A STUDY ON FUEL OIL DESULPHURISATION

A thesis submitted to the University of Glasgow
in accordance with the regulations governing the
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by

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SUMMARY

Three residual fuel oils were characterised and separated by chromatography into aromatic and non-aromatic fractions. Sulphur determinations indicated that most of the sulphur compounds were in the aromatic fractions. Further analysis indicated that the sulphur compounds were essentially thiophenic in nature and relatively unreactive.

Thermal cracking of the oils on glass at 430°C and over copper at the same temperature was studied, and a sulphur balance was carried out on the cracking process. Up to forty percent of the sulphur compounds were removable by this method. Further breakdown of thiophenic material required hydrogenation.

Since it was considered that the hydrogen required could be made available by hydrogen transfer from naphthenes, a study was made of the dehydrogenation of cyclohexane and of a light naphtha fraction over a number of transition-metal sulphide-oxide catalysts of the type generally used in the conventional hydrodesulphurisation processes. It was found that an adequate amount of hydrogen became available at 400°C with a residence time of about twelve seconds on the catalyst. The specific reaction rate constant was calculated, as was the activation energy. The latter was found to be much lower than values reported for the dehydrogenation of cyclohexane over noble metal catalysts.

The direct hydrogenation of thiophene was studied at the same temperature and on the same catalysts. A seventy-eight percent decomposition of thiophene was obtained at 400°C with a residence time of twelve seconds. Since WO_3 had been found to be the most active oxide for dehydrogenation of cyclohexane, and V_2O_3 the most active oxide for the hydrogenation of thiophene, a mixed catalyst of the two oxides was used for hydrogen-transfer studies from cyclohexane to thiophene. It was found that with the apparatus under test a relatively high hydrogen partial pressure, and therefore a high cyclohexane-thiophene ratio, was required. An eighty-five percent decomposition of thiophene could be achieved in a residence time of twenty seconds.

Similar hydrogen-transfer studies with naphtha and thiophene gave parallel results. There were indications, however, that increase of the partial pressure of thiophene could reduce the extent of reaction, possibly due to its adsorption on the active sites of the catalyst.

Hydrogen-transfer studies at 400°C were carried out using mixtures of naphtha and residual fuel oil and optimum experimental conditions were obtained. It was again evident that a low ratio of oil : naphtha would be required to produce effective hydrogenation at the residence time available.

Extended test runs were made with a suitable mixture of naphtha with each of the three residual fuel oils in turn.

On-stream times of up to twenty-four hours were achieved at 400°C with an oil : naphtha ratio of 30/70 (w/w) ; seventy to eighty percent of the sulphur in the oil was removed by this means.

After dehydrogenated naphtha had been separated from the treated oil, it was found that the latter had a viscosity considerably lower than that of the feed oil. Structural group analysis of the treated oil indicated significant hydrogenation of the aromatics and extensive hydrocracking to give an average molecular weight of about half of that of the feed oil.

1. INTRODUCTION.

1.1 Sulphur Compounds in Petroleum.

Crude petroleum is primarily a complex mixture of hydrocarbons ranging from gases such as methane and ethane to asphaltic bitumens. Other elements present include sulphur, oxygen and nitrogen. Vanadium and other minor elements are present in trace quantities. Sulphur when present appears as a divalent element[1]. The more common divalent sulphur compounds include mercaptans, sulphides, disulphides and some aromatic compounds. Within each of the above groups there is a considerable range of variation, so that in the case of the mercaptans one finds primary, secondary and tertiary alkyl thiols as well as aromatic, olefinic and cyclic compounds. Aliphatic mercaptans with five carbon atoms have been identified, as have open-chain sulphides with twelve carbon atoms, and cyclic sulphides with up to five carbon atoms. Higher boiling mercaptans as well as open-chain and cyclic sulphides have also been detected, but not definitely identified.

The study of sulphur compounds in petroleum is complicated by the fact that some of them are readily decomposed on heating. Hydrogen sulphide, although not present in oil as such, is formed during distillation; and thus is found in the gases and light distillates from both distillation and cracking operations. Even mild thermal treatment as in the crude distillation process breaks down higher molecular weight sulphur compounds, and yields low boiling mercaptans, sulphides and disulphides. Variation of distillation conditions may change the range of the sulphur compound products, thus hydrogen sulphide not found in the "Vacuum" distillate is present in the "atmospheric"distillate and may account for nearly four percent of the original total sulphur in the crude oil. Only forty percent of the sulphur compounds in "atmospheric" distillate consists of hydrogen sulphide, mercaptans, sulphides or disulphides. No identifying tests have so far been developed for the remainder. In catalytic cracking a higher degree of decomposition of sulphur compounds takes place than in thermal cracking: among the sulphur compounds that have been identif in cracked petroleum fractions are thiophenol, thiocresol, dimethyl sulphide, thiophene, 2-methyl thiophene and 2:3 dimethyl thiophene. Information on the nature of individual sulphur compounds in petroleum fractions is rather meagre. Smith and Ball[2] have investigated the nature of sulphur bodies in straight-run naphthas boiling up to 250°C. Their results showed that there was considerable variation in the range of sulphur compounds from one crude oil to another. Sulphides, mercaptans and disulphides, hydrogen sulphide and elemental sulphur could be analysed and detected, but mercaptan-type or open-chain and cyclic sulphides were difficult to differentiate. In general, gasoline contains one percent, kerosine five and gas oil and lubricating oil distillate each contain ten percent of the total sulphur in crude oil. The amount of sulphur present in a crude oil is apparently somewhat related to the amount of asphalt in solution. Oils containing the greatest amount of asphalt have the highest sulphur[3] contents in them. The concentration of sulphur in kerosine is generally 0.02 to 0.06% ;

domestic fuel oil 0.3 to 0.72% and industrial or residual fuel oil 2.5 to 4.0%.

The A.P.I project 48 has shown that sulphur compounds in crude oil residues are almost entirely cyclic in nature; and consist of condensed thiophenes of almost every series e.g. thionaphthenes; dibenzothiophenes; naphthothiophenes; benzonaphthothiophenes. These have not yet been isolated or identified as such, however there are indications of condensed molecules containing more than one thiophene nucleus.

1.2 Nature and Characteristics of Residual Fuel Oil.

Residual fuel oils are largely byproducts of refinery operation, which is aimed at maximising the yeild and quality of other more desirable products. This fact explains the wide variation in properties often found in residual fuel oil. During the period in which thermal cracking was an important refinery tool, residual fuel oil consisted largely of tars from thermal cracking operations with only minor proportions of straight-run reduced crudes. When, however, the demand for motor gasoline of higher octane number increased, catalytic cracking was introduced. This change had a marked effect on the make up of residual fuel oil and caused a decrease in the percentage yeild of such material from a crude.

The high boiling residue fraction from the catalytic cracking process is much too heavy for use as fuel oil, and must be adjusted in viscosity by addition of distillate stocks. Thus residual fuel oil from a modern refinery consists mainly of blends of gas oil distillate/....

usually from catalytic cracking operation with the heavy vacuum residue, and minor amounts of tars from thermal cracking operations. Residual fuel oils in the U.K. are classified by British Standard Institute[4]; and in the U.S.A. by the American Society of Testing Material[5]. In the British classification grade F.G. and H. are residual fuel oils, as are No. 4,5,and 6 in the American classification Such classification is largely based on viscosity as may be seen from Tables 1.1 and 1.2.

TABLE No. 1.1

British Classification of Residual Fuel Oils.

	Grade		
	F	G	H
Max. viscosity at 100°F Redwood No. 1.	1000	3500	7000
Gross c.v. Btu/lb.	(18150)	(18000)	(17900)
Flash Point °F minimum	150	150	150
Water Percent Vol. (Max)	1.0	1.0	1.50
Sediment Percent	0.25	0.25	0.25
Sulphur Percent. (Max)	(3.50)	(3.80)	(4.5)

TABLE No. 1.2

American Classification of Residual Fuel Oils.

	4	5	6
Max. viscosity Redwood No.1.	110	708	7520
Flash Point °F minimum	150	150	150
Water and Sediment	0.05	1.0	2.0
Sulphur percent (Max)	(2.2)	(4.7)	(5.2)

It may be seen that the No 4 and 5 grades in the American scheme are much lighter than British class E and F. There is no U.S equivalent of G grade. However, No. 6 and H are almost identical. The G grade fuel, a medium viscosity fuel is also known as "Bunker B", while the H is known as "Bunker C". The U.S bureau of mines in co-operation with American Petroleum Institute conducted in 1955-56 a survey on the properties of burner fuel oils. This survey includes the data on distillate fuel as well as residual fuels[6], and represented the production of 129 refineries in U.S.A. and Canada; according to the survey the sulphur content of No. 4 may vary from 0.10 to 3.27 percent. The carbon residue may also vary from 0.1 to 7.6 percent. This latter variation was due to the fact that some such oils were straight distillates while others were blends of distillate with residual stocks. In general No. 4. grade fuel varied in pour point from -10°F to -50°F; water and sediment from trace to 0.1 percent; and ash from 0.0001 to 0.029 percent; some mineral salts of vanadium and magnesium were also observed in a few parts per million.

In the case of No. 5 fuel or F grade fuel, there was wide variation in Specific Gravity and this varied from 2.3 to 22 A.P.I., and the pour point varied from -20 to 60°F. The sulphur content was higher than that of No. 4; since this value was used primarily by the refiner to classify the fuel; ranging from 0.43 to 4.8 percent. The mineral salts of aluminium, calcium, iron and sodium were also observed to an extent of seventy parts per million.

The H grade fuel oil or No. 6 is the most widely distributed of all residual fuels, and is the grade normally used by power plants and most industrial customers because it is offered at the lowest price. This grade also showed considerable variation in properties. The gravity varied from 2.4 to 19.7 A.P.I. The low gravity products contained large proportions of cracked stocks, while those with the highest gravity were essentially straight un-cracked long residues. Since the low gravity products had a higher heat of combustion on a Btu/gallon basis they were preferred by many industrial users, assuming that the other properties were satisfactory. The viscosity may range from 49 to 1474 cs at 100°F, the pour point from 0 to 65°F, the sulphur content from 0.4 to 5.25 percent. The low carbon residue fuels were generally uncracked long residues and tend to be low in viscosity. The high carbon residue fuels were blends containing heavy residues and possibly cracked residual stocks; their ash content varied from 0.006 to 1.9 percent. The mineral salt present consisted chiefly of zinc, sodium, magnesium and vanadium. Thus it may be seen that there exists for any residual oil quite a wide variation in properties. However if repeated deliveries of fuel oils are obtained from a single refiner much less variation in properties will be encountered.

With improved refinery technique the percentage of residual fuel oil obtained from a given crude is gradually decreasing; but consumption and demand for the heavy oil has increased rapidly, possibly due to its favourable price. The percentage of residual fuel was about twenty-four before but has decreased to about eleven at the present time. It is estimated that this figure could become even lower within a few years; as the refinery yeild has decreased the quality has deteriorated. Today the average heavy oil product is found to have a carbon residue of eighteen percent, a pour point of approximately 50°F, sulphur content of approximately 5 percent and an ash content of about 0.5 percent.

1.3 Sulphur Compounds in Residual Fuel Oils.

Most of the early work on the identification of sulphur compounds in petroleum was done on the lower boiling distillates; since these are more easily analysed than the higher boiling fractions. Information on the nature of higher boiling oils has been obtained from the work of the American Petroleum Institute research project 48; and from the work of Wasson, Wilmington on Middle East Crude oils[7].

It is found that the cyclic nature and aromaticity of the sulphur compounds in oil increases as the boiling range of the oil increases[8]. Sulphur compounds in residual fuel oils are thus mainly consisting of thiophenes. In general, seventy percent of the total sulphur compounds from the crude oil becomes concentrated in the residual fuel; although this residue may only account for twenty percent of the crude oil. Knowledge of the nature of the individual sulphur compounds in cracked petroleum product is even more meagre than for straight run products. It is found however that the cracked products are more highly thiophenic than straight run products[9].

1.4 Disadvantages of Sulphur Compounds in Residual Fuel Oil in relation to its end uses.

Residual fuel oils are used primarily to supply heat and because of their relatively low cost are widely used in many industries; but the heat of combustion of sulphur is 4000 Btu/lb as against 14,450 Btu/lb for carbon. Thus the calorific value of the fuel is lowered by 150 Btu/lb for each one percent of sulphur present.

In certain steam boiler installations fuel oil with a high sulphur content may lead to excessive corrosion, particularly at places where the stack gases are cooled to temperatures below their dew point. However, residual fuel oils are widely used in both stationary and mobile steam boilers of all sizes. Their use not only makes it a cheaper installation but makes it less complicated to operate. The problem of corrosion may be controlled by maintaining the flue gas temperature above its dew point, with an accompanying decrease in overall boiler efficiency. The dew point is high for high-sulphur fuel oil, since appreciable quantities of sulphurous and sulphuric acids are present in the flue gases.

Residual fuels are widely used in furnace industries: among these are open hearth furnaces in the steel industry, kilns in the cement and related industries, various furnaces in the petroleum and chemical industries. The disadvantage presented by sulphur in the fuel in the case of open hearth furnaces is related to the absorption of sulphur by the steel, ~~and~~ resulting in undesirable changes in its properties. ~~of it.~~ Similar troubles are experienced in the glass and ceramic industries, and hence low sulphur fuel is always more attractive.

In the case of diesel engines most are operated on distillate fuels; but certain marine diesel engines and relatively low speed stationary engines are operated on residual fuel oils.

The residual fuel oils are also used as gas enrichment oils to improve the heating value of water gas and other gases. In some areas where coal is not available, residual fuel oil can be used to generate oil gas which is distributed for domestic use. However sulphur must be removed from the resultant gas to a considerable extent before it is passed for domestic use. Sulphur oxides have a considerable effect on plants and human beings[10]. Alfala beans and barley are among the most sensitive crops. In the case of humans even as low as one ppm of sulphur dioxide may cause functional alteration in the lungs' air ways and may cause astmatic attacks. It is quite surprising that the city of New York alone uses residual fuel oil containing 2.5% sulphur and discharges nearly 85,000 tons of sulphur dioxide annually into the air[11]. Anti-pollution laws are becoming more strict and consumers are thus forced to use even lower sulphur content fuels in the vicinity of cities. Thus sulphur content is one of the primary factors in deciding the field of application of a residual fuel oil.

1.5 Removal of Sulphur from Petroleum Products.

The removal of sulphur compounds from distillate petroleum fractions is of obvious interest to the petroleum industry. On most lower boiling distillate fuel oil, specifications have been established limiting the amount of sulphur that may be left in the product. Thus a considerable amount of effort has been made to develop processes for removing sulphur compounds. There is, however, no general specification for the amount of sulphur in residual fuel oil. At the same time very little information is available on commercial methods for reducing the sulphur content of this material. Existing methods for the treatment of distillates may be classified under three headings:-

(a) Treating or Extracting processes.
(b) Thermal and Contact Catalytic processes.
(c) Hydrodesulphurisation processes.

1.5.1 (a) Treating or Extracting processes.

These methods have been developed for relatively simple sulphur compounds in petroleum distillates, and utilise chemicals, clays and solvents. Most of the chemical treating methods developed for use on mercaptans are not effective for thiophenic-type sulphur; lead sulphide treatment oxidises thiols to disulphide and these are left in the distillate[12]. Aqueous sodium and calcium hypochlorites oxidise thiols and alkyl sulphides to water-soluble products, but elemental sulphur and thiophenic sulphur are not affected[13].

The various thiol-dissolving processes using caustic solution and solution promoters such as salts of isobutyric acid, alkyl phenols, methanol, napthenic acid and tannins are used for removing acidic sulphur compounds including hydrogen sulphide and thiols[14]. Clay treatment is useful for improving the odour and colour of various petroleum fractions. Only mercaptan sulphur is removed when concentrated sulphuric acid or anhydrous hydrofluoric acid are used. It is found[15] that not only do they extract all the sulphur containing molecules, but also some of the aromatic hydrocarbons. This may cause large product losses with some petroleum fractions.

In solvent refining Nelson[16] has used sulphur dioxide, furfural and anhydrous hydrogen fluoride for the solvent extraction of catalytic cycle oil. He claimed 69 to 85 percent sulphur removal, but 14 to 35 weight percent of the oil was also extracted. It would thus appear that solvent extraction processes are only partially effective because they not only remove the sulphur bearing molecules but also some hydrocarbons, particularly those with aromatic rings.

Cracked fuel oils are noted for their high aromatic hydrocarbon content. Some straight-run residual oil contains more than forty percent aromatic hydrocarbons[17]. This suggests that this method could not be applied satisfactorily with residual fuel oils.

1.5.2 Thermal and Contact Catalysis processes.

The petroleum industry uses extensively such processes to upgrade residual oils to more marketable products. "Visbreaking" for instance is used to reduce the viscosity of an oil, but does not eliminate sulphur to any material extent. "Coking" is a more severe thermal operation often used in processing residuum. It is however reported[18] that sulphur is not removed during fluid coking.

Morrell[19] has investigated the thermal cracking of various thiophenes and found no decomposition at temperatures as high as 1500°F. This is further supported by the thermodynamic properties of thiophene[20]. The logarithm of equilibrium constant is highly negative even at temperatures as high as 1500°K, this is shown in the Figure 1.1 and Table 1.1

Catalytic Contact decomposition of sulphur compounds in the vapour phase over silicates, bauxites and alumina is effective in decomposing mercaptans, sulphides and disulphides but thiophenes are quite resistant[21]. Some decomposition of thiophene to yield hydrogen sulphide has been observed with bauxite containing iron and titanium oxides, but an exceptionally long contact time in the vapour phase is required[22]. This suggests that since the residual

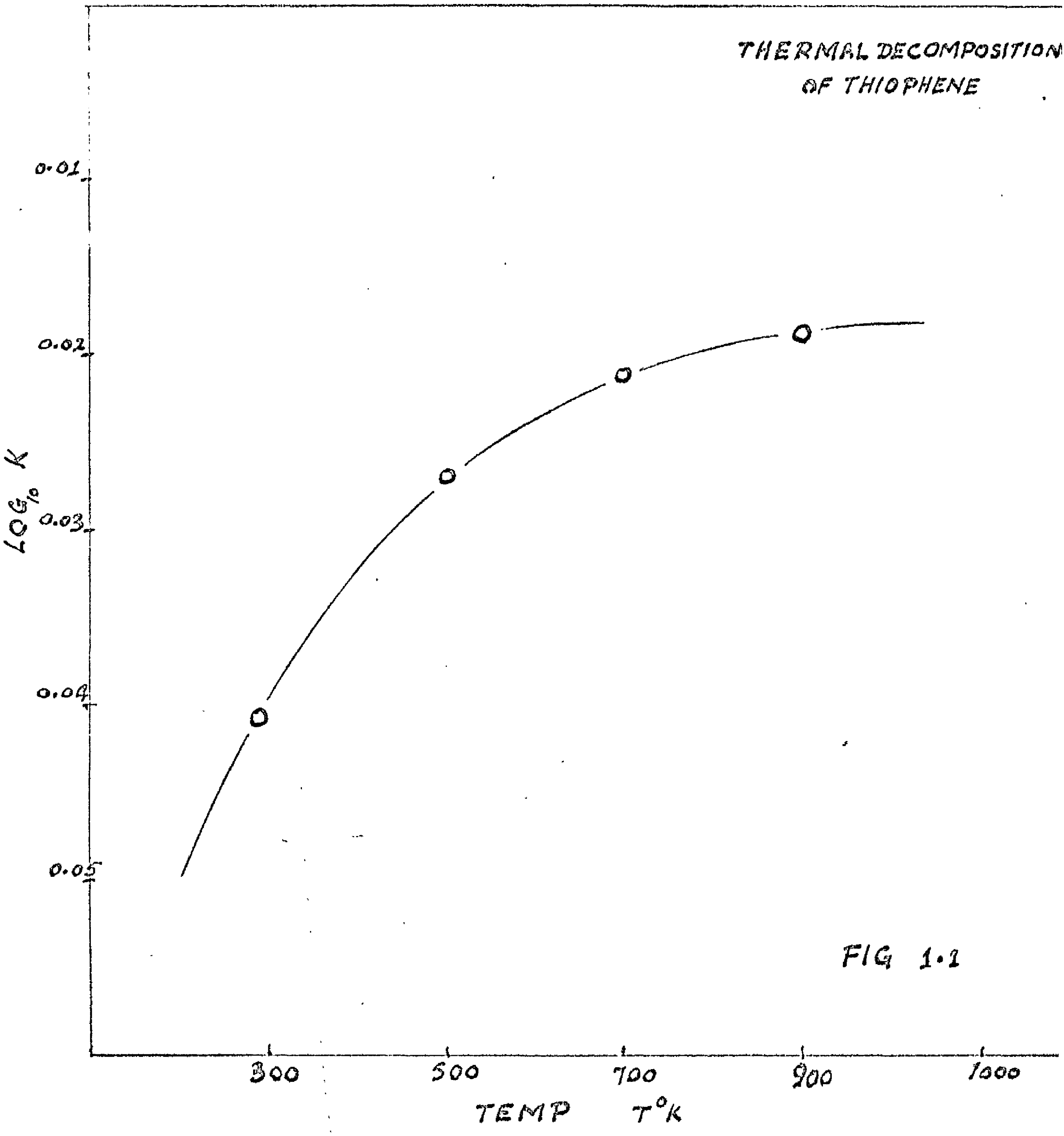

THERMAL DECOMPOSITION
OF THIOPHENE
LOG10 K
0.01
0.02
0.03
0.04
0.05
300
500
700
900
1000
TEMP T°K

FIG 1·1

oils contain the major part of their sulphur as thiophenes, existing Contact Catalytic processes would not be satisfactory.

1.5.3 Hydrodesulphurisation processes.

This type of process is widely used for almost all types of sulphur compounds. Hydrogen and the oil are passed over a suitable catalyst at a particular temperature and pressure, and the hydrogenation of the sulphur compounds is effected and hydrogen sulphide formed. This last is eliminated easily and may be used to prepare sulphur as a byproduct. Now the hydrogen required for the desulphurisation may be obtained either as a byproduct from hydrofining units or by some chemical hydrogen transfer system e.g. "Autofining".

The wide spread installation of hydrogen reforming units with hydrogen availability as a by product has made commercial hydrodesulphurisation operations feasible; but the needs of such commercial plants are ever increasing due to the higher sulphur crudes. At the same time the increasing demand for low sulphur-content middle and heavy distillate fractions can not be satisfactorily obtained at the moment by other desulphurisation methods. McKinley[23] has reported that hydrodesulphurisation is the only method applicable to all types of sulphur compounds. Hughes and Faris[24] have investigated catalytic hydrodesulphurisation of gas oil, reduced crudes, and residual fuels, but relatively very few references show results on the treatment of residual fuel oils.

In the case of a chemical hydrogen transfer system the sulphur is

TABLE No. 1.1

Logarithm of Equilibrium Constant at Various Temperatures for Thermal Decomposition of Thiophene.

		$\log_{10}K$		
Decomposition of thiophene	298°K .041	500 .027	700 .021	900 .019

TABLE No. 1.2

Logarithm of Equilibrium Constant at Various Temperatures for Hydrogenation of Sulphur Compounds.

			$\log_{10}K$		
No.	Type of Sulphur Compound	298°K	500	700	900
A	Sulphur compound + hydrogen to saturated hydrocarbon + H_2S				
	1. Methanethiol to methane	14.28	8.37	6.10	4.59
	2. Thiophene to n-Butane	30.89	12.07	3.85	-.65
	3. Thiacyclopropane to ethane	28.3	15.02	9.26	5.99
B	Sulphur compound + hydrogen to unsaturated hydrocarbon + H_2S				
	1. Ethanethiol to ethylene	-5.98	-.83	+1.34	+2.53

eliminated as hydrogen sulphide by means of catalytic hydrogenation of the sulphur compounds present in the feed stock. The hydrogen required for the reactions is obtained by simultaneous dehydrogenation of six-membered-ring naphthenes, present in the process distillate.

The equilibrium constant for the hydrogenation of various types of sulphur compounds to yield saturated hydrocarbons and hydrogen sulphide at various temperatures is given[25] <u>$\log_{10} K$ versus T°K</u> for open-chain, cyclic and thiophenic types of sulphur compounds are also available[26]. The Figure 1.2 and the Table 1.2 show that the logarithm of equilibrium constant in the temperature range 298 to 900°K are almost all positive. Thus in almost every case the reactions could proceed virtually to completion if hydrogen be present in proper stoichiometric proportion.

Thiols, open-chain and cyclic sulphides are converted to saturated or aromatic hydrocarbons depending upon the particular sulphur compounds involved. Benzothiophenes are converted to alkyl aromatics and dibenzothiophenes are probably converted to biphenyl.

Thus the major reaction mechanism seems to be a simple carbon-sulphur bond rupture followed by saturation of the free valencies. In general, aromatic rings are not saturated even though their hydrogenation may be thermodynamically favoured. This is because of a specific inactivity of the catalyst employed. However, as shown in Table 1.3 in the following page, partial ring saturation may precede carbon-sulphur bond rupture such as in the case of dibenzothiophenes.

