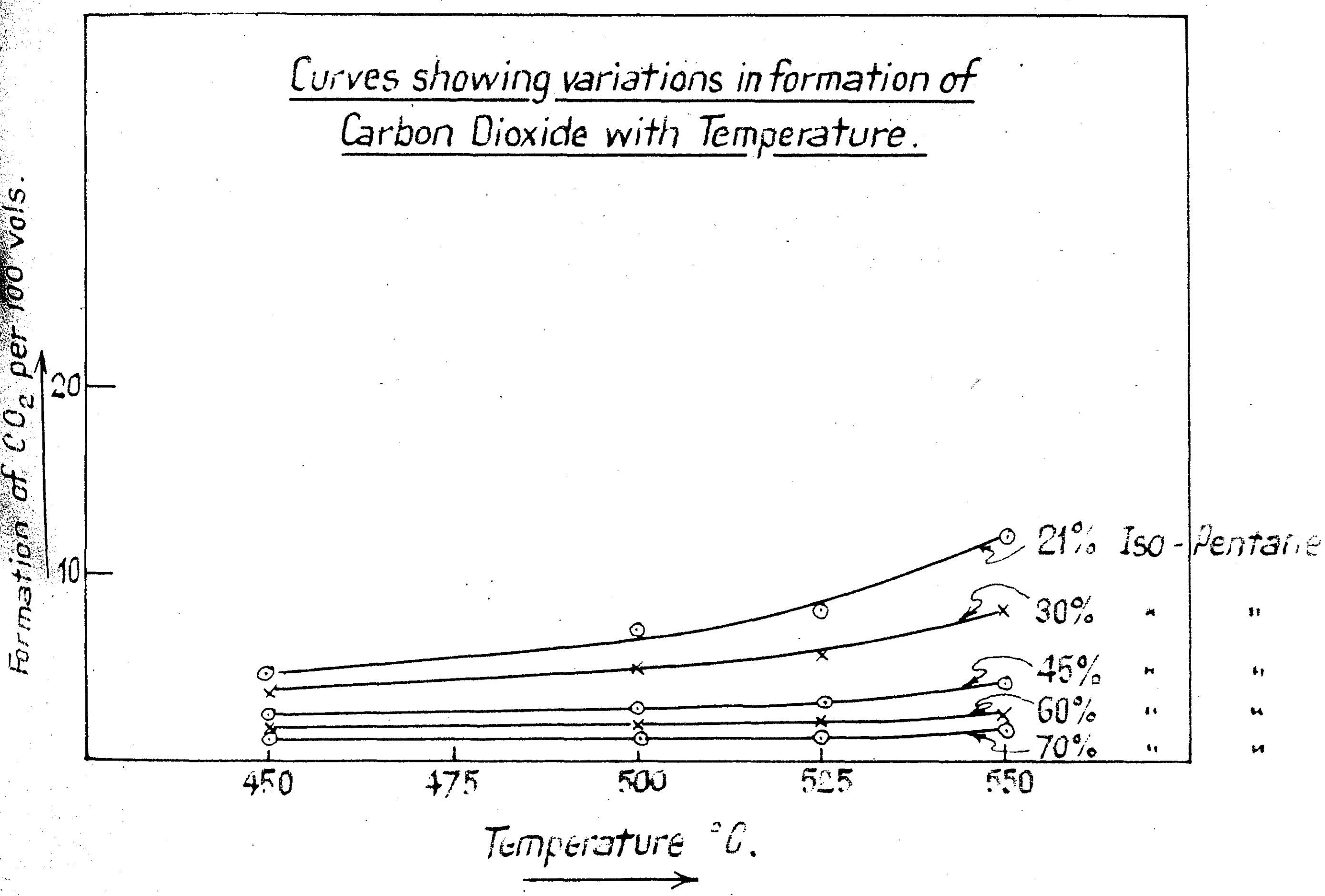
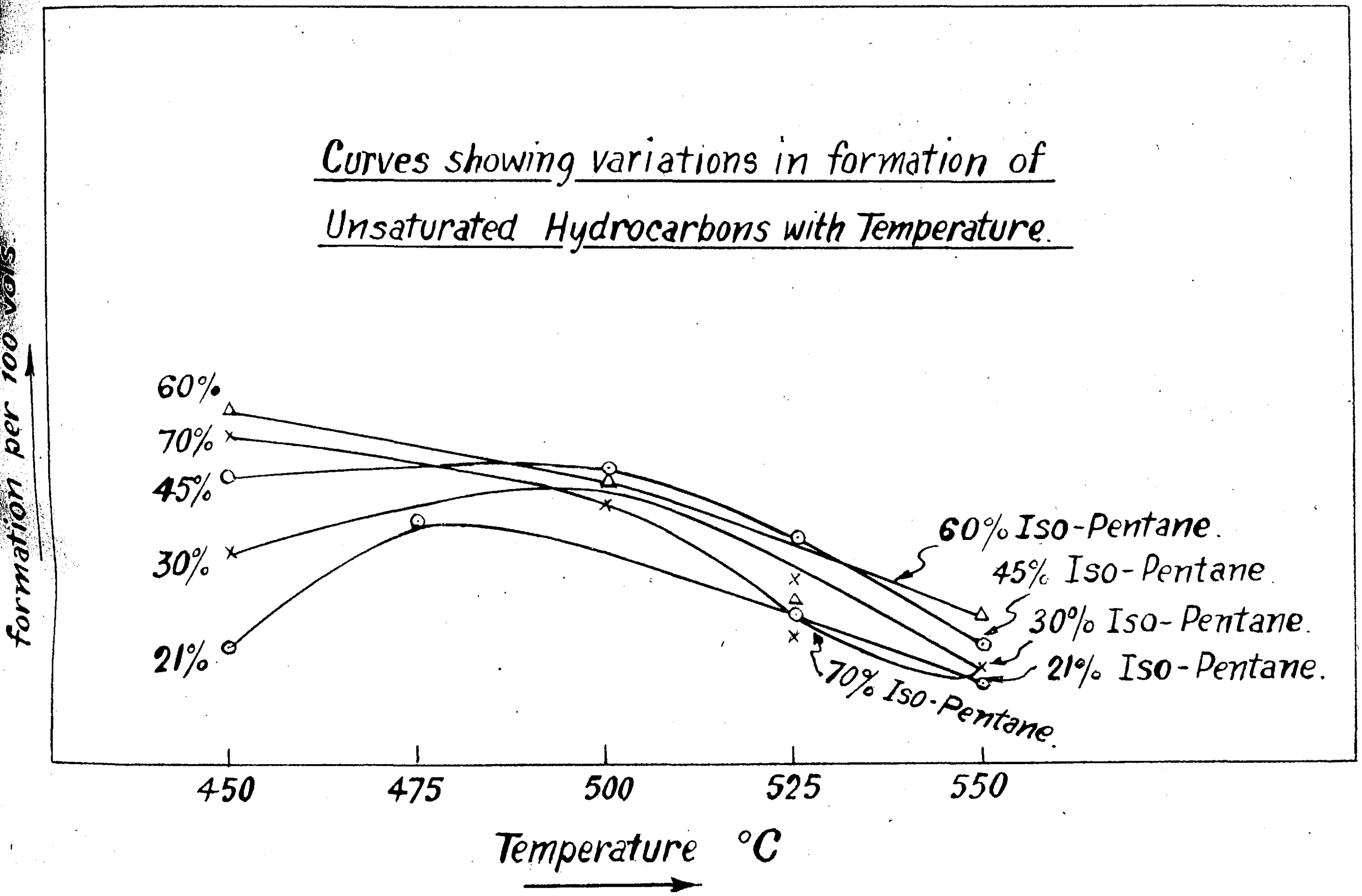

Curves showing variations in formation of Carbon Dioxide with Temperature.
Formation of CO_2 per 100 vols.
20
10
450
475
500
525
550
Temperature °C.
21% Iso-Pentane
30% " "
45% " "
60% " "
70% " "

Fig. 7.



Curves showing variations in formation of Unsaturated Hydrocarbons with Temperature.

Fig. 8.

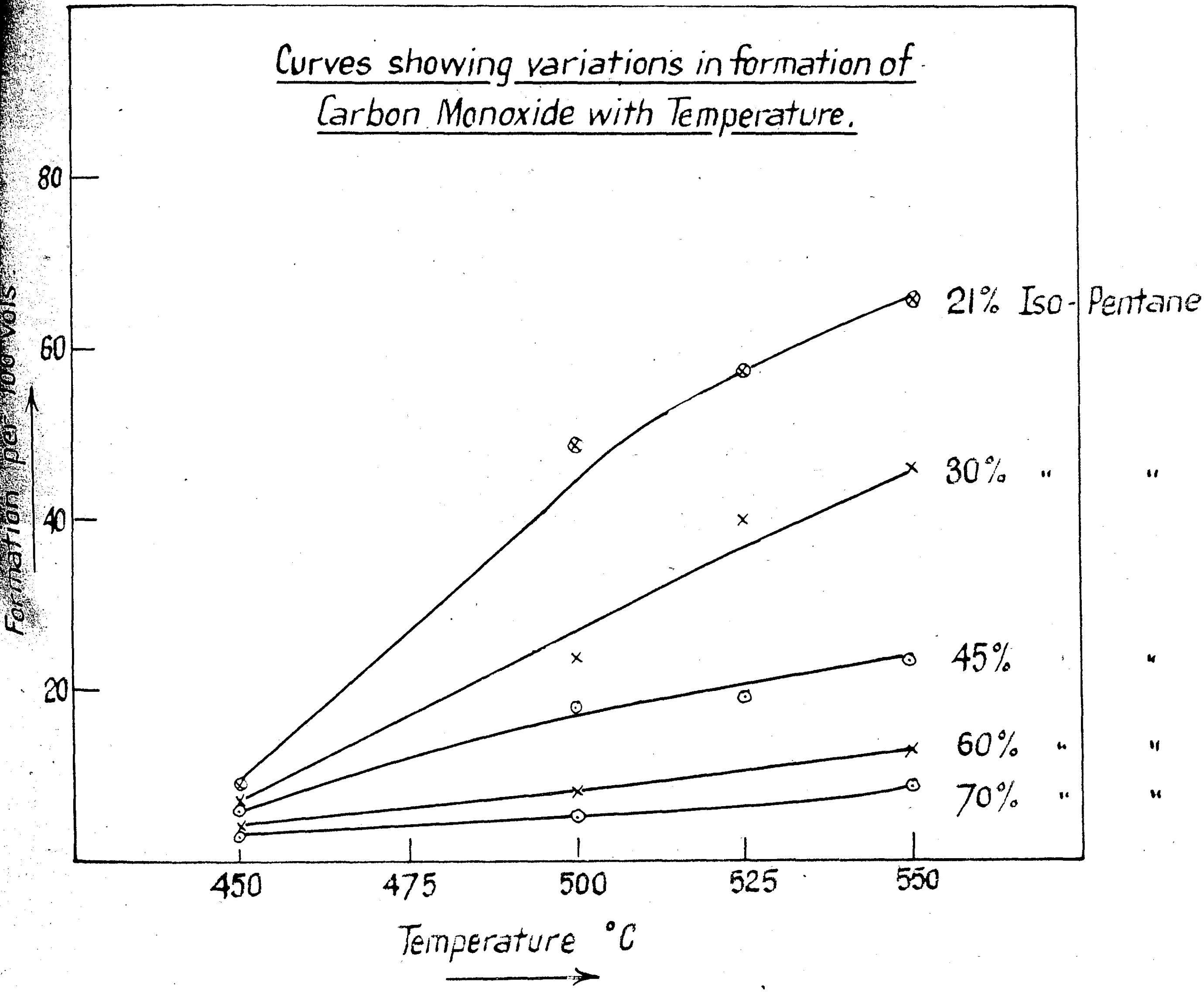

Curves showing variations in formation of Carbon Monoxide with Temperature.
80
60
40
20
Formation per 100 vols.
450
475
500
525
550
Temperature °C
21% Iso-Pentane
30% " "
45% "
60% " "
70% " "

Fig. 9.

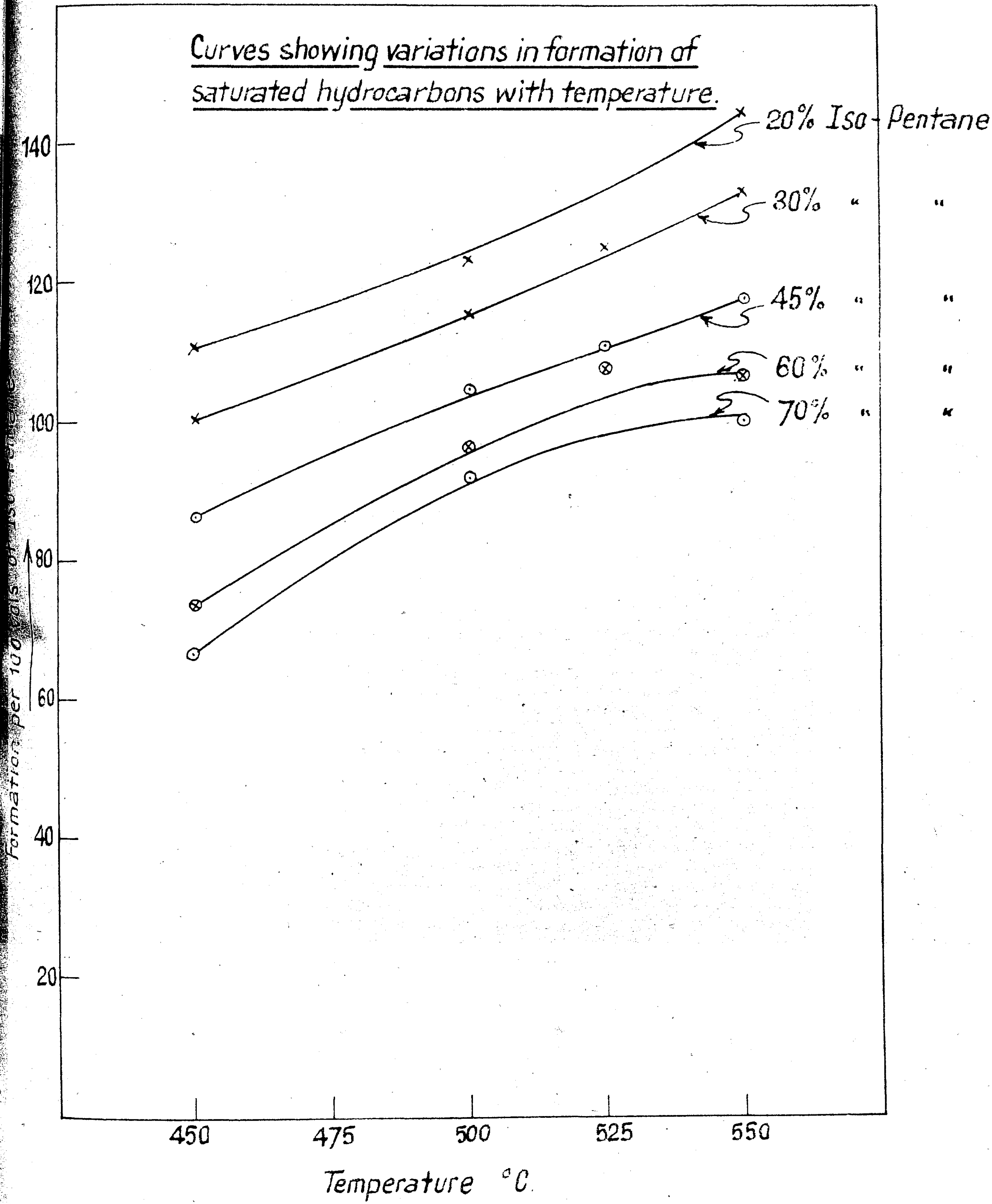

Curves showing variations in formation of saturated hydrocarbons with temperature.
20% Iso-Pentane
30% " "
45% " "
60% " "
70% " "
Formation per 100 cals of Iso-Pentene
140
120
100
80
60
40
20
450
475
500
525
550
Temperature °C

Fig. 10.

V, INFLUENCE OF TIME.

After investigating the effect of varying the proportions of iso-pentane and nitric oxide and the influence of temperature; the influence of increasing the reaction time was examined in detail for the temperature of 500°C. Reaction mixtures having 65.6% iso-pentane and 29.8% nitric oxide were used in all the experiments. The reaction times tried were 20 minutes, 35 minutes, 60 minutes, 120 minutes, 180 minutes, 240 minutes, 300 minutes, 360 minutes and 420 minutes. The results of analysis of the gaseous products of the reaction are tabulated on pages 64-66

It is seen from the tables, that in case of reaction time of 20 minutes (Expt. No.9, temp. 500°C), the amount of nitric oxide left in the gaseous products of the reaction is more than the initial nitric oxide present in the reactants and also the value of carbon dioxide formed which normally increases very gradually (as is mentioned below), is found to be higher than that for a reaction time of 35 minutes and even of 60 minutes. This indicates the possibility of some liquid products condensing. The iso-pentane molecule seems to be broken up to a stage which on cooling to the room temperature i.e. while taking out the sample and analysing, results in partial condensation, it is possible that an appreciable proportion of iso-pentane is left as such.

The curves showing the formation of carbon dioxide, carbon monoxide, unsaturated and saturated hydrocarbons per 100 volumes of iso-pentane, with the variations in reaction time were drawn. Also curves showing the ratio of nitric oxide used to total present and the variations in value of 'n' were made (page67). From these it is seen that the formation of carbon dioxide and carbon monoxide increased steadily with time though the order of increase of carbon monoxide formation is more than that of carbon dioxide. The increase in carbon dioxide formation is very gradual.

The formation of unsaturated hydrocarbons first increases up to a reaction time of about 120 minutes and then decreases with further increase in the time of reaction.

The formation of saturated hydrocarbons increases steadily up to a reaction time of 240 minutes and then the slope of the curve becomes steep, which shows a more rapid increase. The value of 'n' varies from 3.7 in case of the reaction time of 35 minutes to 1.3 in the case of the reaction time of 420 minutes.

In the curve showing the ratio of nitric oxide used to total present, there is a steep rise in the beginning and after that the rise becomes steady but less pronounced. About 80% of nitric oxide present is used when the reaction time is 360 minutes, and about 70% for the reaction time of 180 minutes, which has been used for most of the earlier experiments.

Products of reaction other than gases.

The values for carbon, hydrogen, nitrogen and oxygen left in the residue were calculated as before. These values are given on page 63. It is seen from these that the amount of carbon, hydrogen, nitrogen and oxygen in the residue keeps on increasing with the increase in reaction time. The empirical formula from carbon and hydrogen comes out to be CH_2 except in the case of reaction time of 60 minutes in which case it is C_4H_9.

TABLE V11.

TEMPERATURE 500°C.

Iso-Pentane	65.5
Nitric Oxide	29.8
N_2	4.7

Time of Contact - minutes.	60	120	180	240	300	360	420
Residue:							
Carbon - percent.	.0533 gm	.0676 gm	.0885 gm	.0932 gm	.0973 gm	.1130 gm	.1170 gm
Hydrogen- percent.	.0102	.0118	.0159	.0168	.0172	.0176	.0187
Oxygen - percent.	.0042	.0068	.0082	.0080	.0084	.0878	.0091
Nitrogen- percent.	.0068	.0105	.0130	.0135	.0140	.0150	.0156
Empirical formula for C and H.	$C_4 H_9$	CH_2	CH_2	CH_2	CH_2	CH_2	CH_2

Iso-pentane and nitric oxide.

TABLE V111.

TEMPERATURE 500°C.

1.	Percentage composition of reactants.	1	2	3
	Iso-pentane - %	65.5	65.5	65.5
	NO - %	29.8	29.8	29.8
	N_2 - %	4.7	4.7	4.7
2.	Time of contact - minutes.	60	120	180
3.	NO used - %	10.9	16.8	20.9
4.	Ratio of NO used to total present.	0.37	0.56	0.7
5.	CO_2 formation - %	.97	1.8	1.87
6.	CO_2 formation per 100 vols. of iso-pentane.	1.5	2.7	2.85
7.	$C_n H_m$ formation - %	20.4	22.9	18.2
8.	$C_n H_m$ formation per 100 vols. of iso-pentane.	31.2	33.4	27.8
9.	CO formation - %	2.9	3.6	5.6
10.	CO formation per 100 vols. of iso-pentane.	4.4	5.6	8.5
11.	$C_n H_{2n+2}$ formation - %	53.9	54.5	56.5
12.	$C_n H_{2n+2}$ formation per 100 vols. of iso-pentane.	82.0	83.5	86.8
13.	Contraction / Absorption.	1.0	1.1	1.3
14.	Value of n in $C_n H_{2n+2}$	3.0	2.5	1.8

Iso-pentane and nitric oxide.

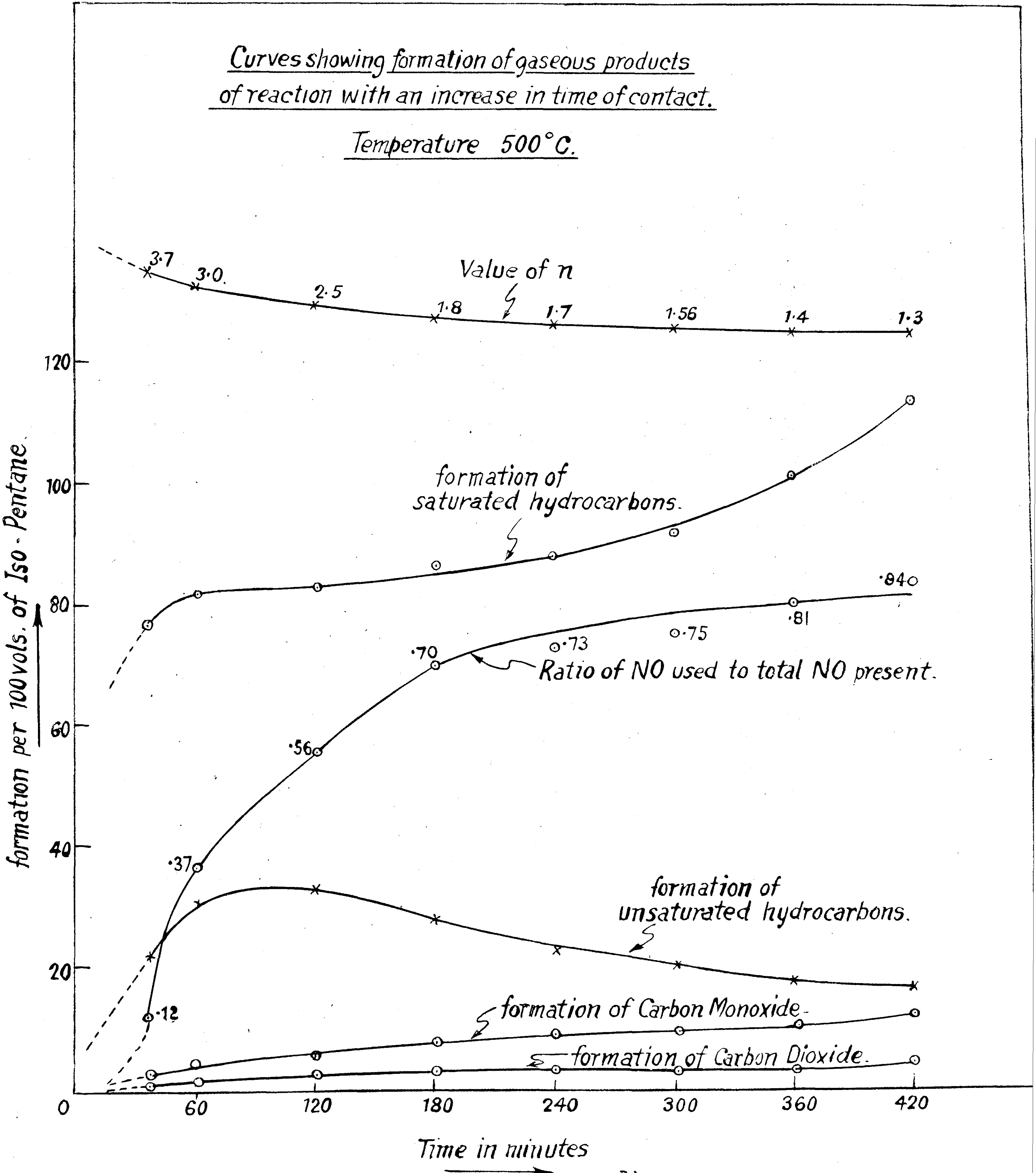
TEMPERATURE 500°C.

		4	5	6
1.	Percentage composition of the reactants.			
	Iso-pentane - %	65.5	65.5	65.5
	NO - %	29.8	29.8	29.8
	N_2 - %	4.7	4.7	4.7
2.	Time of contact - minutes	240	300	360
3.	NO used - %	21.7	22.5	24.0
4.	Ratio of NO used to total present.	0.73	0.75	0.81
5.	CO_2 formation - %	2.24	2.0	2.34
6.	CO_2 formation per 100 vols. of iso-pentane.	3.4	3.0	3.5
7.	$C_n H_m$ formation - %	14.7	14.1	11.7
8.	$C_n H_m$ formation per 100 vols. of iso-pentane.	22.6	21.6	17.9
9.	CO formation - %	6.2	6.8	7.0
10.	CO formation per 100 vols. of iso-pentane.	9.5	10.4	10.7
11.	$C_n H_{2n+2}$ formation - %	59.0	60.5	66.5
12.	$C_n H_{2n+2}$ formation per 100 vols. of iso-pentane.	88	92	102
13.	Contraction / Absorption.	1.37	1.46	1.51
14.	Value of n in $C_n H_{2n+2}$	1.7	1.56	1.4

Iso-pentane and nitric oxide.