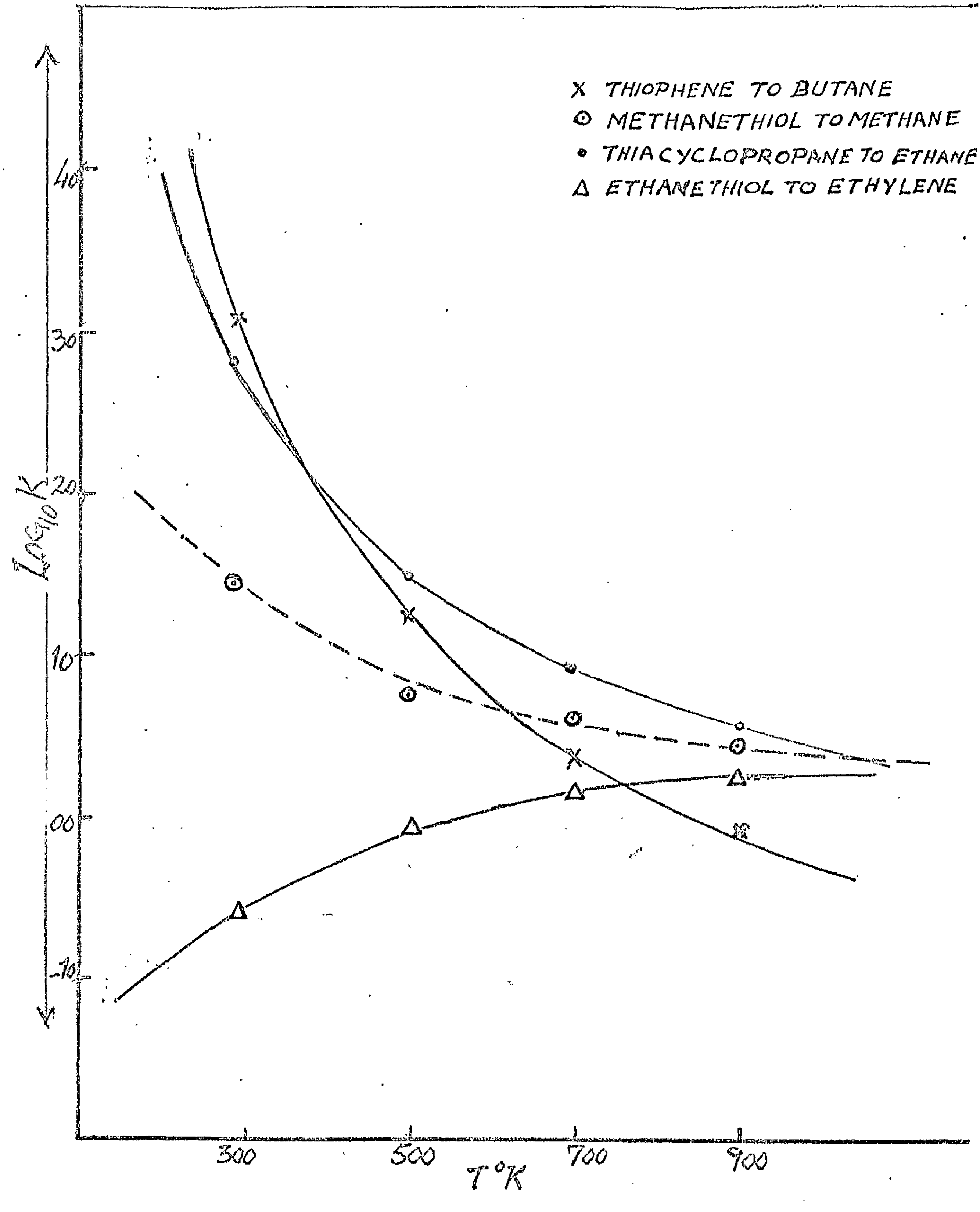

X THIOPHENE TO BUTANE
⊙ METHANETHIOL TO METHANE
• THIACYCLOPROPANE TO ETHANE
Δ ETHANETHIOL TO ETHYLENE
Log10 K
40
30
20
10
00
-10
300
500
700
900
T°K

FIG. 1.2

TABLE No. 1.3

Reaction of Sulphur Compounds under Hydrodesulphurisation

(1) Thiols:-

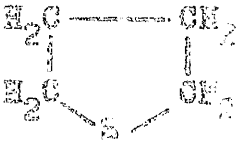
$$RSH + H_2 \longrightarrow RH + H_2S$$

(2) Sulphides:-

(a) open-chain

$$R\text{-}S\text{-}R^1 + 2H_2 \longrightarrow RH + R^1H + H_2S$$

(b) cyclic

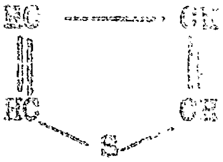


$$+ 2H_2 \longrightarrow CH_3.CH_2.CH_2.CH_3 + H_2S$$

(3) Disulphides:-

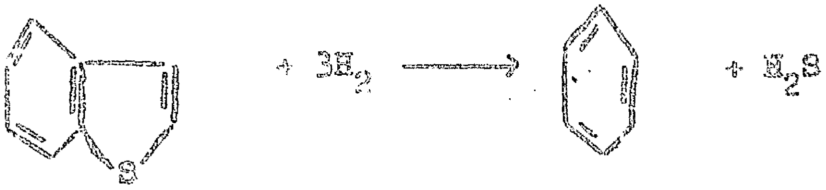
$$RSSR + 3H_2 \longrightarrow 2RH + 2H_2S$$

(4) Thiophenes:-



$$+ 4H_2 \longrightarrow CH_3.CH_2.CH_2.CH_3 + H_2S$$

(5) Benzothiophenes:-



One mole of hydrogen is required per mole of thiol for sulphur removal. Similarily for sulphides the hydrogen consumption would be two moles, and for thiophenes it would require four moles. Assuming a high thiophene content in residual oil a figure of four moles of hydrogen per atom of sulphur may be used. The removal of one percent of sulphur from a barrel of oil about 10° A.P.I. (i.e. weighing 350 lbs per barrel) would require

$$\frac{4(350)359}{100(32)} = 158 \text{ ft}^3 \text{ of hydrogen}$$

Hydrodesulphurisation may be carried out over a wide range of conditions. Choice is generally determined by the feed stock, the desired product, the availability of hydrogen, and other economic requirements. However usually the temperature range of 750 to 780°F is adopted, as below 500°F, the reaction is very slow and above 800°F undesirable side reactions such as hydrocracking tend to increase. Sulphur removal is proportional to the hydrogen partial pressure. Increase in the hydrogen present results in increased hydrogenation. Thus the plant designer has to balance any increased cost of higher pressure against the increase in efficiency, temperature and pressure are inter-related to each other. The use of high temperature (above 800°F) and low pressure (100 psig) promotes catalytic reforming reactions with increased deposition of carbon; while high pressure (1000 psig) and low temperature (600°F) leads to saturation reactions, e.g. conversion of aromatics to naphthenes. Conventional hydrodesulphurisation is an exothermic process and the heat evolved is proportional to the hydrogen consumption. Under properly chosen conditions with saturated feed stock where hydrocracking is eliminated the heat given out may be very small.

In general the physical state of the reactants i.e. liquid, gaseous or mixed phase has little effect on desulphurisation. It is however essential that proper distribution takes place over the catalyst bed, and this has led to a variety of reactor designs. Apparently all commercially available processes for the hydrodesulphurisation of low temperature distillate are of the fixed bed type. Moving bed processes are also employed for high temperature naphtha hydroreforming and desulphurisation. The preference for the fixed bed system is due to the simplicity of operation. This method is applicable to crudes and to residues; particularly at the higher temperature required for residue hydrogenation, continuous fluid and suspended catalyst processes offer advantages over the stand point of catalyst regeneration. The fluidised system has the limitation that the stock must be completely converted to vapourised products in order to maintain the catalyst fluidity.

There are a range of hydrogenation catalysts, one Patent[27] indicates that the oxides and sulphides of group II to VII of the Periodic Table are suitable but that group VIII elements together with the heavy metals of groups I and II are also quite suitable. [illegible] Patent[28] recommends group VI elements and particularly molybdenum tungsten and chromium for general hydrodesulphurisation processes. Hydrodesulphurisation would thus appear to be the most promising method for the desulphurisation of residual oils.

1.6 The Autofining Process.

1.6.1 The theory of the Process.

This is a catalytic process in which desulphurisation of a petroleum distillate is obtained by the fact that sulphur compounds are preferentially attacked and converted into non-substituted molecules by the action of hydrogen. The hydrogen required is provided by the dehydrogenation of part of the stock itself, hence the process becomes self-supporting with respect to the hydrogen.

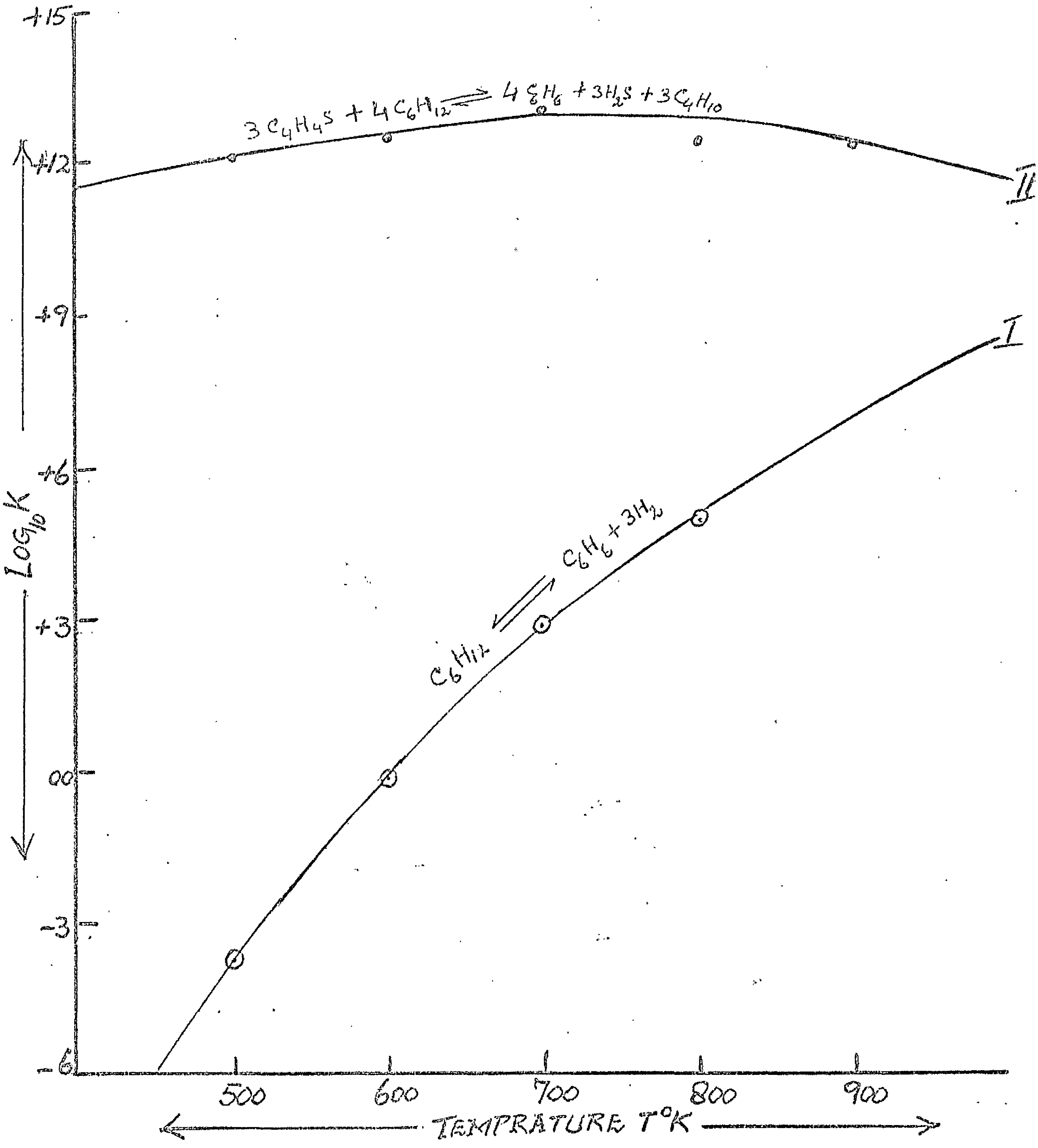
The two reactions involved in the process are dehydrogenation and desulphurisation: the dehydrogenation reaction is increased by raising the temperature and su~~g~~pressed by increase of pressure. Increase in the hydrogen partial pressure increases the rate of desulphurisation[29]. Extensive dehydrogenation leads to a marked change in the product quality, and hence high temperatures are to be avoided. On the other hand, processing at high pressure and moderate temperature would lead to an increase in desulphurisation but a decrease in dehydrogenation with the result that the process could not be made self-supporting with respect to hydrogen. However as reported by Porter[30] the temperature range 760 to 800°F, the pressure 50 to 200 psig, and a space velocity of 5.0 vol/vol.hr. are generally applied to all feed stocks.

Thermodynamic calculations show that the dehydrogenation of a six-membered ring such as cyclohexane is theoretically complete about 660°F. The variation of the logarithm of equilibrium constant with absolute temperature has been calculated and is shown in Figure 1.3. The corresponding calculation has been made for a model autofining process in which cyclohexane provides hydrogen for thiophene decomposition and this is shown also in the Figure. It may be seen therefore that the autofining reaction is quite thermodynamically feasible at the above temperatures.

In general the process operates at pressures of 50 to 300 psig and some sulphur stable catalyst such as cobalt molybdate is used. The catalyst is regenerated periodically. The on-stream period varies with the boiling range of the feed stock, the higher boiling feed stock giving the most trouble. When maximum desulphurisation is required, the unit is run under equilibrium pressure conditions, in which full use of the hydrogen produced is made, and no excess gas is removed from the system except that dissolved in the liquid product.

The two reactions, dehydrogenation and desulphurisation, are endothermic and exothermic respectivley, so that the overall reaction is substantially thermo-neutral.

The rate controlling factors in the case of the hydrodesulphurisation reaction for the formation of hydrogen sulphide and hydrocarbons, have been shown to be catalyst activity, temperature, and hydrogen and oil partial pressures.



$3C_4H_4S + 4C_6H_{12} \rightleftharpoons 4C_6H_6 + 3H_2S + 3C_4H_{10}$
II
I
$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$
$LOG_{10}K$
+15
+12
+9
+6
+3
00
-3
-6
500
600
700
800
900
TEMPRATURE T°K

FIG. 1.3.

It has been reported by Hoog[31], while processing a full boiling-range gas oil (500 to 662°F), that the rate of hydrodesulphurisation of the heavier fraction was considerably slower than the rate for the lighter fraction. Hoog showed that the phenomenon of " light-heavy selectivity" was due to the different type of sulphur compound present. The higher the molecular weight of the sulphur compound the more the sulphur atom is sheilded from the hydrogen atom by hydrocarbon groupings. It appears that the desulphurisation of narrow boiling-range fractions to a level of 95 percent removal could be described by a first order mechanism, viz.,

$$\ln(P_s/P_o) = -K_{H.O.} T$$

where P_s = Partial pressure of sulphur compounds at the end of the catalyst bed.

P_o = The corresponding partial pressure at the inlet to the catalyst bed.

T = Apparent contact time.

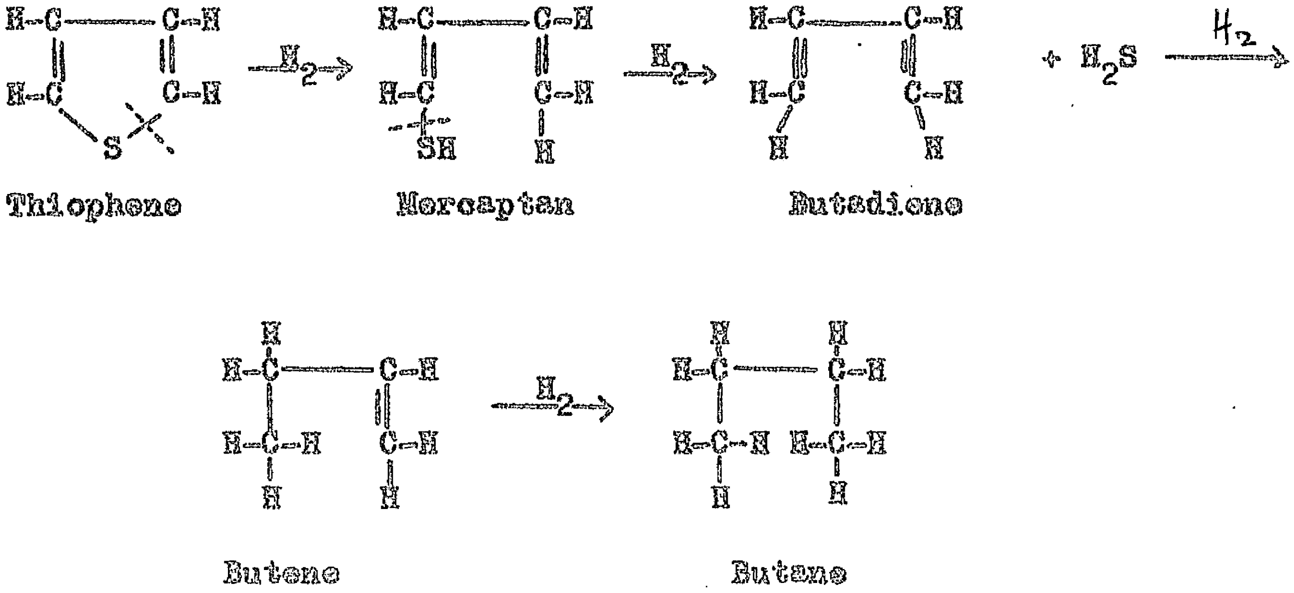
$K_{H.O.}$ = The rate constant for a given hydrogen partial pressure(H). Oil partial pressure (O) temperature and catalyst combination.

The desulphurisation of the full-range oil (500 to 662°F) did not follow this first order relationship. Thus the rate curve for wide range oil is in fact the resultant of an integration of the rate curves for a series of narrow cuts of increasing molecular weight.

The effect of oil partial pressure on the rate of desulphurisation was explained on the assumption that oil molecules are more strongly adsorbed on the catalyst than hydrogen molecules, and may preferentially cover part of the surface leaving less available for the dissociation of the hydrogen molecule. The adsorbed oil molecule is more easily expelled from the surface at a higher hydrogen pressure. This causes a reduction in the influence of oil pressure at higher hydrogen partial pressures.

In order to establish the type of chemical reactions occuring during hydrofining as distinct from cracking hydrogenation, Hoog[32] carried out a series of model experiments in which synthetic blends of sulphur compounds with sulphur free paraffin oil were subjected to hydrofining. The results obtained indicated that no methane or other light hydrocarbon is obtained, the reaction was in fact limited to a rupture of the carbon-sulphur bond, and the hydrogen saturation of the free valencies. In all cases (mercaptans, sulphides, and aromatic thiophenes) virtually complete desulphurisation was obtained. Very promising results were also obtained while autofining sulphur compounds extracted from the gas oil by hydrofluoric acid. These compounds were dissolved in n-heptane; and the solution was subjected to autofining. A sulphur reduction of 98 percent was obtained. Hoog further claimed that the sulphur compounds in light gas oil consisted of 30 to 40 percent simple thiophenes and 60 to 70 percent of homocyclic condensed thiophenes.

As a result of studies on the hydrogenation of thiophene over a vanadium oxide catalyst Komarewsky[33] proposed that the mechanism of this reaction involved the formation of mercaptans and then butadiene as intermediate stages, as shown below.



On the other hand, Kieran found that with tungsten and a molybdenum sulphide catalyst at low hydrogen partial pressures tetrahydrothiophene was formed. The mechanisms proposed by Kieran[34] to account for the effect of increasing hydrogen partial pressure are as follows:-

(a) $C_4H_4S + 2H_2 \longrightarrow C_4H_8S$

(b) $C_4H_4S + 3H_2 \longrightarrow C_4H_8 + H_2S$

(c) $C_4H_4S + 4H_2 \longrightarrow C_4H_{10} + H_2S$

The tetrahydrothiophene formed in the reaction (a) eventually further decomposes into hydrogen sulphide and butane. Since it decomposes ten times faster than the thiophene itself, at a sufficient hydrogen partial pressure reaction (c) is more evident.

It thus appears that at sufficient hydrogen partial pressure the ultimate product in both mechanisms is the formation of hydrogen sulphide and normal butane. This theory is supported by evidence provided by other workers[35,36].

1.6.2 The process in practice.

The autofining process has been applied satisfactorily with light distillates and gas oils. Till now the main interest in the process from a commercial point of view has been in the desulphurisation of lower boiling distillates, which require a relatively extensive refining treatment. The presence of napthenes in kerosines and light gas oil has made it feasible to desulphurise them in this way. Research carried out at Sunbury resulted in the development of a very satisfactory desulphurisation process capable of handling most distillate feed stocks. The first large scale unit of 3500 barrels per day capacity to handle naptha and power kerosine came into operation in 1952 at the Llandarcy refinery of the National Oil Company.

The average on-stream period was 800 hours for gasoline processing, while 400 hours were necessary for naphtha, kerosine, and tractor vaporising oil, and 200 hours for benzine, aromatic extracts, and gas oil. The regeneration was carried out with steam-air mixtures.

When processing naphthas in the above unit at 780°F, 100 psig and with a space velocity of 5.0 vol/vol. hr., not only was nearly complete desulphurisation obtained, but also an increase in octane number and improved lead response was reported. The sulphur content was reduced from 0.081 to 0.0007 percent.

Under the same conditions kerosine containing 0.18 percent sulphur was purified to 0.004 percent. Its char-value was also considerably reduced. The high sulphur content of tractor vaporising oil (0.577 percent) necessitated a lower space velocity of 2.0 vol/vol.hr. The sulphur content was reduced to 0.126 percent. In the case of aromatic benzine extract (0.295 percent sulphur) 98.6 percent of the sulphur was removed and in the case of gas oil (0.720 percent sulphur) fifty percent removal was achieved.

A small commercial unit of 350 barrels per day capacity was installed at Grangemouth refinery for processing a kerosine sulphur dioxide extract. By processing at a temperature of 780°F and a pressure of 100 psig and with a space velocity of 3.0 vol/vol.hr., a sulphur reduction from 1.04 percent in the feed to a product containing 0.45 percent was obtained (56.8 percent). The on-stream period was 200 hours, and regeneration was carried out as before with an air-stream blast.

It has generally been agreed that the autofining of higher boiling distillates and residual oils is difficult technically principally due to the frequent catalyst regeneration requirement (low on-stream periods) and the fact that the relatively low price obtainable for residual fuel oils necessitates a very cheap refining process. This state of affairs may not continue indefinitely due both to growing concern about atmospheric pollution and future shortages of higher grade fuels.

1.7 Purpose of Research.

The purpose of this study was to select typical residual fuel oils and to characterise them as far as possible, and then to make a study of their desulphurisation. To this end it was proposed to find the effect of heat, catalysts and hydrogen on the sulphur content of these oils. It was also intended to make a parallel study with simple model sulphur compounds. Since in the above discussion it was apparent that the autofining process offered an internal source of hydrogen, it was hoped in the end to attempt to develop a process for residual oil desulphurisation using naphtha fractions as a source of hydrogen.

2. CHARACTERISTICS OF OILS.

Three residual oils were obtained for the purpose of this study. Their origin and grade is given in the Table 2.1 below.

Table No. 2.1.

Oil	Origin	Viscosity Redwood No.1. at 100°F	Sulphur %
A	Shell	2220	3.34
B	Esso; atmospheric residue from Iraq Crude.	4450	4.10
C	Esso; atmospheric residue from Kirkuk Crude	3990	4.10

They were all dark oils.

2.1 Determination of Oil Sulphur Content.

A rapid method for the determination of the total sulphur content of such oils has been worked out. This is a modification of the method[37] applied for the determination of sulphate in raw waters, and uses the Thoron indicator. It was found that the new method had a considerable advantage over the conventional gravimetric method[38]. Details of the method and the appropriate calculations are given in the Appendix to this work.

The sulphur contents of the three oils are given in the Table 2.2 below.

Table No. 2.2

Percentage Sulphur in the Oils.

Determination number	Oil A	Oil B	Oil C
1.	3.22	4.08	4.14
2.	3.42	4.12	4.11
3.	3.35	-	4.16
Average	3.34	4.10	4.13

2.2 Seperation of Saturate and Aromatic Fractions of Test Oils.

The saturate and the aromatic fractions of each oil were separated using the chromatographic method, described by Brook and Whitman[39]. The actual procedure is described in the Appendix. A one gram sample of oil was taken for each determination. The results are given in the Table 2.3 on the next page.

Brook and Whitman define the saturate fractions as naphthenes and paraffins. The insoluble residue appeared to consist mainly of carbon (i.e. petroleum coke) and small amounts of mineral matter. As it was determined by difference and was infact the material inseparable from the chromatographic column, it would of course include unaccounted-for errors.

Table No.2.3.

Percentage "Saturate" and "Aromatic" in Test Oils.

Oil	Saturate	Aromatic	Insoluble Residue (by difference)
A	39.20 39.30 39.10 39.20	53.30 53.20 53.60 53.10	7.5 7.5 7.3 7.7
Average	39.20	53.30	7.50
B	38.80 38.40 38.90	54.40 54.80 54.10	6.80 6.80 7.00
Average	38.70	54.43	6.86
C	38.72 38.40 38.80	52.65 53.40 52.95	8.63 8.20 8.25
Average	38.64	53.00	8.36

2.3 Sulphur Balance of Oils.

The saturate and aromatic fractions obtained by the method indicated in 2.2 were further analysed to determine their sulphur content by the method mentioned in 2.1. The over-all sulphur balances are shown in the following table.

Table No. 2.4

Sulphur Balance on Test Oil Fractions.

Oil	Type of fraction	Percentage weight in fraction	Percentage sulphur in fraction	Weight per 100 gms test oil	Percentage Total sulphur in fraction
A	Saturate	39.2	0.80	0.316	9.35
	Aromatic	53.3	5.20	2.781	83.37
	Insoluble residue	(7.5)	–	(0.243)	(7.28)
	Total	100.00		3.34	100.00
B	Saturate	38.71	0.32	0.130	3.16
	Aromatic	54.43	6.80	3.690	90.00
	Insoluble residue	(6.86)	–	(0.280)	(6.84)
	Total	100.00		4.10	100.00
C	Saturate	38.64	0.34	0.132	3.19
	Aromatic	53.00	6.88	3.654	88.24
	Insoluble residue	(8.36)	–	(0.344)	(8.57)
	Total	100.00		4.130	100.00

The values shown in brackets were obtained by difference.

The results show that most of the sulphur compounds are concentrated in the aromatic fractions of the oils. No great importance should be attached to the sulphur content of the insoluble residue since its weight was determined by difference and thus includes all the errors of the method.

2.4 Detection and Classification of Sulphur Compounds in Test Oils.

The methods developed by Karr[40] for qualitative determination of sulphur compounds were applied here to attempt to detect the types of sulphur compounds in these residual fuel oils. The results are shown below.

Table No. 2.5

Detection of Sulphur Compounds.

The oil (A) was dissolved in two parts by volume of carbon tetrachloride and observations were carried out as below:-

Group tested for	Observation	Inference
Aliphatic + Aromatic thiols (1A)	0.5 ml of the mixture + two drops of 2% silver nitrate solution. On shaking white precipitate was formed	Positive
Aliphatic + Aromatic thiols (1B)	0.5 ml of the mixture + two drops of glacial acetic acid + two drops of sodium nitrite solution. No green or red precipitate.	Negative
As 1A (1D)	0.5 ml of the mixture + 0.5 ml of ethanol + two drops of 15% sodium hydroxide + four drops of 10% Phosphomolybdic acid. After agitation, the aqueous layer changed from yellow to green.	Positive
Aromatic thiols (1E)	0.5 ml of the mixture + two drops of 10% phosphomolybdic acid. The aqueous layer changed from yellow to green	Positive
Aliphatic and Aromatic disulphides (2A)	2 ml of the solution + two drops of 2% silver nitrate were agitated and centrifused. The hydrocarbon layer was collected, and 10 small granules of zinc were added + three drops of glacial acetic acid. The mixture was refluxed for a few minutes and then the solution was tested as 1A.	Positive.

Table No. 2.5 continued.

Group tested for	Observation	Inference
Sulphides of all types (3A)	0.5 ml of the mixture + three drops of 41% nitric acid and one drop of H_2SO_4 + one drop of 10% phosphomolybdic acid. No yellow precipitate was obtained, but a dark gelatinous mass was formed.	Inconclusive
Aliphatic and cyclic sulphides (3B)	2.0 ml of the solution + two drops of nitric acid + three drops of 10% phosphomolybdic acid. Yellow precipitate formed, but disappeared on shaking	Inconclusive
Aromatic thiols, disulphides and simple thiophenes	2.0 ml of the solution + three drops of sulphuric acid were agitated for a few minutes. The orange colour in the aqueous layer was observed.	Positive

The numerals and letters given in the left hand column of the above table refer to Karrs original classification of groups. These observations were carried out only on the test oil A. Since the results were in most places rather inconclusive, the scheme of analysis was not applied to the other two oils. It would appear that Karr analysis is not really applicable to residual fuel oils.

2.5 Structural Group Analysis of the Test Oils.

The "carbon distribution" and so called "ring contents" of the test oils were determined by the normal "n, d, M" and "V_k, n, d" methods[41]. The percentage numbers of carbon atoms in paraffinic structure, naphthenic structure, and aromatic structure were calculated by the methods shown in the Appendix. The refractive index (n) and the density (d) were determined at both 20°C and 70°C by Abbe refractometer and accurate pycnometer, respectively. The molecular weights were determined by a modification of Heitlers[42] ebulliometer. The necessary calculation of the molecular weight is included in the Appendix. The kinematic viscosity (V_k) of the test oils at 20°C was determined by means of a standard reverse-flow viscometer[43].

The data obtained ~~is~~ are tabulated below.

Table 2.6

Oil	Refractive Index		Density		Mol. Wt. (M)	Viscosity. cs (V_k)
	n_{20}	n_{70}	d_{20}	d_{70}		
A	1.6340	1.541	0.978	0.968	463	546
B	1.6438	1.548	0.9828	0.972	583	965
C	1.6442	1.552	0.9838	0.976	618	1177

The results of Table 2.6 were used to calculate the structural group analysis by the two well-known methods. The results obtained from the n, d, M at 70°C are shown in Table 2.7; a specimen calculation is included in the Appendix.

Table 2.7

Structural Group Analysis from determinations at 70°C .

Oil	C_A	C_N	C_R	C_P	R_A	R_N	R_T
A	32.09	19.21	51.30	48.70	1.91	1.65	3.56
B	34.59	9.02	43.54	56.46	2.61	0.575	3.18
C	36.48	5.33	41.83	58.17	2.96	0.770	3.83

where:— C_A = Percentage carbon atoms in Aromatic strucuure.
C_N = " " " " Naphthenic "
C_R = " " " " Ring "
C_P = " " " " Paraffinic "
R_A = Total aromatic rings.
R_N = " naphthenic "
R_T = Total rings.

The structural group analysis estimated from the nomograph given in the standard work by Boelhouwer and Cornelissen[44] using the V_k, n, d data at 20°C and shown in the following Table 2.8.

Table 2.8

Structural Group Analysis from V_k, n, d at 20°C

Oil	C_A	C_N	C_R	C_P	R_A	R_N	R_T	Estimated M
A	32.24	16.76	49.0	51.0	2.25	1.05	3.30	480
B	33.50	8.50	42.0	58.0	2.85	0.25	3.10	570
C	34.56	4.44	39.0	61.0	2.90	0.60	3.50	600

The differences between the results given by the two methods are shown in the Table 2.9.

Table 2.9

Oil	C_A	C_N	C_R	C_P	R_A	R_N	R_T	M
A	-.05	+2.45	+2.3	-	-0.34	+0.50	+0.260	-17
B	+1.02	+0.52	+1.54	-	-0.24	+0.325	+0.08	+13
C	+1.92	+0.89	+2.83	-	+0.06	+0.170	+0.33	+18

Where the n-d-M method gave a higher result the difference is preceeded by a plus sign, and an excessive V_k-n-d value by a minus. It may be seen that on the whole the n-d-M method gave slightly higher results but in general the two sets of figures are satisfactorily close.

The carbon and hydrogen contents of the test oils were also determined together with their nuclear magnetic spectra. The latter were obtained on the Perkin Elmer Model 10 of 40 M.C. The results are shown in Table 2.10 and 2.11

Table 2.10

Oil	Percentage carbon	Percentage hydrogen	Percentage sulphur	Total
A	85.08	11.68	3.34	100.00
B	84.24	11.66	4.10	100.00
C	84.24	11.63	4.13	100.00

Table 2.11

Oil	Percentage Aromatic Hydrogen ($\%H_A$)	Percentage Naphthenic + Paraffinic Hydrogen ($\%H_{N+P}$)	C_A	C_{N+P}	C:H Aromatic	C:H non-Aromatic	Formula
A	6 .5	93.50	32.16	67.84	4.93	0.725	$C_{33.5}H_{55}S_{.491}$
B	5.02	94.98	34.04	65.96	6.90	0.688	$C_{40.6}H_{67.2}S_{.632}$
C	5.92	94.08	35.52	64.48	6.15	0.637	$C_{42.7}H_{71}S_{.803}$

In the Table 2.11 the percentage of aromatic hydrogen and of non-aromatic hydrogen estimated from the N.M.R. Spectra, are included together with corresponding average values for carbon already obtained by structural group analysis. The aromatic and non-aromatic carbon-hydrogen ratios calculable from these results are included in the table. While realising that residual fuel oil will contain a vast range of different molecules, it is useful to calculate a so-called formula for a hypothetical average molecule; that may be considered to constitute the unfractionated oil. A specimen calculation is given in the Appendix and the results are included in the last column of the table.

2.6 Discussion.

The experimental results obtained for the three test oils in general show them to be rather similar in constitution, particularly the latter two in spite of their difference in origin. The sulphur balances of the oils show that 80 to 90 percent of the total sulphur is connected to aromatic structure which constitutes more than half of the weight of the oil. The presence of high percentage of aromatic sulphur compounds in the heavy oils has already been indicated by others[45].

The structural group analysis of the oils leads to the same conclusions; in particular the percentage of carbon atoms in aromatic structure (C_A) is remarkably similar. This analysis also shows that about 40 to 50 percent of the total carbon in the oils is in the form of ring structures and that these aromatic sulphur compounds ~~were~~ are likely to be in the form of condensed rings. It appears therefore that most of the sulphur atoms in the oils are linked to condensed aromatic structures of high molecular weight and therefore any physical separation process, e.g. solvent extraction, to remove sulphur compounds must necessarily also remove a large bulk of the oil. It is not possible to obtain a very high sulphur-containing concentrate or to remove a large proportion of the sulphur without breaking up chemical structures.

3. PRELIMINARY PYROLYSIS STUDIES.

One of the simplest ways of breaking a chemical structure is to heat the material to a high temperature. Such a pyrolysis when applied to hydrocarbon materials on an industrial scale is known as "thermal cracking".

It was decided to make a preliminary investigation of the effect of mild thermal cracking on the sulphur content of the oil and on the distribution of sulphur among the products of the pyrolysis.

3.1 General Description of the Apparatus.

The apparatus consisted of three parts (a) the feeder (b) the reactor and (c) the collecting device for the product. The design of the feeder is shown in the Figure 3.1 while the actual connection of the feeder to the reactor is shown in the general Figure 3.2.

One of the open arms of the feeder was connected to a supply of nitrogen from a cylinder through a calibrated manometric flow meter. During the run a constant flow of nitrogen into the reactor was maintained by this means. The other arm was connected to a pressure equalisation tube and manometer. A small thermometer pocket was situated in the centre of the feeder, and during a run a thermometer was fitted into place. The volume of the feeder at different levels was shown by a graduated tape fixed on the outside of the wall of the feeder. The stopcock of the feeder was fitted with a polytetrafluoroethylene plug. The plug had an extension finger and when the plug was turned the finger moved over a calibrated flow scale.

The reactor consisted of a 35.5 inches long pyrex glass tube with

OIL FEEDER.

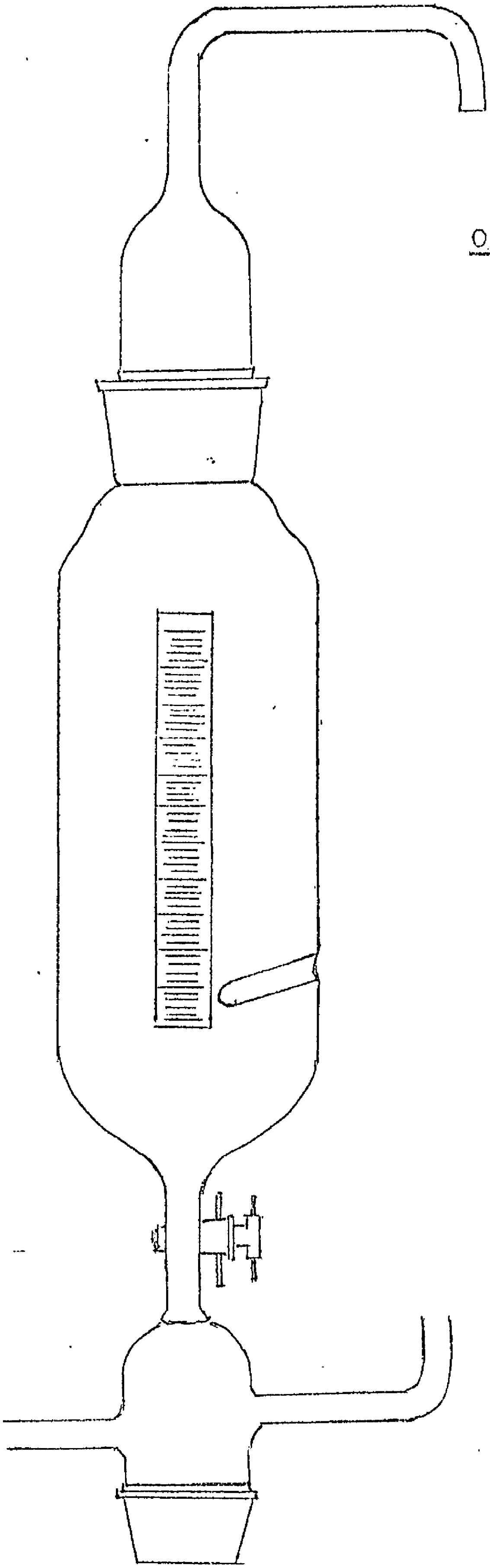


Fig. 3·1

PRELIMINARY PYROLYSIS APPARATUS

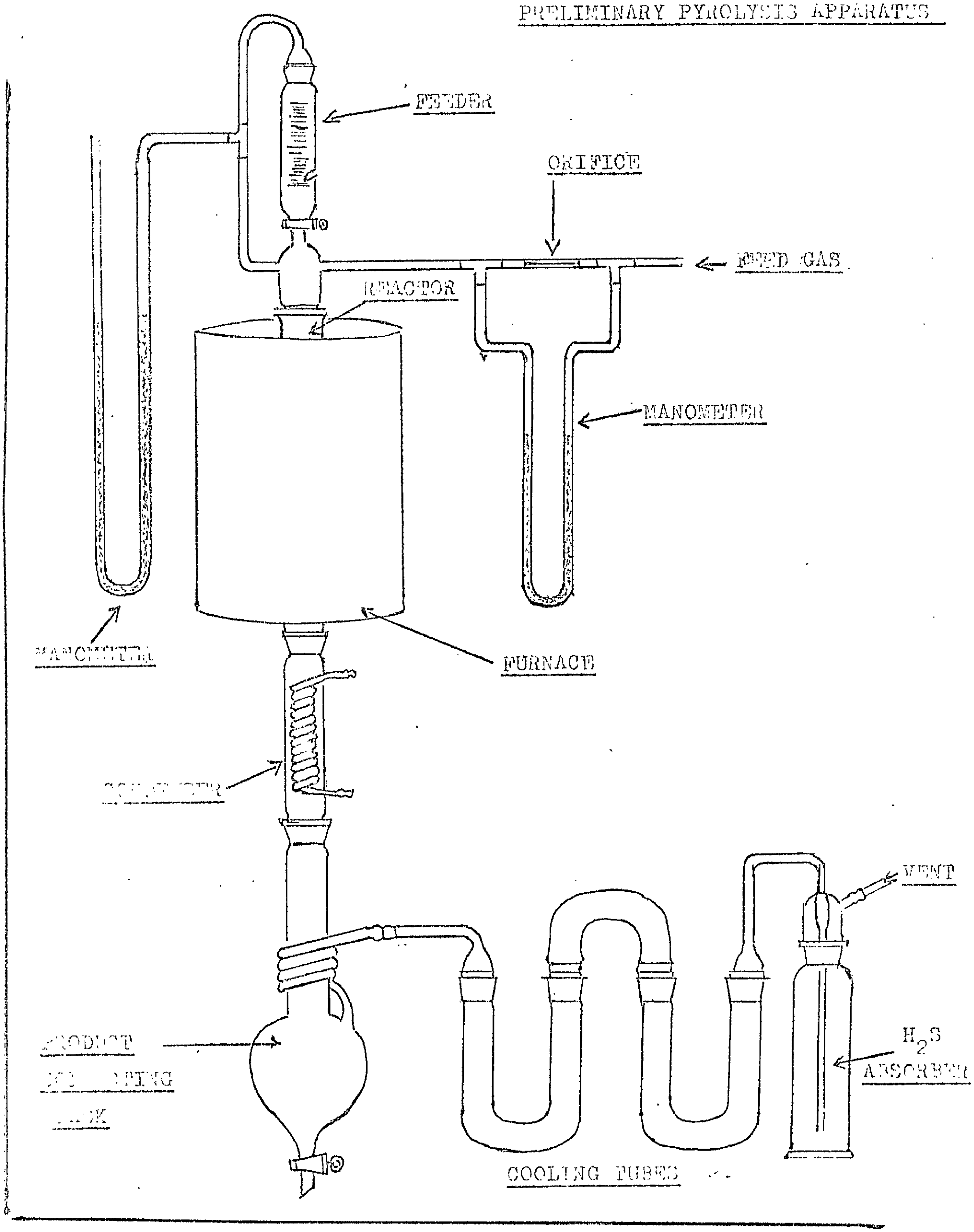


FIG. 3.2

an I.D. of one inch. The design of the reactor is shown in the Figure 3.3. The reactor was fitted with an longitudinal thermocouple pocket of 8mm I.D. tube, and was kept in a vertical position in an electric tube furnace 30.5 inches long and with an internal diameter of 2.5 inches. A chromel-alumel thermocouple was fitted into the pocket. The bottom of the reactor was connected to a spiral water-filled condenser which was intended to cool and condense the cracked oil vapours in a collecting flask. The gases from this flask were led through a spiral into a pair of U-tubes which stood in beakers containing acetone and solid carbon dioxide. The gases leaving the U-tubes were passed through an aqueous solution of cadmium sulphate contained in a gas-absorbing bottle.

3.2 Temperature Distribution of the Furnace.

The equilibrium temperature existing at different points along the length of the furnace was determined by means of a travelling calibrated thermocouple. The temperature at each two inches of length was obtained at three suitable electric current settings and the readings plotted as shown in Figure 3.4. It may be seen that the temperature was slightly higher at the two ends of the furnace to an extent of about 7±2°C than at the middle position. This would allow, however for cooling by radiation etc., from the ends of the furnace and thus the middle twenty inches of the furnace would provide almost constant temperature conditions along that lenght of the reactor.

REACTOR

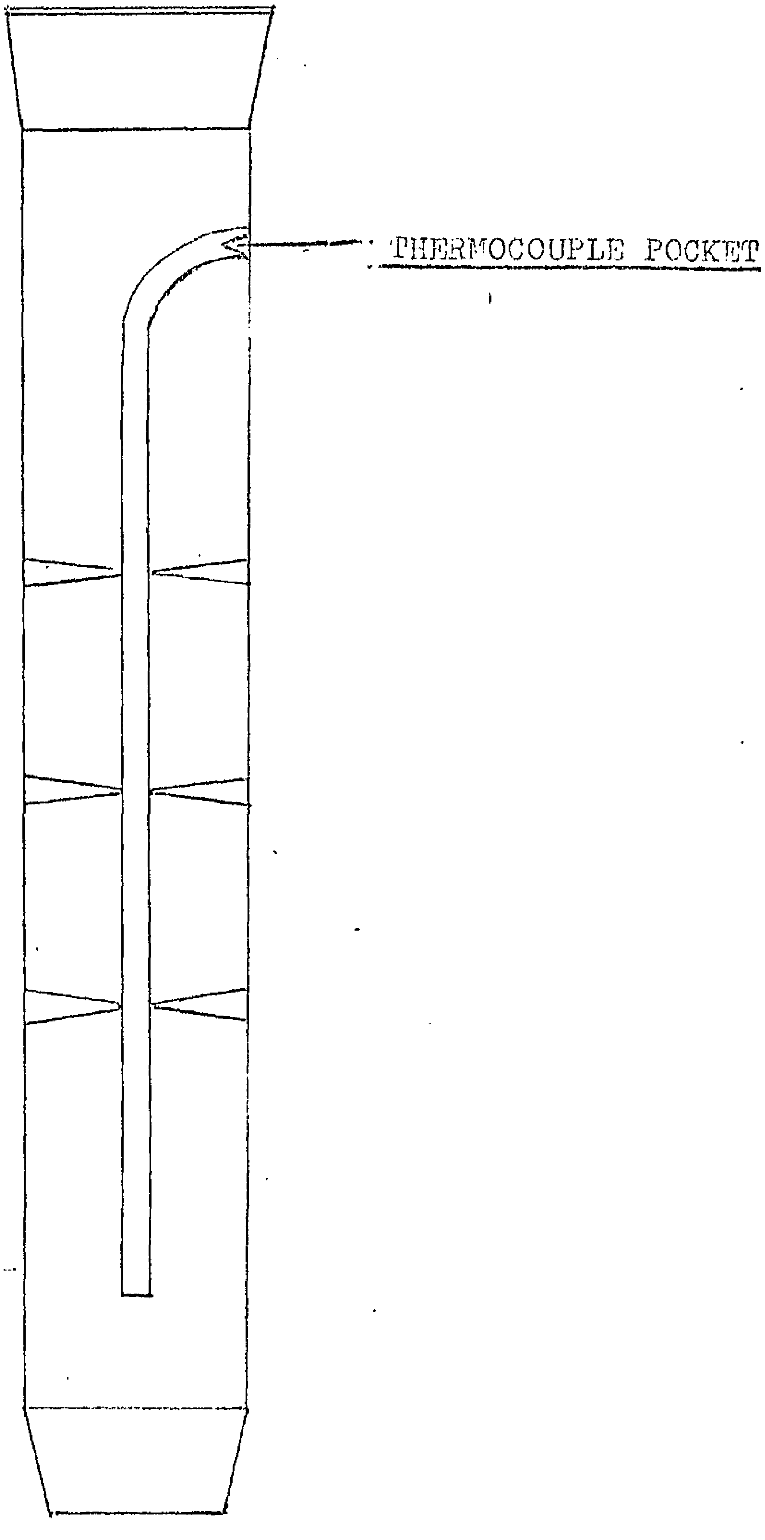
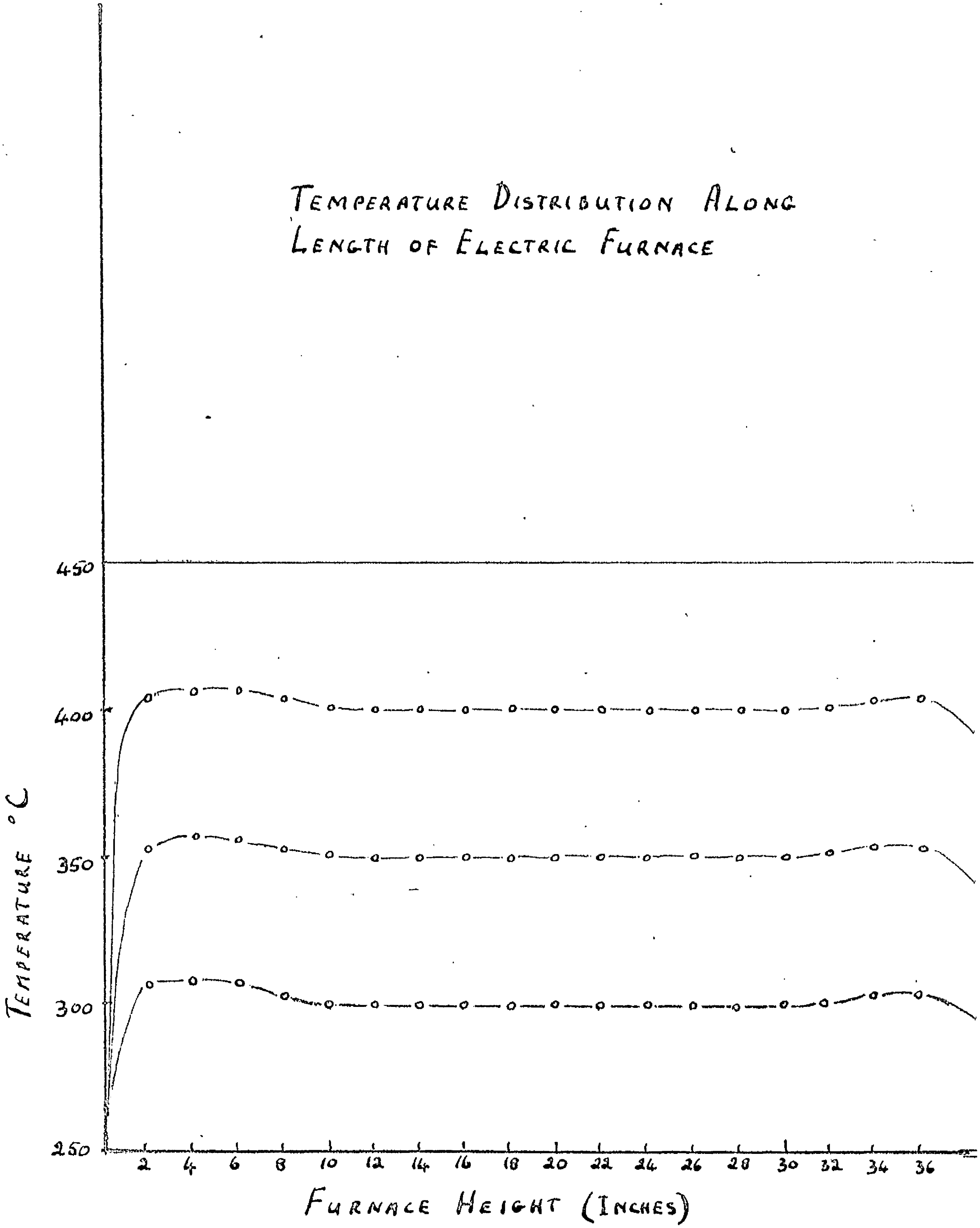


FIG. 3.3.



Temperature Distribution Along Length of Electric Furnace

Fig 3·4

3.3 Thermal Cracking of the Oil on Glass at 430°C.

The reactor was filled with 20 inches of glass helices supported on glass wool as shown in Figure 3.5. The temperature was brought to the required value while nitrogen was passed through the reactor. The test oil A was then run in from the feeder for two hours under the following conditions:-

Reactor temperature = 430°C
Oil flow rate = 2.0 gm/min.
Nitrogen flow rate = 0.0061 ft^3/min at N.T.P.

The hydrogen sulphide coming off with the exit gases was absorbed in ten percent cadmium sulphate solution; and collected for three five-minute periods during the run. The sulphur was then determined by the standard I.P. method[3f]. The oil collected in the condenser recovery-flask was analysed for sulphur by the method described in the Appendix. The percentage removal of sulphur from the oil based on the hydrogen sulphide analysis was compared with the same removal found by determining sulphur content of the liquid product, and the comparison is recorded below:-

Sulphur removal from oil (based on H_2S analysis) = 12.30%
Sulphur removal from oil (based on liquid product) = 16.20%

It may be seen that, although there is some discrepancy between the results possibly due to sampling difficulties, mild thermal cracking appears to remove a significant amount of sulphur from the oil.

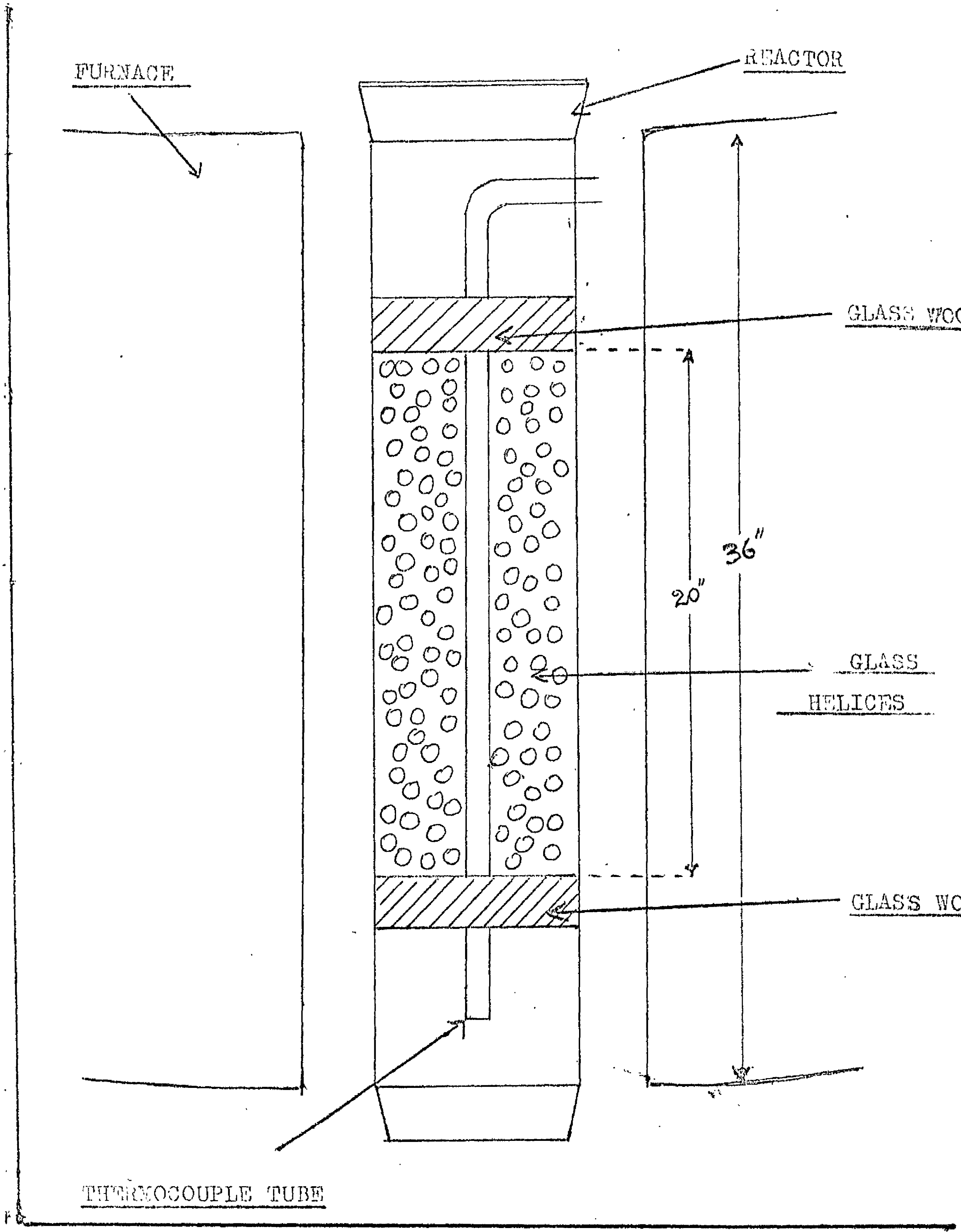

FURNACE
REACTOR
GLASS WOOL
36"
20"
GLASS HELICES
GLASS WOOL
THERMOCOUPLE TUBE

FIG. 3·5.