TEMPERATURE 500°C.

1.	Percentage composition of the reactants.	7	8	9
	Iso-pentane - %	65.5	65.5	65.5
	NO - %	29.8	29.8	29.8
	N_2 - %	4.7	4.7	4.7
2.	Time of contact - minutes	420	35	20
3.	NO used - %	25.1	3.6	-
4.	Ratio of NO used to total present.	0.84	0.12	32
5.	CO_2 formation - %	3.0	0.8	2.8
6.	CO_2 formation per 100 vols. of iso-pentane.	4.5	1.2	4.2
7.	$C_n H_m$ formation - %	11.2	15.0	10.7
8.	$C_n H_m$ formation per 100 vols. of iso-pentane.	16.8	22.2	16.3
9.	CO formation - %	7.5	2.1	1.7
10.	CO formation per 100 vols. of iso-pentane.	11.4	3.2	2.6
11.	$C_n H_{2n+2}$ formation - %	74	51	62.0
12.	$C_n H_{2n+2}$ formation per 100 vols. of iso-pentane.	114	77.5	94.5
13.	Contraction / Absorption.	1.6	0.91	0.9
14.	Value of n in $C_n H_{2n+2}$	1.3	3.7	3.7


Curves showing formation of gaseous products of reaction with an increase in time of contact.

Temperature 500°C.

Fig. 11.

EXPERIMENTAL

B. FLOW EXPERIMENTS.

i, APPARATUS AND PROCEDURE.

The experimental work on the reaction of iso-pentane and nitric oxide under static conditions showed that an appreciable reaction took place at 500°C or above giving carbon dioxide, carbon monoxide, unsaturated hydrocarbons, saturated hydrocarbons and some liquid products along with carbon. It was decided to investigate this reaction more fully by carrying out experiments under streaming conditions. For this purpose, the apparatus as shown in Fig.12 (page 73) was set up. It consisted of an aspirator A1 for the supply of nitric oxide, aspirator A2 was used only when charging A1 with nitric oxide. A1 was connected through a flow-meter F1 to the iso-pentane flask I, which in turn was connected through the three-way stop-cock S to a silica tube (length 50 cms., diameter 0.2 cm.) maintained in an electric furnace, the temperature of which was recorded by a Chromel-Alumel thermocouple. The exit from silica tube was connected to two spiral condensers. The gases were collected over water in the aspirator A5 having Gray's over-flow constant head arrangement[25].

Aspirator A3 contained nitrogen and was connected to three-way stop-cock s.

Nitric oxide was allowed to pass under a constant pressure through the flow-meter F1 to the flask I maintained in a water-bath at a known temperature. Nitric oxide picked up a definite amount of vapour depending on the temperature of the bath. The total amount of is-pentane converted to gas could be calculated from the vapour pressure of iso-pentane at that temperature and from a knowledge of the amount of nitric oxide passed. A check on this calculation was provided by knowing the exact volume of iso-pentane vapourised. This was determined by means of the burette attached to the flask. The flask was filled to a definite mark with iso-pentane just before the experimental initial observations were made, and after the experiment, the level was made up to the same mark again by adding iso-pentane from the burette. The amount thus added gave the quantity of iso-pentane vapourised.

The mixed stream of nitric oxide and

and iso-pentane gas from the flask I passed through the stop-cock S and the silica-tube to the condensing system. Condenser G1 was kept in ice and G2 in Drikold (solid carbon dioxide), - the addition of the ice and the drikold was made, to the respective containers only after the apparatus had been swept with the reaction mixture.

Before each experiment, the apparatus was freed from oxygen by passing nitrogen through the system for about 15 minutes. The reaction mixture was then swept through the apparatus for 15-30 minutes, after which the apparatus was ready for various initial observations to be made and recorded.

During each experiment, some carbon and a little tarry product was deposited in the silica-tube. These were burned off before using the tube for the next experiment.

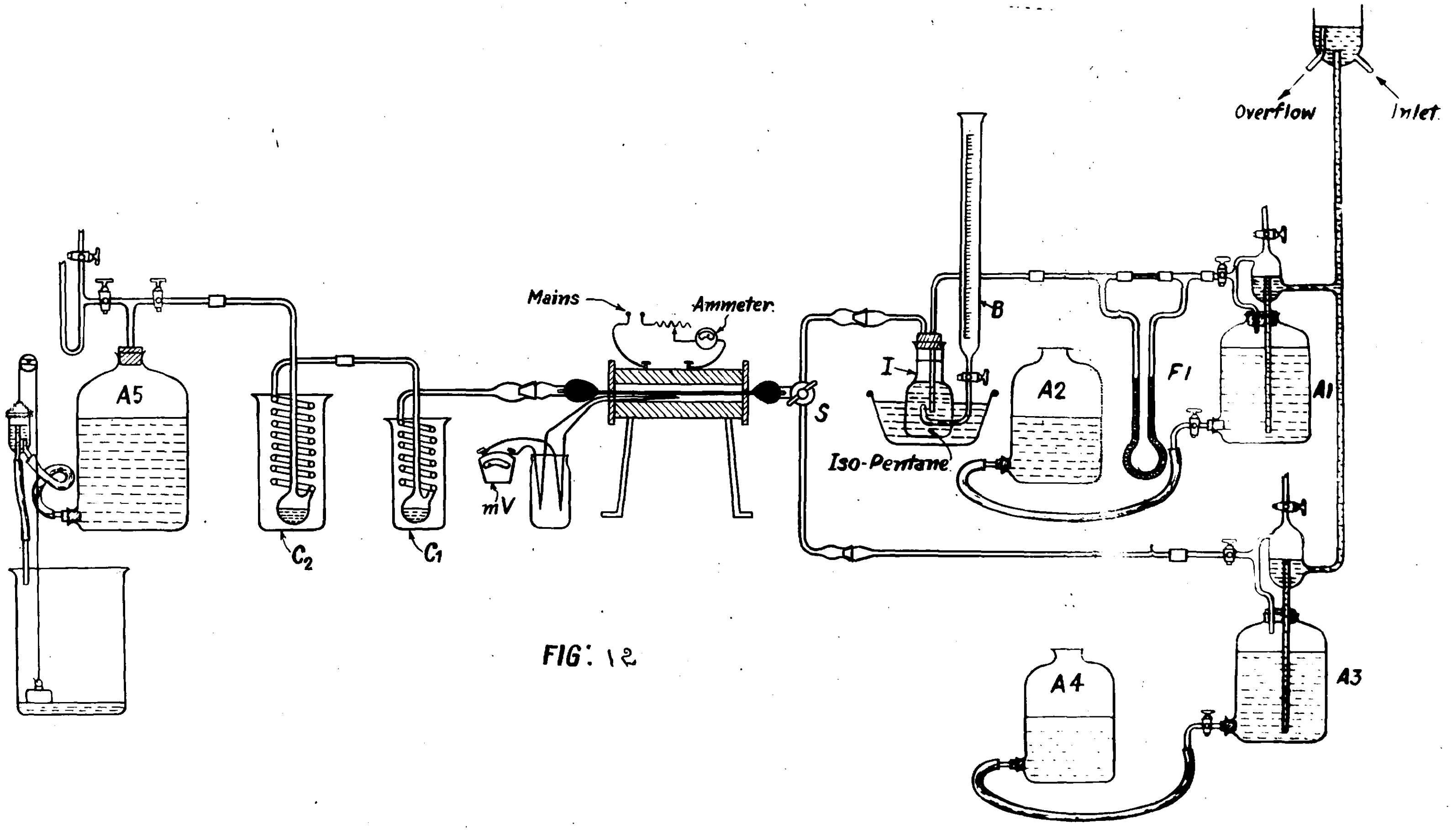

Overflow
Inlet
Mains
Ammeter
B
I
F1
A1
A2
S
Iso-Pentane
A5
C2
C1
mV
A3
A4

FIG: 12

ii, Reactions - General discussion and the influence of varying contact times.

The first series of experiments was carried out at 750°C. The iso-pentane bath was kept at 20°C and the ratio of iso-pentane to nitric oxide used was 3:1. The various observations such as the volume of nitric oxide passed, amount of iso-pentane vapourised, volume of gases collected, etc., were recorded. The contact time was calculated as the period of retention in the silica tube used, assuming that the reactants behaved as perfect gases and that no reaction occurred, that is

$$\text{Contact time (in seconds)} = \frac{\text{Volume of the reaction tube in c.c.}}{\text{Quantity of the reaction mixture in c.c., per second.}}$$

After a few preliminary runs, a number of experiments was made with varying times of contact which could be obtained by varying the rate of flow of nitric oxide through the flow-meter F1. In all these experiments the ratio of iso-pentane to nitric oxide was kept constant. The results of these experiments are given in Table IX .

The reaction products were found to be both liquid and gaseous. The liquid consisted of unreacted iso-pentane, some unsaturated hydrocarbon and a trace of brown coloured liquid which contains nitrogen and was easily soluble in a concentrated solution of caustic potash. In experiment No.4, Table IX , in which the time of contact of iso-pentane and nitric oxide was 0.36 second, the yield of the liquid condensed was 10.0 c.c. (total iso-pentane vapourised, 15.1 c.c.); the yield of unsaturated compounds per c.c. of iso-pentane vapourised was found to be 0.065 c.c; identification of these liquid products will be discussed in detail later.

The gaseous products of the reaction consisted of unreacted nitric oxide, carbon dioxide, unsaturated hydrocarbons, carbon monoxide, hydrogen and saturated hydrocarbons. These were estimated in an improved Bone and Wheeler Gas Analysis Unit. The estimation of NO, CO_2, C_nH_m and CO was done by absorption as mentioned for the Macfarlane Unit. Hydrogen was estimated by combustion with copper oxide at 250° - 300°C and the saturated hydrocarbons by explosion over mercury.

Curves were plotted showing the variations in the formation of the various gases with varying times of contact (page 84). These show that there is an increased production of all of the gases with increase in time of contact. The increase in the yield of carbon dioxide and carbon monoxide is of a small order.

The value of 'n' in C_nH_{2n+2} varied from 2.0 with a contact time of 0.12 second to 1 for the contact time of 0.6 second and 1.0 second.

Comparison of the reaction of iso-pentane and nitric oxide with pyrolysis of iso-pentane.

Before studying the influence of the other variables such as temperature and variations in the percentage composition of the reactants, the pyrolysis of iso-pentane was studied. Iso-pentane was vapourised by passing nitrogen through the iso-pentane flask instead of nitric oxide. The results of a number of experiments made with varying times of contact are given in Table X.

The products of reaction consisted of gases as well as liquids. The liquid consisted of unreacted iso-pentane, unsaturated hydrocarbons and a trace of a dark brown liquid. This dark brown liquid did not contain any nitrogen and was not soluble in caustic potash. It was fairly soluble in organic solvents such as benzene, ether, etc.

In experiment No.2 (Table X), made with a contact time of 0.33 second, the yield of liquid condensed was 16 cc. (total iso-pentane vapourised, 21.3c.c.) and the yield of unsaturated compounds in this, per c.c. of iso-pentane vapourised was 0.015 c.c.

The gaseous products consisted of unsaturated hydrocarbons, hydrogen and saturated hydrocarbons. Curves were plotted showing the variations in the yields of the various gaseous products with increase in time of contact (pages 85). These show an increased yield of unsaturated compounds, hydrogen and saturated hydrocarbons with the increase in contact time.

Comparison of the results of the set of experiments on the interaction of iso-pentane and nitric oxide, and the set of experiments made with iso-pentane vapourised by passing nitrogen, shows that:-

1. the production of oxides of carbon can take

place only when nitric oxide is present.

2. addition of nitric oxide to iso-pentane results in a reduction, in the yield of hydrogen. A possible explanation lies in the oxidation of the pyrolytic hydrogen to water by the nitric oxide. Evidence of this was obtained by inserting a small detector tube filled with anhydrous copper sulphate into the system between the reaction tube and the condenser C-1 during one experiment, when a distinct blue colour was developed.

3. the presence of nitric oxide increases the yields of unsaturated hydrocarbons in both the liquid and gaseous products.

4. the yield of saturated hydrocarbon is greater in presence of nitric oxide than in case of pure pyrolytic decomposition of iso-pentane.

5. thermal decomposition is accompanied by the formation of a tarry deposit whereas decomposition in presence of nitric oxide gives rise to traces of a complex material containing primary nitro groups.

Solubility of nitric oxide in iso-pentane.

During the experiments nitric oxide was found to be soluble in iso-pentane. The solubility was experimentally determined by titrating the solution of nitric oxide in iso-pentane with a standard potassium permanganate solution. A blank was necessary.

Volume of N/10 $K Mn O_4$ used for 10 c.c. of the solution of nitric oxide in iso-pentane = 1.2 c.c.

∴ Solubility of nitric oxide in iso-pentane

= .036 gm/100 c.c.

= 26.8 c.c. per 100 c.c.

or 268 c.c. of nitric oxide per litre of iso-pentane.

Iso-pentane and nitric oxide.

Table IX

Experiment No.	1	2	3
Temperature.	750°C	750°C	750°C
Time of Contact.	0.12 sec.	0.2 sec.	0.3 sec.
Duration of the run.	39 min.	60 min.	126 min.
Vol. of nitric oxide passed.	1500 cc	1250 cc	1750 cc
Iso-pentane used.	17.2 cc	19.7	23.7
Temperature of iso-pentane bath.	20°C	20°C	20°C
Volume of gas collected.	1630 cc	3000 cc	3920 cc
Analysis of gaseous products:-			
NO - %	68.0	33.0	36.8
CO_2 - %	0.5	1.2	1.8
$C_n H_m$ - %	3.8	14.3	12.0
CO - %	1.0	1.0	1.1
H_2 - %	25.0	6.1	8.0
$C_n H_{2n+2}$ - %		43.0	36.0
C/A	1.25	1.4	1.6
n	2.0	1.6	1.5
Yield of gaseous products per cc of iso-pentane:-			
CO_2	0.47 cc	1.8 cc	3.0 cc
$C_n H_m$	3.6 cc	21.8 cc	20.0 cc
CO	0.95 cc	1.5 cc	2.5 cc
H_2	23.7 cc	9.1 cc	13.2 cc
$C_n H_{2n+2}$		60.5 cc	60.0 cc

Iso-pentane and nitric oxide.

Experiment No.	4	5	6	7
Temperature.	$750^{\circ}C$	$750^{\circ}C$	$750^{\circ}C$	$750^{\circ}C$
Time of contact.	0.36 sec.	0.45 sec.	0.6 sec.	1.0 sec.
Duration of the run.	55 min.	70 min.	140 min.	70 min.
Vol. of nitric oxide passed.	1000 cc	1000 cc	1000 cc	1000 cc
Amount of iso-pentane used.	15.1 cc	14.15 cc	14.0 cc	6.5 cc
Temperature of iso-pentane bath.	$20^{\circ}C$	$20^{\circ}C$	$20^{\circ}C$	$20^{\circ}C$
Volume of gas collected.	2350 cc	2100 cc	2320 cc	1550 cc
Analysis of gaseous products:-				
NO - %	27.5	32.5	32.8	24.1
CO_2 - %	1.0	1.0	1.0	3.6
$C_n H_m$ - %	12.1	12.7	16.5	13.2
CO - %	2.2	3.0	1.5	4.3
H - %	5.9	50.0	10.2	16.7
$C_n H_{2n+2}$ - %	23.3		39.4	32.0
C/A	1.6	1.5	2.0	2.0
n	1.4	1.5	1.0	1.0
Yield of gaseous products per c.c. of iso pentane:-				
CO_2	1.5 cc	1.5 cc	1.6 cc	8.5 cc
$C_n H_m$	20.0 cc	19.1 cc	27.4 cc	31.5 cc
CO	3.5 cc	4.5 cc	2.5 cc	10.3 cc
H	10 cc	74.5 cc	16.9 cc	39.8 cc
$C_n H_{2n+2}$	40 cc		65.5 cc	76.0 cc

<u>Iso-pentane only.</u>

Table IX

Experiment No.	1.	2.	3.
Temperature	750°C	750°C	750°C
Time of Contact	0.24 sec.	0.33 sec.	0.42 sec.
Duration of the run	37 min.	80 min.	107 min.
Volume of nitrogen passed	1000 cc.	1500 cc	1500 cc.
Amt. of Iso-pentane used	14 cc	21.3 cc	24.2 cc
Temperature of iso-pentane bath	20°C	20°C	20°C
Volume of gas collected	2000 cc	3520 cc	4450 cc
Analysis of gaseous products			
$C_n H_m$ - %	11.1	13.7	9.2
H - %	18.1	20.2	23.8
$C_n H_{2n} + 2$ - %	18.8	22.6	33.2
$C/_A$ - %	1.25	1.3	1.7
n - %	2.0	1.9	1.3
Yield per c.c. of iso-pentane			
C_nH_m	15.8 cc	22.6 cc	17.0 cc
H	25.6 cc	33.2 cc	44.0 cc
$C_n H_{2n} + 2$	26.4 cc	37.4 cc	61.0 cc

Iso-pentane only.

Experiment No.	4	5
Temperature	750°C	750°C
Time of contact	0.75 sec.	1.0 sec.
Duration of the run	126 min.	70 min.
Volume of nitrogen passed	1000 cc	500 cc.
Amt. of iso-pentane used	16.4 cc	6.2 cc
Temp. of iso-pentane bath	20°C	20°C
Volume of gas collected	3250 cc	1200 cc
Analysis of gaseous products		
$C_n H_m$ - %	8.4	10.0
H - %	25.0	29.0
$C_n H_{2n+2}$ - %	32.0	35.6
$C/_A$ - %	2.0	2.0
n - %	1.0	1.0
Yield per c.c. of iso-pentane		
$C_n H_m$	16.7	26.4
H	50.0	56.0
$C_n H_{2n+2}$	63.5	69.0

ISO-PENTANE AND NITRIC OXIDE (TEMP. 750°C.)

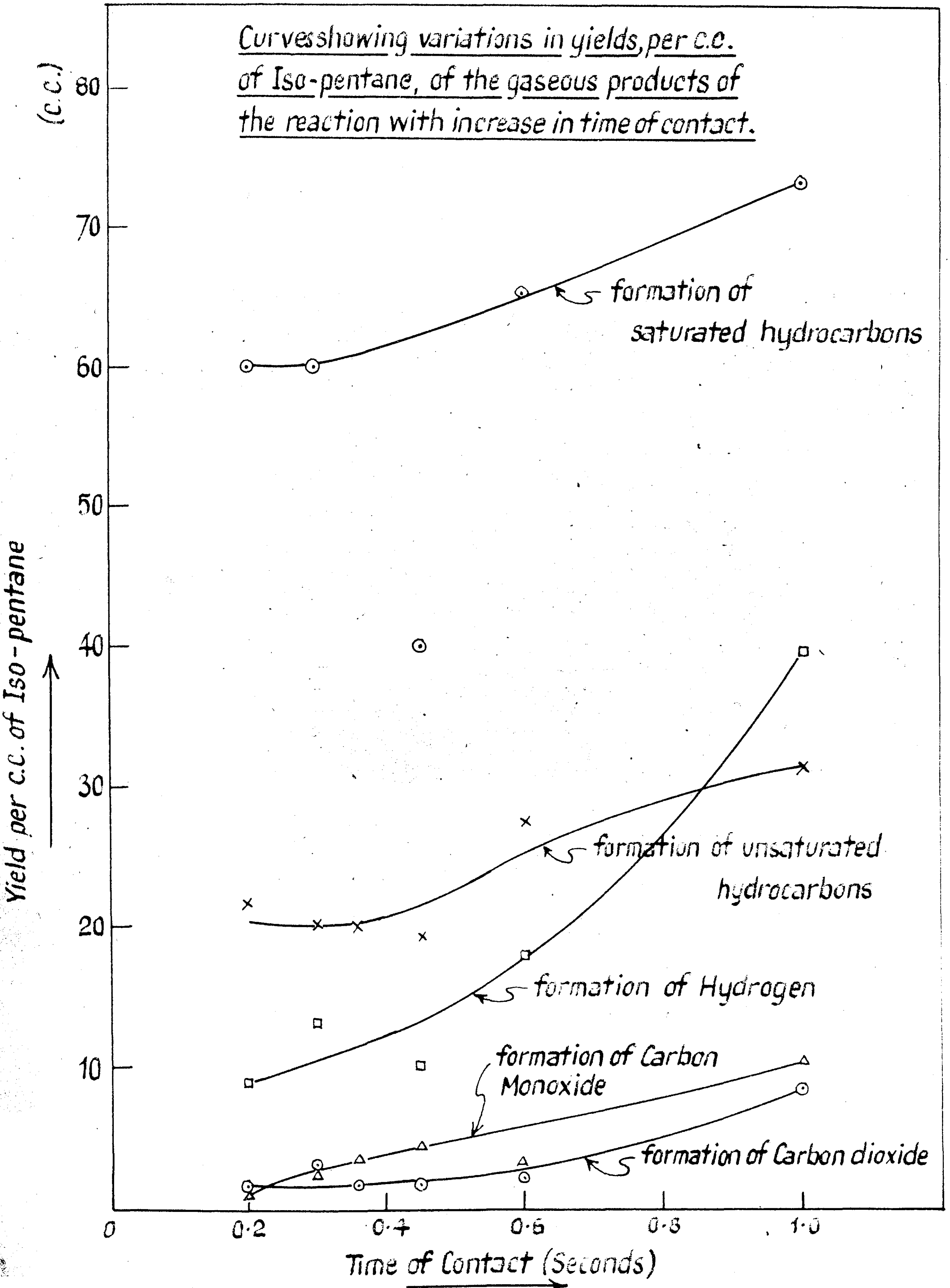


Fig. 13.

ISO PENTANE ALONE (TEMP. 750°C.)

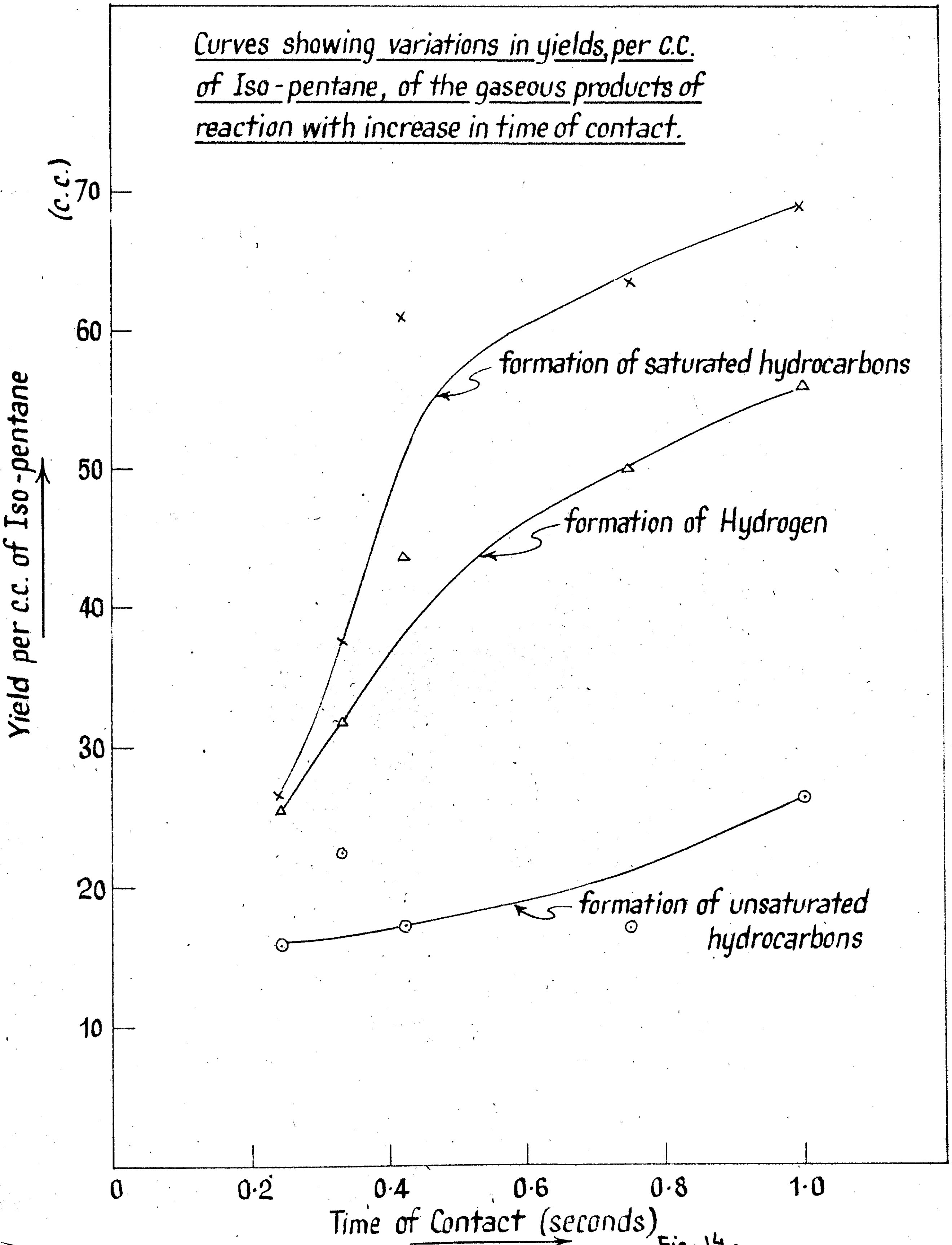

Curves showing variations in yields, per C.C. of Iso-pentane, of the gaseous products of reaction with increase in time of contact.

Fig. 14.

iii. Influence of Composition of Reacting Mixture.

A set of experiments was made at 750°C with varying proportions of iso-pentane and nitric oxide. The proportions of the reactants were varied by keeping the iso-pentane flask at different temperatures and varying the rate of passage of nitric oxide through iso-pentane. The total volume of the reaction mixture passing through the silica tube was kept constant so as to give similar times of contact, 0.6 second, in all these experiments. The iso-pentane bath temperatures used were 9°C, 15°C, 17°C and 20°C. The results of these experiments are given in Table XI .

From these it is seen that, when the proportion of nitric oxide in the reaction mixture is very large, the amount of the unreacted iso-pentane condensed is very small and the liquid products contain comparatively more of the dark-coloured product and a large amount of unsaturated compounds. There is hardly any coloured product formed when the concentration of nitric oxide is about 27%.

The ratio of nitric oxide used to total nitric oxide passed is a maximum for about 60% concentration of iso-pentane in the reaction mixture.

Curves were drawn showing, per c.c. of iso-pentane, variations in the yield of the gaseous products of the reaction. These indicate:

1. Increased yield of unsaturated hydro-carbons with decrease in the proportion of iso-pentane down to about 60% iso-pentane. Further decrease in the proportion of iso-pentane results in a decreased yield of these hydrocarbons.
2. A steady increase in the yield of saturated hydrocarbon with a decrease in the proportion of iso-pentane.
3. The yield of hydrogen is fairly steady up to 60% iso-pentane and then increases rapidly.
4. There is not very much change in the yield of carbon dioxide. The yield of carbon monoxide shows an increase with the decrease in the proportion of iso-pentane, especially pronounced at the lowest concentration investigated.

Iso-pentane and nitric oxide.

Table XI

Effect of varying proportions of iso-pentane.

Experiment No.	1	2	3	4
Temperature.	750°C	750°C	750°C	750°C
Time of contact.	0.6 sec.	0.6 sec.	0.6 sec.	0.6 sec
Duration of the run.	58 min.	66 min.	75 min.	85 min
Vol. of nitric oxide passed.	1000 cc	1000 cc	1000 cc	1000 cc
Amt. of iso-pentane used.	6.2 cc	8.3 cc	10.2 cc	13.5 cc
Temp. of iso-pentane bath.	9°C	15°C	17°C	20°C
Percentage iso-pentane present in the reaction mixture.	55%	61.5%	66%	72.5%
Volume of gas collected.	1820 cc	1680 cc	1900 cc	1950 cc
Analysis of gaseous products:-				
NO - %	14.7	37.4	36.2	34.0
CO_2 - %	0.5	1.2	1.5	1.0
$C_n H_m$ - %	11.3	19.2	14.2	14.6
CO - %	1.5	0.6	0.5	1.0
H - %	9.6	4.9	5.0	7.2
$C_n H_{2n+2}$ - %	26.6	30.1	31.3	35.4
$C/_A$	2.0	2.0	2.0	2.0
n	1.0	1.0	1.0	1.0

	1	2	3	4
Yield of gaseous products per cc of iso-pentane:-				
CO_2	1.5 cc	2.5 cc	2.8 cc	1.4 cc
$C_n H_m$	33.1	38.8	26.6	21.0
CO	4.5	1.2	0.5	1.4
H	28.0	9.8	9.0	10.8
$C_n H_{2n+2}$	78.0	61.0	58.0	51.5
Liquid products.				
Vol. collected in dry-ice cooled condenser.	1.8 cc	5.5 cc	6.5 cc	9.0 cc
	(very large amt. of coloured product).			
Yield of liq. unsaturated hydrocarbons per cc of iso-pentane.	0.1	0.025 cc	0.03 cc	0.02 cc
Ratio of nitric oxide to total nitric oxide passed.	0.25	0.37	0.31	0.33

ISO-PENTANE AND NITRIC OXIDE

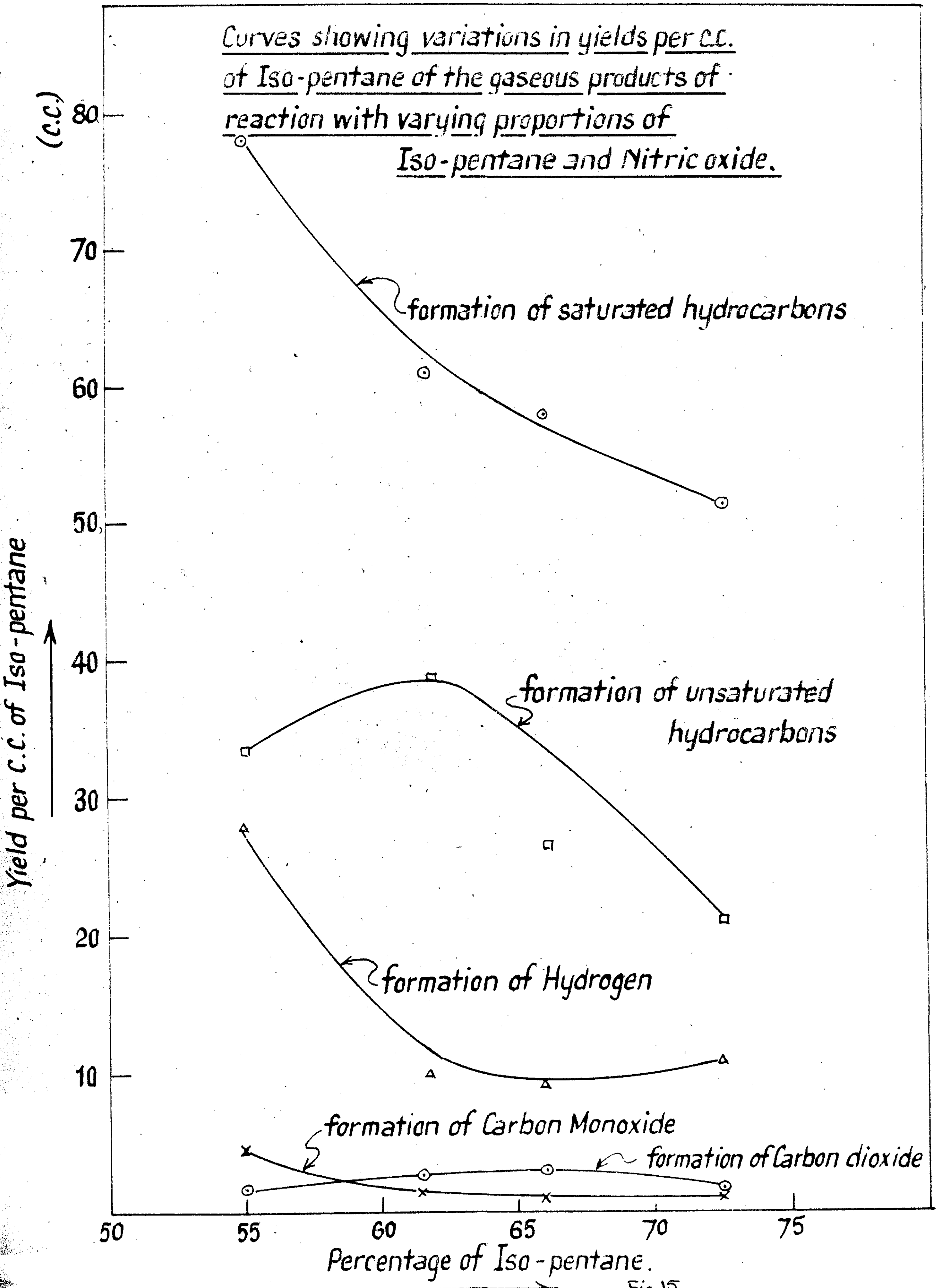


Fig. 15.

iv, Influence of Temperature.

After studying the influence of time of contact and the influence of varying the composition of the reaction mixture, the influence of temperature was examined. Experiments were made using a ratio of iso-pentane to nitric oxide of 3:1 and a contact time of 0.35 second at the temperatures of 600°C, 650°C, 750°C, 800°C, 850°C, 875°C and 900°C. The gaseous and the liquid products were analysed in each case; the result of these experiments are given in TableXII .

At 875°C and 900°C, the liquid products contained a large percentage of the tarry product, this was found by extracting the coloured liquid with a concentrated solution of caustic potash. The insoluble portion was found to be fairly soluble in organic solvents. The amount of unreacted iso-pentane as would be expected, is considerably small for temperatures above 800°C.

It is seen from the Table XII that the

amount of unsaturated hydrocarbons in the liquid products, calculated per c.c. of iso-pentane vapourised, increases with the increase in temperature.

Curves showing the variations in the yields per c.c. of iso-pentane, of the gaseous products of the reaction with the increase in temperature are given in Fig. 16. These show:

1. An increase in carbon dioxide and carbon monoxide with increase in temperature. The increase is very small.

2. There is increased yield of hydrogen, the increase is very marked at 800°C and above.

3. The yield of saturated hydrocarbons increases with the increase in temperature, slowly at first and then rapidly at temperatures of 800°C and above.

4. There is increased yield of unsaturated hydrocarbons, this increase is also very noticeable at about 800°C and above.

Iso-pentane and nitric oxide.

Table XII

Effect of Temperature.

Experiment No.	1.	2.	3.	4.
Temperature	600°C	650°C	750°C	800°C
Time of contact	0.38 sec.	0.35 sec.	0.36 sec.	0.35 sec.
Duration of run	60 min.	55 min.	55 min.	55 min.
Vol. of nitric oxide passed.	1000 cc	1000 cc	1000 cc	1000 cc
Amt. of iso-pentane used	13.7 cc	15.3 cc	15.1 cc	15.4 cc
Temp. of iso-pentane bath	20°C	20°C	20°C	20°C
Volume of gas collected	1410 cc	2250 cc	2350 cc	3520 cc
Analysis of gaseous products:				
NO - %	69.0	31.4	27.5	21.5
CO_2 - %	3.0	1.0	1.0	2.0
$C_n H_m$ - %	4.0	3.0	12.1	15.7
CO - %	1.5	1.5	2.2	1.0
H - %	2.0	7.5	5.9	7.8
$C_n H_{2n+2}$ - %	10.2	48.0	23.3	23.8
C/A - %	1.1	1.4	1.6	2.0
n - %	2.4	1.7	1.4	1.0

Yield of gaseous products per cc of iso-pentane	1.	2.	3.	4.
CO_2	3.7 cc	1.5 cc	1.5 cc	4.5 cc
$C_n H_m$	4.0 cc	4.0 cc	20.0 cc	36.0 cc
CO	1.5 cc	2.0 cc	3.5 cc	3.8 cc
H	2.2 cc	11.0 cc	10.0 cc	11.6 cc
$C_n H_{2n+2}$	10.5 cc	72.0 cc	40.0 cc	54.5 cc
Liquid products				
Vol.collected in solid dioxide cooled condenser	11.0 cc	11.0 cc	10.0 cc	8.5 cc
Yield of $C_n H_m$ (liq.) per cc of iso-pentane	0.05 cc	0.05 cc	0.065 cc	0.073 cc
Ratio of NO used to total NO passed	0.025 cc	0.29 cc	0.36 cc	0.24 cc

Iso-pentane and nitric oxide.

Effect of Temperature.

Experiment No.	5.	6.	7.
Temperature	850°C	875°C	900°C
Time of contact	0.35 sec.	0.38 sec.	0.38 sec.
Duration of the run	55 min	60 min	60 min
Vol. of nitric oxide passed	1000 cc	1000 cc	1000 cc
Amt. of iso-pentane used	15.1 cc	13.5 cc	13.5 cc
Temp. of iso-pentane bath	20°C	20°C	20°C
Volume of gas collected	5920 cc	7350 cc	7670 cc

Analysis of gaseous products:

NO	- %	13.9	8.5	6.1
CO_2	- %	1.1	1.2	1.1
$C_n H_m$	- %	28.5	14.8	20.0
CO	- %	2.0	1.8	1.6
H	- %	10.0	9.1	10.0
$C_n H_{2n} + 2$	- %	30.8	57.2	58.0
C/A	- %	2.0	2.0	2.0
n	- %	1.0	1.0	1.0

Yield of gaseous products per cc of iso-pentane	5.	6.	7.
CO_2	4.3 cc	6.0 cc	6.7 cc
$C_n H_m$	110.0 cc	82.0 cc	108.5 cc
CO	7.2 cc	10.0 cc	9.2 cc
H	39.2 cc	49.7 cc	57.3 cc
$C_n H_{2n} + 2$	112.0 cc	311.0 cc	330.0 cc
Liquid products			
Vol. collected in solid dioxide cooled condenser	2.5 cc	2.0 cc (dark brown colour)	1.0 cc (very dark colour)
Yield of $C_n H_m$ (liq.) per c.c. iso-pentane	0.101 cc	-	-
Ratio of NO used to total NO passed	0.17	0.38	0.52

ISO-PENTANE AND NITRIC OXIDE EFFECT OF TEMPERATURE

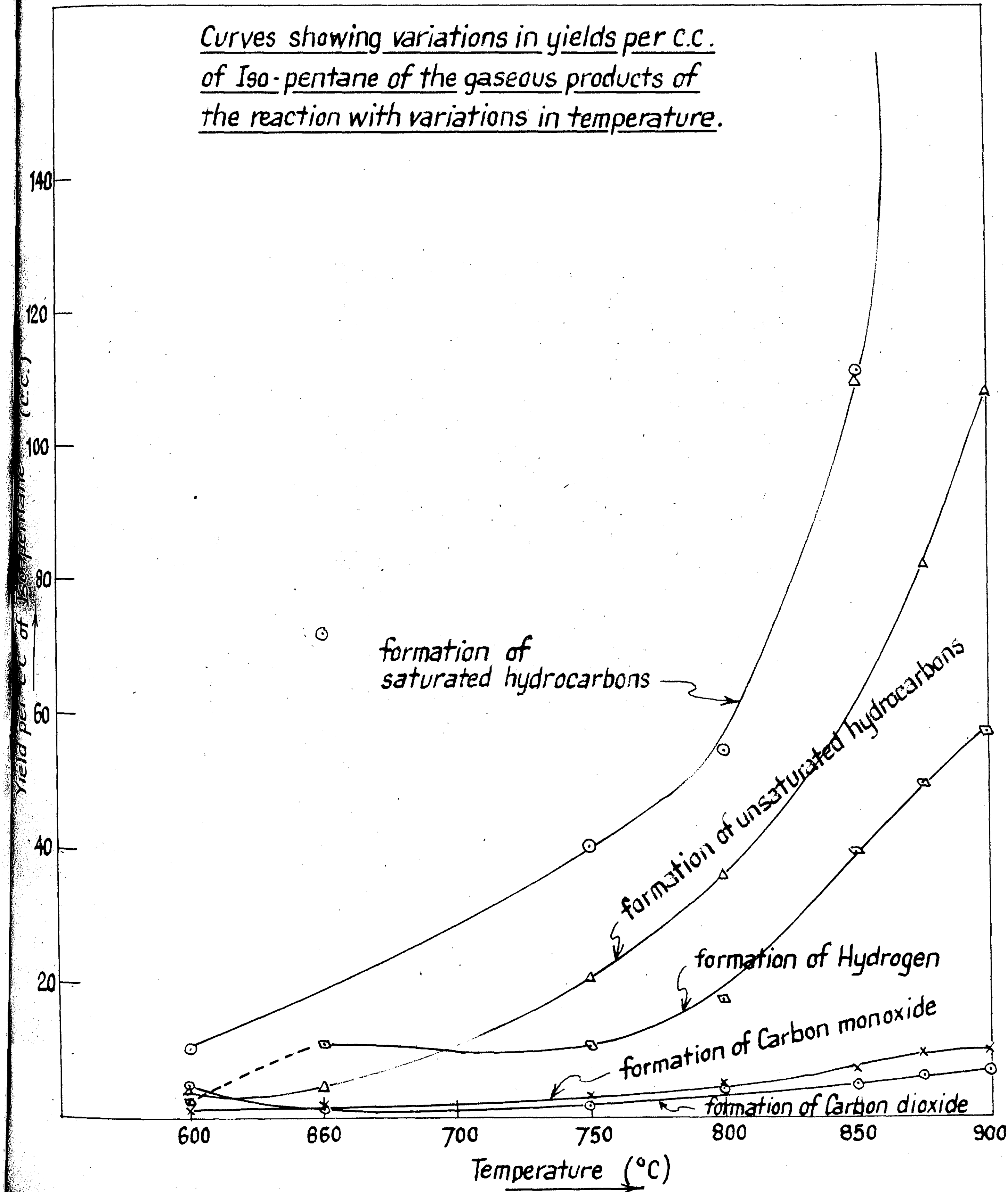


Fig. 1c.

V, Identification of the unsaturated hydrocarbons and the liquid products of the reaction.

As described earlier, the liquid products of the reaction were collected in two spiral condensers, one of which was kept in ice and the other in drikold. Distillation of the liquid products showed that all the liquid distilled off from 22° to 30°C leaving in the flask a few drops of a light brown oily liquid. Examination of these two fractions was carried out as follows:-

Distillate.

Examination of the distillate for the constituent elements revealed the absence of nitrogen. No evidence could be obtained for the presence of any functional grouping such as acidic, ketonic, aldehydic, etc.

On treating a portion of the liquid with potassium permanganate solution, immediate decolourisation of the permanganate solution took place. This gave an indication of the presence of unsaturated compounds which was confirmed by the following tests.

1. About 1 c.c. of the liquid was dissolved in a c.c. or two of carbon tetrachloride and treated with 1% solution of bromine in carbon tetrachloride. The colour of bromine was discharged without the evolution of hydrogen bromide. This gave positive evidence for the presence of unsaturated compounds. Substances which are readily brominated such as phenols not only discharge the colour of bromine but also simultaneously liberate hydrogen bromide.

2. 2 c.c. of the liquid was mixed with 3 c.c. glacial acetic acid and to this was added a known volume (about 5 c.c.) of fuming sulphuric acid. After a little agitation the mixture was allowed to stand for 2 hours and the level of the layers read off. This method gives essentially complete solution of olefines in presence of active saturated hydrocarbons like iso-octane which have a tendency to go into the solution with sulphuric acid. Also the use of fuming sulphuric acid with glacial acetic acid avoids the possibility of polymerisation of the olefines or formation of saturated hydrocarbons through the complex reactions[26].

The amounts of unsaturated hydrocarbons found in the liquid products are given in Tables IX – XII .

Residue.

This was a yellow oily liquid found to be very easily soluble in a concentrated solution of sodium hydroxide. On applying the Lassaigne test, evidence was obtained for the presence of nitrogen.

To a portion of the alkaline solution, excess of sodium nitrite solution was added and on careful acidification with sulphuric acid, an intense red colour was produced which disappeared on further addition of acid. This indicated the presence of a primary nitro group.

No further test could be applied on account of the extremely small quantity of the residue.

Identification of the unsaturated hydrocarbons.

For the identification of the various unsaturated hydrocarbons produced during the reaction it was thought desirable to prepare a fair quantity of their bromo-derivatives. This was done by using only one spiral condenser cooled in ice, to condense the unreacted iso-pentane, passing the gaseous products through two absorption bottles and collecting the remaining gases as before. Each of the absorption bottles contained 5 c.c. bromine covered with about 20 c.c. of 10% potassium bromide solution, these were kept in ice to condense any bromides being carried with the gas stream.

The bromo-derivatives so formed were collected and submitted to fractionation after the removal of excess of bromine. The fractions collected were:

A) fraction boiling between 120° - 129°C
B) fraction boiling between 136° - 143°C
and C) fraction boiling between 145° - 150°C

The last two were obtained in fair yields. The boiling points of these fractions correspond with following boiling points[27]:

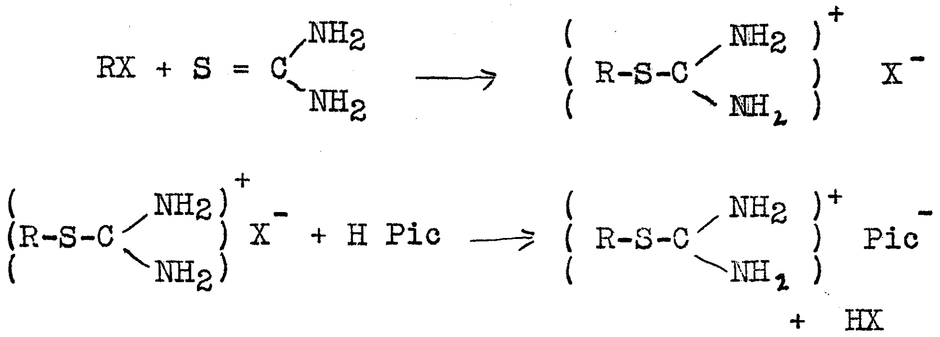
a)	Ethylene dibromide $CH_2Br \cdot CH_2Br$	B.pt. 129°C
b)	Propylene dibromide $CH_3 \cdot CHBr \cdot CH_2Br$	B.pt. 142°C
c)	Iso-butylene dibromide $(CH_3)_2CBr \cdot CH_2Br$	B.pt. 149°C

The three fractions A, B and C were refractionated. From A, a fraction boiling between 127° - 129°C was isolated. Similarly from B, a fraction boiling between 139° - 142°C, and from C, a fraction boiling between 146° - 149°C were collected.

The identity of these was confirmed by determination of the density (by means of a 2 c.c. pycnometer) and the refractive index by Abbe's Refractrometer at 20°C). The result of these determination are given below:

	B.Pt.	Density	Refractive Index.
Fraction A	127° - 129°C	-	1.5360
Ethylene dibromide	129°C	-	1.5380
Fraction B	139° - 142°C	1.931	1.5195
Propylene dibromide	142°C	1.926	1.5203
Fraction C	146° - 149°C	1.771	1.5101
Iso-butylene dibromide	149°C	1.765	1.5090

The amount of fraction A was too small for the determination of density. Advantage was taken of the method of Brown and Campbell[28] for the identification of alkyl bromides by preparing their iso-thio-urea picrates. This formation of the picrate can be represented by the following equations:



$$RX + S = C\begin{matrix}NH_2\\NH_2\end{matrix} \longrightarrow \left(R{-}S{-}C\begin{matrix}NH_2\\NH_2\end{matrix} \right)^+ X^-$$

$$\left(R{-}S{-}C\begin{matrix}NH_2\\NH_2\end{matrix} \right)^+ X^- + H\,Pic \longrightarrow \left(R{-}S{-}C\begin{matrix}NH_2\\NH_2\end{matrix} \right)^+ Pic^- + HX$$

$$H\,Pic \equiv HO\,C_6\,H_2\,(NO_2)_3$$

This picrate was prepared by taking about 0.5 gm of the fraction A, 0.5 gm of powdered thio-urea, 10 c.c. alcohol and heating together in a reflux for about 30 minutes. Then 0.5 gm of picric acid was added and the mixture heated till a clear solution was obtained. On cooling, the picrate separated out. This was re-crystallised from alcohol. The melting point of the picrate was found to be 254° - 257°C (Melting pt. Ethylene dibromide - iso-thio-urea picrate 250°C).

PART I.

DISCUSSION OF RESULTS.

Discussion of Results.

According to Rice's theory of Free Radicals, iso-pentane on pyrolysis will give rise to the following products:-

a) Saturated hydrocarbons - methane, ethane and propane.

b) Unsaturated hydrocarbons - ethylene, propylene, iso-butylene, 1 - butene, and 2 - butene.

and c) Hydrogen.

Nitric oxide on the other hand is thermally stable at temperatures up to 500°C and is decomposed slightly up to 900°C. On account of this slight decomposition of nitric oxide, there may be some combustion of the hydrocarbon or its products, when iso-pentane and nitric oxide are heated together at 500°C to 900°C. Also, on heating, if iso-pentane does not react instantaneously with nitric oxide to give stable compounds, it would undergo thermal decomposition.

Nitric oxide, which possesses an odd electron, is known to combine instantly in solution with tri-phenyl - methyl, diphenyl - nitrogen and their analogues. Again with the salts of the transition metals such as iron and cobalt which possess unpaired d electrons, it forms co-ordination compounds - the nitrosyls. By analogy nitric oxide may be expected to form nitroso compounds by combining with the free radicals formed during the pyrolysis of iso-pentane:

$$R - \ + \ {}^{\cdot}N{:}O \longrightarrow R\,.\,NO$$

$$(R \equiv \text{a free radical})$$

The work carried out on the interaction of iso-pentane and nitric oxide has shown that no appreciable reaction takes place below 500°C but at higher temperatures carbon dioxide, unsaturated hydrocarbons, carbon monoxide, hydrogen, saturated hydrocarbons, water, primary nitro compounds along with some tarry products and carbon are formed. The effect of increase of contact time, temperature and the concentration of nitric oxide in the reacting mixture have been studied and show increased yields of all the products of reaction except unsaturated hydrocarbons. The yield of the unsaturated hydrocarbons increases with increase in temperature and contact time; but with increasing concentration of nitric oxide in the reacting mixture, the yield of these increases at first, reaches a maximum and then decreases (fig. 15). From the yields of the reaction products, it is seen that the thermal decomposition of the hydrocarbon is the principal reaction and is accompanied by some oxidation.