3.3.1 Material balance on thermal cracking.

The over-all material balance of the above process was determined. The reactor was heated to 150°C, and benzene was run through to collect benzene-soluble material. The benzene extract was heated to remove the solvent and the residue weighed. The increase in weight of the reactor itself gave the petroleum coke formed. The material balance obtained is shown in the Table 3.1.

Table 3.1

Material Balance (Thermal Cracking)

Input Oil	Output		% Recovery
240.00 gm	Oil	= 209.60	87.10
	Benzene soluble	= 7.20	3.00
	Petroleum coke	= 16.04	6.70
	H_2S	= 0.64	0.26
	Loss	= 6.52	2.94
Total = 240.00 gm	Total	= 240.00	100.00

3.3.2 Sulphur balance on thermal cracking.

From the sulphur determinations on various products an overall sulphur balance was calculated. The results are tabulated over the page.

Table 3.2

Sulphur Balance (Thermal Cracking)

Based on 100 gm of oil

Percentage sulphur in Input oil = 3.34
" " " Output oil = 2.85
Percentage sulphur in Benzene soluble oil = 2.82

Input oil	Output	Percentage of Total sulphur
3.34 gm	Oil = 2.485	74.30
	Benzene soluble = 0.084	2.52
	H_2S = 0.402	12.30
	Loss = 0.369	10.88
Total = 3.34 gm	Total = 3.34	100.00

The results showed an unaccounted for sulphur loss of about 11.0 percent. This could be accounted by inaccuracies in the sampling of the hydrogen sulphide-containing gas and other experimental errors.

3.4 Thermal Cracking of the Oil on Copper at 430°C.

The glass helices in the reactor were replaced with 150 gms of pure copper foil cut into small pieces of approximately $\frac{1}{4}$ inch square. This weight of foil occupied the same volume as the glass helices used in the previous experiment. The run conditions i.e. temperature feed rate, etc., were as before.

The run was carried out over three hours, and the product oil was collected in seperate increments every fifteen minutes. The sulphur content of each fifteen minute fraction was determined and the results are shown in the Table 3.3. No cadmium sulphide was precipitated in the gas bottle indicating that no hydrogen sulphide had escaped from the reactor. When the copper foil was removed from the reactor at the end of the run it was found blackened due to the formation of copper sulphide. The total sulphur content of the foil was determined by the method described in the Appendix.

Material and sulphur balances were calculated as before.

Table 3.3

Thermal Cracking of oil on Copper

Sample No.	Duration	Input Percentage Sulphur	Output Percentage Sulphur	Percentage Reduction
1.	0—15'	3.34	2.42	27.6
2.	15—30'	"	2.40	28.1
3.	30—45'	"	2.36	29.4
4.	45—60'	"	2.16	35.4
5.	60—75'	"	2.09	37.6
6.	75—90'	"	2.09	37.6
7.	90—105'	"	2.06	38.6
8.	105—120'	"	2.06	38.6
9.	120—135'	"	2.08	37.8
10.	135—150'	"	2.05	38.5
11.	150—165'	"	2.05	38.5
12.	165—180'	"	2.05	38.5

Table 3.4

Material Balance - Thermal Cracking on Copper.

Input Oil	Output	Percentage
360 gm	Oil = 305.15	84.60
	Benzene soluble = 19.35	5.34
	Petroleum coke = 26.80	7.45
	Loss = 8.70	2.61
Total = 360.00	Total = 360.00	100.00

Table 3.5

Sulphur Balance - Thermal Cracking on Copper.

Based on 100 gm of oil

Sulphur contents in products

Percentage sulphur in output oil = 2.060

Percentage sulphur in benzene soluble product = 2.820

Percentage sulphur in 100 gm copper = 0.821

Input oil	Output	Percentage Sulphur in fraction
3.34 gm	Output oil = 1.7450	52.30
	Benzene soluble = 0.1503	4.50
	Copper Foil (150 gm) = 1.2310	36.83
	Loss = 0.2137	6.37
Total = 3.34 gm	Total = 3.3400	100.00

3.5 The Effect of Copper Contact Time on Sulphur Reduction of the Test Oil.

The effect of contact time was determined by taking a new bed of copper foil. The total volume occupied by 150 grams of copper was obtained by water displacement. The corresponding volume obtained from the true density for this amount of copper was subtracted from the former total volume. The bed voidage was thus obtained, and hence the residence time for each flow rate was calculated. The calculation is shown in the Appendix. The reactor temperature and nitrogen gas flow rate were kept constant for all succeeding runs. Each run was carried out for two hours, and the extent of desulphurisation was determined from the analysis of the product oil.

The results are tabulated below.

Table 3.6

Effect of Contact Time

Test Oil flow rate	Residence time in seconds	Sulphur weight percentage in product	Percentage total sulphur removal
1.0 gm/min	62"	2.19	34.21
2.0 "	31"	2.28	31.80
3.0 "	20.6"	2.63	21.42
4.0 "	15.5"	2.79	16.30
5.0 "	12.4"	2.92	12.51

3.6 The Effect of Repeated Contact with Copper.

The last nine fifteen-minute samples of the run described in Section 3.4 were collected together and this mixed oil was utilised to determine the further sulphur removal possible by a series of contacts with fresh samples of copper foil. Experimental conditions were as before.

The results are tabulated below.

Table 3.7

Effect of repeated contact with copper.

Number of contacts	Total contact time (secs)	Percentage sulphur in feed	Percentage sulphur in product	Percentage removal of sulphur	Overall total percentage sulphur reduction
1.	31"	2.06	2.02	1.02	39.32
2.	62"	2.02	2.02	nil	39.32
3.	93"	2.02	2.02	nil	39.32

It was found, as shown above, that the copper foil could not reduce the sulphur content to any material extent by further contacts after the first run. It would appear therefore that chemical equilibrium for the reaction between the sulphur compounds in the oil and the copper was virtually reached in about thirty seconds of contact time.

3.7 Discussion.

This preliminary pyrolysis study was intended to find the extent of desulphurisation of the test oil by thermal cracking at a temperature range which would be used in later hydrodesulphurisation studies.

A removal of 16.2 percent of the sulphur in the oil at a temperature of 430°C and in contact with relatively inert gaseous surfaces establishes that hydrogen produced by the cracking was hydrogenating the sulphur compounds to produce hydrogen sulphide. The possibility of thermal decomposition of complex thiophenes is not likely even at 1500°K (1227°C) as has been shown in the Figure 1.1. The logarithm of equilibrium constant for the decomposition is highly negative at 430°C.

It was felt that the thermal cracking process and the production of hydrogen sulphide would not necessarily have reached equilibrium in the contact time possible in the apparatus.

Thus a catalyst was sought which if possible would also be a chemical material capable of removing hydrogen sulphide from the system, so that the hydrodesulphurisation reaction could go to completion. Loudon[46] mentions the use of copper[47] in the estimation of sulphur from chemical compounds. In view of this pure copper foil was used for the subsequent thermal cracking experiments. It was found that using the same experimental conditions as with glass helices the copper foil caused the removal of 38 to 39 percent of the sulphur in the oil. This indicates that the copper is either, promoting the thermal cracking of the hydrocarbons which produces the hydrogen for the subsequent hydrodesulphurisation, or is acting as an absorbent for hydrogen sulphide and effectively reducing its partial pressure and thus promoting the hydrogenation of the sulphur compounds. Possibly both effects take place to some extent.

Since it was found that repeated contact of the treated oil with further amounts of fresh copper at 430°C did not produce further sulphur removal, it would appear that the treated oil was now stable to cracking at 430°C or that all the sulphur compounds that could be hydrogenated under the experimental conditions had been removed by the earlier treatment. It is possible that further sulphur removal could be achieved by carrying out the thermal cracking process at a higher temperature, but this would markedly increase the loss of oil as carbon, thus it was not felt suitable to continue on this line.

4. DEHYDROGENATION STUDIES.

In the previous section it was shown that only a limited amount of hydrogen could be obtained by thermal cracking at 430°C. This was sufficient to hydrogenate only about forty percent of the sulphur compounds.

From a consideration of the stoichiometry of the system, an oil containing "S" percent (w/w) sulphur would require 2S/32 grams of hydrogen to react with the sulphur in 100 grams of oil.

In a fuel oil of the following analysis[40] ;

C = 85.1, H = 10.9 and S = 4.0

removal of all the sulphur as hydrogen sulphide would give in theory a residual oil containing C = 89.35, H = 10.65. However owing to the nature of the thermal cracking process the dehydrogenation of the oil cannot normally come about without simultaneous deposition of carbon, and this results in a loss of valuable material. It is therefore necessary to add to the system another petroleum fraction which can be dehydrogenated to a useful material; and provide sufficient hydrogen to remove all the sulphur from the heavy oil as hydrogen sulphide.

The parts of this work which follow have been arranged to study the various aspects of such a process; viz., the dehydrogenation of suitable hydrocarbon, hydrogenation of thiophene and the selection of a suitable catalyst combination which would permit both reactions to be carried out consecutively in the one system.

4.1 Catalytic Activity.

It is known that certain metals and their oxides are suitable hydrogenating and dehydrogenating catalysts. This is associated both with their ability to adsorb hydrogen and with the electronic configuration of the metal atom. If one considers the IV, V and VI periods of the Periodic Table, it is found that with the transition elements the 3d, 4d and 5d orbitals are unfilled. With such elements adsorption of hydrogen take place at a high rate and the amount adsorbed corresponds to the coverage of a large part of the metal surface.

The specific catalytic activity of such an element is associated with the bond energy between the hydrogen and the metal surface, and the number of unpaired "d" electrons. It is found that the activity passes through a maximum viz., Scandium and Titanium have little activity, Vanadium through to Nickel are active, and Copper which has a completely filled "d" shell has again little activity. Hydrogen is not chemisorbed on copper to any great extent until a temperature in excess of 400°C is reached.

Holling and Griffith[49] have measured to adsorption of hydrogen on various transition metallic oxides at different temperatures. The results are shown in Table 4.1.

Table 4.1

Adsorption of Hydrogen on Metal Oxides.

Catalyst	Temperature				
	100°C	200°C	300°C	400°C	450°C
	ccs adsorbed per 100 grams catalyst				
V oxide	27	30	490	1950	1974
Cr oxide	152	280	400	392	385
W oxide	3	76	57	38	210
Fe oxide	40	80	360	1676	1800
Co oxide	613	993	1014	1013	1013

It is to be anticipated that the oxides will show maximum catalytic activity at the temperature of maximum hydrogen adsorption.

In the hydrogenation of sulphur compounds sulphur-sensitive catalysts have to be avoided. Such sulphur sensitive catalysts are exemplified by iron, cobalt and nickel metal or oxides. The active hydrogenation sites of such catalyst are readily poisoned by traces of sulphur and also by organic peroxides and unsaturated polymers which may be present in petroleum products. Sulphur-insensitive catalysts include vanadium, chromium , tungsten and molybdenum oxides and sulphides. These catalysts display their maximum activity only at relatively high temperatures, but are quite active in the temperature range employed for hydrodesulphurisation.

Tungsten disulphide is a strong hydrogenation and hydrocracking catalyst and may be more active than molybdenum. It may also be used for olefin hydrogenation and for the hydrogenation of aromatics.

Extensive use of a cobalt-molybdenum type catalyst is made in the industrial hydrodesulphurisation of the naphtha and light gas oil. Since molybdenum falls in the $4d^4$ transition series and chromium and tungsten in the $3d^4$ and $5d^4$ respectively, the last two elements also could be satisfactorily utilised for such processes. Vanadium being in the $3d^3$ state should also bear a close resemblance to chromium in its catalytic activity.

4.2 Preparation of Catalysts.

The oxides of five elements were selected as possible suitable catalysts. These were vanadium, tungsten, molybdenum, chromium and cobalt oxides. All the reagents used were of analytical grade.

4.2.1 Preparation of Vanadium Oxide (V_2O_5).

Excess concentrated nitric acid was carefully added to a hot saturated solution of ammonium metavanadate (NH_4VO_3). The dark brown precipitate was filtered and washed until freed from nitrate. It was then dried at 120°C. When required, the powder was slightly dampened with water and made into pellets by means of a pharmaceutical pelleting machine. The pellets had an average thickness of 1/8" and a diameter of 3/16".

4.2.2 Preparation of Tungsten Oxide (WO_3).

Ammonium tungstate $(NH_4)_{10}W_{12}O_{41}$ solution was treated as above. The precipitate was yellow.

4.2.3 Preparation of Molybdenum Oxide (MoO_3).

Ammonium molybdate $(NH_4)_6MoO_{24}$ solution was treated as above. A white precipitate was obtained which gradually turned to yellow.

4.2.4 Preparation of Chromium (Cr_2O_3) and Cobalt Oxide (Co_2O_3)

Both the oxides were obtained as such. Before use the powder was dampened with water and pelleted as before.

4.2.5 Preparation of a mixed catalyst.

173.5 grams of tungsten oxide and 100 grams of vanadium oxide, prepared as above, were thoroughly mixed and the mixture pelleted. The above quantities were calculated to give a volume percentage of each component in the mixture of 50 percent.

4.2.6 Firing of Pellets.

Each batch of pellets was dried in an oven at 120°C and thereafter in a furnace to 800 - 900°C for three hours. This gave a stable and strong pellet; except in the case of vanadium oxide (V_2O_5) which was later found to give a stable pellet by heating to 700°C.

4.3 Dehydrogenation of Cyclohexane and of a Naphtha Fraction.

The reactor used in the preliminary studies was again used here but with some modification viz:-

(a) The feeder was replaced by a "dosing pump" (type MHRE-72 by Watson Marlow Ltd.)

(b) The hydrogen sulphide absorbing flask was duplicated.

(c) A manifold and series of gas sampling bottles connected with a vacuum pump was attached to the gas outlet line.

(d) A wet test gas meter was also fitted to the gas outlet line.

During the earlier work it had been found difficult to obtain a sufficiently low feed rate of oil (i.e. $<$ 1.0 gm/min). This difficulty was overcome by introducing a dozing pump whose flow rate could be easily adjusted from 0.5 ml to 0.1 ml per minute by selecting a suitable thin diameter neoprene tube as feed line. This is shown in the Figure4.1. One end of the neoprene tube was fixed to a burette-type graduated tube, while the other end was connected to a hypodermic needle. The needle was pushed through a serum cap fitted to the top of the reactor, the flow of feed material was from the needle point into the reactor.

In order to obtain a continuous analysis of the hydrogen sulphide, two absorbing flasks were connected in parallel through a single two-way stopcock. This is also shown in the general diagram Figure4.2a. In order to analyse the product gases a series of gas sampling bottles were attached to the outlet line through a manifold. The gas meter was intended to measure the total quantity of off gases. The loss in recovery due to the "snap" sample collection of gas was also thus accounted for.

REPLACEMENT OF FEEDER
BY DOZING PUMP

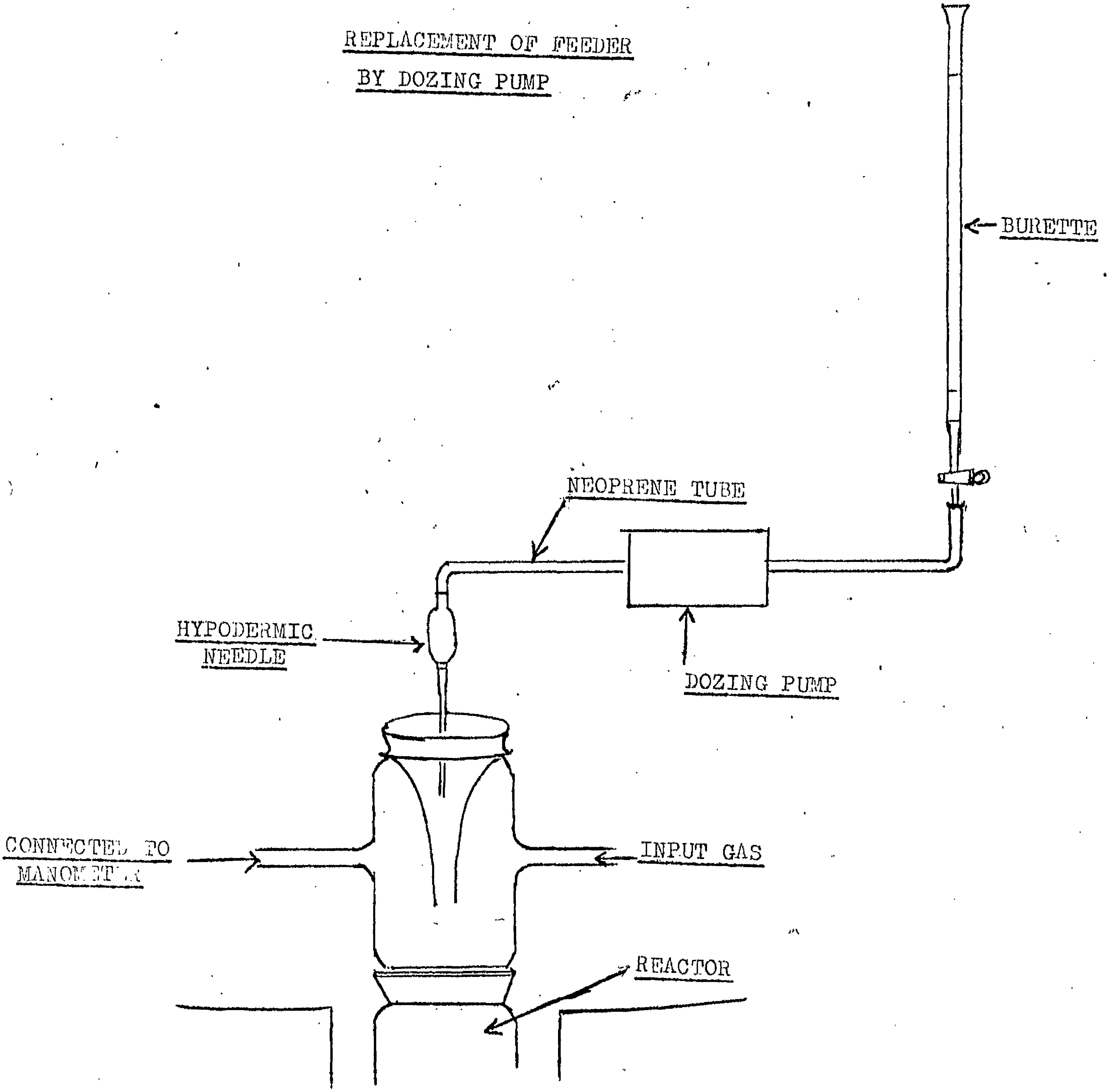
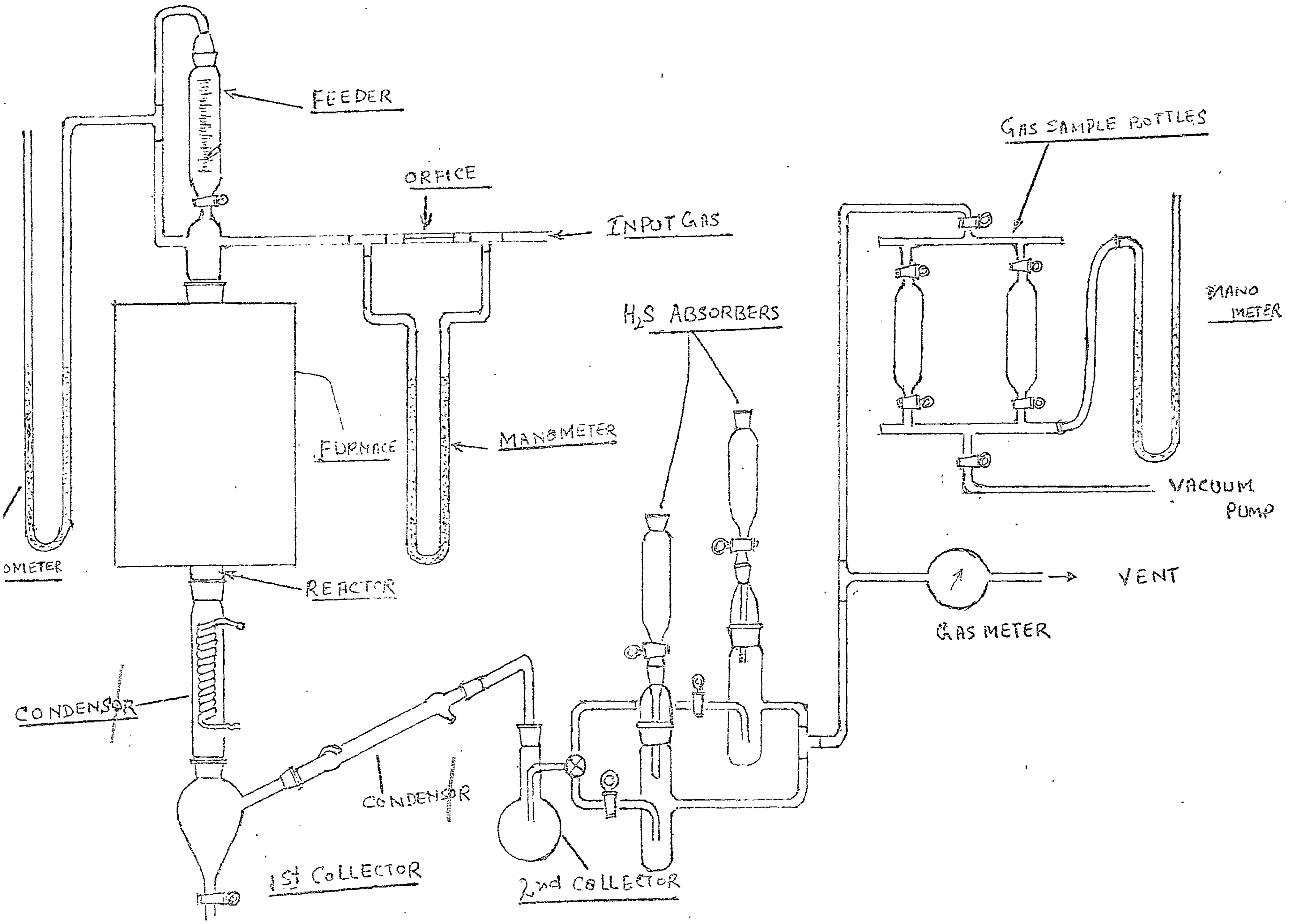


FIG. 4.1


FEEDER
ORFICE
INPUT GAS
GAS SAMPLE BOTTLES
MANO METER
H$_2$S ABSORBERS
FURNACE
MANOMETER
VACUUM PUMP
OMETER
REACTOR
VENT
GAS METER
CONDENSOR
CONDENSOR
1st COLLECTOR
2nd COLLECTOR

4.3.1 Catalyst Used.

The dehydrogenation studies with cyclohexane and a naphtha fraction were carried out with all the catalysts shown in the following table.

Table 4.2

Catalyst	Type	Superficial Volume (c.c./ 100 gm.)
A	Chromium oxide-sulphide	33.0
B	Vanadium "	24.4
C	Tungsten "	14.10
D	Cobalt "	19.30
E	Molybdenum "	22.20
F	°Vanadium + Tungsten "	17.70

° A mixture of 173.5 grams of tungsten oxide and 100 grams of vanadium oxide to get 50 percent volume of each catalyst.

4.3.2 Raw Material Used.

The cyclohexane used was an Analar grade reagent obtained from B.D.H. Its purity was reported to be 99.98 percent. When passed through an F - 11 Perkin Elmer gas chromatograph using a Benzyl di-phenyl column at 120°C, no other peak except that of the cyclohexane (C_6H_{12}) was observed.

The naphtha fraction was obtained locally[50] and was known as LPD-100 with a sulphur content of 0.5 ppm.

The physical characteristics of the naphtha were as follows:-

Boiling range = 40 to 150°C (the distillation curve prepared according to I.P 123 is given in Figure 8.1.

Specific gravity, 60/60°F, (I.P.59) = 0.684.

Mean molecular weight (I.P.86) = 89.

4.3.3 Analysis of Products.

Initial dehydrogenation tests on cyclohexane in this apparatus showed that the liquid product was benzene and small traces of cyclohexene. This made it possible to analyse quantitatively the dehydrogenated product by means of a refractive index determination and to check this by gas chromatograph. A standard curve of refractive indices at 20°C over a range of mixtures of cyclohexane and benzene was prepared. Similarily calibration peaks for the same mixtures were recorded by means of the F-11 Perkin Elmer gas chromatograph.

The extent of dehydrogenation of naphtha was determined by gas chromatographic analysis of the exit gases obtained from the reacting system. In this case a Perkin Elmer chromatograph No. 452 with a silica column at 50°C was used. No other permanent gas except hydrogen was shown on the record obtained. A suitable calibration curve for hydrogen was prepared.

4.3.4 Reaction Procedure and Results.

Before each dehydrogenation run the selected volume of catalyst pellets was activated in the reactor in a slow stream of hydrogen (0.0003 ft^3/min at 20°C) for a period corresponding to one hour per ml of catalyst volume, while the temperature was slowly raised to 400°C. During this activation period all the oxide catalysts were sulphided by treatment either with thiophene or with hydrogen sulphide.