Theories of Pyrolysis and the Interaction of Iso-pentane and nitric oxide.

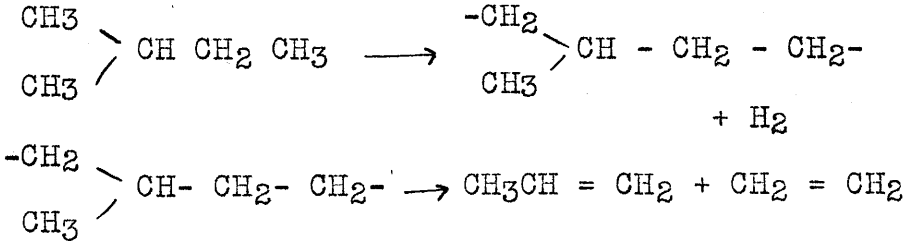
The unsaturated hydrocarbon found in the products of the reaction were:-

1. $CH_2 = CH_2$ Ethylene
2. $CH_3\,CH = CH_2$ Propylene
3. $(CH_3)_2C = CH_2$ Iso-butylene

The last two were obtained in fair yields. Frey and Hepp[29] have obtained almost similar results; these workers obtained maximum yields of iso-butylene as compared with other unsaturated hydrocarbons while carrying out a series of flow experiments on the pyrolysis of iso-pentane at 575°C.

As mentioned above, according to the theory of free radicals, the unsaturated hydrocarbon which would be expected to be formed are ethylene, propylene, iso-butylene, 1 - butene and 2 - butene. 1 - butene does not appear to be a product of the decomposition of iso-pentane as it has not been found by any of the investigators[30]. 2 - Butene has been obtained in small yields by Frey and Hepp[29], but it has not been found in the products of the reaction in the experiments described above, probably on account of its relative instability in presence of nitric oxide, at the temperatures and contact times used. Hurd and Spence[31] have shown in their work on the thermal decomposition of butylenes that iso-butylene is much more stable than n. butenes.

The theories of Kassel and Creigee discussed in the introduction, fail to explain the formation of iso-butylene and also the quantity in which it is formed. According to Kassel's theory, in the case of iso-pentane two hydrogen atoms are brought together into close proximity and united to yield hydrogen. The resulting carbon chain is broken in the centre to furnish a molecule of ethylene and a molecule of propylene.



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!>CH\;CH_2\;CH_3 \longrightarrow \begin{matrix}-CH_2\\ CH_3\end{matrix}\!>CH - CH_2 - CH_2- \quad + H_2$$

$$\begin{matrix}-CH_2\\ CH_3\end{matrix}\!>CH- CH_2- CH_2- \longrightarrow CH_3CH = CH_2 + CH_2 = CH_2$$

Creigee suggests in his theory that the thermal rupture of carbon chain occurs by removal of hydrogen atom in 1:4 position, the resulting di-radical undergoing stabilisation by cleavage between carbon atoms 2 and 3. Applying this theory to iso-pentane, result similar to Kassel's theory is obtained, which is not in agreement with the experimental results.

Additional support to the free radical theory is given in this work by the value of n i.e. the number of carbon atoms in the saturated hydrocarbons, which was generally found to vary from 1.5 to 1.0, showing that the saturated hydrocarbons produced consisted mostly of lower alkanes. Also during the preferential combustion of hydrogen at 250° to 300°C, no carbon dioxide was formed, had C_4 or C_5 saturated hydrocarbons been present, carbon dioxide would have been formed. According to the theory of free radicals, saturated hydrocarbons produced during pyrolysis would consist of methane, ethane and propane only. Appleby and co-workers[9] in their studies of thermal decomposition of n. heptane, over a temperature range of 550°- 630°C, have indicated that the composition of the saturated hydrocarbons produced is in agreement with the theory of Free Radicals.

Liquid Products of the reaction.

No nitroso compounds as postulated above have been found. There is not much possibility of finding these in the reaction products as they are unstable. The formation of nitro compounds is probably a result of the reaction of nitrogen dioxide formed by oxidation of a small fraction of nitric oxide. The yield of nitro compounds is small on account of oxidation taking place only to a limited extent.

The small quantities of dark coloured products formed may be a result of polymerisation of some unsaturated hydrocarbons. Nitric oxide is known to aid in the polymerisation of unsaturated hydrocarbons, which in some cases form what is known as vapour-phase gum.

Formation of oxides of carbon.

The oxides of carbon are probably a result of:-

a) oxidation of the hydrocarbon followed by degradation or

b) the rupture of iso-pentane followed by oxidation of the degradation products.

An increase in time of contact, temperature or concentration of nitric oxide would mean an increase in the decomposition of nitric oxide which would result in an increase in yields of carbon dioxide and carbon monoxide. This is found to be the case.

Comparison with thermal decomposition of iso-pentane alone.

In this work, a comparison of the interaction of iso-pentane and nitric oxide with the thermal decomposition of iso-pentane alone shows (figs. 17, 18 and 19) that in presence of nitric oxide the yield of saturated and unsaturated hydrocarbons are greater but of hydrogen less; also iso-pentane molecule is found degraded to a greater extent. This may be explained as follows:-

a). The yield of hydrogen is less probably on account of the oxidation of pyrogenic hydrogen to water, which is found as one of the products of the reaction.

b) The increased yields of unsaturated hydrocarbons, saturated hydrocarbons and the greater degradation of iso-pentane are difficult to explain conclusively.

Nitric oxide decomposes slightly; above 500°C. The walls of the silica reaction-tube might be catalysing the decomposition of nitric oxide, also carbon which is a product of the reaction is known to aid in decomposition of nitric oxide. It is probably this decomposition of nitric oxide, which is an exothermic reaction, assisting in the greater degradation of the hydrocarbon molecule.

The production of increased amounts of unsaturated hydrocarbons may also be explained by the removal of hydrogen. Considering some of the reactions involved in the thermal decomposition of iso-pentane according to the free radical theory,

1. $(CH_3)_2\ CH\ CH_2\ CH_3 \longrightarrow CH_3\ CH(CH_3)- \ + \ -CH_2\ CH_3$ (Primary)

2. $CH_3\ \ CH(CH_3)- \longrightarrow CH_3\ CH = CH_2 + H$ (Secondary)

it is seen from the reaction (2) that if hydrogen is removed, there would be increased yield of unsaturated hydrocarbons.

Thus it is seen from the above discussion that nitric oxide and iso-pentane react on heating at 500°C or above. The principal reaction is thermal decomposition of the hydrocarbon which is degraded to a greater extent in the presence of nitric oxide, and is accompanied by some oxidation. The products obtained are in general agreement with the theory of free radicals if it is postulated that some oxidation is taking place on account of a little decomposition of nitric oxide.

Inhibition of the thermal decomposition of paraffin hydrocarbons by nitric oxide has been studied by various authors under static conditions; the concentration of nitric oxide in such investigations being usually small. Only a very few authors have given any details of the products of the reaction. Steacie and Folkin[56] who have investigated the inhibition by nitric oxide of the thermal decomposition of n. butane find that the products of the inhibited reaction were the same as those of the normal decomposition. This is probably due to the fact that nitric oxide was present in small amounts, and the effect of the slight decomposition of this small amount of nitric oxide would be negligible on the thermal decomposition of the hydrocarbon.

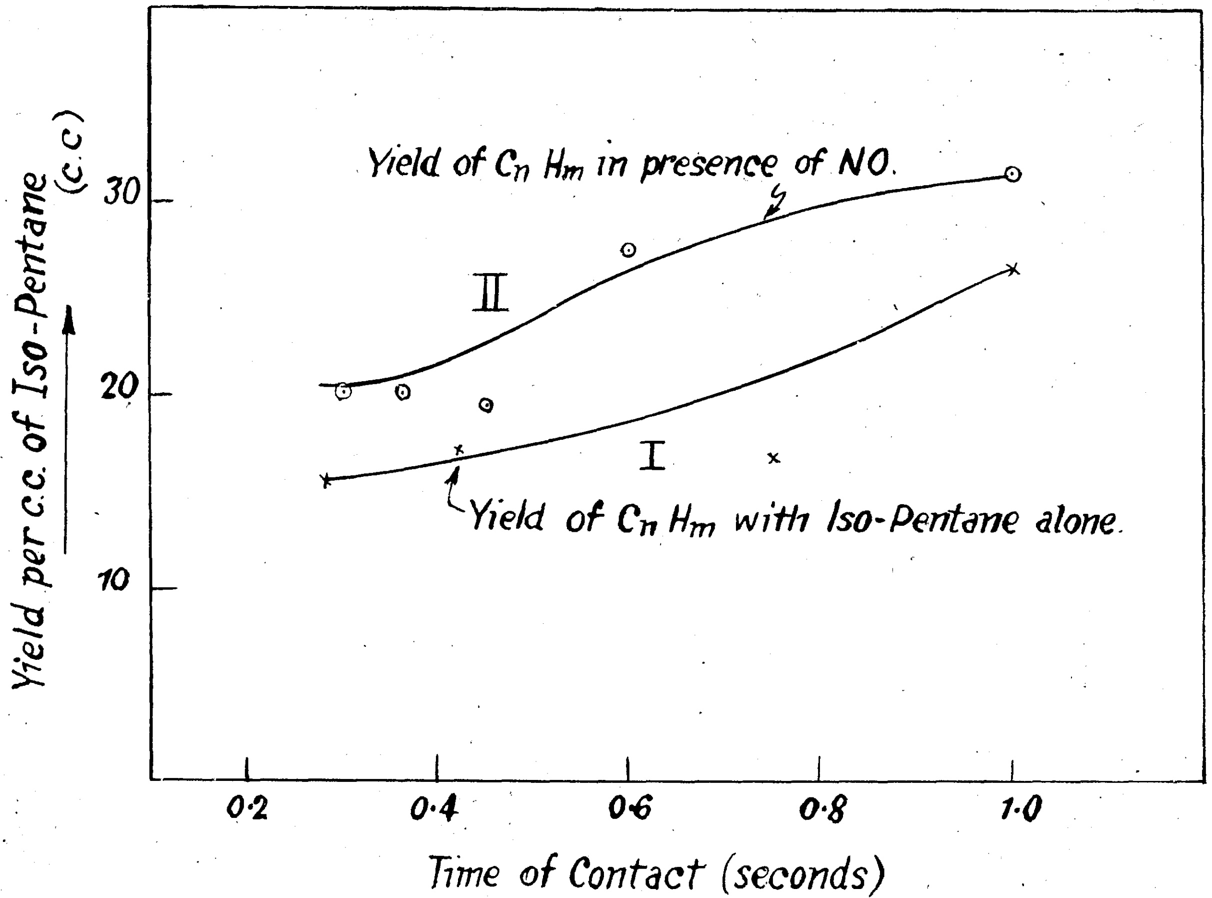

Yield of $C_n H_m$ in presence of NO.
II
I
Yield of $C_n H_m$ with Iso-Pentane alone.
Yield per c.c. of Iso-Pentane (c.c)
30
20
10
0·2
0·4
0·6
0·8
1·0
Time of Contact (seconds)

Fig. 17.

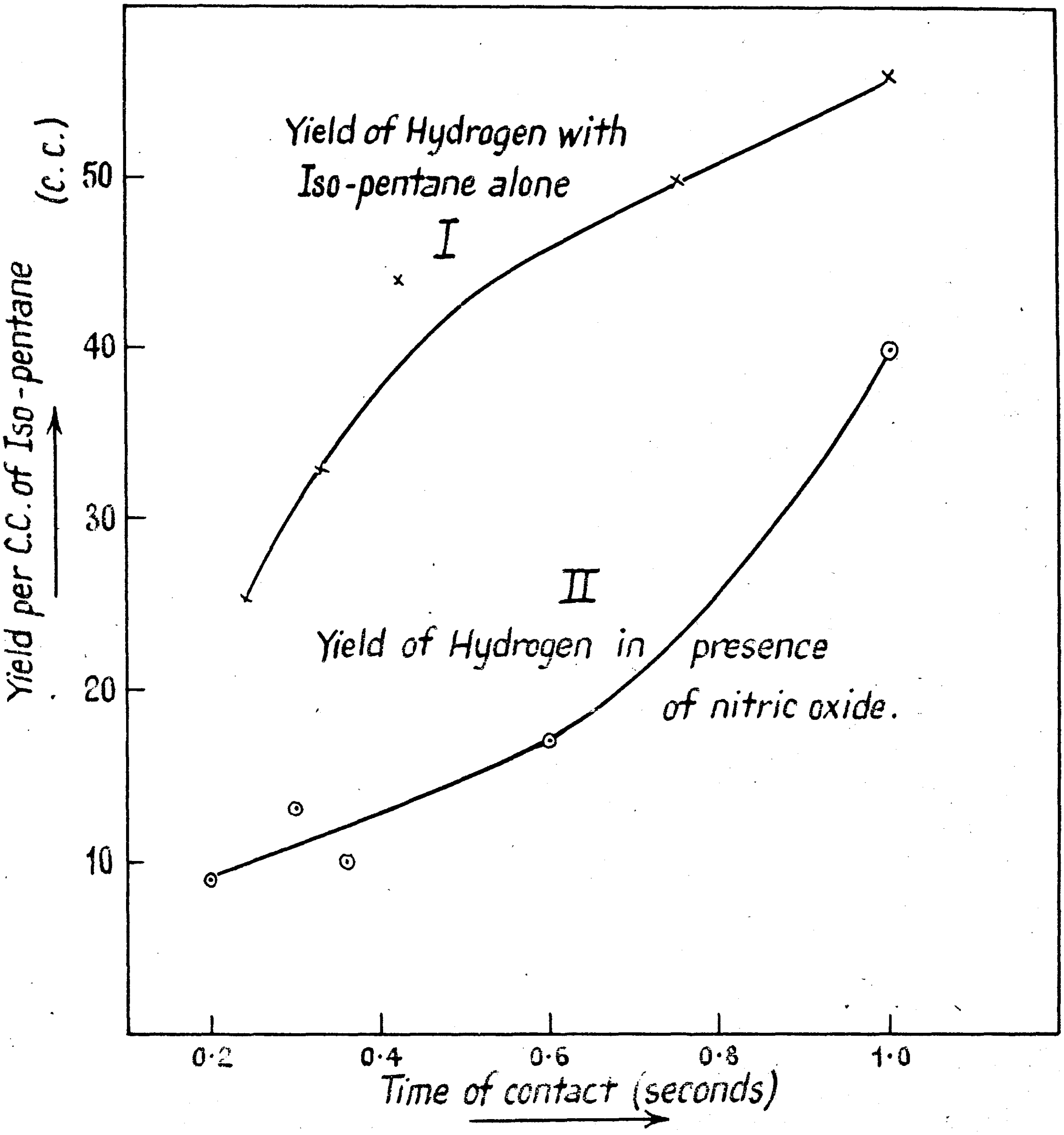
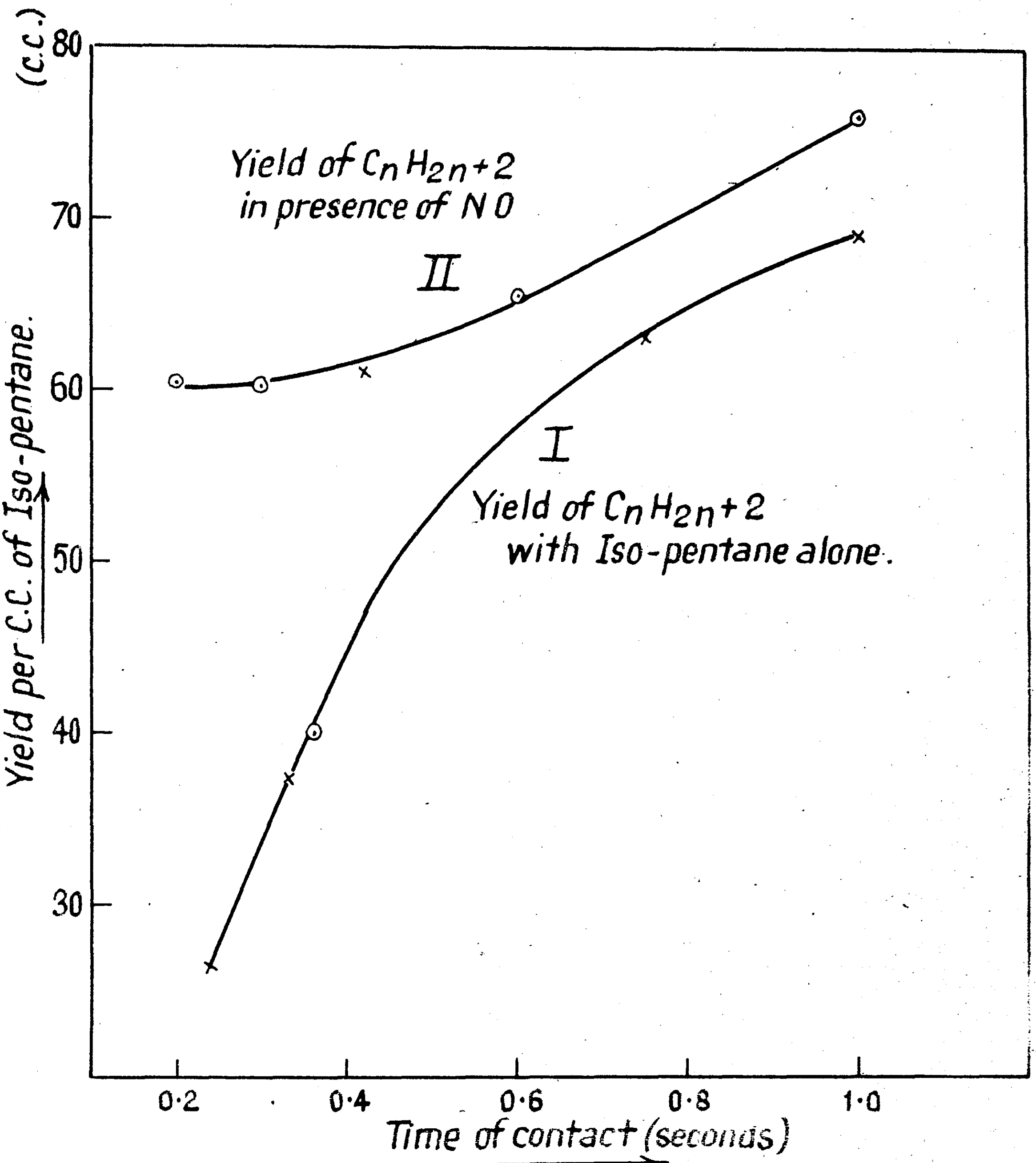

Yield of Hydrogen with
Iso-pentane alone
I
II
Yield of Hydrogen in presence
of nitric oxide.
Yield per C.C. of Iso-pentane (c.c.)
10
20
30
40
50
0·2
0·4
0·6
0·8
1·0
Time of contact (seconds)

FIG. 18.



(c.c.)
80
70
60
50
40
30
Yield per C.C. of Iso-pentane.
Yield of C_nH_{2n+2} in presence of NO
II
I
Yield of C_nH_{2n+2} with Iso-pentane alone.
0·2
0·4
0·6
0·8
1·0
Time of contact (seconds)

FIG. 19.

PART II.

INTERACTION OF ISO-PENTANE AND NITROGEN DIOXIDE.

INTRODUCTION AND REVIEW OF PREVIOUS WORK.

Introduction and Review of previous work.

In recent years there has been considerable interest in the production of nitro-paraffins. Generally, alkane hydrocarbons resist direct nitration, but improved methods of nitration at high temperatures and pressures have made available a number of liquid nitro-paraffins at low cost. These liquids are useful solvents for a number of organic compounds including cellulose esters, resins, oils, fats and waxes. Various derivatives of nitro-paraffins have a great commercial application, for example:-

a) their amines formed by reduction,

$$\underset{\text{2 nitro-propane}}{CH_3\ CH(NO_2)CH_3} + 3\ H_2 \longrightarrow \underset{\text{Iso propylamine}}{CH_3\ CH(NH_2)CH_3} + 2H_2O$$

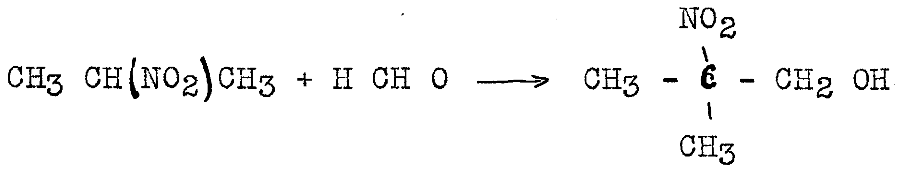
are useful raw materials for the synthesis of pharmaceuticals, dyestuffs, rubber chemicals and emulsifying agents.

b) Choloro-nitro compounds prepared by chlorinating the sodium salt of nitro-paraffins,

$$CH_3\ CH(NO_2)CH_3 + Na\ OH + Cl_2 \longrightarrow CH_3\ C(Cl)(NO_2)\ CH_3 + NaCl + H_2O$$

are used as insecticides, antigelling agents in rubber cements and for chemical synthesis.

c) Aliphatic nitro-hydroxy compounds prepared by the condensation of aliphatic aldehydes in presence of basic catalysts.



$$CH_3\ CH(NO_2)CH_3 + H\ CH\ O \longrightarrow CH_3 - \overset{NO_2}{\underset{CH_3}{C}} - CH_2\ OH$$

2 - nitro - 2 - methyl - 1 - propanol

have found applications as heat sensitizer for rubber latex, high boiling solvents for cellulose esters, oil-soluble dyes, etc.,

d) the amino-hydroxy compounds, formed by the reduction of the aliphatic nitrohydroxy compounds, are useful for synthesis of wetting agents and surface active agents, pharmaceuticals, photographic developers, resins, dystuffs, etc.

In some cases the nitro-paraffins are useful intermediates in the synthesis of well known chemicals like chloropicrin, hydro-xylamine, etc.

The first aliphatic nitro compounds, di-nitroethane was prepared in 1864[32] and a general method for the preparation of nitro-paraffins was established in

1872 (Victor Meyer and Stuber)[33]. At that time aromatic nitro-derivatives were already of substantial importance, since mauveine had been made by Perkin sixteen years before and the aniline dye was in active development. Great interest was therefore aroused by this discovery of Meyer; and before the end of the year Kolbe[34] had announced the production of nitromethane by reaction between sodium nitrite and sodium chloro-acetate. Eight years later Beilstein and Kurbatov[35] found that cyclo-paraffins could be nitrated in the liquid phase. In case of a petroleum fraction boiling at 95° - 100°C, and having a density between that of a paraffin and a cyclo-paraffin of seven carbon atoms, selective nitration was used in a successful effort to purify it from naphthenic components. The nitro-derivative boiled for the most part at 193° to 197°C and had a composition corresponding to the formula $C_7 H_{15}NO_2$. The next two decades witnessed many efforts to find a practical way in which the nitration reaction might be carried out, but it was concluded that the reactions were slow and accompanied by oxidation resulting in poor yields of the nitro compounds so that between 1900 and 1930 relatively little work was done in the field of nitro-paraffins.

The work done in recent years on nitro-paraffins can be divided in two groups:-

A. Work on the nitration of alkanes in the gaseous phase primarily due to Hass and his co-workers[36] of the Purdue University of the United States of America,

and B. work on the nitration of olefines by Levy and Rose[37] of Imperial Chemical Industries, Ltd..

A. Vapour Phase Nitration of Alkanes.

In the United States, Hass and his co-workers[36] have extensively studied the vapour phase nitration of methane, ethane, propane, butanes, pentanes and hexanes, using nitric acid as the nitrating agent. Developments in Great Britain are indicated in the patents assigned to Imperial Chemical Industries.

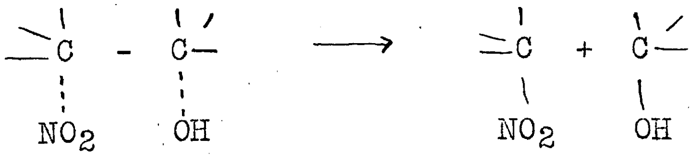
As a result of their work, Hass and his co-workers have made the following generalisations:-

1. On nitration with nitric acid in the vapour phase at temperatures from 350° to 500°C alkanes give all the mono-substitution products which could result if the nitro group is assumed to substitute any hydrogen or any alkyl group, that is, all those possible by C - C rupture or C - H rupture.

2. The vapour phase nitration of lower paraffins at temperatures in excess of 250°C, does not yield di-nitro-paraffins.

A free radical mechanism has been proposed for these nitration reactions which accounts for the specific mono-nitro-paraffins formed in all cases, small amounts of the expected olefines (according to the proposed mechanism) are also found. On the other hand it seems unlikely to explain the proportions of various products, like the production of 27% nitro-methane and 73% nitro-ethane from the nitration of ethane, or the fact that the nitration of iso-butyl chloride leads to mono-nitro derivatives of the parent substance (1 - chloro - 3 nitro - , 1 - chloro - 2 nitro - , 1 - chloro - 1 - nitro - 2 - methyl propane), 1 - chloro - 2-nitro propane and nitro-methane, but no chloro-nitro methane or 2 - nitro-propane. The alternative theory mentioned by Hass of complex formation between nitric acid and the hydrocarbon, for example:-

and



while providing for the formation of alcohols, small amounts of which survive, also fails to explain satisfactorily the formation of the above products.