Catalysts A and B were sulphided by hydrogenating thiophene (4% v/v of thiophene in benzene) at 400°C at a flow rate of 0.5 ml/min and a hydrogen flow rate of 0.002 ft^3/min. The thiophene-benzene mixture was started at the halfway point of the activation period and continued until a steady maximum flow of hydrogen sulphide appeared in the exit gases from the reactor. This sulphiding occupied about four to six hours.

The remaining catalysts (C to F) were sulphided from the half-way point of the activation period by a slow stream of hydrogen sulphide from a cylinder. This flow was again continued until no further absorption of hydrogen sulphide took place.

If at any time the flow of hydrogen had to be interrupted it was replaced by a similar flow of purified nitrogen. At the end of the activation period the flow of hydrogen was replaced by purified nitrogen, which was then passed during the dehydrogenation run continuously at a rate of 0.0061 ft^3/min. The furnace temperature was then adjusted to the required value for the run, and the liquid to be dehydrogenated was passed into the reactor at a rate of 0.5 ml/min and its flow continued for two hours. The observations were as follows:-

(i) *For cyclohexane runs.* Four, half-hour samples of liquid product were collected and the refractive index of each sample measured. The four samples were then combined and a gas chromatographic analysis was made on a sample of the mixture.

(ii) *For naphtha runs.* The total volume of exit gas produced was measured and gas chromatographic analysis made on snap samples collected after every 20 minutes. An average analysis was calculated from the values found for each six gas samples.

In calculating the total volume of gas produced at N.T.P. allowance was made for the volume of gas lost in snap sampling. A typical set of experimental values for a cyclohexane run and for a naphtha run are recorded in tables 4.3(i) and 4.3(ii).

Dehydrogenation runs were carried out on each of the catalysts with various volumes of catalyst in the reactor and at various temperatures as shown in the following tables.

In the left hand column of each table 4.4 the letters (a) to (f) signify the following , viz:-

(a) signifies the mean residence time (seconds).

(b) signifies percentage (w/w) decomposition of cyclohexane determined by refractive index.

(c) signifies percentage (w/w) decomposition of cyclohexane determined by gas chromatography.

(d) signifies the benzene gram moles produced per 100 gram moles of cyclohexane fed.

(e) signifies the hydrogen gram moles produced per 100 gram moles of cyclohexane fed.

(f) signifies $\text{Log}_{10}K$, $K = (pH_2)^3(pC_6H_6)/(pC_6H_{12})$, the partial pressure ratio determined from the experimental values.

Table 4.3(i)

Dehydrogenation of Cyclohexane by Catalyst "F" at 400°C.

Cyclohexane flow rate = 0.5 ml/min.

Nitrogen flow rate = 0.0061 ft^3/min at N.T.P

Volume of catalyst = 48.8 ml.

Time (min)	n_D^{20} of sample	Percentage Decomposition w/w	Gas Chromatograph (% decomposition)
0 - 30'	1.4484	40.50	40.80
30 - 60'	1.4492	40.70	
60 - 90'	1.4493	40.90	
90 - 120'	1.4493	40.90	
Average decomposition = 40.70%			

Table 4.3(ii)

Dehydrogenation of Naphtha by Catalyst "F" at 400°C

Naphtha flow rate = 0.5 ml/min.

Nitrogen flow rate = 0.0061 ft^3/min at N.T.P

Volume of catalyst = 48.8 ml.

Time of run = 120 mins.

Measured outlet gas volume = 1.206 ft^3 at N.T.P

Snap gas sample volume = 250 mls at 20°C, 0.0079 ft^3 at N.T.P

Time	% H_2 in outlet gas	Volume H_2 in snap sample ft^3	Total outlet hydrogen ft^3	Total outlet gas
0 - 20'	38.4	.0032	.080	
20 - 40'	41.3	.0034	.086	
40 - 60'	41.8	.0034	.087	
60 - 80'	38.9	.0032	.081	
80 - 100'	40.8	.0034	.085	
100 - 120'	41.3	.0034	.086	
		Total		1.206 + 6 x .0079 = 1.253 ft^3

Table 4.4(i)

Dehydrogenation of Cyclohexane and Naphtha over Catalyst A at different temperatures.

Temperature (^{o}C)	300	350	400	450
Cyclohexane				
Run No.	1	2	3	4
Catalyst Volume (mls)		16.5		
(a)	2.63	2.43	2.18	2.09
(b)	2.00	4.50	11.00	15.10
(c)	2.00	4.30	10.90	14.85
(d)	1.99	4.54	11.00	15.00
(e)	6.03	13.62	33.00	45.00
(f)	-5.445	-4.098	-2.724	-2.274
Run No.	5	6	7	8
	Naphtha			
H_2 mole/100 mole Naphtha	7.56	–	40.90	58.10

Temperature (^{o}C)	300	350	400	450
Cyclohexane				
Run No.	9	10	11	12
Catalyst Volume (mls)	33.0			
(a)	5.13	4.74	4.29	4.07
(b)	5.00	10.01	18.10	22.90
(c)	5.10	10.20	–	–
(d)	4.84	10.02	18.00	22.90
(e)	14.52	30.06	54.00	68.70
(f)	-3.987	-2.861	-2.022	-1.693
Run No.	13	14	15	16
	Naphtha			
H_2 mole/100 mole Naphtha	18.10	–	71.40	85.20

Table 4.4(i) continued.

Temperature ($^{\circ}C$)	300	350	400	450
		Cyclohexane		
Run No.	17	18	19	20
Catalyst Volume (mls)		49.5		
(a)	7.70	7.13	6.39	6.13
(b)	7.10	15.10	24.50	29.45
(c)	6.80	14.90	24.45	29.40
(d)	6.67	14.40	23.10	27.40
(e)	20.01	43.20	69.30	82.20
(f)	-3.480	-2.33	-1.687	-1.460
Run No.	21	22	23	24
		Naphtha		
H_2 mole/100 mole Naphtha	24.90	40.80	89.30	105.10

Temperature ($^{\circ}C$)	300	350	400	450
		Cyclohexane		
Run No.	25	26	27	28
Catalyst Volume (mls)		66.00		
(a)	10.25	9.50	8.58	8.18
(b)	8.50	17.80	29.00	33.40
(c)	8.50	-	28.65	33.30
(d)	8.29	17.30	27.40	31.40
(e)	24.87	51.90	82.20	94.20
(f)	-3.146	-2.078	-1.461	-1.283
Run No.	29	30	31	32
		Naphtha		
H_2 mole/100 mole Naphtha	30.90	58.20	108.50	114.50

Table 4.4(ii)

Dehydrogenation of Cyclohexane and Naphtha over Catalyst "B" at different temperatures.

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	33	34	35	36
Catalyst Volume (mls)	12.2			
(a)	3.71	3.46	3.06	2.94
(b)	5.10	8.40	14.50	18.90
(c)	4.95	8.30	14.50	18.70
(d)	5.05	7.95	14.05	18.02
(e)	15.15	23.85	42.75	54.06
(f)	-3.917	-3.213	-2.369	-2.022
Run No.	37	38	39	40
	Naphtha			
H_2 mole/100 mole Naphtha	18.70	30.30	53.40	69.90

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run NO.	41	42	43	44
Catalyst Volume (mls)	24.4			
(a)	7.24	6.70	6.00	5.74
(b)	7.20	13.50	21.20	27.00
(c)	7.10	13.40	-	26.80
(d)	7.19	13.00	19.85	25.60
((e)	21.57	39.00	59.55	76.80
(f)	-3.359	-2.484	-1.891	-1.550
Run No.	45	46	47	48
	Naphtha			
H_2 mole/100 mole Naphtha	27.60	50.30	80.20	103.50

Table 4.4(ii) continued.

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	49	50	51	52
Catalyst Volume (mls)	36.6			
(a)	10.04	9.20	8.70	8.33
(b)	9.80	18.20	28.00	35.20
(c)	9.65	18.10	28.20	35.10
(d)	9.75	17.30	26.30	32.80
(e)	28.25	51.90	78.90	98.40
(f)	-2.004	-2.078	-1.513	-1.225
Run No.	53	54	55	56
	Naphtha			
H_2 mole/100 mole Naphtha	36.90	67.40	101.60	141.20

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	57	58	59	60
Catalyst Volume (mls)	48.8			
(a)	14.45	13.40	12.00	11.50
(b)	16.50	25.10	32.00	42.20
(c)	16.45	24.90	31.80	41.90
(d)	15.50	23.80	30.30	39.30
(e)	46.50	71.40	90.90	117.90
(f)	-2.230	-1.646	-1.329	-0.989
Run No.	61	62	63	64
	Naphtha			
H_2 mole/100 mole Naphtha	60.80	93.50	115.10	150.80

Table 4.4(iii)

Dehydrogenation of Cyclohexane and Naphtha over Catalyst "C" at different temperatures.

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	65	66	67	68
Catalyst Volume (mls)	7.05			
(a)	1.91	1.76	1.58	1.52
(b)	3.40	6.40	11.45	17.50
(c)	3.35	6.30	11.25	-
(d)	3.79	6.40	11.15	15.10
(e)	11.37	19.20	33.45	45.30
(f)	-4.379	-3.522	-2.70	-2.264
Run No.	69	70	71	72
	Naphtha			
H_2 mole/100 mole Naphtha	13.70	23.20	42.90	59.70

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	73	74	75	76
Catalyst Volume (mls)	14.10			
(a)	3.69	3.43	3.07	2.93
(b)	6.20	11.50	19.20	23.60
(c)	6.20	11.35	19.20	23.40
(d)	6.39	11.00	18.40	22.40
(e)	19.17	33.00	55.20	67.20
(f)	-3.522	-2.724	-1.995	-1.730
Run No.	77	78	79	80
	Naphtha			
H_2 mole/100 mole Naphtha	23.50	43.80	74.00	86.40

Table 4.4(iii) continued

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	81	82	83	84
Catalyst Volume (mls)	28.20			
(a)	7.24	6.70	6.01	5.74
(b)	8.60	19.60	28.20	39.00
(c)	8.40	19.60	28.00	38.70
(d)	8.55	18.40	26.70	36.30
(e)	25.65	55.20	80.10	108.90
(f)	-3.081	-1.995	-1.495	-1.095
Run No.	85	86	87	88
	Naphtha			
H_2 mole/100 mole Naphtha	31.70	70.70	101.50	142.50

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	89	90	91	92
Catalyst Volume (mls)	42.30			
(a)	10.70	9.90	8.87	8.50
(b)	10.90	22.80	34.00	53.00
(c)	10.68	22.45	33.90	52.65
(d)	10.45	21.70	32.10	45.40
(e)	31.35	65.10	66.30	136.20
(f)	-2.799	-1.774	-1.254	-0.797
Run No.	93	94	95	96
	Naphtha			
H_2 mole/100 mole Naphtha	42.90	81.80	124.50	185.10

Table 4.4(iv)

Dehydrogenation of Cyclohexane ams Naphtha over Catalyst "D" at different temperatures.

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	97	98	99	100
Catalyst Volume (mls)	48.8			
(a)	13.55	12.40	11.58	10.85
(b)	8.40	17.60	27.50	33.10
(c)	8.20	17.60	27.20	32.75
(d)	8.10	16.95	26.50	30.80
(e)	24.30	50.85	79.50	92.40
(f)	-3.146	-2.070	-1.420	-1.281
Run No.	101	102	103	104
	Naphtha			
H_2 mole/100 mole Naphtha	31.70	67.80	105.80	114.50

Table 4.4(v)

Dehydrogenation of Cyclohexane and Naphtha over Catalyst "E" at different temperatures.

Temperature (°C)	300	350	400	450
	Cyclohexane			
Run No.	105	106	107	108
Catalyst Volume (mls)	48.8			
(a)	13.55	12.40	11.58	10.85
(b)	2.80	5.10	15.10	23.50
(c)	2.40	5.45	15.10	-
(d)	3.07	5.04	14.60	22.30
(e)	9.21	15.12	43.80	66.90
(f)	-4.63	-3.917	-2.316	-1.730
Run No.	109	110	111	112
	Naphtha			
H_2 mole/100 mole Naphtha	12.60	28.50	66.70	-

Table 4.4(vi)

Dehydrogenation of Cyclohexane and Naphtha over Catalyst "P" at different temperatures.

Temperature ($^{\circ}C$)	300	350	400	450
	Cyclohexane			
Run No.	113	114	115	116
Catalyst Volume (mls)	48.8			
(a)	13.15	12.10	10.85	10.40
(b)	9.20	23.10	40.70	54.00
(c)	9.10	22.80	40.80	53.65
(d)	9.20	21.80	37.50	46.50
(e)	27.60	65.40	112.50	139.50
(f)	-2.99	-1.763	-1.051	-0.765
Run No.	117	118	119	120
	Naphtha			
H_2 mole/100 mole Naphtha	44.60	108.50	150.00	177.00

Table 4.5

Dehydrogenation of Cyclohexane and Naphtha over Catalyst "P" at 400°C (Effect of Flow Rate).

Temperature = 400°C

Nitrogen Flow Rate = 0.0061 ft^3/min at N.T.P.

Volume of Catalyst = 48.8 ml.

Flow rate ml/min	0.4	0.3	0.2	0.1
Run No.	117	118	119	120
(a)	14.35	19.65	28.50	59.30
(b)	54.70	67.20	75.80	75.60
(c)	54.30	67.00	75.20	75.10
(d)	51.30	64.10	72.60	73.20
(e)	153.90	192.30	217.60	219.60
Run No.	121	122	123	124
	Naphtha			
H_2 ole/100 mole Naphtha	192.50	254.50	289.00	303.

4.4 Discussion.

It may be seen from Figures 4.1A to 4.6 that the sulphided-oxides tested are all reasonably good dehydrogenating catalysts. They of course vary slightly in their relative ability. It would appear that most of them would be suitable for making hydrogen available for desulphurisation.

As has been shown already (1.5.3), only a small amount of hydrogen is stoichiometrically necessary to remove the 4 percent sulphur found in most residual fuel oils. Assuming that the sulphur in the residual fuel oil was thiophene (C_4H_4S) four moles of hydrogen would be theoretically required for complete desulphurisation. Thus an oil with 4 percent sulphur would require 0.5 mole of hydrogen per 100 gram of oil. The complete dehydrogenation of cyclohexane provides three moles of hydrogen. Thus a mixture of equal quantities of oil and cyclohexane would only require 16.7 percent decomposition of the naphthene. This, of course, does not take into account the value of the equilibrium constant for the dehydrogenation reaction, and the excess naphthene and thus of the hydrogen required to push the reaction to the desired extent in the reaction time available. Figures 4.1A to 4.4B show the hydrogen made available by each catalyst as a function of mean residence time. It appears that the curves will go on rising to some extent by increase in mean residence time.

Catalysts "A", "B" and "C" were ~~all~~ each tested over a range of values and the results are compared with those given for one mean

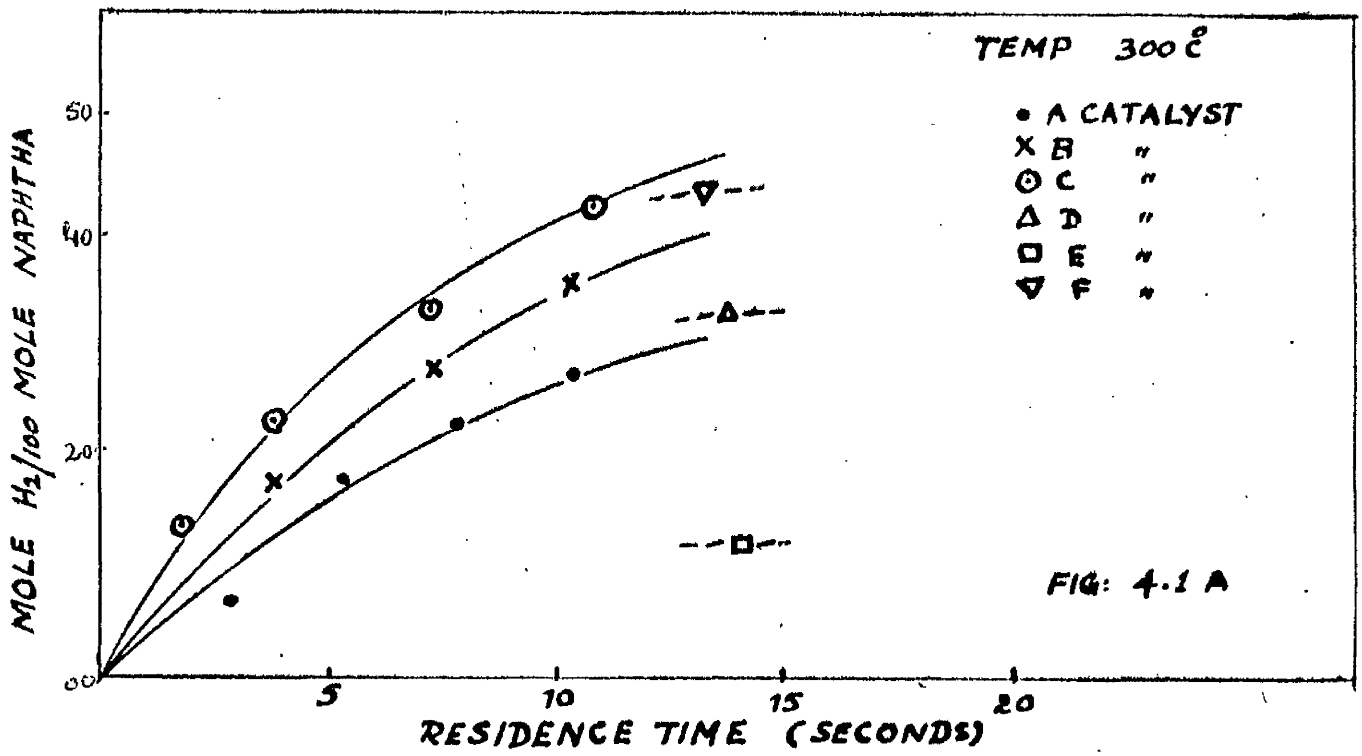


FIG: 4.1 A

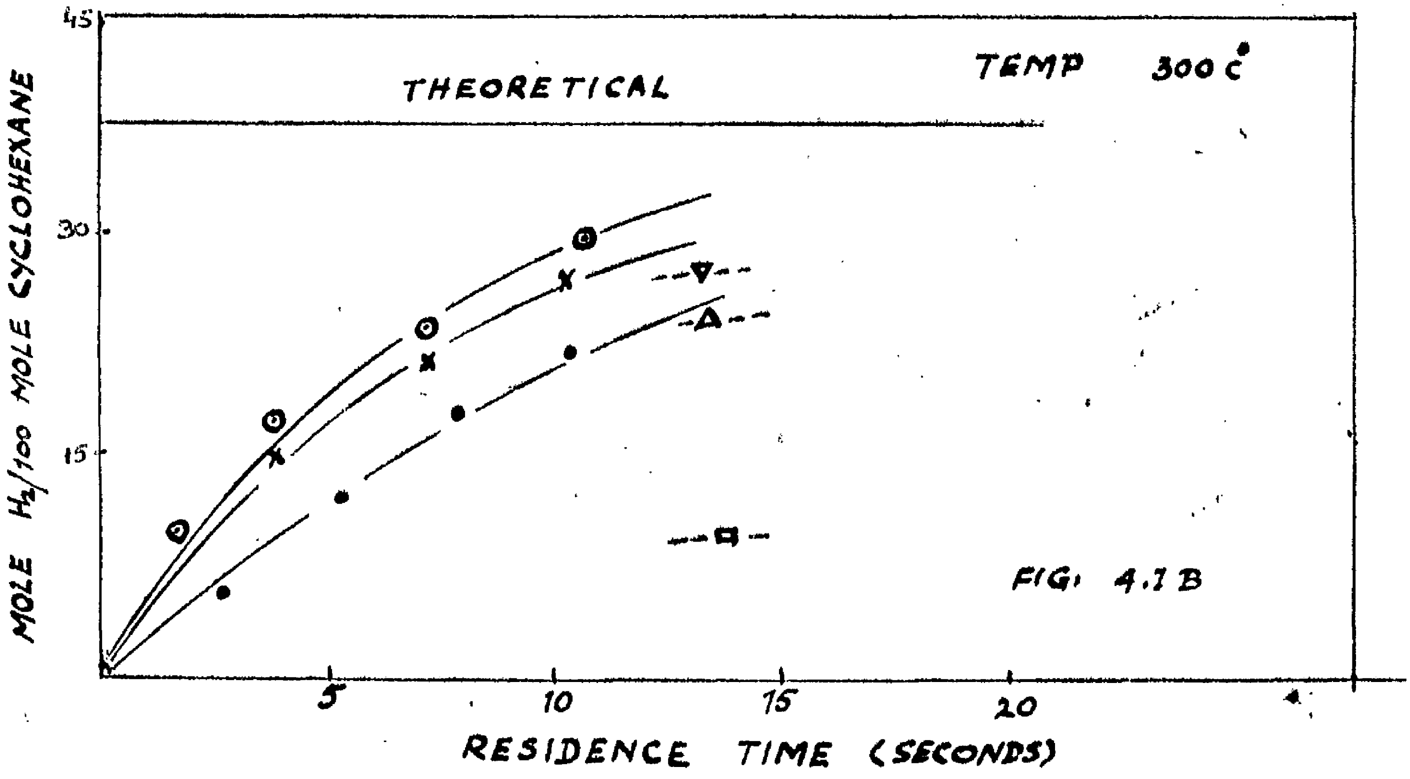


FIG: 4.1 B

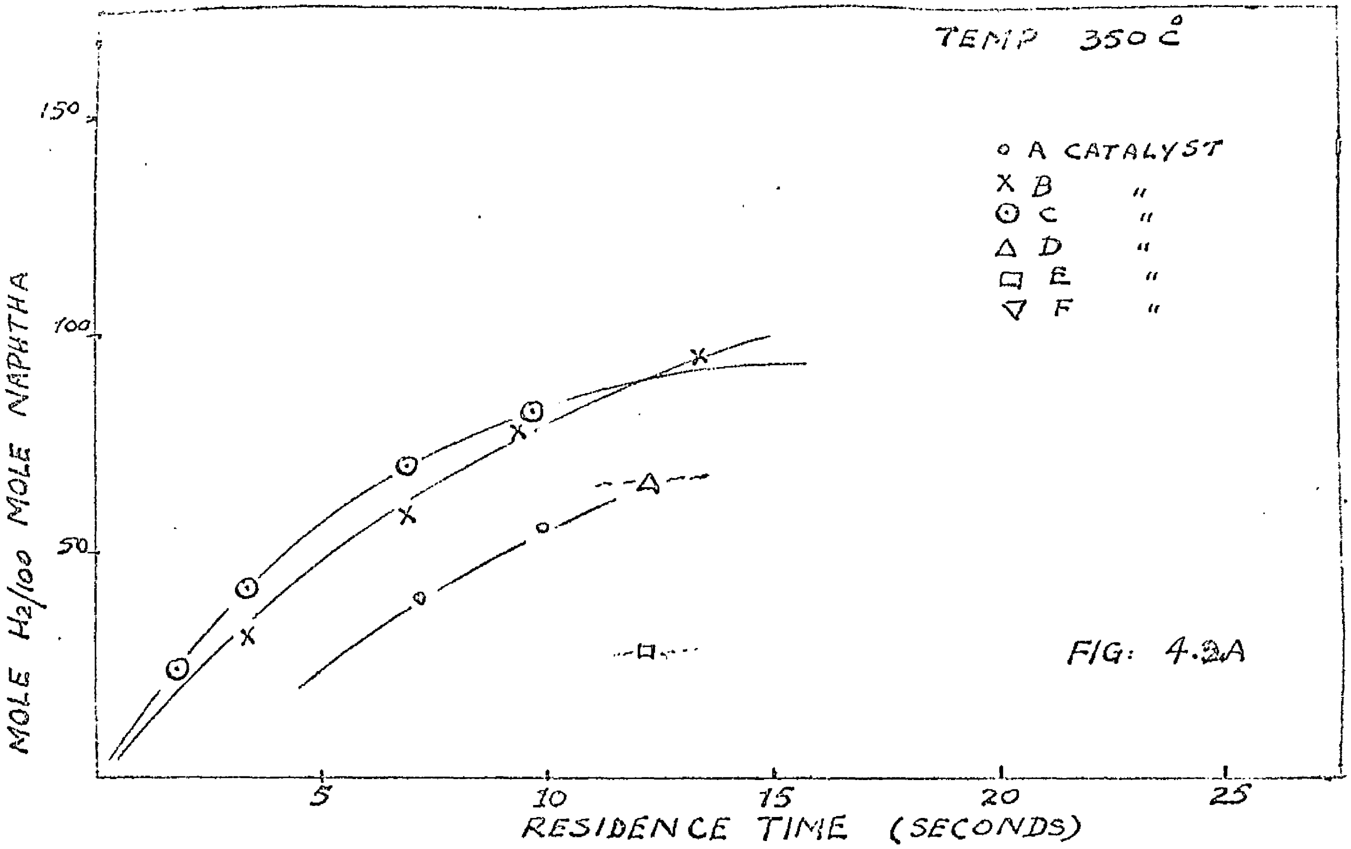


FIG: 4.2A

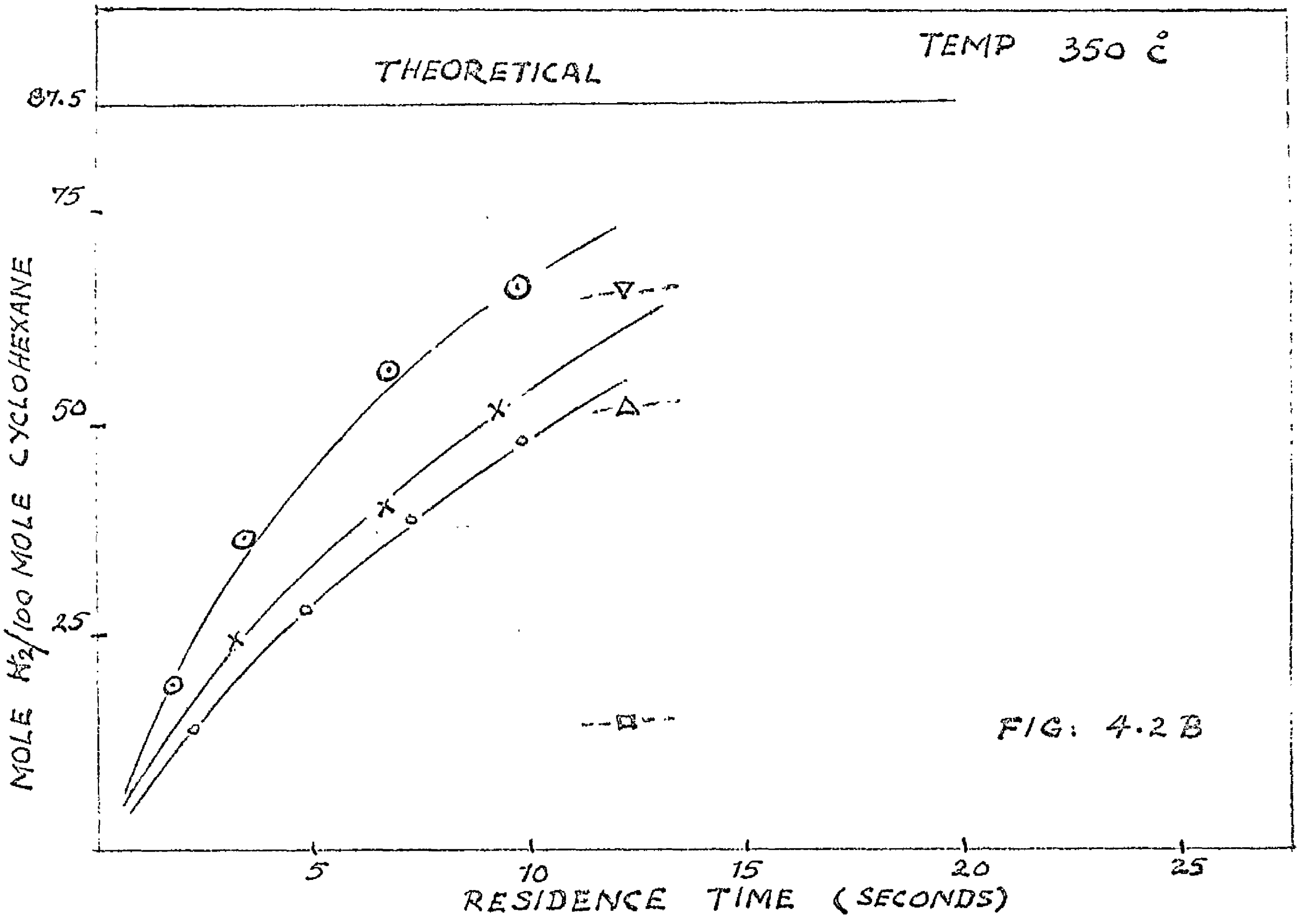


FIG: 4.2B

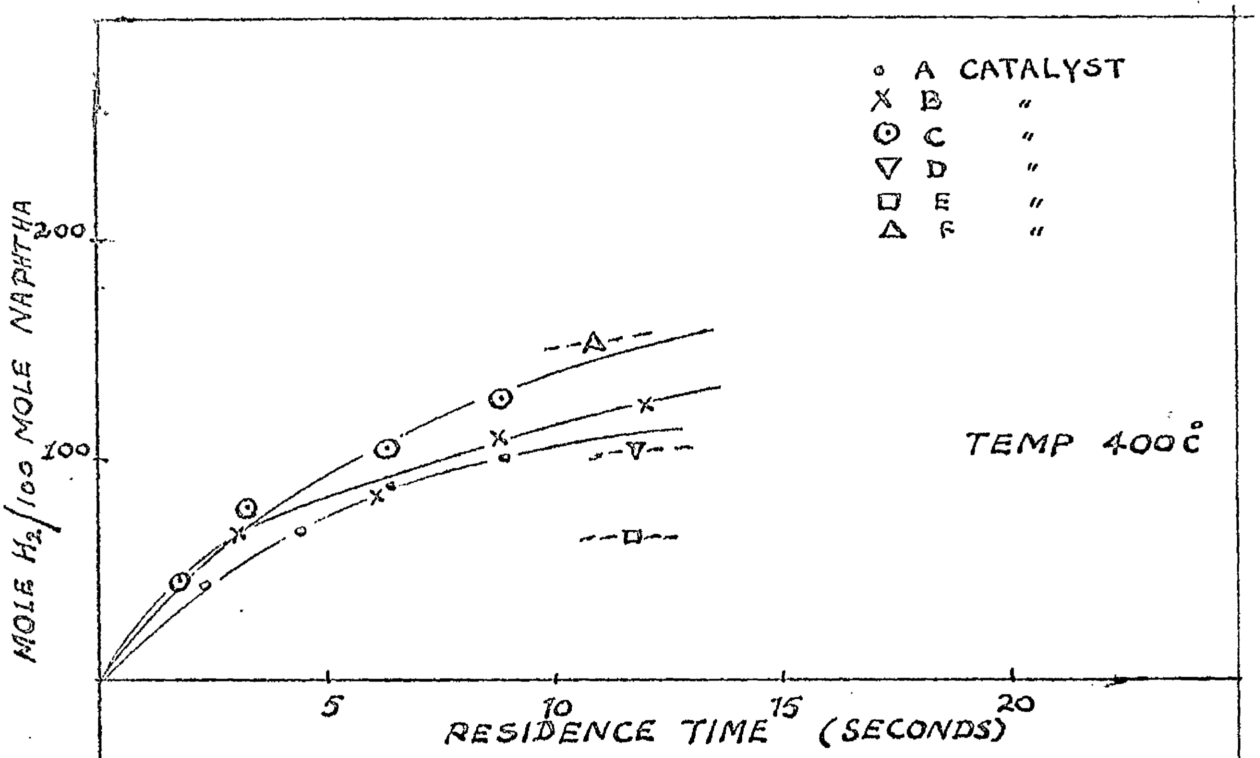


FIG 4.3 A

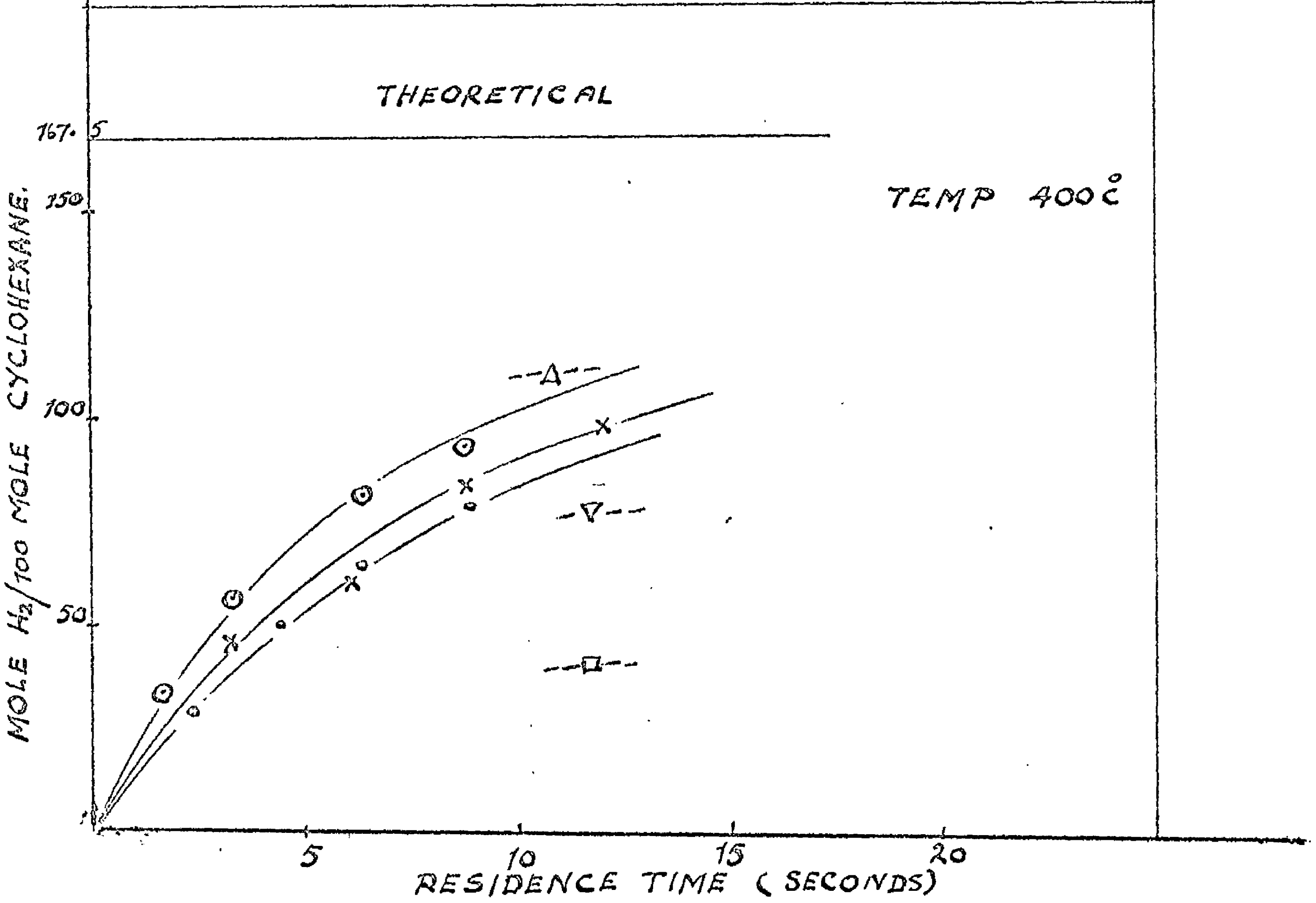


FIG 4·3B

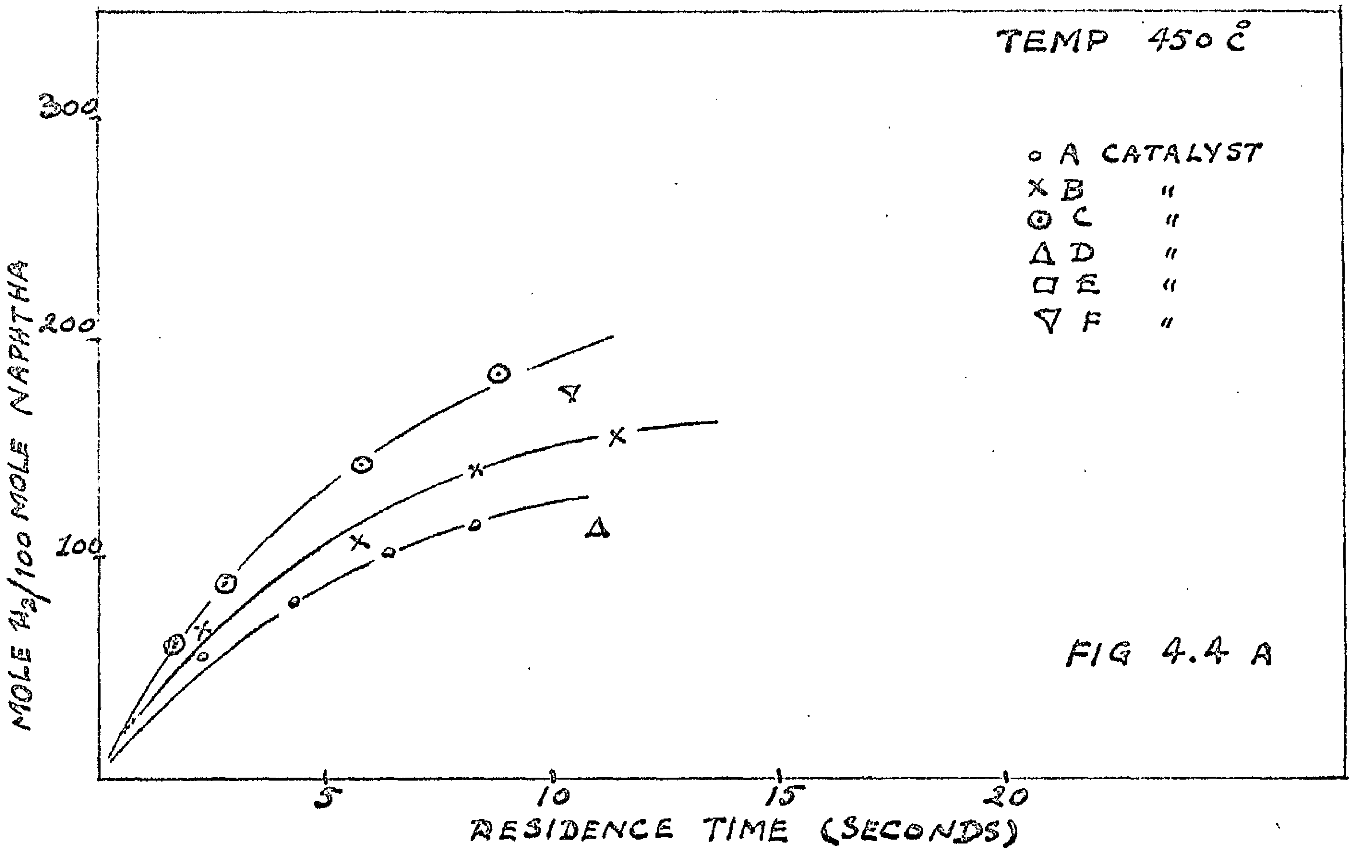


FIG 4.4 A

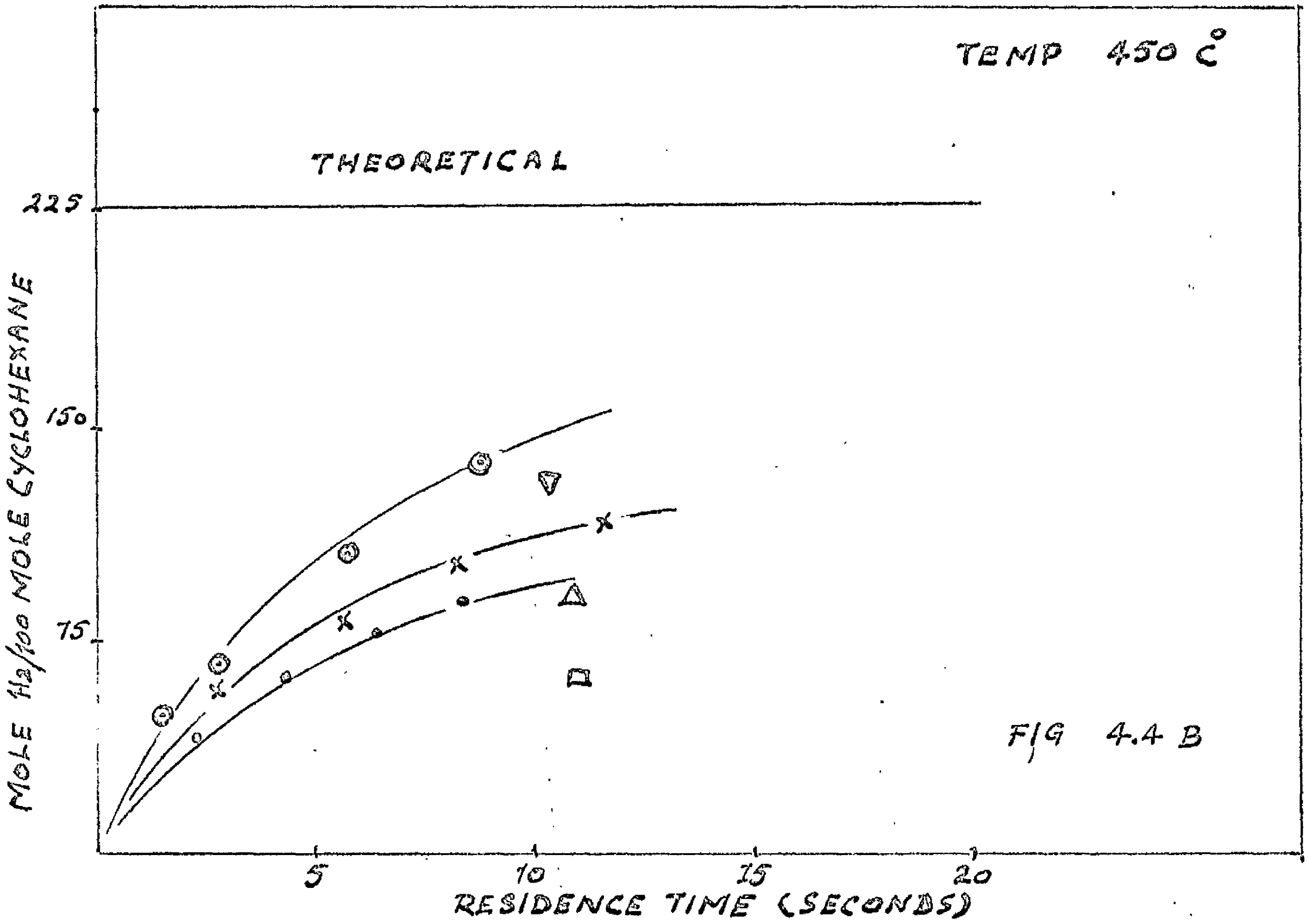


FIG 4.4 B

residence time study for two catalysts "D"(Co_2O_3) and "E" (MoO_3) which are recognised desulphurising catalysts. Catalyst "F" a composite mixture is included here since desulphurisation studies to be described later showed that this mixture was an excellent hydrogen transfer catalyst. Catalyst "C" (WO_3) was found to be the best material, while catalyst "B" followed it closely. This is shown in Figure 4.5A. and 4.5B.

The results for the naphthene dehydrogenation were also parallel to that of cyclohexane, in this case also the Catalyst "C" proved to be the most suitable.

The extent of naphthene decomposition increases with reaction temperatures as could be seen from Figure 4.5A.

The catalyst "E" (MoO_3), "A" (Cr_2O_3) and "D" (Co_2O_3) have low hydrogen production as compared to "B", "F" and "C". The catalyst "C" amongst all showed the maximum production of hydrogen while "F" showed higher than "C" in some cases as could be seen from Figures 4.1A to 4.4B. The corresponding results for the dehydrogenation of naphtha at the fixed mean residence time is shown in Figure 4.5A. The production of hydrogen in each case is slightly higher (10 to 15 %) than for cyclohexane. This may be accounted for by the fact that the density of cyclohexane (.776) is slightly higher than that of the naphtha (.689), and the lighter molecules may decompose more easily. During the analysis of the naphtha off-gases, no other gas (except in some cases traces of methane) than hydrogen was observed, indicating

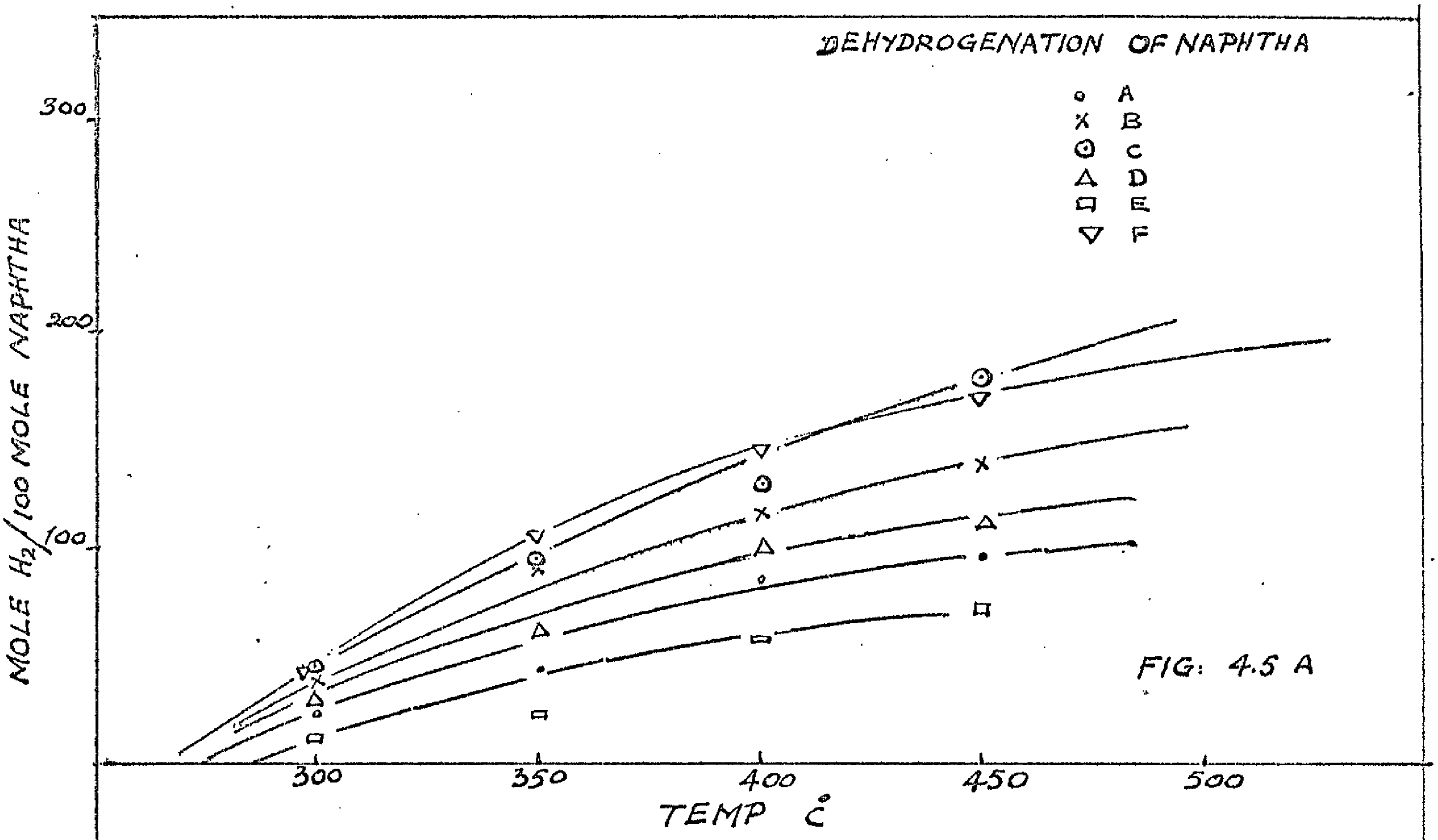


FIG: 4.5 A

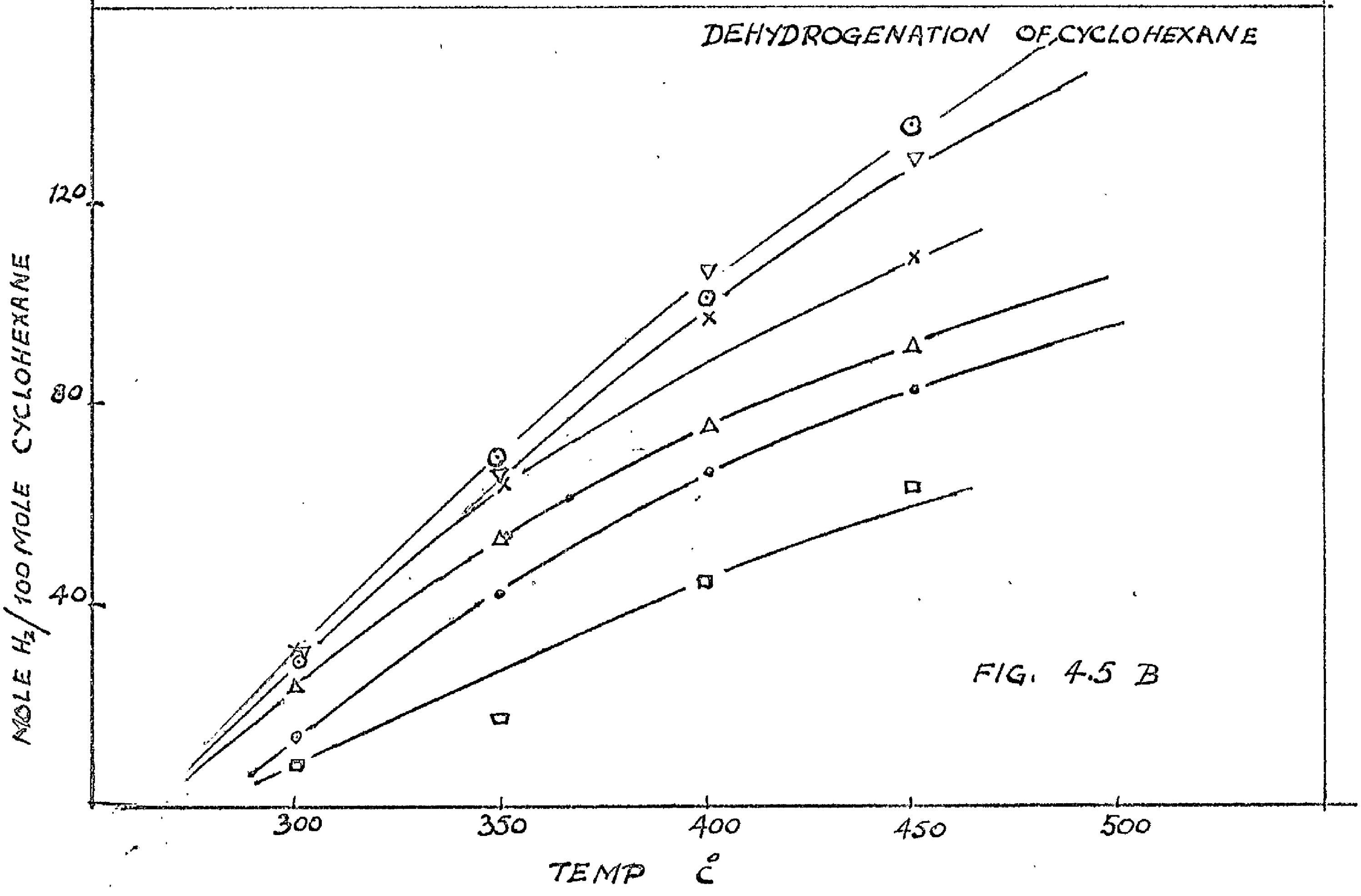


FIG. 4.5 B

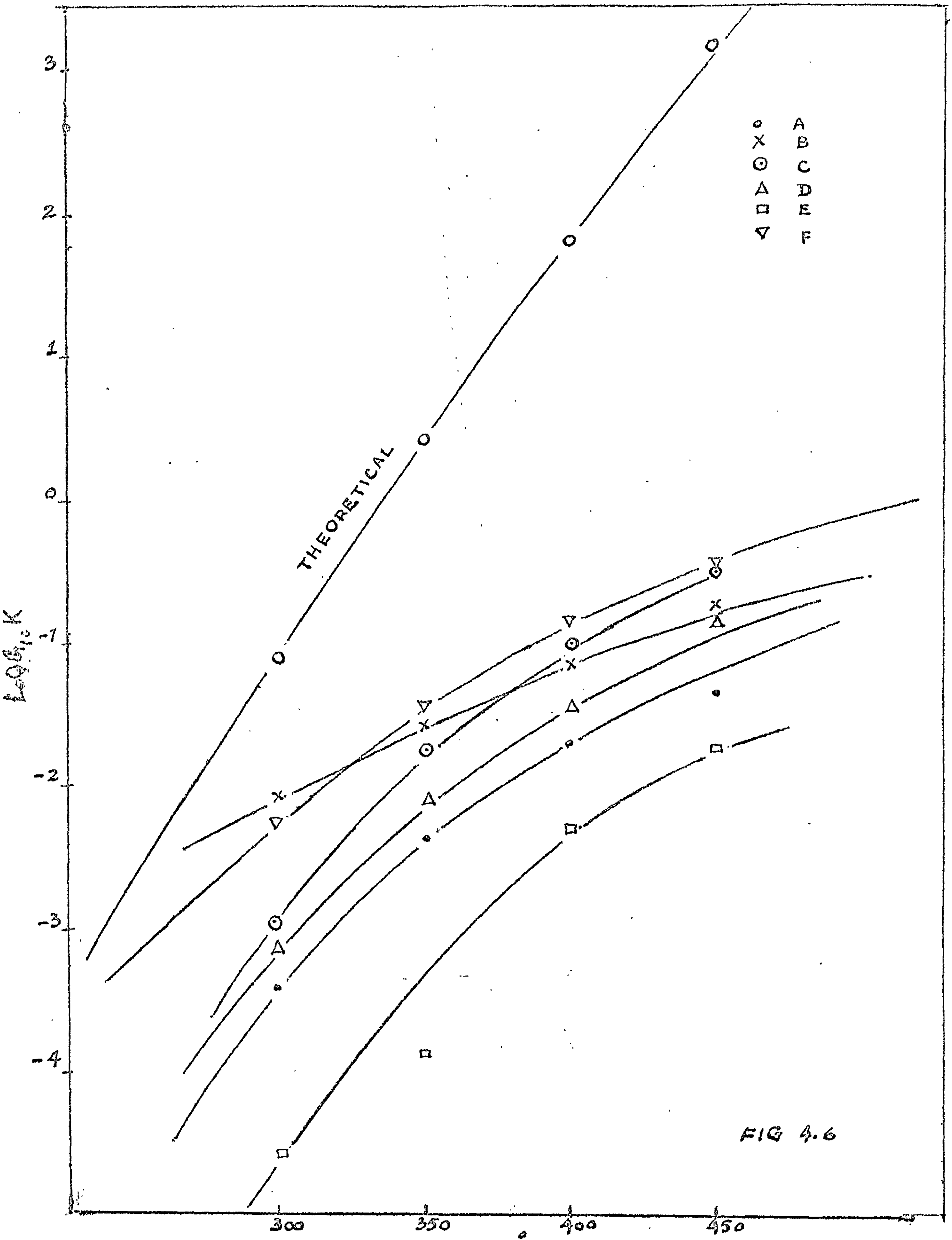

3
2
1
0
-1
-2
-3
-4
$Log_{10} K$
300
350
400
450
TEMP C°
THEORETICAL
• A
X B
⊙ C
Δ D
□ E
∇ F

FIG 4.6

that no other severe breaking of bonds takes place during the dehydrogenation reaction.