B. Liquid Phase nitration of Olefines with Nitrogen Tetroxide.

Since the work of A. Semenor[38], over 80 years ago on the reaction between pure ethylene and apparently pure nitrogen tetroxide, persistent attempts have been made to achieve satisfactory preparation of aliphatic nitro-compounds from olefines and oxides of nitrogen and nitric acid, but without any real success[39].

During the last few years Levy and Rose have investigated the addition of nitrogen tetroxide to ethylene, propylene, iso-butene, but - 1 - ene, but - 2 - ene and cyclo-hexane in the liquid phase[37]. They found that the reaction could be best carried out at - 10° to 25°C. Their method consisted in absorbing gaseous olefines in pure dry nitrogen tetroxide, as liquid or concentrated solution the reaction mixture being kept cooled, and liquid olefines by mixing with drop-wise addition. Ethylene was found to react fairly slowly though the higher olefines reacted more rapidly. Propylene, iso-butene and the n. butenes required an ether or ester type of solvent, since otherwise oxidation took place. Oxidation reactions and the interference by nitrogen trioxide addition was avoided by the use of excess of nitrogen tetroxide or where convenient by the addition of oxygen.

The following generalizations were made as a result of the above work:-

1. The addition of nitrogen tetroxide to the double bond can take only two forms:-

   a) as two NO_2 groups to give di-nitro compounds

   b) as one NO_2 group and one O-NO to give nitro-nitrites.

2. Nitro-nitrate is usually formed in small amounts as a result of the oxidation of nitro-nitrite. In presence of oxygen, nitro-nitrate is formed even at the expense of di-nitro compound.

3. In the formation of nitro-nitrites from unsymmetrical olefines (propylene, iso-butene, but - 1 - ene, etc.) the nitro group invariably attaches to the carbon atom with greater number of hydrogen atoms and the nitrite group to the other

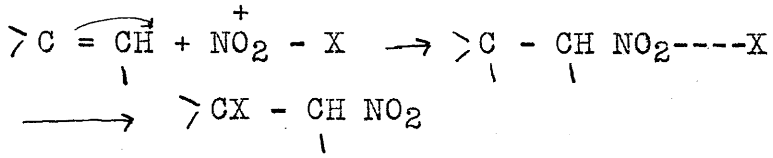
side of the double bond, for example:-

$$CH_3 - CH = CH_2 \xrightarrow{NO_2\ ONO} CH_3\ CH(O(NO)CH_2\ NO_2$$

$$(CH_3)_2\ C = CH_2 \longrightarrow (CH_3)\ \ C(O\ NO)\ CH_2\ NO_2$$

Levy and Rose have suggested that the reaction is electrophilic and concerns the polar forms of nitrogen tetroxide where the initial attack is by the positive nitro group followed by release and attachment of the remaining group as

$- NO_2$ or $- O\ NO$:



$$>C \overset{\frown}{=} \underset{|}{CH} + \overset{+}{NO_2} - X \longrightarrow >\underset{|}{C} - \underset{|}{CH}\ NO_2{-}{-}{-}{-}X \longrightarrow >CX - \underset{|}{CH}\ NO_2$$

$(X = NO_2,\ O\ NO,\ \text{or}\ NO)$

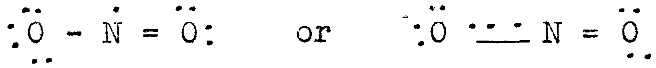
Nitrogen dioxide - Properties and Structure.

Nitrogen tetroxide has long been regarded as an equilibrium mixture, as indicated by the following equation:

$$N_2\ O_4 \rightleftharpoons 2\ NO_2$$

The dimolecular form is predominant at lower temperatures, but vapour density measurements indicate complete conversion to the mono molecular form above 140°C. In appearance nitrogen tetroxide varies from colourless crystals at $-50^{\circ}C$ to black vapour at 183°C; near room temperature the mixture is brown. The colour changes are assumed to be related to the state of the equilibrium. It is believed that above 140°C, nitrogen dioxide decomposes to form nitric oxide and oxygen, a change which is complete at 619.5°C. The boiling point of nitrogen tetroxide, as given in the International Critical Tables is 21.3° at 760 m.m.

Nitrogen dioxide, like nitric oxide, is another simple paramagnetic molecule which has a resonance structure

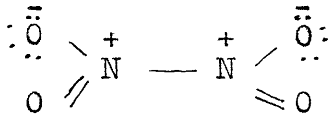


$$:\ddot{\underset{\cdot\cdot}{O}} - \dot{N} = \ddot{O}: \quad \text{or} \quad {}^{-}:\ddot{O} \,\dot{-}\dot{-}\, N = \underset{\cdot\cdot}{O}$$

but it has much greater tendency to dimerize.

The structure of the dimeride, has not been clearly established. Spectral evidence and entropy measurements indicate that the molecule is symmetrical. This is usually taken as indicative of the di-nitro-structure

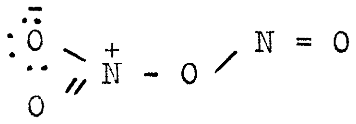
$O_2N - NO_2$ or



I

but since this has two positively charged nitrogen atoms in adjacent positions, it should be less stable than nitro - nitroso structure:

$O_2 N\ ONO$ or



II

Chemical evidence rather favours formula II though nitration with nitrogen tetroxide may be explained by formula I.

Reactions of Nitrogen Dioxide and Paraffin Hydrocarbons.

Urbanski and Slon[40] have made a study of the nitration of methane, propane, n. pentane, n. hexane, n. heptane, n. octane and n. nonane by nitrogen dioxide in the vapour phase at 200°C using a glass apparatus. Yields with methane were reported to be insignificant but the higher hydrocarbons gave mono-nitro derivatives $CH_3\ (CH_2)_n\ NO_2$ and the di-nitro-derivatives $ON_2\ CH_2\ (CH_2)_n\ CH_2\ NO_2$. These products consisted of mostly primary isomers though secondary nitro-paraffins were found to be present in small amounts. Some water soluble oxidation products which do not appear to have been examined, were also reported.

The only other work of significance is of Hass, Hodge and Dorsky[41] who have investigated the action of nitrogen dioxide on propane in the vapour phase at a temperature of 248°C in a Pyrex glass apparatus and at 425° to 600°C in a stainless steel nitrator. At a temperature of 600°C, approximately equal quantities of nitro-methane, nitro-ethane, 1-nitro propane and 2-nitro propane were formed. Lower temperature favoured the formation of 2-nitro propane. At 248°C, a long contact time was necessary for substantially complete reaction of nitrogen dioxide. In addition to the nitro-paraffins mentioned, miscellaneous oxidation products including acids and aldehydes were formed in the products of the reaction but no details have been given about these.

Oxidation Reactions.

The reaction of methane and nitrogen dioxide has been studied at temperatures of 440°C - 680°C, in presence of various catalysts, including platinum, vanadium pentoxide, pumice and nickel by Frolick, Harrington & Waitt[42]. Formaldehyde was produced, yields being about 25% based on methane used. Methanol was not found among the products. Bibb[43] has carried out similar work. The formation of formaldehyde by the action of nitrogen dioxide on methane is the subject of a French patent[44] and a U.S. patent[45.].

Chemists have been attracted by the hope of devising schemes of oxidizing paraffins to aliphatic acids[35]. At best, one could expect a relatively complex mixture. Granacher and Schaufelberger[46] have reported on the oxidation of paraffins when treated with nitrogen dioxide at 140°C for 8 to 10 hours, to give products completely soluble in alkali, but no mention has been made of the nature of these products. Schaarschmidt[47] also has studied the action of nitrogen dioxide on paraffins but the constituents of the complex product were not completely identified.

It was, therefore, considered that the interaction of nitrogen dioxide and iso-pentane warranted further study with respect to the possibilities of both nitration and oxidation of the hydrocarbons taking place and comparing it with the work carried out in the reaction between nitric oxide and iso-pentane and reported above.

PART II.

EXPERIMENTAL.

i, APPARATUS AND PROCEDURE.

At ordinary temperatures, neither nitrogen, dioxide nor nitrogen tetroxide react with iso-pentane. Moreover, iso-pentane and nitrogen tetroxide being mutually soluble, it was decided to study the interaction of these in the vapour phase. For this purpose, the apparatus which is shown in fig. 20. was set up.

The aspirator A3, which contained nitrogen for the vapourisation of nitrogen tetroxide, was connected through the flow-meter F2 to the graduated nitrogen tetroxide vapouriser N, which in turn was connected to the three-way stop-cock S. Similarly the aspirator A, having nitrogen to be used for vapourisation of iso-pentane was connected to the iso-pentane flask I through the flow-meter F1. The flask I. was connected to the three-way stop-cock S.

The arrangement of the apparatus after the stop-cock was same as that used in experiments with nitric oxide and iso-pentane.

Nitrogen from the aspirator A3 was made to pass under a constant pressure through the flow-meter F2 and the nitrogen tetroxide vapouriser N kept in a water bath at a known temperature where it picked up a definite amount of nitrogen tetroxide vapour; to the stop-cock S. There it met the stream of iso-pentane gas and nitrogen coming from the aspirator A1, flow-meter F1 and the flask I.

The concentrations of nitrogen tetroxide and iso-pentane in the inlet gases were adjusted by controlling the rates of flow of nitrogen through the two vapourising flasks and also the temperatures of the baths surrounding these flasks. In making these adjustments due allowance was made for the fact that the combined volume and rate of flow of the inlet gases had to be of such values that the required time of contact with the reaction zone of the silica tube was obtained. Immediately on entering the reaction tube, which was generally maintained at 450°C, nitrogen tetroxide was changed to nitrogen dioxide, so that the reaction which took place was between iso-pentane and nitrogen dioxide.

The mixed stream of the reactants passed from the silica-tube maintained in the electric furnace at a known temperature to the condensing system consisting of two spiral condensers, one kept in ice and the other in drikold. The gases evolved during the reaction were collected over water, in the aspirator A5 fitted with constant head arrangement.

Before each experiment, the apparatus was swept with the reaction mixture for 15-30 minutes to expel oxygen. The condenser C1 was then placed in ice and C2 in drikold, iso-pentane in the flask filled to its mark to enable the exact amount vapourised to be measured accurately, and the aspirator A5 completely filled with water.

The presence of nitrogen dioxide in the reacting gases precluded the use of rubber connections and as far as possible ground glass joints were used. Some difficulty was experienced in obtaining satisfactory connections between the silica-tube and the glass apparatus at either end, but this was finally overcome by the use of Polythene which when warmed, could be moulded to give a tight joint between the silica-tube and the glass apparatus.

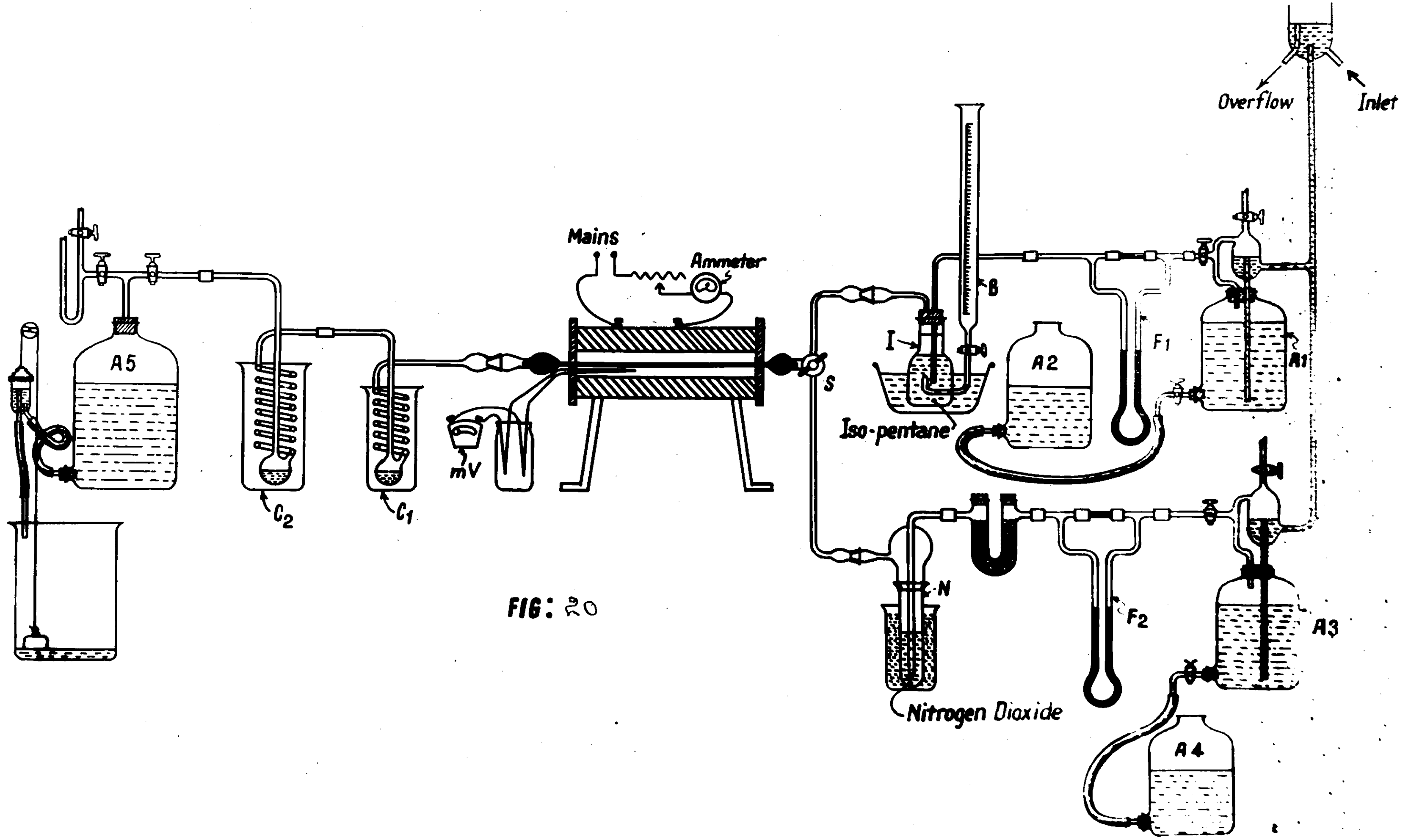

Overflow
Inlet
Mains
Ammeter
A5
C2
C1
mV
S
B
I
A2
F1
A1
Iso-pentane
N
F2
A3
A4
Nitrogen Dioxide

FIG: 20

ii, REACTIONS - GENERAL DISCUSSION.

A few trial runs were made to get a preliminary idea of the temperature to be used for studying the inter-action of iso-pentane and nitrogen dioxide. At 250°C and 300°C, the quantity of the liquid products formed was very small, so that the temperature of 450°C at which the liquid products were found to be in fair yields, was selected for carrying out the experiments. Earlier work on the inter-action of iso-pentane and nitric oxide had shown that at 450°C, there was not any appreciable decomposition of the iso-pentane molecule. The ratio of iso-pentane to nitrogen dioxide used was 4:1.

The products of the reaction consisted of gases as well as liquids. The liquid product formed two distinct layers. The upper layer on distillation gave unreacted iso-pentane and a light blue liquid which on keeping turned pale yellow. This was found to be mostly a mixture of nitro-paraffins. The lower layer was yellow to brown in colour depending on contact time, temperature and concentration of nitrogen dioxide in the reactants; contained oxidation products, oxides of nitrogen and water. Identification of the liquid products will be described in detail later.

The gases produced were analysed as before in the improved Bone and Wheeler Gas Analysis Unit and were found to contain nitric oxide, carbon dioxide, unsaturated hydrocarbons, carbon monoxide and hydrogen. No saturated hydrocarbons could be detected in any of the experiments.

Compared with the experiments on the reaction of iso-pentane and nitric oxide, very little carbon was seen in the silica-tube probably on account of the lower temperatures used; consequently silica tube was made free from carbon only after completing a set of experiments.

A systematic study of the reaction was made by investigating the influence of the following factors:

1. Temperature.
2. Contact times.
3. Variations in the concentrations of iso-pentane and nitrogen dioxide in the reaction mixture.

iii, INFLUENCE OF TEMPERATURE.

To investigate the influence of temperature on the reaction, a number of experiments was made at a 4:1 ratio of iso-pentane to nitrogen dioxide and a contact time of 3.0 seconds. The yields of the liquids as well as of the various gases produced were determined; the result of these experiments are given in Table XIII.

It is seen from the results of the experiments that no saturated hydrocarbons could be found even at temperatures as high as 600°C and with a contact time of 3.0 seconds; this is surprising, as on the basis of earlier work iso-pentane would be expected at 500°C and above to yield saturated hydrocarbons in an appreciable quantity as decomposition products. It means that the free radicals, cleavage products, etc., are being nitrated or oxidized or both as soon as these are formed; only some unsaturated hydrocarbons are left in the gases.

After calculating the yields of carbon dioxide, carbon monoxide, unsaturated hydrocarbons and hydrogen, per c.c. of iso-pentane; curves were drawn showing the yield of these gases with increase in temperature. It was found that the yields of all the gases produced increased with temperature, though the order of the increase of production of hydrogen and unsaturated hydrocarbons is greater than that of the oxides of carbon. The yield of unsaturated hydrocarbons is very high at 450°C and above as compared with the yields at temperatures lower than 450°C.

Curves were also plotted showing the variations in the yields of the liquid products with increase in temperature. These curves show:

1. that the yield of nitro products increases up to 450°C, and at higher temperatures there is a sharp decline. The reduced yields at temperatures above 450°C are probably the result of an increase in the rate of oxidation of the original hydrocarbon or products of the reaction with nitrogen dioxide.

2. the yield of aqueous acidic products increases up to 450°C, but at higher temperatures instead of a sharp decrease as in case of the

nitro-products, the yields show only a slight decrease up to the maximum temperature investigated. Reduction in the yield of this fraction is probably the result of an increase in oxidation to gaseous products and more decomposition of the hydrocarbons, as is seen from the high yields of hydrogen and unsaturated hydrocarbons.

Another factor which is likely to exert its influence at temperatures above 450°C especially when the contact time is long, is the increased dissociation of nitrogen dioxide into nitric oxide and oxygen, resulting in the reduced yields of the liquid products. The percentage nitric oxide found in the gaseous product at 450°C and above, as is seen from Table XIII is very high.

Iso-Pentane and Nitrogen dioxide.

TABLE XIII

Effect of Temperature.

Experiment No.	1	2	3	4
Temperature	250°C	300°C	350°C	400°C
Vol. of nitrogen passed for iso-pentane vapourisation.	2050 cc	2050 cc	2200 cc	2250 cc
Iso-pentane bath temperature.	15°C	15°C	15°C	15°C
Iso-pentane used.	17.2 cc	17.1 cc	17.5 cc	17.8 cc
Vol. of nitrogen used for NO_2 vapourisation.	1000 cc	1050 cc	1200 cc	1150 cc
Temp. of N_2O_4 bath.	8°C	8°C	8°C	8°C
Amount of N_2O_4 used.	2.2 cc	2.1 cc	2.2 cc	2.2 cc
Duration of the run.	180 mins.	180 mins.	180 mins.	180 mins
Time of contact.	3 secs.	3 secs.	3 secs.	3 secs
Vol. of gas collected.	3250 cc	3700 cc	4250 cc	4650 cc
Analysis of the gaseous products of the reaction:-				
NO - %	2.0	3.9	9.0	11.3
CO_2 - %	1.1	1.5	1.5	1.6
C_nH_m - %	0.8	1.5	2.0	2.3
CO - %	-	0.8	1.0	1.0
H_2 - %	5.0	7.0	8.0	9.3
C_nH_{2n+2} - %	-	-	-	-

	1	2	3	4
Yield of the gaseous products of the reaction per c.c. of iso-pentane:-				
CO_2	2.0 cc	3.2 cc	3.6 cc	4.2 cc
$C_n H_m$	1.4 cc	3.2 cc	4.8 cc	5.3 cc
CO	-	1.1 cc	2.3 cc	2.6 cc
H_2	9.0 cc	15.1 cc	18.8 cc	24.2 cc
Liquid products of the reaction:-				
A. Nitro products (yield)	0.4 cc	0.5 cc	0.7 cc	1.0 cc
Yield per 100 cc of iso-pentane of these	2.3 cc	2.9 cc	4.0 cc	5.7 cc
B. Aq. Acidic products (yields)	0.3 cc	0.5 cc	0.7 cc	1.0 cc
Yield per 100 cc of iso-pentane of these	1.74 cc	2.9 cc	4.0 cc	5.7 cc

Iso-pentane and Nitrogen dioxide.

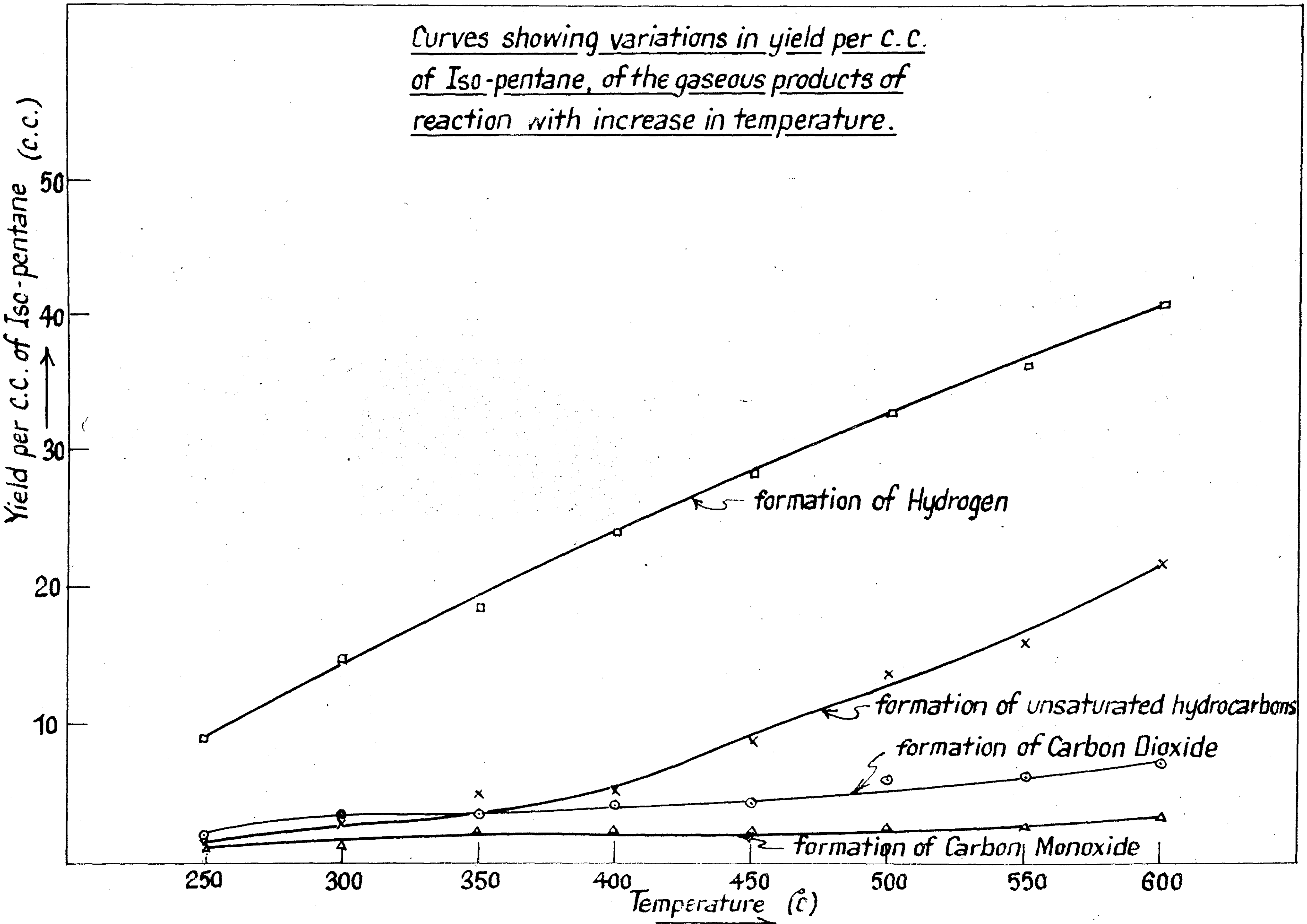
TABLE XIII (continued).

Effect of Temperature.