The commercial autofining process which is carried out with cobalt-molybdate catalyst is described by Porter[30]. He reports that the reaction temperature must be kept low, as beyond 450°C greater breakdown of molecular structure of the hydrocarbons takes place leading to carbon deposition on the catalyst which in turn soon loses its activity.

A study with catalyst "F" at 400°C and different flow rates (0.5 to 0.1 ml/min) was carried out. The results are shown in Table 4.5. Decrease of flow rate increases the percentage decomposition and only at the lower flow rate tested does the decomposition approach constancy. From free energy data for the reaction the theoretical equilibrium constant are then the theoretical extent of decomposition was calculated. The theoretical decomposition for this temperature is related on Figure 4.7 where it may be seen to be slightly less than the mean value experimentally obtained. The difference is possibly due to a combination of errors, but we may conclude that the reaction reaches equilibrium after about thirty seconds of reaction time.

From the stand point of later desulphurisation however, the rate of production of hydrogen is more important. This was found to be a maximum at the flow rate of 0.3 ml/min in the case of cyclohexane, while in the case of naphtha the rate was constant for the flow rates of 0.4 ml/min and 0.3 ml/min.

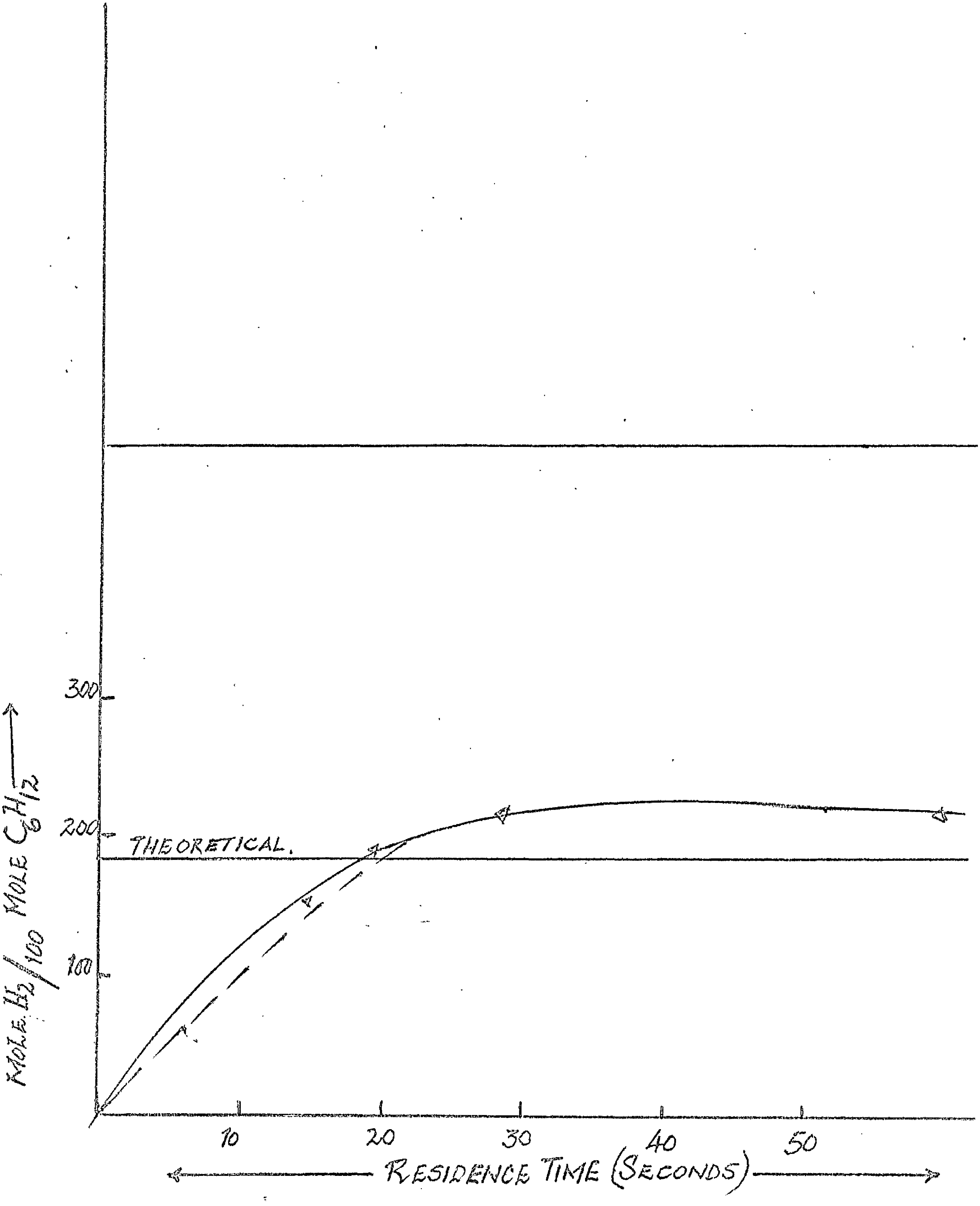

Mole H2/100 Mole C6H12
300
200
100
THEORETICAL.
10
20
30
40
50
RESIDENCE TIME (SECONDS)

Fig-4.7.

In Figure 4.6 the degree of approach to equilibrium in the dehydrogenation of cyclohexane is visualised. The logarithm of equilibrium constant is plotted against temperature. The figure shows the theoretical value and the approach of the actual values. It may be seen that owing to the great rise in the equilibrium constant with temperature, the approach to equilibrium was greater at 300°C than at 450°C.

The results shown in the Tables 4.4(i) to 4.4(iii) for catalysts "A", "B" and "C" indicate a first order reaction. From a suitable plot the specific reaction rate constant was evaluated and is given for the various catalysts and reaction temperatures in Table 4.6. From a plot of the logarithm rate constant versus $1/T$ °K the activation energy was determined. The value for the three catalysts is shown in Table 4.6.

All three catalysts show a relatively similar low activation energy for cyclohexane dehydrogenation . This value is similar to that reported by Balandin[51] for the dehydrogenation of cyclohexane over charcoal supported rhenium. Other authors[52] who dehydrogenated cyclohexane at slightly lower temperatures over such catalysts as nickel-alumina, platinum on silica-alumina and platinised asbestos report activation energies in the range of 15 to 18 K cals/mol. It would appear that the transition metal oxide catalysts tested here are superior to noble metal catalysts for such dehydrogenation purposes and have the added advantage of being resistant to sulphur poisoning.

Table 4.6

Catalyst	Temperature °C	Rate Constant (sec^{-1})	Activation Energy K.cal/mol
A	300	3.2×10^{-3}	8.05
	350	6.4×10^{-3}	
	400	12.0×10^{-3}	
	450	20.1×10^{-3}	
B	300	10.6×10^{-3}	6.9
	350	18.1×10^{-3}	
	400	30.9×10^{-3}	
	450	40.1×10^{-3}	
C	300	8.5×10^{-3}	8.1
	350	16.2×10^{-3}	
	400	29.0×10^{-3}	
	450	51.0×10^{-3}	

5. HYDROGENATION STUDIES.

Having shown that hydrogen is easily made available from cyclohexane and naphtha dehydrogenation at about 400°C; it was now necessary to determine the ease with which it could be utilised to hydrogenate thiophene. To this end a number of experimental runs were carried out to determine the suitability of the selected catalysts for thiophene hydrogenation.

In these runs hydrogen gas was supplied externally from cylinders and a constant mole ratio of hydrogen to thiophene (8:1) was maintained.

5.1 Raw Materials used.

All materials used were of Analar grade. The benzene and thiophene used to calibrate the gas chromatograph showed no other peak.

5.2 Analysis of Products.

The hydrogen sulphide in the exit gases was absorbed in the gas absorbing flask which contained 10% aqueous cadmium chloride solution. The cadmium sulphide thus formed was determined by Iodometric titration. The actual procedure and calculation are shown in the Appendix (3.4. The liquid condensed from the exit gases was analysed by gas chromatograph. It was found to contain only benzene and thiophene. A reference curve for use with the gas chromatograph was prepared from standard mixtures of benzene and thiophene.

5.3 Reaction Procedure and Results.

The sulphided-oxides were left in the reactor at the required temperature in a current of purified nitrogen. This was then replaced by hydrogen at a rate of 0.0008 ft^3/min at N.T.P; and this gas fed for one hour. With steady hydrogen flow a two percent v/v thiophene in benzene solution was then fed into the reactor at a rate of 0.5 ml/min. This gave a mole ratio of hydrogen to thiophene in the reactor of 8:1 (the stoichiometric reaction requirement is 4:1). The hydrogenation run was continued for two hours, and during this time six samples each of twenty minutes duration were passed through the gas absorbing flasks containing cadmium chloride solution. The exit gas freed from hydrogen sulphide was passed through the wet test gas meter. Periodic snap samples of this exit gas were analysed by gas chromatograph to check that only hydrogen was present.

The total condensed liquid product collected after the run was analysed by means of gas chromatograph using a benzyl-diphenyl column at 120°C. It was thus possible to compare the extent of thiophene hydrogenation by two methods.

The hydrogenation studies were carried out with all catalysts A, B, C, D, E and F. Catalysts A, B and C were studied at different temperatures and different bed depth of catalyst; while each of the catalysts D, E and F was studied at different temperatures while at a constant bed volume. The results are in Tables 5.2(i) to 5.2(vi). The catalysts B, C, and F were studied at different ratios of hydrogen to thiophene viz., 4:1, 8:1, 12:1 and 16:1 while at a constant temperature (400°C). The catalyst F was studied over a range of thiophene flow rates, while maintaining the ratio of hydrogen to thiophene at 8:1. Four different flow rates 0.5, 0.4, 0.3 and 0.2 ml/min were studied. The results are shown in Table 5.4. A typical set of experimental values for hydrogenation run is shown in the Table 5.1, while the results of all the catalysts are shown in Table 5.2i to 5.4.

In the left hand column of each table the letters (a) to (m) signify the following:-

(a) signifies the mean residence time in seconds.

(g) signifies percentage gm-mole decomposition of thiophene by hydrogen sulphide collection.

(h) signifies percentage gm-mole decomposition of thiophene by gas chromatography.

(k) signifies total hydrogen gm-mole in off gases.

(l) signifies mole hydrogen per mole of thiophene used.

(m) signifies $\mathrm{Log}_{10}K$, $K = \dfrac{(H_2S)\ (C_4H_{10})}{(C_4H_4S)/(H_2)^4}$

Table 5.1

Hydrogenation of thiophene by Catalyst "F" at 400°C.

Liquid flow rate = 0.5 ml/min (2% v/v of thiophene in benzene)

Hydrogen flow rate = 0.0008 ft^3/min at N.T.P

Volume of catalyst = 48.8 mls.

Time of run = 120 mins.

Time	Input Sulphur Wt. (gm)	Output Sulphur As H_2S (gm)	% decomposition of thiophene (Wt.)	Gas chromatograph decomposition of thiophene (wt)
0 - 20'	0.0805	0.0517	64.3	
20 - 40'	"	0.0537	66.8	68.4
40 - 60'	"	0.0542	67.3	
60 - 80'	"	0.0520	65.2	
80 - 100'	"	0.0541	67.3	
100 - 120'	"	0.0541	67.3	

Table 5.2(1)

Hydrogenation of thiophene with Catalyst "A" at different temperatures and bed volumes.

Temperature °C	300	350	400	450
Run No.	1	2	3	4
Catalyst Volume (ml)	16.5			
(a)	2.63	2.43	2.18	2.09
(g)	1.20	2.70	16.90	23.20
(h)	1.40	2.75	17.60	23.60
(k)	0.112	0.118	0.112	0.106
(l)	-	-	4.0:1	4.57:1
(m)	-.005	-.09	+.581	+.921

Temperature °C	300	350	400	450
Run No.	5	6	7	8
Catalyst Volume (ml)	33.0			
(a)	5.13	4.74	4.27	4.07
(g)	1.90	6.90	24.60	30.60
(h)	2.20	7.00	25.40	31.20
(k)	0.118	0.115	0.103	0.098
(l)	-	7.0:1	5.14:1	5.23:1
(m)	-.002	-.07	+.97	+1.02

Temperature °C	300	350	400	450
Run No.	9	10	11	12
Catalyst Volume (ml)	49.5			
(a)	7.70	7.23	6.39	6.13
(g)	2.60	11.10	31.40	41.40
(h)	3.20	11.80	31.80	42.10
(k)	0.116	0.112	0.096	0.092
(l)	14.9:1	5.9:1	5.53:1	4.85:1
(m)	-.06	+.118	1.04	1.298

Table 5.2(i) continued.

Temperature °C	300	350	400	450
Run No.	13	14	15	16
Catalyst Volume (ml)	66.0			
(a)	10.25	9.50	8.58	8.18
(g)	3.10	14.80	36.80	48.50
(h)	3.90	14.80	37.10	48.80
(k)	0.116	0.112	0.094	0.088
(l)	12.1:1	4.55:1	5.09:1	4.67:1
(m)	−.04	+0.3	1.18	1.54

Table 5.2(ii)

Hydrogenation of thiophene with Catalyst "B" at different temperatures and bed volumes.

Temperature °C	300	350	400	450
Run No.	17	18	19	20
Catalyst Volume (ml)	12.2			
(a)	3.71	3.46	3.06	2.94
(g)	8.70	17.90	52.10	59.40
(h)	9.10	18.40	52.70	59.60
(k)	−	.110	.086	.083
(l)	−	−	4.49:1	9.3:1
(m)	−.06	.514	1.589	1.717

Temperature °C	300	350	400	450
Run No.	21	22	23	24
Catalyst Volume (ml)	24.4			
(a)	7.24	6.70	6.00	5.74
(g)	11.40	29.70	64.30	69.70
(h)	11.80	−	64.80	69.70
(k)	0.112	0.099	0.082	0.074
(l)	5.3:1	4.89:1	4.03:1	4.7:1
(m)	−.015	1.02	1.82	2.01

Table 5.2(ii) continued.

Temperature °C	300	350	400	450
Run No.	25	26	27	28
Catalyst Volume (ml)	36.6			
(a)	10.04	9.20	8.70	8.33
(g)	12.70	36.20	71.40	77.80
(h)	12.90	36.80	71.00	78.40
(k)	.108	.094	.070	.068
(l)	6.85:1	5.0:1	4.65:1	4.57:1
(m)	0.12	1.19	2.01	2.24

Temperature °C	300	350	400	450
Run No.	29	30	31	32
Catalyst Volume (ml)	48.8			
(a)	14.45	13.40	12.00	11.50
(g)	14.20	43.40	78.10	82.40
(h)	14.60	43.80	78.80	82.60
(k)	0.112	0.091	0.068	0.064
(l)	4.28:1	4.62:1	4.53:1	4.63:1
(m)	+.32	1.42	2.24	2.32

Table 5.2(iii)

Hydrogenation of thiophene with Catalyst "C" at different temperatures and bed volumes.

Temperature °C	300	350	400	450
Run No.	33	34	35	36
Catalyst Volume (ml)	7.05			
(a)	1.91	1.76	1.58	1.51
(g)	4.80	14.10	38.60	44.20
(h)	5.10	13.90	39.20	44.10
(k)	-	-	0.088	0.084
(l)	-	-	5.7:1	5.8:1
(m)	-.05	+.38	+1.29	1.32

Table 5.2(iii) continued.

Temperature °C	300	350	400	450
Run No.	37	38	39	40
Catalyst Volume (ml)	14.10			
(a)	3.69	3.43	3.07	2.93
(g)	8.90	20.20	43.10	51.00
(h)	9.40	20.60	43.60	51.70
(k)	0.108	0.088	0.088	0.084
(l)	10.1:1	10.9:1	5.07:1	4.8:1
(m)	-.025	.613	1.325	1.584

Temperature °C	300	350	400	450
Run No.	41	42	43	44
Catalyst Volume (ml)	28.20			
(a)	7.24	6.70	6.01	5.74
(g)	12.80	24.90	50.20	55.40
(h)	13.40	25.10	50.40	55.90
(k)	0.109	0.102	0.088	0.080
(l)	6.3:1	5.14:1	4.34:1	4.94:1
(m)	.24	.945	1.546	1.688

Temperature °C	300	350	400	450
Run No.	45	46	47	48
Catalyst Volume (ml)	42.30			
(a)	10.70	9.90	8.87	8.50
(g)	14.20	28.80	56.60	58.20
(h)	14.40	29.30	56.80	58.20
(k)	0.110	0.096	0.082	0.080
(l)	5.24:1	5.82:1	4.59:1	4.66:1
(m)	0.325	1.01	1.67	1.725

Table 5.2 (iv)

Hydrogenation of thiophene with Catalyst "D" at different temperatures and bed volumes.

Temperatures °C	300	350	400	450
Run No.	49	50	51	52
Catalyst Volume (ml)	48.8			
(a)	13.55	12.40	11.58	10.85
(g)	11.20	28.60	34.10	39.20
(h)	11.30	29.10	34.00	39.30
(k)	0.112	0.096	0.089	0.085
(l)	5.28:1	5.82:1	6.28:1	6.1:1
(m)	.125	1.02	1.18	1.29

Table 5.2 (v)

Hydrogenation of thiophene with Catalyst "E" at different temperatures

Temperature °C	300	350	400	450
Run No.	53	54	55	56
Catalyst Volume	48.8			
(a)	13.55	12.40	11.58	10.85
(g)	6 .90	24.80	29.20	34.80
(h)	7.10	25.10	29.60	34.60
(k)	0.115	0.103	0.097	0.094
(l)	6.0:1	4.87:1	5.45:1	5.29:1
(m)	-.06	.845	1.02	1.21

Table 5.2(vi)

Hydrogenation of thiophene with Catalyst "F" at different temperatures

Temperature °C	300	350	400	450
Run No.	57	58	59	60
Catalyst Volume (ml)	48.8			
(a)	13.15	12.10	10.85	10.40
(g)	16.40	37.40	68.70	74.80
(h)	16.50	37.60	68.80	75.20
(k)	0.102	0.094	0.072	0.068
(l)	8.0:1	4.83:1	4.8:1	4.7:1
(m)	.545	1.22	2.01	2.24

Table 5.3(i)

Hydrogenation studies at different mole ratio of thiophene to hydrogen. Catalyst "B" at 400°C.

Mole ratio (H_2:C_4H_4S)	4:1	8:1	12:1	16:1
Run No.	61	62	63	64
Catalyst Volume (ml)	48.8			
(a)	←—— 12.00 ——→			
(g)	69.20	78.10	84.30	87.00
(h)	69.30	78.80	84.30	87.20
(k)	0.014	0.068	0.128	0.188
(l)	4.66:1	4.53:1	4.28:1	4.13:1
(m)	2.01	2.26	2.32	2.61

Table 5.3(ii)

Hydrogenation studies at different mole ratio of thiophene to hydrogen. Catalyst "C" at 400°C

Mole ratio ($H_2:C_4H_4S$)	4:1	8:1	12:1	16:1
Run No.	65	66	67	68
Catalyst Volume (ml)	42.3			
(a)	8.87			
(g)	39.20	56.60	62.40	65.10
(h)	39.20	56.80	62.40	65.40
(k)	0.034	0.082	0.142	0.202
(l)	4.58:1	4.58:1	4.31:1	4.1:1
(m)	1.29	1.68	1.78	1.84

Table 5.3(iii)

Hydrogenation studies at different mole ratio of thiophene to hydrogen. Catalyst "F" at 400°C.

Mole ratio ($H_2:C_4H_4S$)	4:1	8:1	12:1	16:1
Run No.	69	70	71	72
Catalyst Volume (ml)	48.8			
(a)	10.85			
(g)	56.20	68.70	74.40	78.80
(h)	56.50	68.80	74.50	78.80
(k)	0.021	0.072	0.132	0.191
(l)	4.74:1	4.76:1	4.51:1	4.33:1
(m)	1.650	2.01	2.21	2.26

Table 5.4

Hydrogenation studies at different flow rates.
Catalyst "F" at 400°C.

Flow rate ml/min	0.4	0.3	0.2
Run No.	73	74	75
Catalyst Volume (ml)		48.8	
(a)	14.35	19.65	28.50
(g)	79.80	84.40	84.40
(h)	79.60	84.60	84.40
(k)	0.054	0.039	0.027
(l)	4.4:1	4.2:1	4.23:1
(m)	2.26	2.381	2.381

5.4 Discussion.

The hydrogenation studies with all the sulphided oxide catalysts show excellent results. It may be seen from the Figures 5.1 to 5.4 that the catalysts have different relative efficiences. The corresponding value for theoretical decomposition possible at each temperature obtained from theoretical equilibrium data is included in Figure 5.5. The nature of the curves in Figures 5.1 to 5.4 show that at lower temperatures the extent of desulphurisation is largely dependent on residence time, while at higher temperatures vis., 400°C and 450°C, the curves show the approach to equilibrium and a resultant smaller change in percentage decomposition.

Figure 5.5 shows that the equilibrium line acts as a "bottle-neck" to the extent of reaction. At low temperature (300°C) the reaction rate is too slow to allow the high extent of decomposition possible at this temperature to be achieved. At higher temperature although the reaction rate is greater the equilibrium is less favourable. Thus over a range of temperature there is a maximum conversion possible in any given apparatus, which is determined by residence time. Thus with the apparatus used here and the residence time selected the maximum extent of hydrogenation is obtained at about 450°C.