Experiment No.	5	6	7	8
Temperature	450°C	500°C	550°C	600°C
Vol. of nitrogen passed for iso-pentane vapourisation.	2150 cc	2150 cc	2200 cc	2200 cc
Iso-pentane bath temperature.	15°C	15°C	15°C	15°C
Iso-pentane used.	17.5 cc	17.3 cc	17.5 cc	17.1 cc
Vol. of nitrogen used for NO_2 vapourisation.	1150 cc	1150 cc	1150 cc	1200 cc
Temp. of N_2O_4 bath.	8°C	8°C	8°C	8°C
Amount of N_2O_4 used.	2.1 cc	2.1 cc	2.1 cc	2.2 cc
Duration of the run.	180 mins.	180 mins.	180 mins.	180 min.
Time of contact.	3 secs.	3 secs.	3 secs.	3 secs.
Vol. of gas collected.	4900 cc	5300 cc	5650 cc	6250 cc
Analysis of the gaseous products of the reaction:-				
NO - %	17.5	19.0	17.5	16.1
CO_2 - %	1.5	2.0	2.2	2.2
$C_n H_m$ - %	3.1	4.5	5.0	6.1
CO - %	0.8	1.0	0.8	0.9
H_2 - %	10.2	10.8	11.2	11.2
$C_n H_{2n+2}$ - %	-	-	-	-

	5	6	7	8
Yield of the gaseous products of the reaction per c.c. of iso-pentane:-				
CO_2	4.2 cc	6.1 cc	6.6 cc	7.3 cc
$C_n H_m$	8.7 cc	13.8 cc	16.2 cc	22.0 cc
CO	2.3 cc	3.0 cc	2.6 cc	3.3 cc
H_2	28.5 cc	33.0 cc	36.6 cc	41.0 cc
Liquid products of the reaction:-				
A. Nitro products (yield)	1.1 cc	.6 cc	0.3 cc	0.2 cc
Yield per 100 c.c. of iso-pentane of these.)	6.3 cc	3.4 cc	1.7 cc	1.2 cc
B. Aq. Acidic products (yields)	1.2 cc	1.1 cc	1.0 cc	0.8 cc
Yield per 100 c.c. of iso-pentane of these.)	6.85 cc	6.4 cc	5.7 cc	4.7 cc

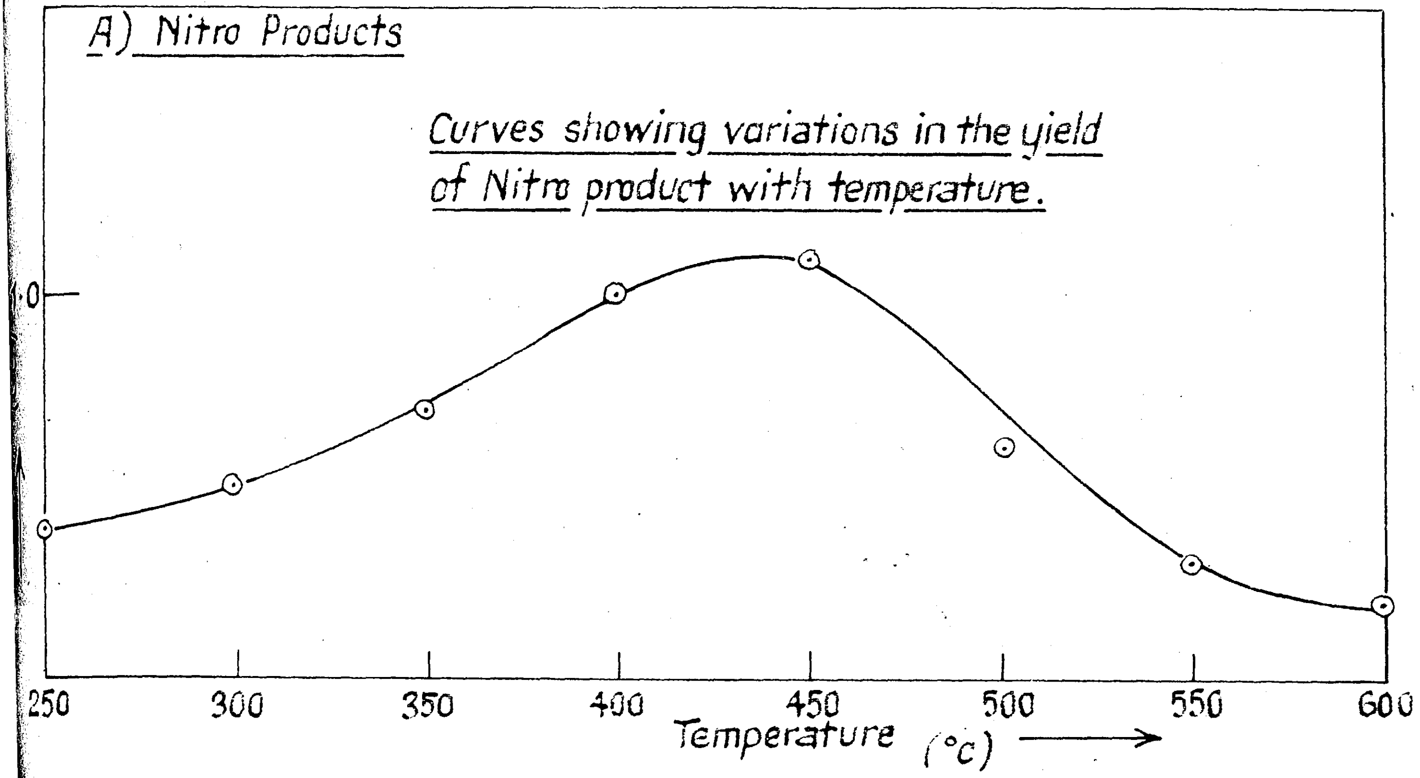
ISO-PENTANE AND NITROGEN DIOXIDE — EFFECT OF TEMPERATURE



Curves showing variations in yield per C.C. of Iso-pentane, of the gaseous products of reaction with increase in temperature.

Fig. 21

ISO-PENTANE AND NITROGEN DIOXIDE EFFECT OF TEMPERATURE



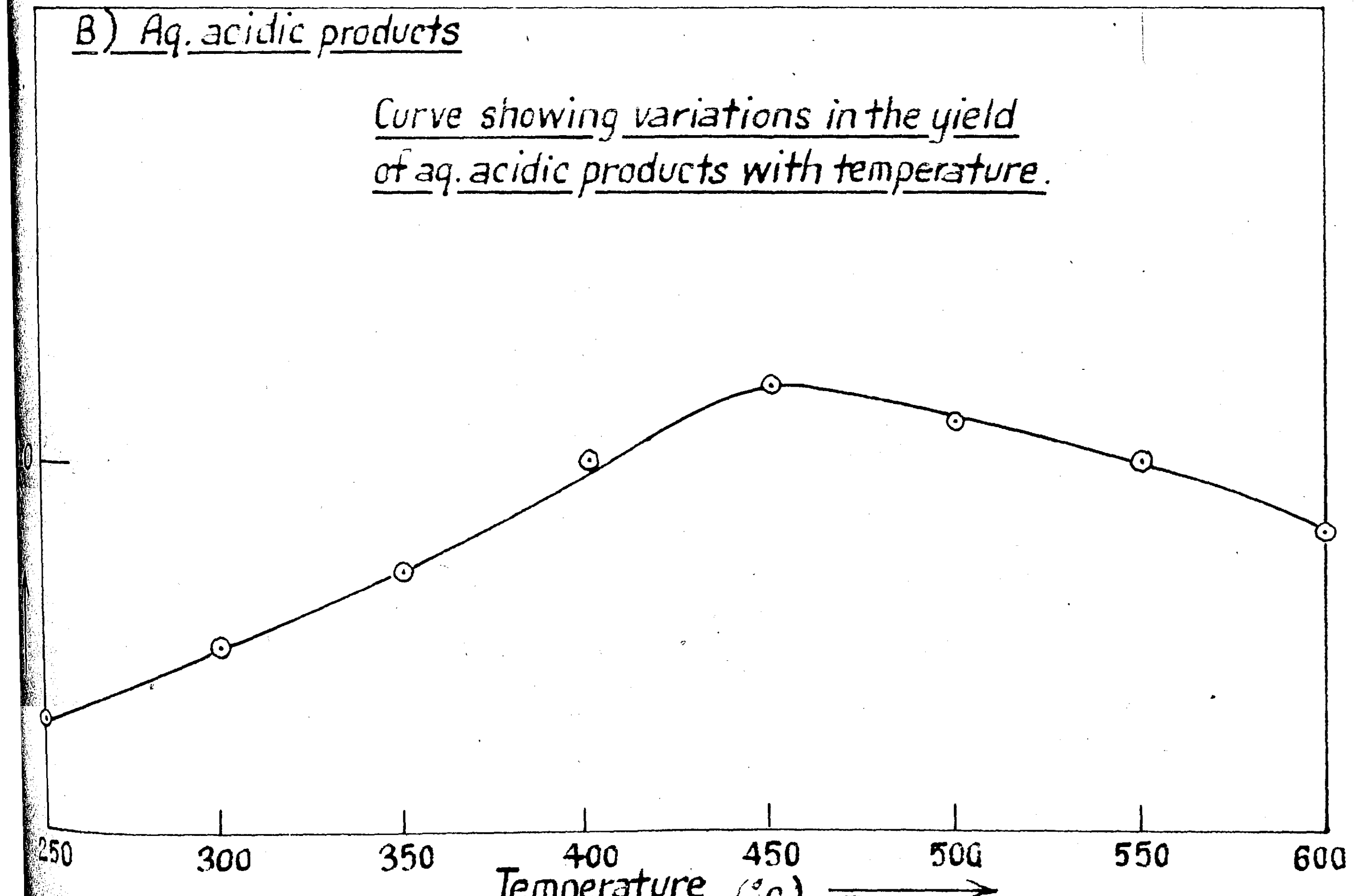


Fig. 22.

iv, INFLUENCE OF TIME OF CONTACT.

Experiments were made at 450°C (the temperature which was found to be most suitable for the formation of liquid products) with varying times of contact from 0.31 second to 3.0 second. The rates of flow of nitrogen through the flow-meters F1 and F2, were carefully calculated so that, though the rate of passage of the reaction mixture was varied to get different times of contact, the ratio of iso-pentane to nitrogen dioxide was kept the same, that is, 4:1. The results of these experiments are given in Table XIV.

GASEOUS PRODUCTS.

The gases produced were found to be nitric oxide, carbon dioxide, unsaturated hydrocarbons, carbon monoxide and hydrogen. No saturated hydrocarbons were found. Yields of the gases produced were calculated per c.c. of iso-pentane and curves drawn (fig. 23) showing variations in the yields of these gases with increase in contact times. These show:

1. An increase in the production of carbon dioxide with increase in contact times.

2. An increase in the yield of carbon monoxide up to a contact time of 1.5 second. A little decrease in the yield is seen for the contact time of 3.0 seconds.

3. With an increase in contact time up to 1 second, an increase in the yield of the unsaturated hydrocarbons results; further increase in contact time results in a decreased yield.

4. The yield of hydrogen shows a considerable increase, with increase in contact time.

LIQUID PRODUCTS.

The amount of the liquid products formed, both nitro as well as aqueous acidic were calculated per 100 c.c. of iso-pentane vapourised. Curves were plotted showing the variations in the amounts produced with increase in times of contact (fig. 24). These indicate:

1. The production of nitro compounds

increases only up to a contact time of about 1 second, then decreases with further increase in the contact time.

2. The yield of the aqueous acidic products rises steadily with increase in time of contact.

Iso-pentane and Nitrogen Dioxide.

TABLE. XIV

EFFECT OF TIME OF CONTACT.

Experiment No.	1.	2.	3.
Temperature.	450°C	450°C	450°C
Vol. of Nitrogen passed for (iso-pentane vapourisation)	2150 cc	2000 cc	1600 cc
Iso-pentane bath temp.	15°C	20°C	20°C
Iso-pentane used.	17.5 cc	20 cc	22.3 cc
Vol. of Nitrogen passed for NO_2 vapourisation ( )	1150 cc	925 cc	610 cc
Temp. of N_2O_4 bath	8°C	12°C	15°C
Amt. of N_2O_4 used	2.1 cc	2.8 cc	3.3 cc
Duration of the run	180 min.	150 min.	90 min.
Time of contact	3.0 secs.	1.5 secs.	0.9 secs.
Vol. of gas collected	4900 cc	4600 cc	4000 cc

Analysis of the gaseous products of reaction.

		1.	2.	3.
NO	%	17.5	15.0	24.7
CO_2	%	1.5	0.6	1.0
C_nH_m	%	3.1	2.6	8.5
CO	%	0.8	2.0	-
H_2	%	10.2	8.5	5.2
C_nH_{2n+2}	%	-	-	-

Yield of the gaseous products per c.c. of Iso-pentane.

	1.	2.	3.
CO_2	4.2 cc	1.4 cc	1.8 cc
C_nH_m	8.7 cc	6.0 cc	15.2 cc
CO	2.3 cc	4.6 cc	-
H_2	28.5 cc	19.5 cc	9.3 cc

Liquid products - Yields per 100 cc iso-pentane.

		1.	2.	3.
A.	Nitro products	6.3 cc	9.0 cc	10.8 cc
B.	Aq-acidic products	6.8 cc	4.0 cc	3.4 cc

Iso-pentane and Nitrogen Dioxide.

TABLE. XIV

EFFECT OF TIME OF CONTACT.

Experiment No.		4.	5.
Temperature		450°C	450°C
Vol. of Nitrogen passed for iso-pentane vapourisation		1400 cc	1150 cc
Iso-pentane bath temp.		22°C	22°C
Iso-pentane used		22.0 cc	19.7 cc
Vol. of Nitrogen passed for NO_2 vapourisation		420 cc	380 cc
Temp. of N_2O_4 bath		16°C	17°C
Amt. of N_2O_4 used		3.0 cc	3.0 cc
Duration of the run		45 min.	25 min.
Time of contact		0.5 secs.	0.31 secs.
Vol. of gas collected		3100 cc	2675 cc
Analysis of the gaseous products of reaction.			
NO	%	25.8	22.8
CO_2	%	1.1	-
C_nH_m	%	6.7	7.1
CO	%	1.3	0.7
H_2	%	1.6	2.1
C_nH_{2n+2}	%	-	-

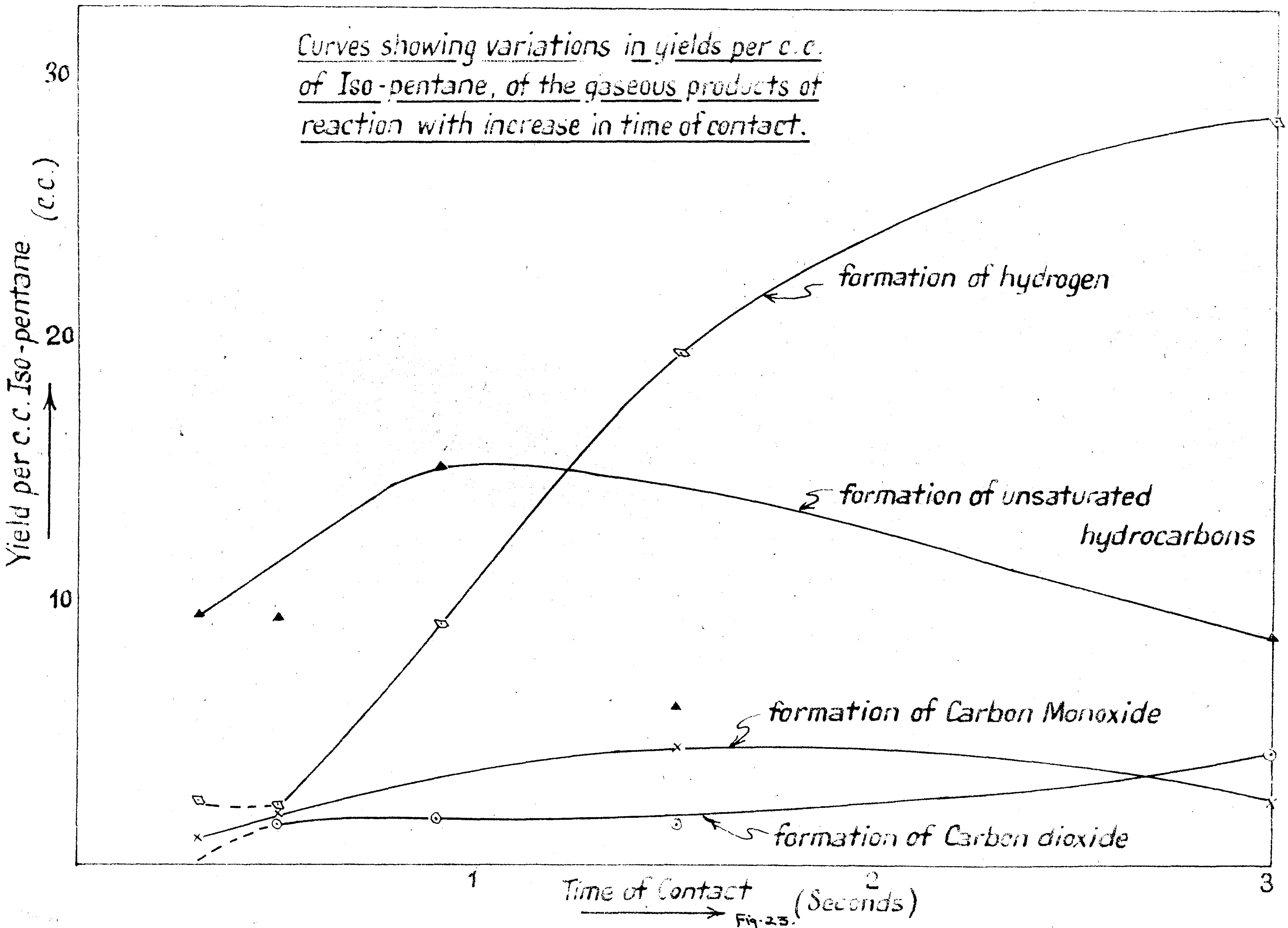
Yield of the gaseous products per c.c. of iso-pentane.

	4.	5.
CO_2	1.5 cc	-
C_nH_m	9.4 cc	9.6 cc
CO	1.8 cc	0.96 cc
H_2	2.2 cc	2.8 cc

Liquid products - Yields per 100 cc iso-pentane.

A.	Nitro products	8.2 cc	7.1 cc
B.	Aq. Acidic products	4.5 cc	3.1 cc

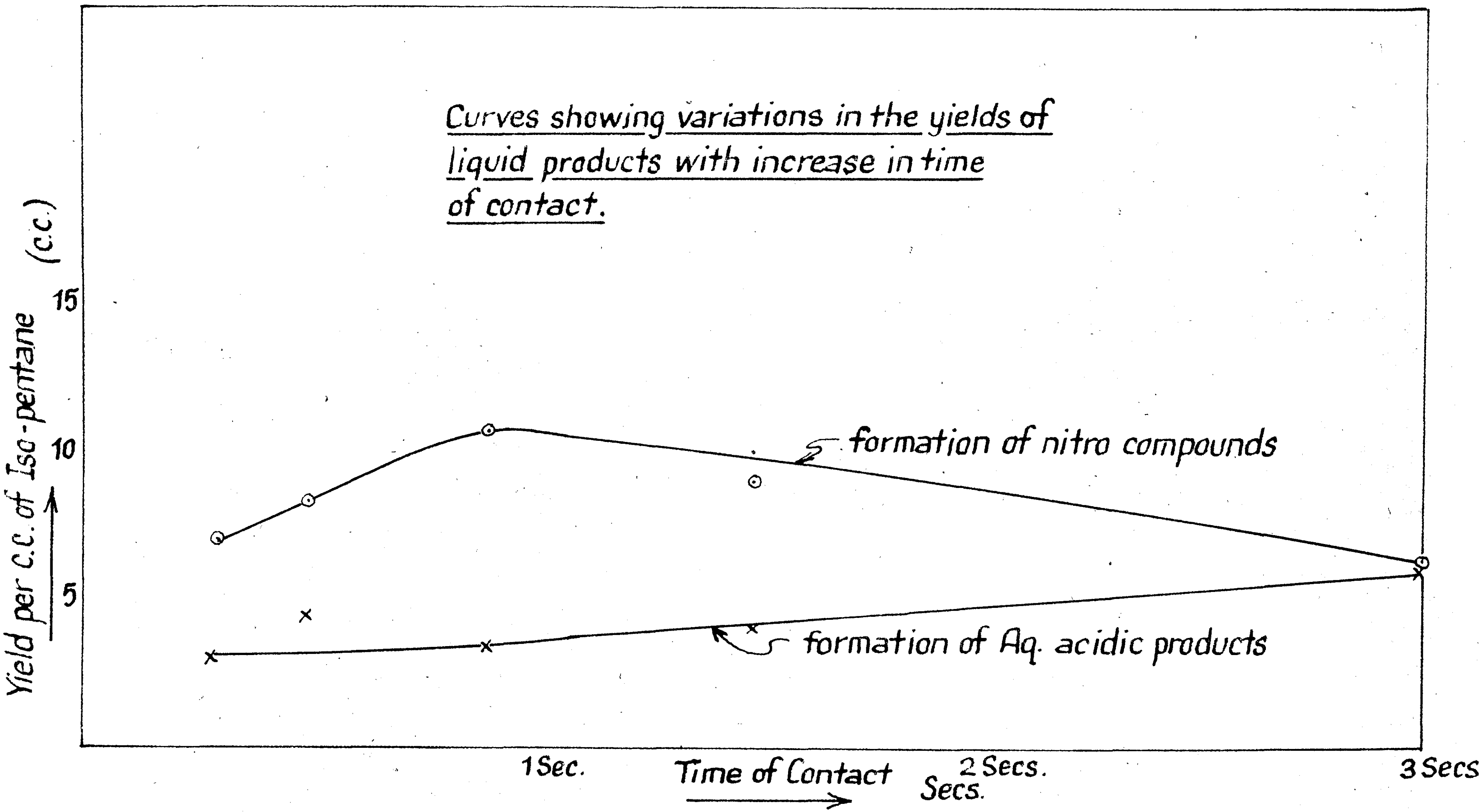
ISO-PENTANE AND NITROGEN DIOXIDE



Curves showing variations in yields per c.c. of Iso-pentane, of the gaseous products of reaction with increase in time of contact.

Fig. 23.

ISO-PENTANE AND NITROGEN DIOXIDE



Curves showing variations in the yields of liquid products with increase in time of contact.

Fig. 24.

v, INFLUENCE OF COMPOSITION OF REACTING MIXTURE.

After examining the influence of temperature and of the time of contact, a set of experiments at 450°C, was made to study the influence of variations in the composition of the reacting mixture. The rates of vapourisation of iso-pentane and nitrogen tetroxide were so arranged that though the ratio of iso-pentane to nitrogen dioxide was varied for the various experiments, the total volume of reaction mixture passing through the reaction tube was kept the same, to obtain a time of contact 1.5 second in each of the experiments. The proportions of iso-pentane to nitrogen dioxide used varied from 12:1 to 13:1. The results of the experiments are given in Table XV .

GASEOUS PRODUCTS.

As before the gases produced consisted of nitric oxide, carbon dioxide, unsaturated hydrocarbons, carbon monoxide and hydrogen. Yields of these gases per c.c. of iso-pentane vapourised, were calculated and curves were drawn showing the variations in the yields with varying concentration of iso-pentane (fig.25). These show increased yields of all of the gases with decrease in concentration of iso-pentane in the reaction mixture.

LIQUID PRODUCTS.

The amounts of the liquids obtained in the various experiments were estimated, as previously, as the total nitro-products and the total aqueous acidic products. Yields of these per 100 c.c. of iso-pentane were calculated and the curves plotted showing the variations in the yields with varying proportions of iso-pentane (fig.25). These indicate a considerable increase in the yields of the nitro products as well as of the aqueous acidic products with decrease in the concentration of iso-pentane in the reaction mixture, up to the limits investigated.

Iso-pentane and Nitrogen Dioxide.

TABLE XV

EFFECT OF VARYING PROPORTIONS OF ISO-PENTANE.

Experiment No.	1.	2.	3.
Temperature	450 C	450 C	450 C
Vol. of Nitrogen passed for iso-pentane vapourisation	2300 cc	1750 cc	2300 cc
Iso-pentane bath temp.	20 C	20 C	20 C
Iso-pentane used	33.2 cc	22.4 cc	28.2 cc
Vol. of Nitrogen passed for NO_2 vapourisation	820 cc	940 cc	890 cc
Temp. of N_2O_4 bath	8 C	8 C	10 C
Amt. of N_2O_4 used	1.4 cc	1.5 cc	2.5 cc
Duration of the run	150 min.	150 min.	150 min.
Time of contact	1.5 sec.	1.5 sec.	1.5 sec.
Vol. of gas collected	3350 cc	2800 cc	3050 cc
Percentage iso-pentane	92.5	89.0	86.0

Analysis of the gaseous products of reaction.

		1.	2.	3.
NO	%	8.3	12.8	19.1
CO_2	%	1.0	2.0	4.9
C_nH_m	%	2.0	2.8	1.4
CO	%	1.5	0.5	-
H_2	%	10.0	7.9	6.5
C_nH_{2n+2}	%	-	-	-

Yield of the gaseous products of iso-pentane.

	1.	2.	3.
CO_2	1.0 cc	2.5 cc	5.3 cc
C_nH_m	2.0 cc	3.5 cc	1.6 cc
CO	1.5 cc	0.62 cc	-
H_2	10.0 cc	9.9 cc	7.0 cc

Liquid products - Yields per 100 cc iso-pentane.

A. Nitro products	1.8 cc	4.5 cc	3.9 cc
B. Aq. acidic products	0.3 cc	2.2 cc	2.1 cc
Ratio of (Iso:NO)	12:1	8:1	6:1

Iso-pentane and Nitrogen Dioxide.

TABLE XY

EFFECT OF VARYING PROPORTIONS OF ISO-PENTANE.

Experiment No.	4.	5.	6.
Temperature	450 C	450 C	450 C
Vol. of Nitrogen passed for (iso-pentane vapourisation)	2000 cc	1600 cc	1700 cc
Iso-pentane bath temp.	20° C	18° C	15° C
Iso-pentane used	20.0 cc	16.1 cc	16.0 cc
Vol. of Nitrogen passed (for NO_2 vapourisation)	925 cc	1035 cc	1090 cc
Temp. of N_2O_4 bath	12° C	13° C	15° C
Amt. of N_2O_4 used	2.8 cc	5.5 cc	6.5 cc
Duration of the run	150 min.	150 min.	150 min.
Time of contact	1.5 sec.	1.5 sec.	1.5 sec.
Vol. of gas collected	4600 cc	5600 cc	6200 cc
Percentage iso-pentane	80.0	61.5	56.5

Analysis of the gaseous products of the reaction.

NO	%	15.0	29.8	32.4
CO_2	%	0.6	2.0	3.2
C_nH_m	%	2.6	5.0	4.9
CO	%	2.0	0.4	1.1
H_2	%	8.5	7.0	6.6
C_nH_{2n+2}	%	-	-	-

Yield of the gaseous products of iso-pentane.

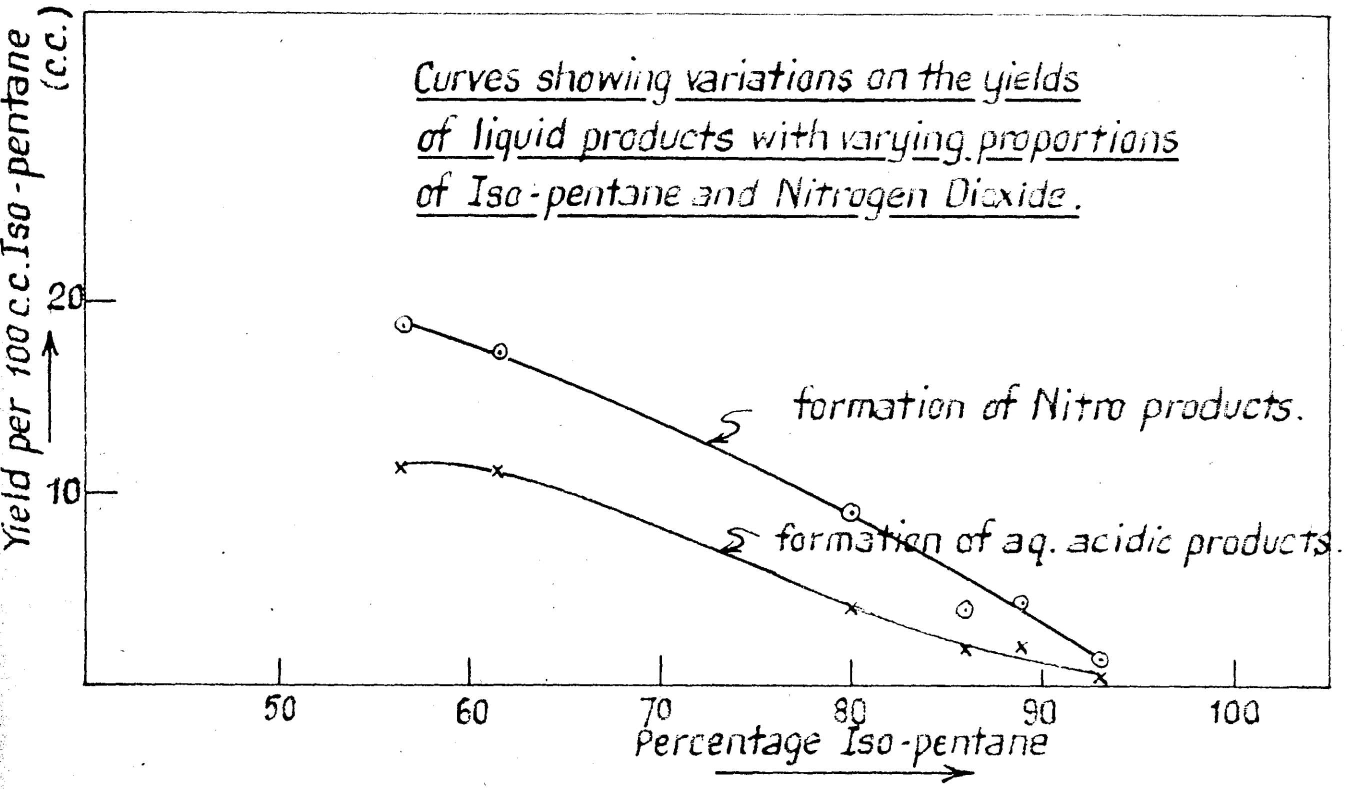
	4.	5.	6.
CO_2	1.4 cc	6.9 cc	12.3 cc
C_nH_m	6.0 cc	17.5 cc	19.0 cc
CO	4.6 cc	1.4 cc	4.2 cc
H_2	19.5 cc	24.0 cc	27.0 cc

Liquid products - Yields per 100 cc iso-pentane.

A. Nitro products	9.0 cc	17.4 cc	18.7 cc
B. Aq. acidic products	4.0 cc	11.2 cc	11.2 cc

Ratio of (Iso:NO)	4:1	1.6:1	1.3:1

ISO-PENTANE AND NITROGEN DIOXIDE


Curves showing variations on the yields of liquid products with varying proportions of Iso-pentane and Nitrogen Dioxide.

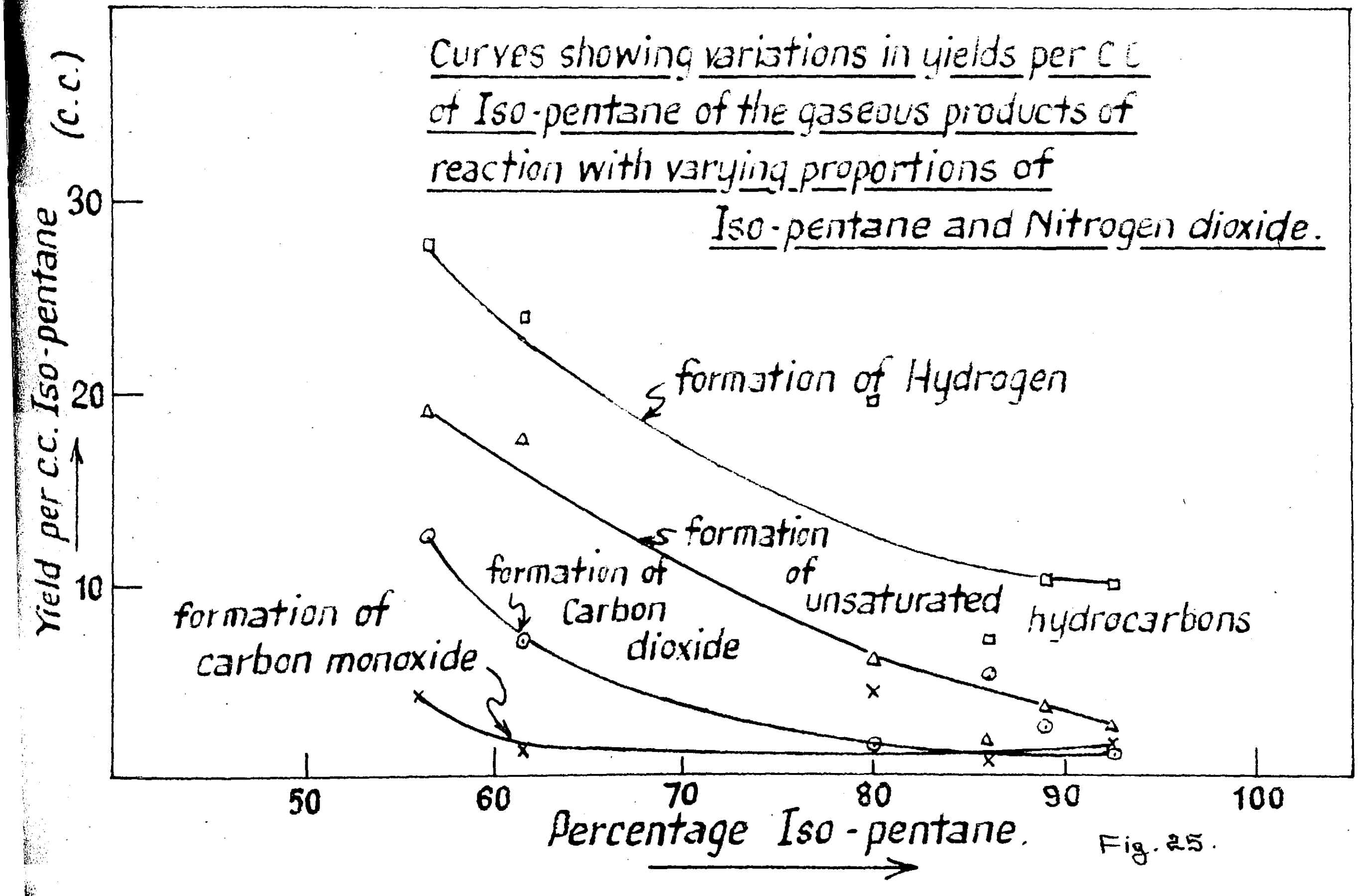

Curves showing variations in yields per c.c of Iso-pentane of the gaseous products of reaction with varying proportions of Iso-pentane and Nitrogen dioxide.

Fig. 25.

vi. IDENTIFICATION OF THE LIQUID PRODUCTS OF THE REACTION.

As mentioned earlier, the liquid products were obtained in two distinct layers:

I. Upper layer - light blue to pale yellow in colour.

II. Lower layer - varied in colour from pale yellow to brown.

Identification of these layers is described below:

The upper layer after washing with a dilute solution of sodium carbonate to remove the oxides of nitrogen and water was distilled. It was found to consist of unreacted iso-pentane, b.pt. 27-29°C and some nitro-products. When sufficient of these nitro-products had been collected, they were fractionated in a column packed with Fenske helices. A little boric acid (1 in 1,000) was added to prevent possible decomposition[48]. The fractions collected were:

A. Distilling Range - 78° - 82°C.
B. Distilling Range - 98° - 102°C.
C. Distilling Range - 112° - 115°C.
D. Distilling Range - 120° - 128°C.
E. Distilling Range - 140° - 143°C.
and F. Residue.

The yields of fractions A to D were rather small compared with that of fraction E or the quantity of the residue left in the flask.

After the fraction E at 143°C, no further fraction could be obtained. A little charring of the products was seen throughout the fractionation but a rapid increase in charring was noticed after the fraction D had been obtained. In order to avoid the charring and in an effort to obtain some additional fractions, an attempt was made to fractionate the nitro-products (Upper layer) under reduced pressure but without success.

Analytical Examination of the above fractions.

I. General.

1. Detection of nitrogen.

Nitrogen was found to be present in each of the above fractions including the residue, by applying the Lassaigne test.

2. Nitroso group.

Its absence was established by applying Liebermann's reaction which consisted in treating about 0.1 gm of the substance with an equal quantity of phenol and about 2 c.c. of sulphuric acid. Nitroso compound gives a blue colour which on pouring into water changes to red and on addition of sodium hydroxide solution changes back to blue. No such colour was produced. All the fractions gave a negative indication.

3. Nitro group.

The presence and the nature of nitro group was established by the following tests:-

a) Action of alkali.

Compounds containing primary and secondary nitro groups dissolve in alkali and are regenerated on acidification.

b) Bose's Method[49].

It depends on the hydrolysis of nitro compounds to yield nitrous acid

$$R\,NO_2 + HO\,H \text{ (alkali)} \longrightarrow R\,OH + H\,NO_2$$

which can be detected by Greiss-Ilosvay's reagent. This reagent is said to have a sensitiveness of 1 in 1,000,000,000 and was prepared by mixing 0.5 gm sulphanilic acid + 150 c.c. of 2 N acetic acid with a colourless solution of 0.1 gm of pure a-naphthylamine in 20 c.c. of boiling water.

In carrying out the test, a small quantity (0.01 to 0.05 gm) of the substance was boiled in a Pyrex test-tube with 1 c.c. of a concentrated solution of potassium hydroxide (10 gms in 6 c.c. H_2O) for a period not exceeding 2 minutes. The colour of the solution deepened during boiling and finally a yellow to dark brown product was obtained. The test-tube was then cooled and about 1 c.c. of water added. A few drops of this alkaline solution were acidified with about 1 c.c. of 50% acetic acid and then treated with about 0.5 c.c. of Greiss-Ilosvay's reagent. The development of a rose red colour indicated the presence of free $H\ NO_2$ and indirectly that of a nitro group in the substance taken.

c) Hearon and Gustavson's Method[50].

This method is based on the oxidation of ferrous hydroxide to ferric hydroxide in presence of a nitro compound. The test is not applicable in presence of nitroso compounds, aliphatic nitrites and nitrates, quinones or hydroxylamine.

Two solutions are required:-

1. Iron solution.

250 c.c. of distilled water was boiled for 15 minutes to remove any dissolved air. After cooling 12.5 gms of ferrous ammonium sulphate and 2 c.c. of concentrated sulphuric acid were added.

2. Base solution.

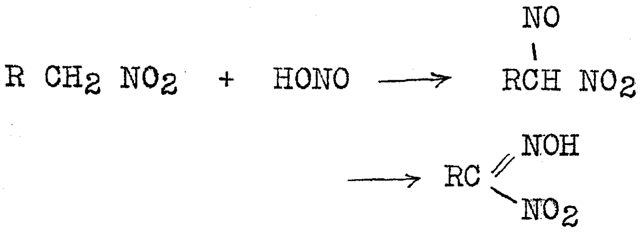
30 gms of caustic potash were dissolved in 30 c.c. of distilled water and then added to 200 c.c. of 95% alcohol.

To carry out the test, 0.7 c.c. of the iron solution was pipetted into a small test-tube and a little quantity (10m gm) of the unknown added. Then 0.5 c.c. of the base solution was added and stream of nitrogen passed through the test-tube to remove air. The tube was quickly stoppered and shaken. A positive test was indicated by the formation of a red-brown to brown precipitate of ferric hydroxide within about 2 minutes.

d) <u>Action of nitrous acid (Victor Meyer's)</u>[51].

Although this is only of historical importance for classifying the alcohols as primary, secondary or tertiary by conversion to the iodide and then to the nitro-derivative which is treated with nitrous acid; the last step is considered of great value in determining the nature of nitro group in case of aliphatic nitro compounds. The action of HNO_2 is as follows:-

1. With primary nitro



$$R\,CH_2\,NO_2 + HONO \longrightarrow RCH(NO)NO_2 \longrightarrow RC(=NOH)NO_2$$

Nitrolic Acid (salts are red)

2. With secondary nitro

$$R_2\,CH\,NO_2 + HONO \longrightarrow R_2C(NO)(NO_2)$$

Pseudo-nitrole (blue)

3. With tertiary nitro

$$R_3\,C\,NO_2 + HONO \longrightarrow \text{No reaction}$$

The test was carried out by dissolving a few drops of the nitro group in a concentrated solution of sodium hydroxide and adding excess of sodium nitrite solution. Upon cautious acidification with dilute sulphuric acid, added dropwise, production of a red colour indicated a primary nitro group and of a blue colour the presence of a secondary nitro group.

e) Reduction to amines.

The presence of the nitro group can be detected by the reduction of the compounds having nitro group, with acid reducing agents, to amines. The possibility of secondary and tertiary amines formation by condensation must also be considered.

The reduction to amines also helps in the characterization of the nitro groups as a mixture of amines can be easily separated into primary, secondary or tertiary amines by treatment with benzene sulphonyl chloride or p. toluene sulphonyl chloride in presence of dilute sodium hydroxide[52]. The reactions involved are:-

1. With primary amines

$$RNH_2 + Cl\,SO_2\,C_6\,H_5 \xrightarrow{Na\,OH} R.N\,(Na)\,SO_2\,C_6\,H_5$$

(water soluble)

$$\xrightarrow{H\,Cl} RNH\,SO_2\,C_6\,H_5$$

(water insoluble)

2. With secondary amines

$$R_2\,NH + Cl\,SO_2\,C_6\,H_5 \xrightarrow{Na\,OH} R_2\,N\,SO_2\,C_6\,H_5$$

(insoluble in alkali)

3. With tertiary amines

$$R_3\,N + Cl\,SO_2\,C_6\,H_5 \longrightarrow \text{No reaction.}$$

The tertiary amines can be isolated by steam distillation or by solvent extraction.

The reduction of the nitro-products was carried out by treating about 1 c.c. of the products with 3 gms of granulated tin in a 100 c.c. flask. About 20 c.c. of dilute hydrochloric acid (1:1) was added gradually with thorough shaking. After about

10 minutes of the addition of acid, the mixture was refluxed for approximately two hours at 100°C. A trap containing hydrochloric acid was arranged to absorb any amines which might pass through the condenser while refluxing. The flask was cooled after refluxing and the contents made alkaline with 20 - 40% sodium hydroxide solution. The liberated amines were then extracted by ether and treated with p. toluene sulphonyl chloride for characterization.

f) Davidson's Indicator Method[53].

This method is useful in determining the presence of a tertiary nitro-derivative and the absence of primary and secondary nitro groups, after establishing the presence of a nitro group in the compound. The procedure adopted consisted of adding a drop of the sample to be tested, to 1 c.c. of the indicator A (described below) which was red in colour to establish the presence of an acidic group. The colour changes produced were compared with those given in the table below. Then a drop of the sample found to be acidic was treated with 1 c.c. of indicator B to classify the acidic group present. If the colour did not change or was converted to yellow, dichromate purple, or red, it would depend on whether the acidic group was weak, or intermediate or strong. Primary and secondary nitro-paraffins are classified as weak acids (pH 8 - 12); the tertiary do not show any acidic reaction.

TABLE XVI

	Strong Acid	Intermediate Acid.	Weak Acid	Non-acid.
Indicator A.	Yellow		Green	Purple
Indicator B.	Red	Yellow	Blue-Voilet	

Stock solutions of indicator A and B were prepared by mixing the following in proportions given:

	Indicator A.	Indicator B.
Bromothymol blue in CH_3 OH (0.1%)	25 c.c.	25 c.c.
2 M. KOH in CH_3 OH	25 c.c.	25 c.c.
CH_3 OH	425 c.c.	887.5 c.c.
Alizarin-Yellow R in CH_3 OH (0.1%)	25 c.c.	-
Pyridine.	500 c.c.	-
Thymol blue in CH_3 OH (0.1%)	-	25.0 c.c.
Bromo-Cresol purple in CH_3 OH (0.1%)	-	37.5 c.c.

II. Examination of each individual fraction.

Fraction A. (b.pt. 78° - 82°C).

The fraction was found to contain a primary nitro group, no other functional group was found.

Fraction B. (b.pt. 98° - 102°C)

Positive evidence of the presence of primary nitro group was obtained and the boiling point indicated the substance to be nitro-methane (B.pt. Nitro-methane, 101°C); this was confirmed by the following tests:-

1. Refractive Index Determination.

The fraction was redistilled and the refractive index determined by Abbe's Refractometer at 20°C.

$$n_D^{20} \quad \text{(Fraction B)} = 1.3835$$

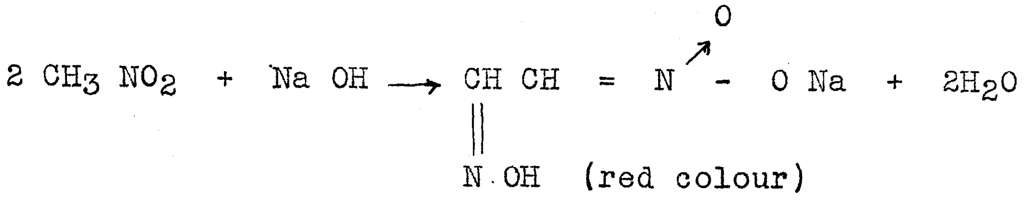
$$n_D^{20} \quad \text{(Nitro-methane)} = 1.3818$$

2. Rosenthaler Test[54].

The test consists in heating the unknown substance with ammonium hydroxide and vanillin. In presence of nitro-methane, a red colour develops which disappears on cooling. The fraction B gave a positive indication.

3. On treating a portion of the fraction B with concentrated solution of sodium hydroxide, a red colour was developed due to the formation of

sodium salt of methazonic acid.



$$2\ CH_3\ NO_2 + Na\ OH \longrightarrow \underset{\underset{N\cdot OH}{\|}}{CH}\ CH = \overset{\overset{O}{\nearrow}}{N} - O\ Na + 2H_2O$$

(red colour)

Fraction C (b.pt. 112° - 115°C)

This fraction was also found to contain a primary nitro group. The boiling point of the fraction corresponds to that of nitro-ethane which is 114°C. The identity was confirmed by redistillation and the determination of the refractive index.

Refractive index as determined of fraction C - 1. 3895.

Refractive index of pure nitro-ethane - 1.3916

Another confirmatory test[55] used was based on the formation of a persistent pink colour when an excess of hydrochloric acid containing ferric chloride was added to an alkaline solution of nitro-ethane. According to Scott and Treon[55] stable coloured complexes were also formed by 1 - nitro propane and 1 - nitrobutane while 2 - nitropropane and 2 - nitrobutane gave colours which faded rapidly. Nitro-methane did not react.

The procedure adopted consisted in treating a few drops of the fraction C in about 5 c.c. of water with 1.5 c.c. of a 20% solution of sodium hydroxide in a 25 c.c. flask. After allowing to stand for 15 minutes, the solution was acidified with 6.0 c.c. of dilute hydrochloric acid (diluted 1 in 7) and 0.5 c.c. of 10% ferric chloride solution added immediately after. A pink colour was produced which did not fade showing the presence of nitro-ethane.

Fraction D. (b.pt. 120° - 128°C)

A secondary nitro group ($-CH\,NO_2$) was found to be present. The boiling point and the presence of secondary nitro-group showed it to be 2 - nitro-propane (b.pt. 2 - nitro-propane, 120.8°C). It was confirmed by the determination of the refractive index.

Refractive index as determined of the redistilled fraction.	1.3930
Refractive index of 2 - nitro-propane.	1.3941

Fraction E. (b.pt. 140° - 143°C).

The fraction E was found to be a mixture of nitro-paraffins. When an alkaline solution of a portion of the fraction with sodium nitrite was treated with a little sulphuric acid (Victor-Meyer's reaction), the red colour of nitrolic acid salts as well as the blue colour of pseudo-nitrole were produced. The identity of the nitro compounds was established by reduction of a small amount of the fraction with tin and hydrochloric acid. (See page 171) The amines produced were extracted with ether. For separation, the amines were treated with p. toluene sulphonyl chloride (Hinsberg's Method). After cooling, the mixture was treated with ether and shaken vigorously. The ether layer would be expected to contain the unchanged tertiary amines and the sulphonamide of the secondary amine. No tertiary amine was found since extraction of the ether layer with hydrochloric acid followed by the addition of excess alkali to the acid extract, no precipitate was produced.

The sulphonamide of the secondary amine was obtained, by distilling off the ether from the ether layer. It was recrystallised from alcohol. The melting point was found out to be 53° - 55°C showing the secondary amine to be 2 - aminobutane which meant that the nitro compound present was 2 - nitrobutane.

The alkaline aqueous layer was made acid with hydrochloric acid; a precipitate was formed which was filtered off and recrystallised from dilute alcohol. The melting point was experimentally determined to be 77° - 78°C which corresponds to that of the p. toluene sulphonamide of iso-butylamine, indicating the presence of iso-nitrobutane in the fraction E. Thus fraction E contained 2 nitro-butane and iso-nitrobutane.

Fraction F. (Residue).

The residue was a light brown and very viscous though clear liquid. No other functional group besides a primary nitro was found to be present.

To summarize, the nitro-paraffins found were:-

	1.	Nitro - methane	$CH_3\ NO_2$
	2.	Nitro - ethane	$CH_3.CH_2\ NO_2$
	3.	2 - nitro-propane	$CH_3.CH\ NO_2.CH_3$
	4.	2 - nitro-butane	$CH_3.CH\ NO_2.CH_2.CH_3$
and	5.	iso - nitrobutane	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.NO_2$

II. Identification of the products of reaction present in the lower layer.

The lower layer varied in colour from pale yellow to brown and was found to consist mostly of water, oxides of nitrogen and some oxidation products. On distilling, most of the liquid distilled off at 98° - 110°C leaving a brown viscous residue similar in appearance to the one left by the upper layer after distillation of the nitro-paraffins. Nitrogen was found to be absent when the residue was examined for its presence.

A systematic qualitative examination of the products for the presence of various functional groups, showed only the presence of ketonic and carboxylic groups. Identification of the compounds containing ketonic and carboxylic groups present in the reaction products was carried out as described below:-

1. Ketonic group.

A portion of the products was heated to boiling with 0.25 gm of 2:4 di-nitrophenyl hydrazine in 15 c.c. of methyl alcohol, cooled and 0.5 c.c. of concentrated hydrochloric acid added. The reaction mixture was boiled again for a few minutes and allowed to cool to crystallise the di-nitro-phenyl hydrazone, which was filtered off and recrystallised from dilute alcohol. The melting point was found to be 127°, showing the ketone present to be acetone (m.pt. of di-nitro-phenyl hydrazone of acetone, 128°C).

Carboxylic group.

Great difficulty was experienced in the identification of the carboxylic acids on account of the large amount of water present. Attempts to prepare amides, anilides or toluides of the acids present were not successful probably on account of the small quantity of the acids present and the dilution in which these were present. S - Benzyl - iso - thiuronium salts, p. Phenyl-phenacyl esters or p. Bromophenacyl esters could not be prepared as the required reagents were not available at the time, so an indirect method was adopted which consisted in preparing the barium salts of the acids present by treating a portion of the products with barium hydroxide solution. The precipitate of the barium salts was filtered off, washed and treated with methyl alcohol and a little sulphuric acid to prepare the methyl esters. On distillation of the esters, the following 3 fractions were collected:-

1. boiling point 55° - 57°C
2. boiling point 64° - 65°C
3. boiling point 76° - 79°C

From the boiling point it is seen that fraction 1. corresponds to methyl acetate, fraction 2. to methyl alcohol and fraction 3. to methyl propionate, thereby, indicating the presence of acetic acid and propionic acid in the products of the reaction.

To summarize, the products found in the aqueous layer were:-

1. Acetone.
2. Acetic acid.

and 3. Propionic acid.

PART II.

DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS.

Nitrogen tetroxide is an equilibrium mixture as indicated by the following equation:

$$N_2O_4 \rightleftharpoons 2NO_2$$

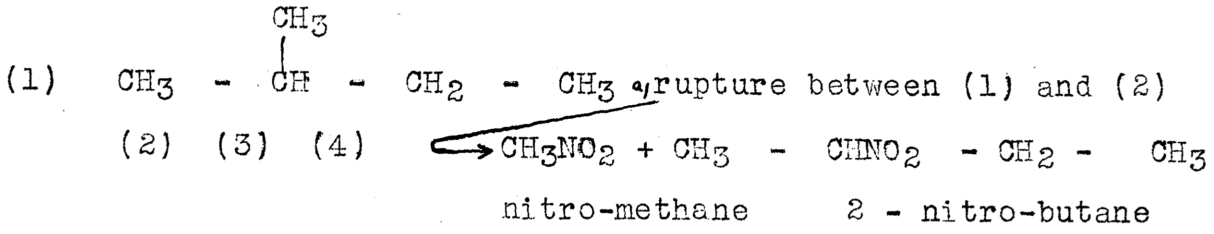
The di-molecular form is predominant at lower temperatures. The vapour density measurements indicate a complete conversion to the mono-molecular form at about 140°C. On heating above 140°C, nitrogen dioxide decomposes into nitric oxide and oxygen and this decomposition is complete at 619°C.

The behaviour of iso-pentane on heating has already been discussed in Part I. So when iso-pentane and nitrogen dioxide are heated together, it would be expected that a molecule of nitrogen dioxide which possesses an odd electron, on collision with a free radical under suitable conditions might result in formation of a stable bond. Also, due to the readily available oxygen from nitrogen dioxide the oxidation of the hydrocarbon, and/or its thermal decomposition products would be expected to take place.

On passing a mixture of nitrogen dioxide and iso-pentane gas through a reaction tube maintained at temperatures varying from 250°C to 600°C, it was found that the products of the reaction consisted of nitration products (nitro-paraffins), oxidation products such as carboxylic acids, oxides of carbon, water, etc.; thermal decomposition products like hydrogen, unsaturated hydrocarbons; and nitric oxide. This multiplicity of reaction products makes the interpretation of the experimental work difficult.

NATURE OF NITRATED PRODUCT AND THEIR FORMATION.

If it is considered that iso-pentane is nitrated in the vapour phase by substitution of any of the alkyl groups present in the hydrocarbon, with a nitro group, the following nitro-paraffins might result:



(1) $CH_3 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - CH_3$ a, rupture between (1) and (2)

(2) (3) (4) $\longrightarrow CH_3NO_2 + CH_3 - CHNO_2 - CH_2 - CH_3$

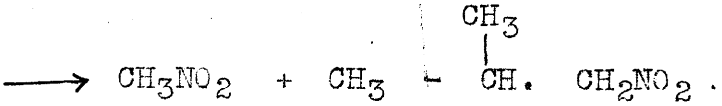
nitro-methane 2 - nitro-butane

b, rupture between (2) and (3)

$$\longrightarrow CH_3CHNO_2\ CH_3 + CH_3\ CH_2\ NO_2$$

2 - nitro-propane nitro-ethane

c, rupture between (3) and (4)

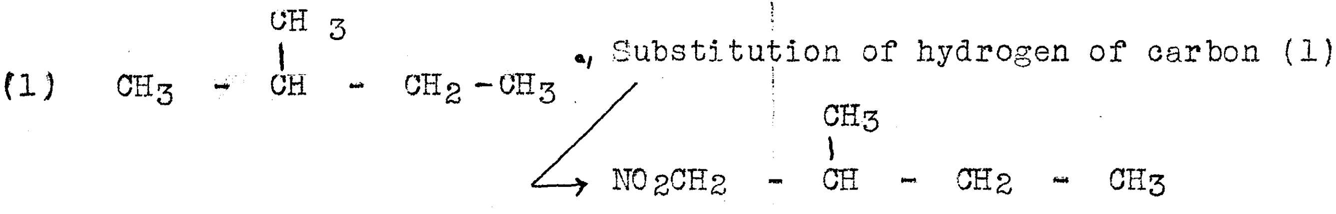


$$\longrightarrow CH_3NO_2 + CH_3 - \overset{CH_3}{\overset{|}{CH}}.\ CH_2NO_2.$$

nitro-methane iso-nitro-butane.

that is, nitro-methane, nitro-ethane, 2 - nitro-propane, 2 - nitro-butane, and iso-nitro-butane.

Similarly considering the substitution of any hydrogen by a nitro group, the resulting nitro-paraffins would be:



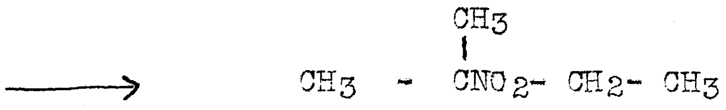
(1) $CH_3 - \overset{CH\ 3}{\overset{|}{CH}} - CH_2 - CH_3$ a, Substitution of hydrogen of carbon (1)

$$\longrightarrow NO_2CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - CH_3$$

(2) (3) (4)

Iso-pentane (2 - methyl-butane) | 1 - nitro - 2 - methyl butane

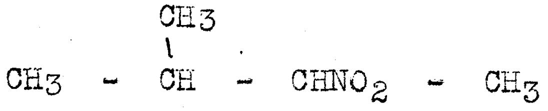
b, Substitution of hydrogen of carbon (2)



$$\longrightarrow CH_3 - \overset{CH_3}{\overset{|}{CNO_2}} - CH_2 - CH_3$$

2 - nitro - 2 - methyl butane

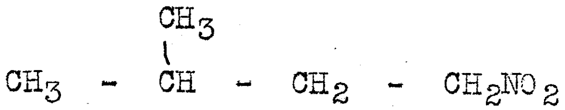
c, Substitution of hydrogen of carbon (3)



$$CH_3 - \overset{CH_3}{\overset{|}{CH}} - CHNO_2 - CH_3$$

3 - Nitro 2 - methyl-butane

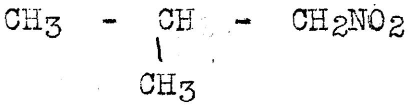
d, Substitution of hydrogen of carbon (4)



$$CH_3 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - CH_2NO_2$$

4 - nitro 2 - methyl-butane

The nitro-paraffins found in the products of the reaction are:

1.	CH_3NO_2	nitro-methane
2.	$CH_3CH_2NO_2$	nitro-ethane
3.	$CH_3CHNO_2CH_3$	2-nitro-propane
4.	$CH_3CHNO_2CH_2CH_3$	2-nitro-butane
5.	 $CH_3 - \underset{CH_3}{\underset{|}{CH}} - CH_2NO_2$	iso-nitro-butane

that is, all those and only those which would result from substitution of any alkyl of hydrocarbon by a nitro group.

None of the products which would result from the substitution of any hydrogen of the hydrocarbon, have been found. This gives support to the assumptions on which free radical theory is based; that is, in the thermal decomposition of a hydrocarbon, the dissociation occurs preferentially through the rupture of C - C bond and any breaking of a C - H bond is negligible in comparison. An examination of the bond strength of:

	i.	$C - C$	59 K.Cals.
	ii.	$C - H$	87 K.Cals.
	iii.	$C = C$	100 K.Cals.
and	iv.	$C \equiv C$	123 K.Cals.

shows that the C - C bond is the weakest.

No evidence has been obtained of the presence of any di-nitro-paraffins. Hass and co-workers[36] in their study of nitration of hydrocarbons with nitric acid at 300° - 500°C, have likewise not obtained any di-nitro-paraffins but Urbanski and Slon[40] in their work on the reaction of nitrogen dioxide and n.pentane, n.hexane, etc., at 200°C, have obtained di-nitro-paraffins. It can be that the formation of di-nitro- compounds in the vapour phase takes place only at lower temperatures of reaction, i.e., about 200°C.

It was found that the yields of the nitro-paraffins by this action of nitrogen dioxide and iso-pentane increased up to 450°C, further increase in temperature resulting in decreased yields. The increase in yield up to 450°C may be explained by the fact that the velocity of the nitration reaction

increases with increase in temperature.
Increase in temperature above 450°C, results in increase of the process of pyrolysis of the hydrocarbon, this is supported by the investigation of the interaction of nitric oxide and iso-pentane. Also, there is considerable increase in the decomposition of nitrogen dioxide to nitric oxide and oxygen, which also would lead to a reduction in the yield of nitro-alkanes.

At 450°C, a maximum yield of nitro-paraffins is obtained with a contact time of about 1 second. A longer contact time than 1 second, results in increase of oxidation and thermal decomposition products at the expense of nitration products (fig. 24).

McCleary and Degering[60] have reported that flashes of fires could be seen in the reaction tube when a mole ratio of iso-pentane to nitric acid of about 2.0 or lower was used. In this work though the ratio of iso-pentane to nitrogen dioxide varied from 12:1 to 13:1, no such flash was seen probably on account of the presence of an inert gas - nitrogen, as a diluent. The yield of nitro-paraffins increased with increase in concentration up to the limits of the concentration of nitrogen dioxide investigated.

NATURE OF THE OXIDATION PRODUCTS AND THEIR FORMATION.

The oxidation products found to be present are:

1. Oxides of carbon.
2. Water.
3. Acetone.
4. Acetic acid and propionic acid.

These products are probably the result of oxidation by nitrogen dioxide, which decomposes during the reaction. $2NO_2 \longrightarrow 2NO + O_2$

Nitric oxide is one of the gaseous products of the reaction.

The oxidation products may be accounted for by assuming:

a) direct oxidation of the parent hydrocarbon,

b) oxidation of the nitro-paraffin,

c) oxidation of free radicals, cleavage products and olefines.

M. Konowaloff[61] who studied the liquid phase nitration of a variety of compounds, has given as one of his conclusions that oxidation occurs on the carbon atom to which the nitro group is attached.

In the ~~the~~ oxidation of aliphatic hydrocarbons at atmospheric pressures, the oxidation reactions are probably stepwise, each successive step occurring with greater ease, as the reactions are exothermic and accompanied by free energy decreases. The type of reaction for the successive steps is the same, and, when a carbon compound containing oxygen is oxidized further, it is the hydrogen atoms joined to the carbon atoms already in combination with oxygen that are attacked. Ewell[58] has shown that the chlorination of paraffins follows a similar pattern. Thus the point of first attack continues to be the point for successive attacks. This has been clearly shown, in the oxidation of the isomeric octanes, where the methyl group at the end of the longest free straight chain is first attached and oxidation continues along the chain to a point where a resistance to further oxidation is encountered. At such a point - represented by the formation of a ketone structure at the point where the chain branch ends in the case of the iso-octanes- oxidation may be partly arrested, and the product recovered before decomposition or oxidation can destroy it. However, as Pope, Dykstra and Edgar[63] have found, a considerable portion of the hydrocarbon will have been destroyed when this point is reached, a large amount of heat will consequently have been liberated; and only a low yield of any ketone will be obtained. This explains the formation of acetone and its small amount.

The carboxylic acids, i.e., acetic and propionic acids were also found in small quantities. No formic acid, which is comparatively unstable, has been found showing that the oxidation reactions had proceeded almost to completion, that is to water and carbon dioxide. The large amounts of water and carbon dioxide produced in the reaction support this view. To obtain useful and desirable intermediate products of oxidation, in fair yields, it would be necessary to control this process of oxidation either by using lower temperatures of reaction or by using a lower concentration of nitrogen dioxide in the reacting mixture.

NATURE OF THE THERMAL DECOMPOSITION PRODUCTS AND THEIR FORMATION.

The products expected to be formed by the thermal decomposition of iso-pentane are saturated hydrocarbons, unsaturated hydrocarbons and hydrogen. In the reaction of iso-pentane and nitrogen dioxide, the reaction products contained hydrogen and unsaturated hydrocarbons only; no saturated hydrocarbons were found. In this reaction, the absence of saturated hydrocarbons, which are produced in the reaction of iso-pentane and nitric oxide, shows that the saturated hydrocarbons or the free radicals produced which lead to their formation are being nitrated or oxidized as soon as those are found.

The unsaturated hydrocarbons, besides being produced by the thermal decomposition of the hydrocarbons, may also be a result of some of the oxidation reactions or of pyrolysis of the nitration products. Steacie and Plewes[59] suggest that the first step in the oxidation of a hydrocarbon is its dehydrogenation to unsaturated compounds; ethane, for example, gives

$$C_2H_6 + \frac{1}{2}O_2 \longrightarrow C_2H_4 + H_2O$$

Seigle[62], who has studied the pyrolysis of nitro-ethane and 1-nitro-propane found the products of reaction to consist of aldehydes, unsaturated hydrocarbons, nitrogen and oxides of carbon; no lower nitro-alkanes were found.

To summarize, the following conclusions can be made as a result of this work:

1. When iso-pentane and nitrogen dioxide react, the reactions taking place are complex and include nitration, oxidation and thermal decomposition of the hydrocarbons.

2. During nitration of iso-pentane with nitrogen dioxide at 450°C and with the contact times used, all mono-substitution products are formed which could result if the nitro group is assumed to substitute any alkyl group of the hydrocarbon. No carbon skeleton rearrangement occurs during the nitration. The mechanism suggested for the nitration reactions is

$$\text{Iso-pentane} \longrightarrow R + R'$$
$$+ NO_2 \longrightarrow RNO_2 + R'NO_2$$
$$(R, R' \equiv \text{Alkyl radicals})$$

3. At 450°C or so, no di-nitro-paraffins are formed.

4. The rates of nitration and oxidation increases with increase in concentration of nitrogen-dioxide in the reacting mixture.

5. It is possible to get the hydrocarbon oxidized to carboxylic acids with nitrogen dioxide in the vapour phase, though the yield of these acids is small

COMPARISON OF THE INTERACTION OF NITRIC OXIDE AND NITROGEN DIOXIDE WITH ISO-PENTANE.

Nitric oxide which possesses an odd electron is very stable and shows little tendency to dimerize. This stability of nitric oxide is explainable by its possessing a resonance structure. Nitric oxide acts as a mild oxidizing agent at higher temperatures and in presence of catalysts; on combination with an alkyl group, nitric oxide will give R - NO ($R \equiv$ alkyl group) which are unstable. On the other hand, nitrogen dioxide is found in equilibrium with its dimer, N_2O_4, at ordinary temperatures. Nitrogen dioxide is a powerful oxidizing agent as it readily loses oxygen. If it is assumed that nitrogen dioxide - which possesses an odd electron - combines with an alkyl radical, the resulting $R-NO_2$ are stable.

The action of nitric oxide and nitrogen dioxide on iso-pentane is in keeping with their above mentioned characteristics as is seen from a comparison of the two interactions. This comparison reveals that:

1. The primary reaction in case of nitric oxide and iso-pentane was the thermal decomposition of the hydrocarbon. This thermal decomposition of iso-pentane was greater in presence of nitric oxide than in a pure pyrolysis. The products of pyrolysis were unsaturated hydrocarbons, hydrogen and saturated hydrocarbons. In the case of iso-pentane and nitrogen dioxide, the hydro-carbon was decomposed though only to a limited extent on account of the lower temperature used for the reaction. The products found consisted of hydrogen and unsaturated hydrocarbons. No saturated hydrocarbons were found in the gaseous products of the reaction.

2. Oxidation took place with nitric oxide as well as with nitrogen dioxide. With nitric oxide, the oxidation was very limited and no products other than oxides of carbon and small amount of water were found. In the reaction of nitrogen dioxide and iso-pentane the oxidation products consisted of acetone, some carboxylic acids besides oxides of carbon and water. Some of the unsaturated hydrocarbons formed are also likely to be the result of

the dehydrogenating action of nitric oxide, and of nitrogen dioxide.

3. The yield of nitro-products which were primary derivatives only, was very small with nitric oxide. Nitrogen dioxide gave all the nitro-paraffins which would result from the substitution of any alkyl group of hydrocarbon by a nitro group.

SUMMARY.

SUMMARY.

Interaction of Iso-pentane and Nitric Oxide.

The interaction of iso-pentane and nitric oxide has been studied under static as well as streaming experimental conditions. It was found that the reaction first becomes appreciable at 500°C. The products of the reaction were carbon dioxide, carbon monoxide, unsaturated hydrocarbons, hydrogen, saturated hydrocarbons, water, primary nitro-compounds along with some tarry products and carbon.

Experiments were also made to study the thermal decomposition of iso-pentane alone. A comparison of the interaction of iso-pentane and nitric oxide with the thermal decomposition of iso-pentane alone, revealed that the hydrocarbon molecule is degraded to a greater extent in the presence of nitric oxide. The yields of gaseous unsaturated hydrocarbons and saturated hydrocarbons are increased

but that of gaseous hydrogen is decreased probably on account of its combustion to water, in presence of nitric oxide.

The influence of the three principal factors - contact time, temperature and variations in concentration of nitric oxide in the reacting mixture - have been examined in detail. It was found that an increase in any of the three factors results in:

a) increased yields of the decomposition products - saturated hydrocarbons, unsaturated hydrocarbons and hydrogen,

b) an increase in oxidation products such as oxides of carbon, and

c) an increase in tarry and polymerised products.

The unsaturated hydrocarbons produced which were identified by the formation of their dibromides, were found to be ethylene, propylene and iso-butylene. The last two were obtained in fair yields. On the basis of the theory of free radicals[6], the unsaturated compounds, which would be expected to be formed are ethylene, propylene, iso-butylene, 1 - butene and 2 - butene. 1 - Butene has not been found by any of the investigators who have studied the pyrolysis of iso-pentane[30]. 2 - Butene has been found in small quantities by Frey and Hepp[29]. In the present work 2 - butene has not been found in the products of the reaction probably on account of its relative instability in presence of nitric oxide. Hurd and Spence[31] have shown in their work on thermal decomposition of butylenes that n. butylenes are less stable than iso-butylene.

Interaction of Iso-pentane and Nitrogen dioxide.

The interaction of nitrogen dioxide and iso-pentane has been studied by passing a mixture of these through a silica reaction-tube maintained in an electric furnace at a known temperature. The products of the reaction were found to consist of nitro-paraffins, oxidation products, and thermal decomposition products such as hydrogen and unsaturated hydrocarbons. No gaseous saturated hydrocarbons were found. The influence of temperature, time of contact and composition of the reacting mixture have been investigated. The conditions for maximum production of nitro-paraffins by this reaction, using a 2:1 ratio of iso-pentane to nitrogen dioxide (to avoid danger of excessive oxidation), were a temperature of 450°C and a time of contact of 1 second.

Products of the reaction.

The liquid products of the reaction were obtained in two layers, the upper consisted of nitro-paraffins along with unreacted hydrocarbon while the lower contained oxides of nitrogen, water and other oxidation products. These oxidation products were found to be acetone, acetic acid and propionic acid.

The nitration products obtained were nitro-methane, nitro-ethane, 2 - nitro-propane, 2 - nitro-butane, and nitro-isobutane, that is, all the nitro-paraffins which would result from substitution of any alkyl group of the hydrocarbon by a nitro group. None of the nitro products which would result from substitution of any hydrogen was found. This gives support to the assumptions on which free radical theory is based, that is, in thermal decomposition of a hydrocarbon, the dissociation occurs preferentially through a rupture of C - C bond and any breaking of C - H bond is negligible compared with that of a C - C bond.

No evidence has been obtained of the presence of any di-nitro-paraffin.

BIBLIOGRAPHY.

BIBLIOGRAPHY.

1.	Ostergood et al,	Petroleum Processing	1947,	2-no.10,	753
2.	Egloff and Wilson	Ind. Eng. Chem.	1935,	27 ,	917
3.	Callingeart	J.Amer.Chem.Soc.	1923,	45 ,	130
4.	Kassel	J. Chem.Phys.	1933,	1 ,	749
5.	Creigee	Ber.	1935,	68 ,	665
6.	Rice et al	J. Am.Chem.Soc.	1931,	53 ,	1959
		ibid	1932,	54 ,	3529
		ibid	1933,	55 ,	3035
		ibid	1934,	56 ,	2381
		Trans. Faraday Soc.	1934,	30 ,	247
7.	Pareth and Hofeditz	Ber	1929,	62 ,	1335
8.	Bonhoeffer and Haber	Z.Physik.Chem.	1928,	A.137 ,	263
9.	Appleby	J.Am. Chem.Soc.	1947,	69 ,	2279
10.	Dintses and Frost	J.Gen.Chem.U.S.S.R.	1933,	3 ,	747
11.	Dintses and Zherke	ibid	1936,	6 ,	68
12.	Beeck	Nature	1935,	136 ,	1028
13.	Bone	Trans. Faraday Soc.	1934,	30 ,	148
14.	Hinshelwood et al	Proc. Roy. Soc.	1936,	A.154 ,	335
		ibid	1937,	A.159 ,	192
		ibid	1937,	A.162 ,	1568
		ibid	1939,	A.179 ,	131
15.	Staveley	Proc.Roy. Soc.	1937,	A.152 ,	557
16.	Gray,Travers and White	ibid	1938,	A.167 ,	15

17. Steacie and Shane Canad. J. Res. 1940, 18B, 351

18. Kuhlmann Annalender Pharmacie 1838, 29, 284

19. Huntington British Patent 14855

20. Elod and Nedelmann Z. Electrochem 1927, 33, 217

21. Bredig, Elod and Kortum Z. Electrochem 1930, 36, 991

22. Staveley and Hinshelwood Trans. Faraday Soc. 1939, 35, 845

23. (Beller and Hans U.S. Patent 2,216,222
(Paul U.S. Patent 2,244,210
(Thomas U.S. Patent 2,365,851

24. Platonov and Shaikind J. Gen. Chem. U.S.S.R. 1934, 4, 434

25. Gray and King Fuel Research Technical Paper No. 24.

26. Berg and Parker Anal. Chem. 1948, 20, 456

27. Clarke A handbook of Organic Analysis, p.170

28. Brown and Campbell J.C.S. 1937, 1699

29. Frey and Hepp. Ind. Eng. Chem. 1933, 25, 441

30. Kossiakoff and Rice J. Amer. Chem. Soc. 1943, 65, 590

31. Hurd and Spence ibid 1929, 51, 3353

32. Sidgwick Organic Chemistry of Nitrogen (1937)

33. Meyer and Stuber Ber 1872, 5, 203

34. Kolbe J. Pr. Chem. 1872, 5, 427

35. Beilstein and Kurbatr Ber 1880, 13, 1818

36. Hass et al Ind. Eng. Chem. 1936, 28, 339
ibid 1938, 30, 67
ibid 1939, 31, 118
ibid 1946, 38, 251
ibid 1939, 31, 648

Hass et al — Ind.Eng. Chem. 1947, 39, 817

Chem. Rev. 1943, 32, 373

Ind. Eng. Chem. 1943, 35, 1146

37. Levy and Rose — Quarterly Reviews 1948, Vol.I.no.4, 358

J.C.S. 1946, 1093

ibid 1946, 1096

ibid 1946, 1100

ibid 1948, 52

38. Semenov — Z. Chem. Pharm. 1864, 7, 129

39. Riebsomer — Chem. Rev. 1945, 36, 157

40. Urbanski and Slon — Compt. rend. 1936, 203, 620

ibid 1937, 204, 870

Chem. Abstracts 1939, 32, 42

41. Dorsky, Hodge, Hass — Ind. Eng. Chem. 1938, 33, 1138

42. Frolich, Harrington and Waitt — J.Am. Chem.Soc. 1928, 50, 3216

43. Bibb — Ind. Eng. Chem. 1932, 24, 10

44. French Patent — 709,825 (Chem.Abstracts, 1932, 26, 1302)

45. Bailey — U.S. Patent 1,319,748

46. Granacher and Schaulfelberger — P.Helv.Chim.Acta. 1922, 25, 392

47. Schaarschmidt — Z. angerv.Chem. 1924, 37, 933

48. Hass et al — Ind. Eng.Chem. 1938, 33, 1142

49. Bose — Analyst 1931, 56, 504

50. Hearon and Gustavson — Ind. Eng.Cham.Anal.Ed. 1937, 9, 352

51. Victor Meyer — Annalen 1875, 175, 93

52.	Hinsberg	Quantitative Organic Analysis by Openshaw, p.72.			
53.	Davidson	J. Chem.Ed.	1942,	19 ,	154
54.	Rosenthaler	Ind.Eng.Chem.Anal.Ed.	1937,	9 ,	352
55.	Scott and Treon	ibid	1940,	12 ,	189
56.	Steacie and Folkins	Canad J. Res.	1940,	B18 ,	1
57.	Pease	J.Am.Chem.Soc.	1935,	57,	2296
58.	Ewell	p.174 Unit Process in Organic Synthesis (Groggins)			
59.	Steacie and Plewes	Proc. Roy. Soc.	1934,	A146,	583
60.	McCleary and Degering	Ind. Eng. Chem.	1938,	30,	64
61.	Konowaloff	Ber.	1902,	35,	1584
62.	Seigle	Ph.D. Thesis(1939) Purdue University (Indiana)			
63.	Pope, Dykstra and Edgar.	J.Am.Chem.Soc.	1929,	51,	2203