The Figures 5.1 to 5.4 indicate that in general the catalyst "B" has the highest hydrogenation efficiency while catalysts "F" and "C" follow it. The catalysts A, D and E on the other hand have a relatively poor hydrogenation efficiency. The Figure 5.5 drawn

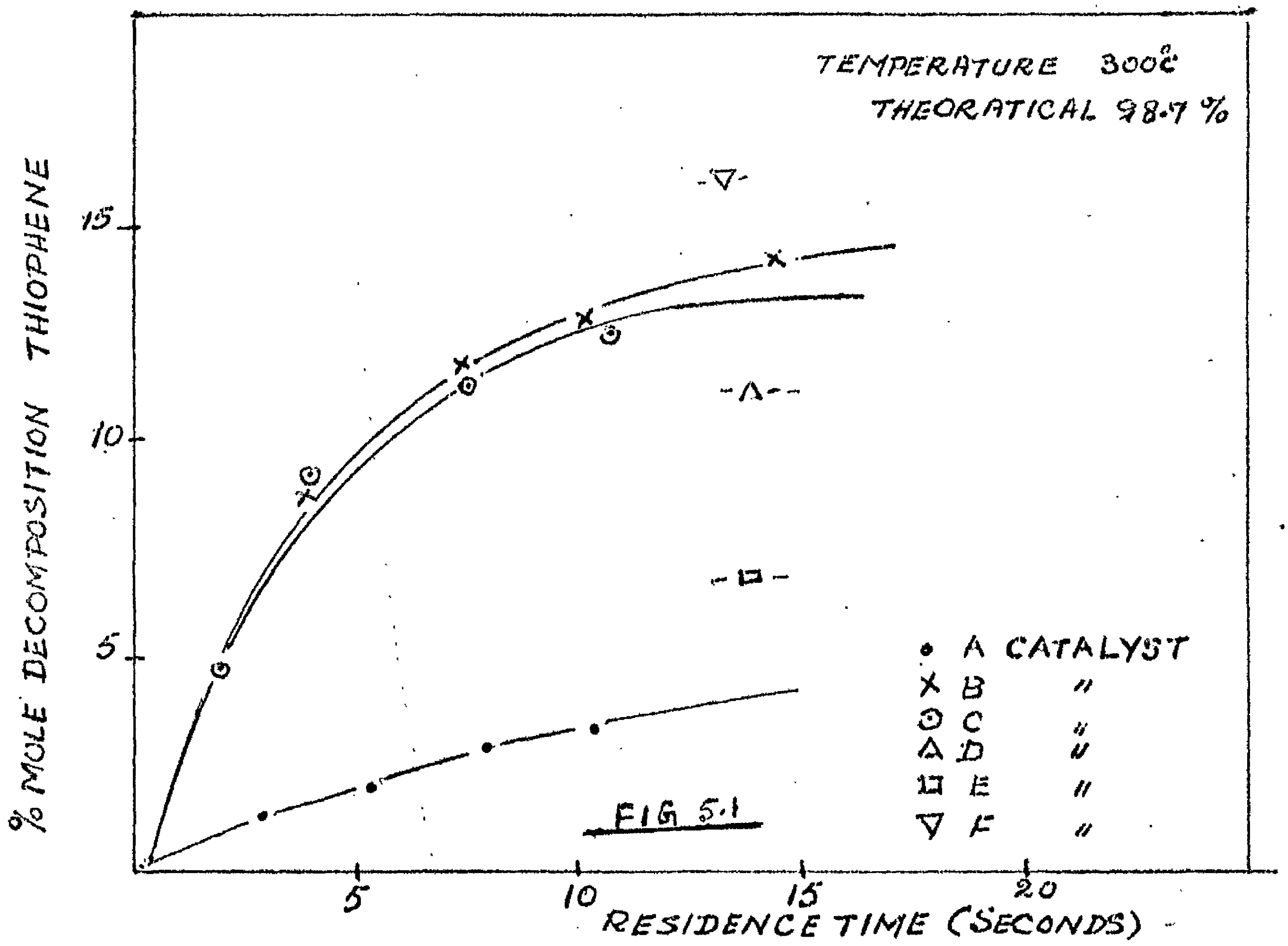

TEMPERATURE 300°C
THEORATICAL 98.7 %
% MOLE DECOMPOSITION THIOPHENE
15
10
5
5
10
15
20
RESIDENCE TIME (SECONDS)
• A CATALYST
× B "
⊙ C "
△ D "
⌑ E "
▽ F "

FIG 5.1

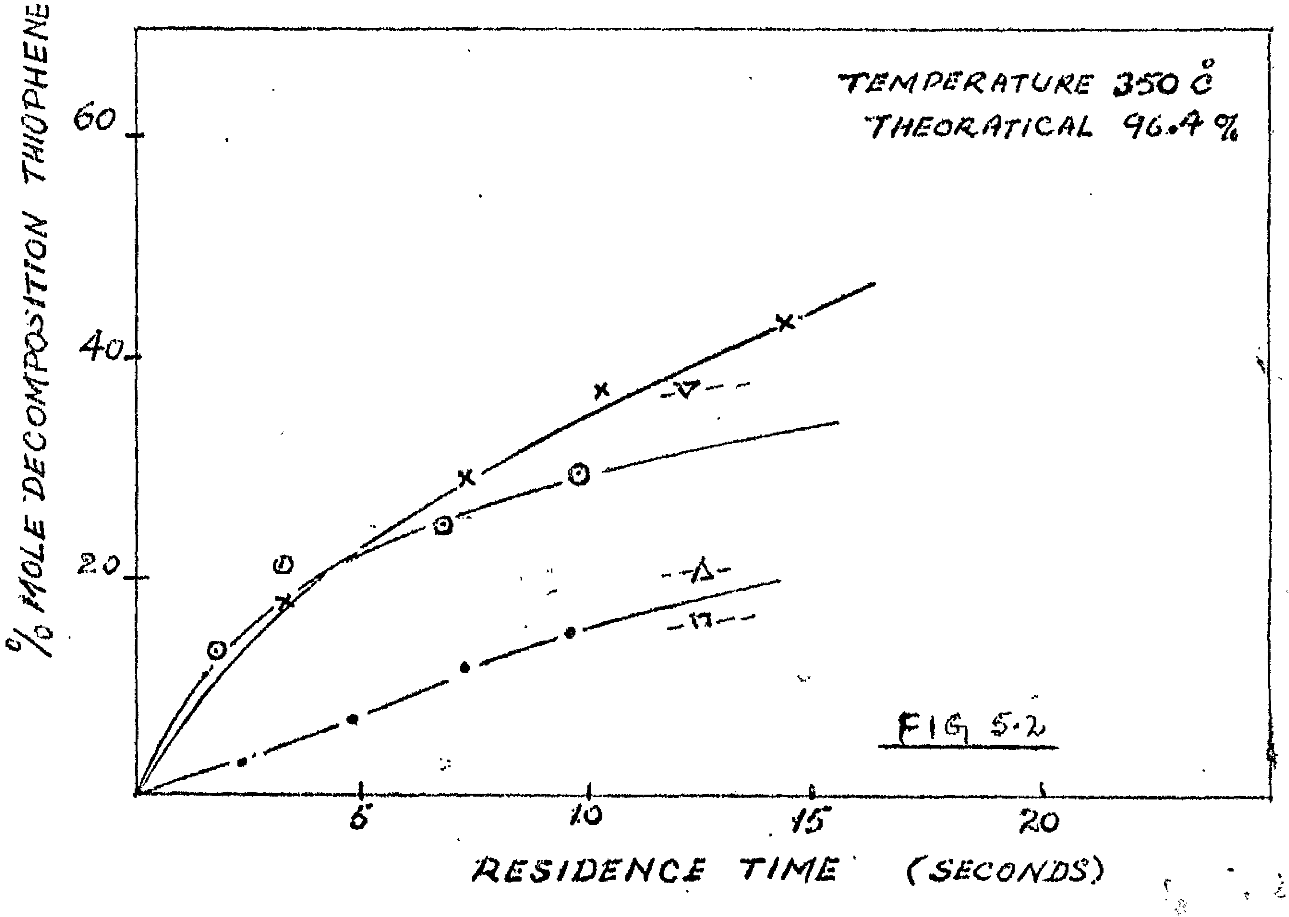

TEMPERATURE 350°C
THEORATICAL 96.4 %
% MOLE DECOMPOSITION THIOPHENE
60
40
20
5
10
15
20
RESIDENCE TIME (SECONDS)

FIG 5.2

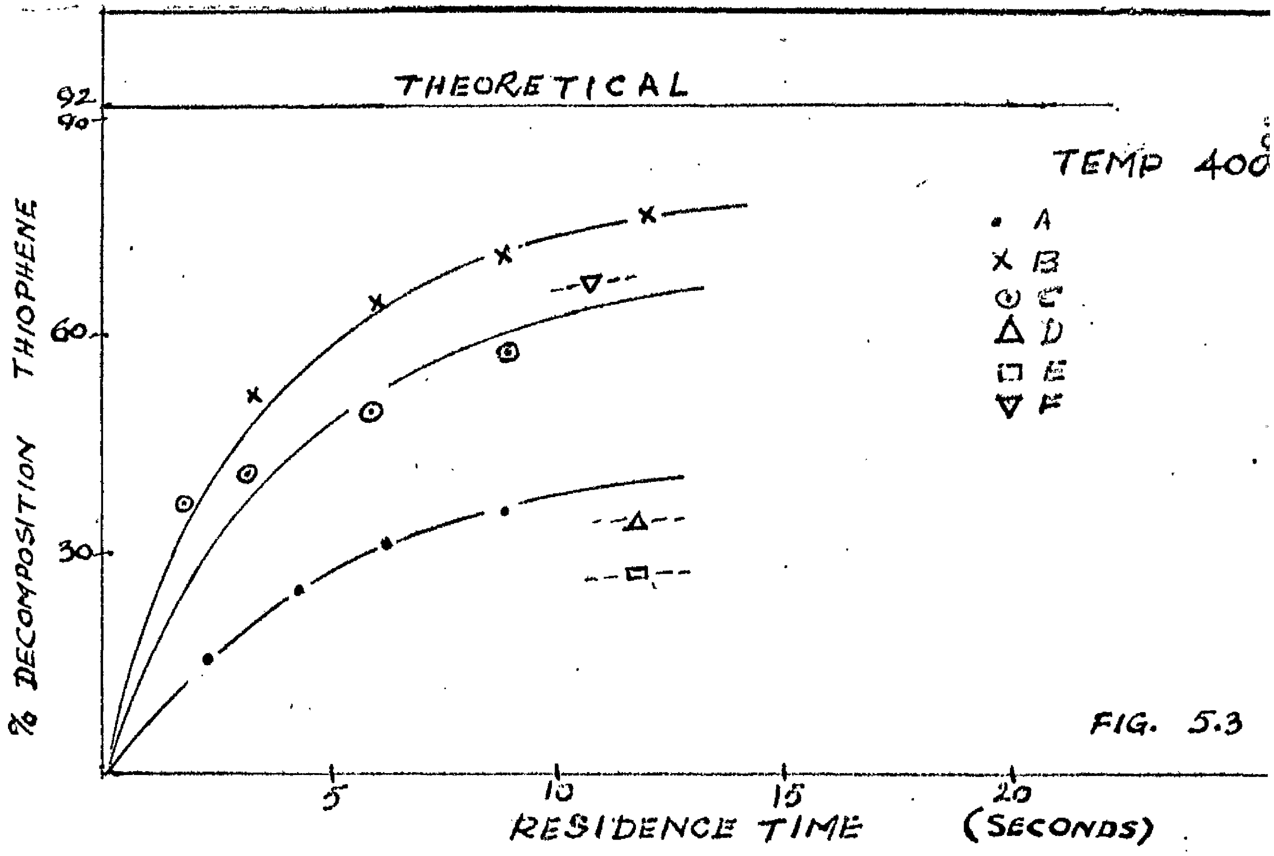

THEORETICAL
92
90
60
30
% DECOMPOSITION THIOPHENE
TEMP 400
• A
× B
⊙ C
△ D
□ E
▽ F
5
10
15
20
RESIDENCE TIME (SECONDS)

FIG. 5.3

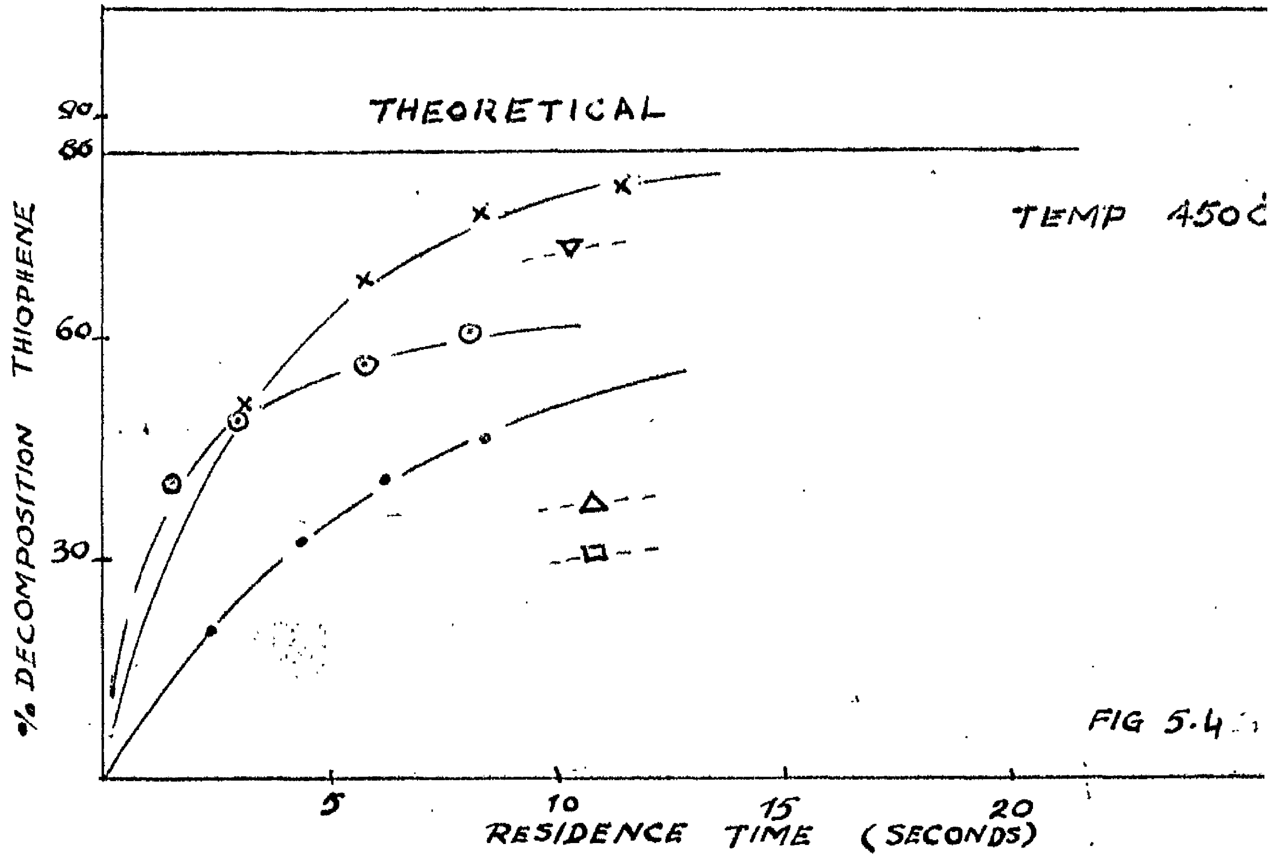
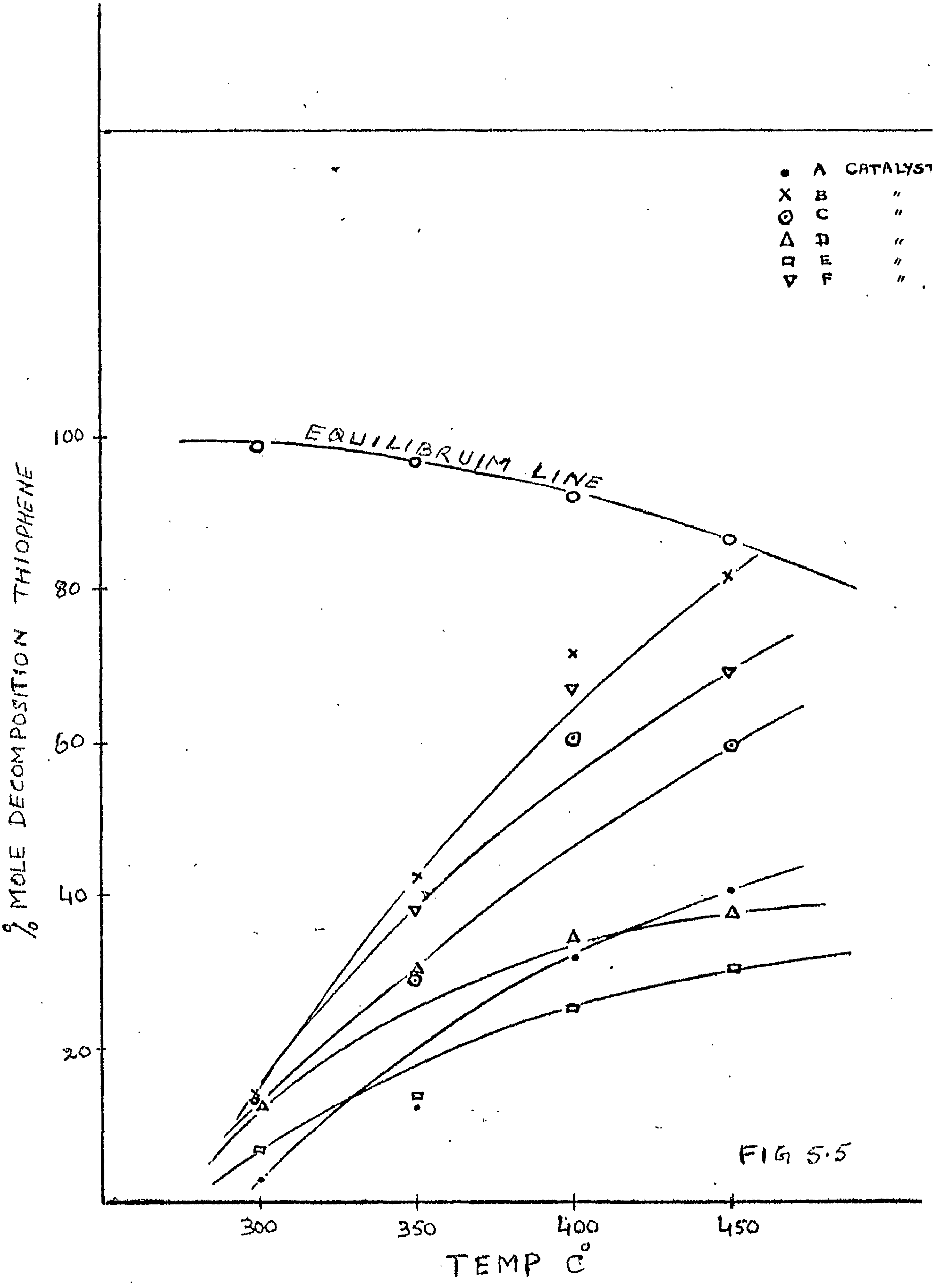

THEORETICAL
90
86
60
30
% DECOMPOSITION THIOPHENE
TEMP 450
5
10
15
20
RESIDENCE TIME (SECONDS)

FIG 5.4



% MOLE DECOMPOSITION THIOPHENE
100
80
60
40
20
300
350
400
450
TEMP C°
EQUILIBRUIM LINE
● A CATALYST
X B "
⊙ C "
Δ D "
◻ E "
∇ F "

FIG 5.5

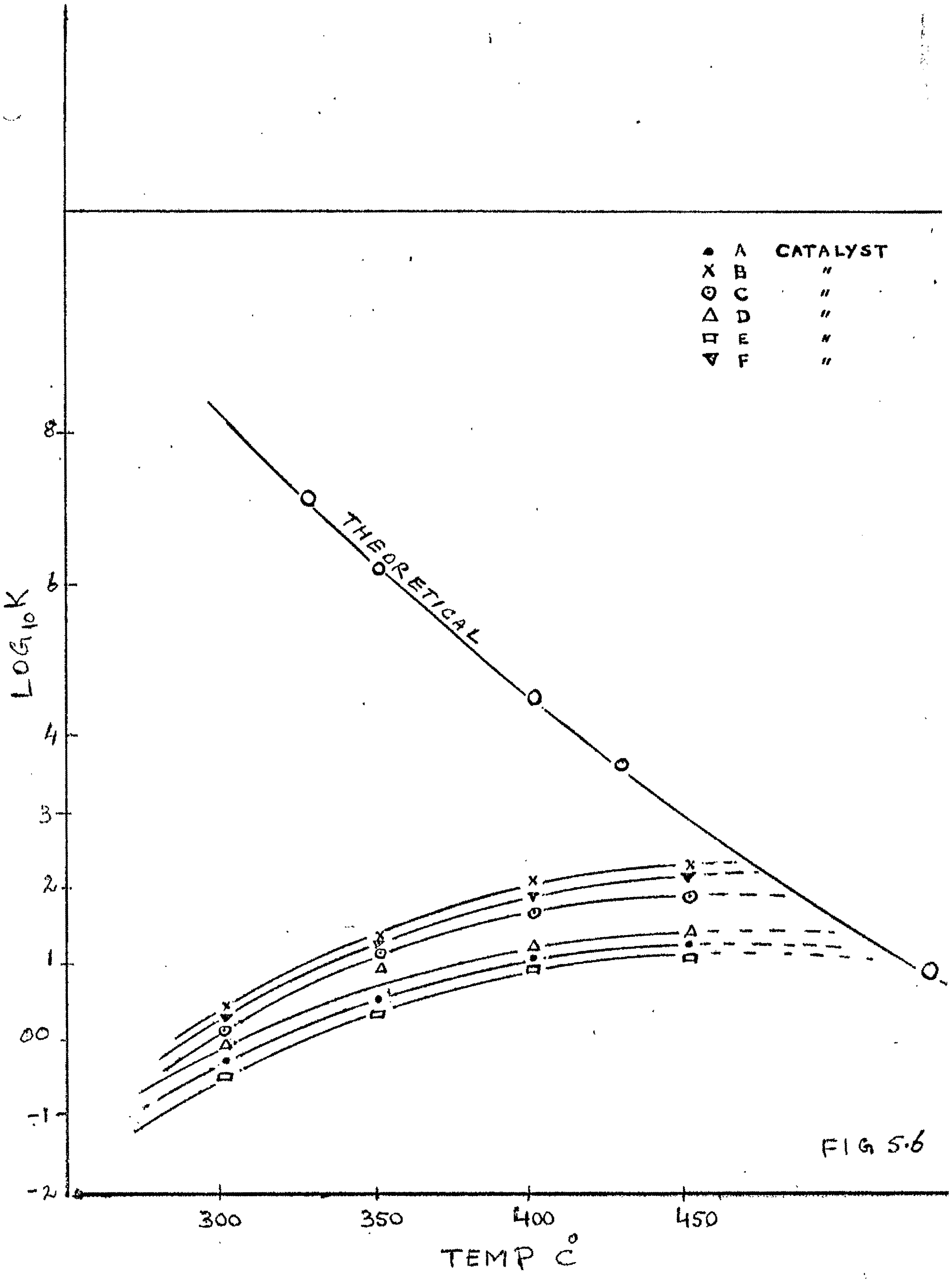

● A CATALYST
X B "
⊙ C "
Δ D "
⊓ E "
▼ F "
THEORETICAL
LOG10 K
8
6
4
3
2
1
00
-1
-2
300
350
400
450
TEMP C°

FIG 5.6

from the Figures 5.1 to 5.4 at a fixed residence time shows the extent of hydrogenation at different temperatures. In view of the unfavourable equilibrium these lines will not extend indefinitely as temperatures are raised above 450°C. The theoretical decomposition is shown by an equilibrium line included in the Figure. This line represents the maximum decomposition possible at infinite residence time.

The effect of the partial pressure of hydrogen on the extent of reaction at a constant residence time for catalysts "F" and "Z" is shown in Figure 5.8. It appears that increase of hydrogen partial pressure increases the degree of hydrogenation. This agrees with the findings of Hoog in desulphurising a gas oil. It may be seen from the Figure and from the results in 5.3(i) to 5.3(ii) that there is relatively little effect after a partial pressure of hydrogen equivalent to a mole ratio of 1:12. It is also shown in the figure that the system is relatively near to equilibrium, and thus there is nothing much to be gained in increasing the partial pressure of hydrogen further.

The Figure 5.7 shows the effect of longer residence time with catalyst "F" at 400°C. It may be seen that the extent of decomposition approaches the value to equilibrium in about twenty seconds of residence time. The maximum experimental decomposition was 84.6 percent while a theoretical value of 91.5 percent was required at this temperature. It may also be

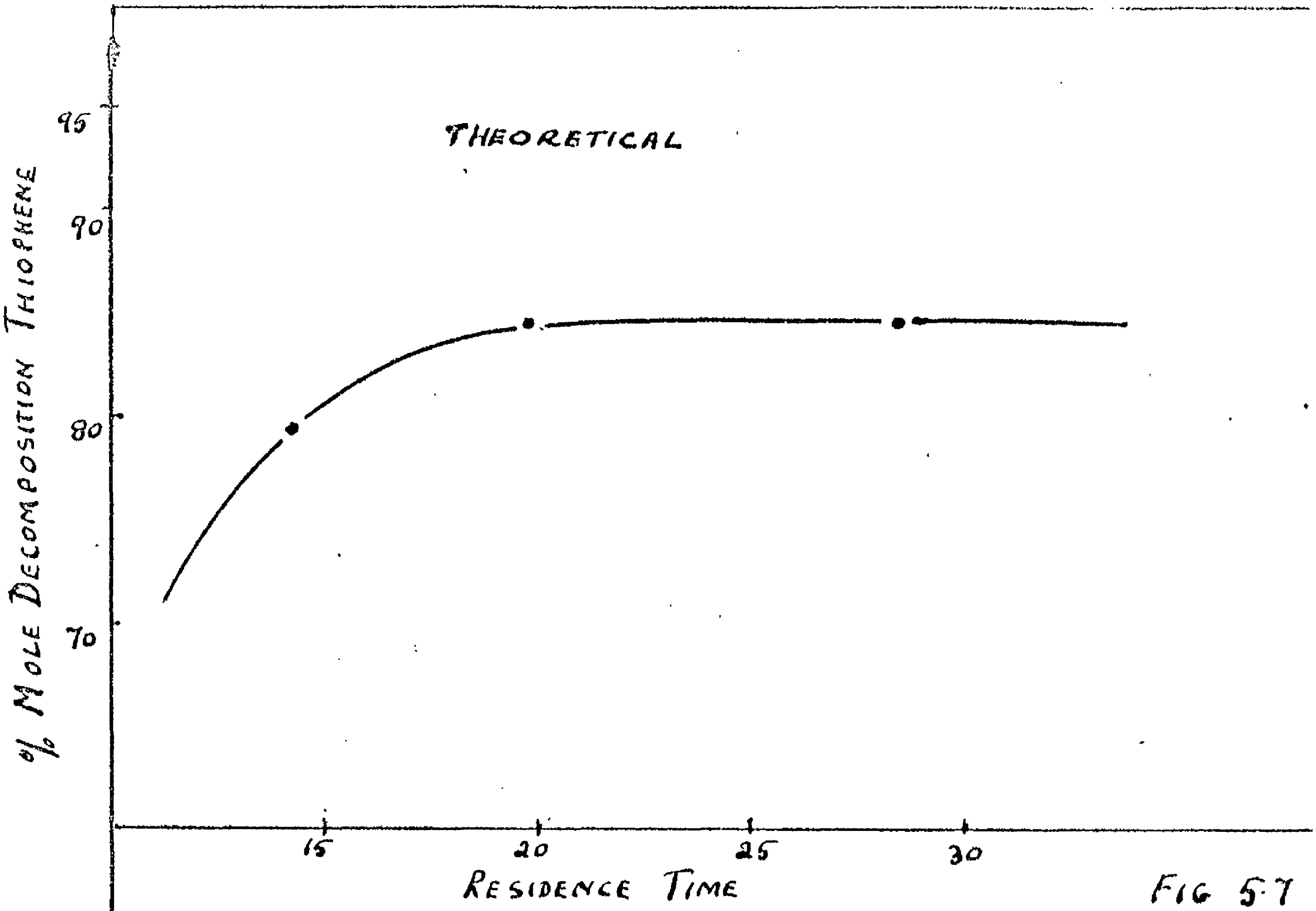

THEORETICAL
95
90
80
70
% MOLE DECOMPOSITION THIOPHENE
15
20
25
30
RESIDENCE TIME

FIG 5·7

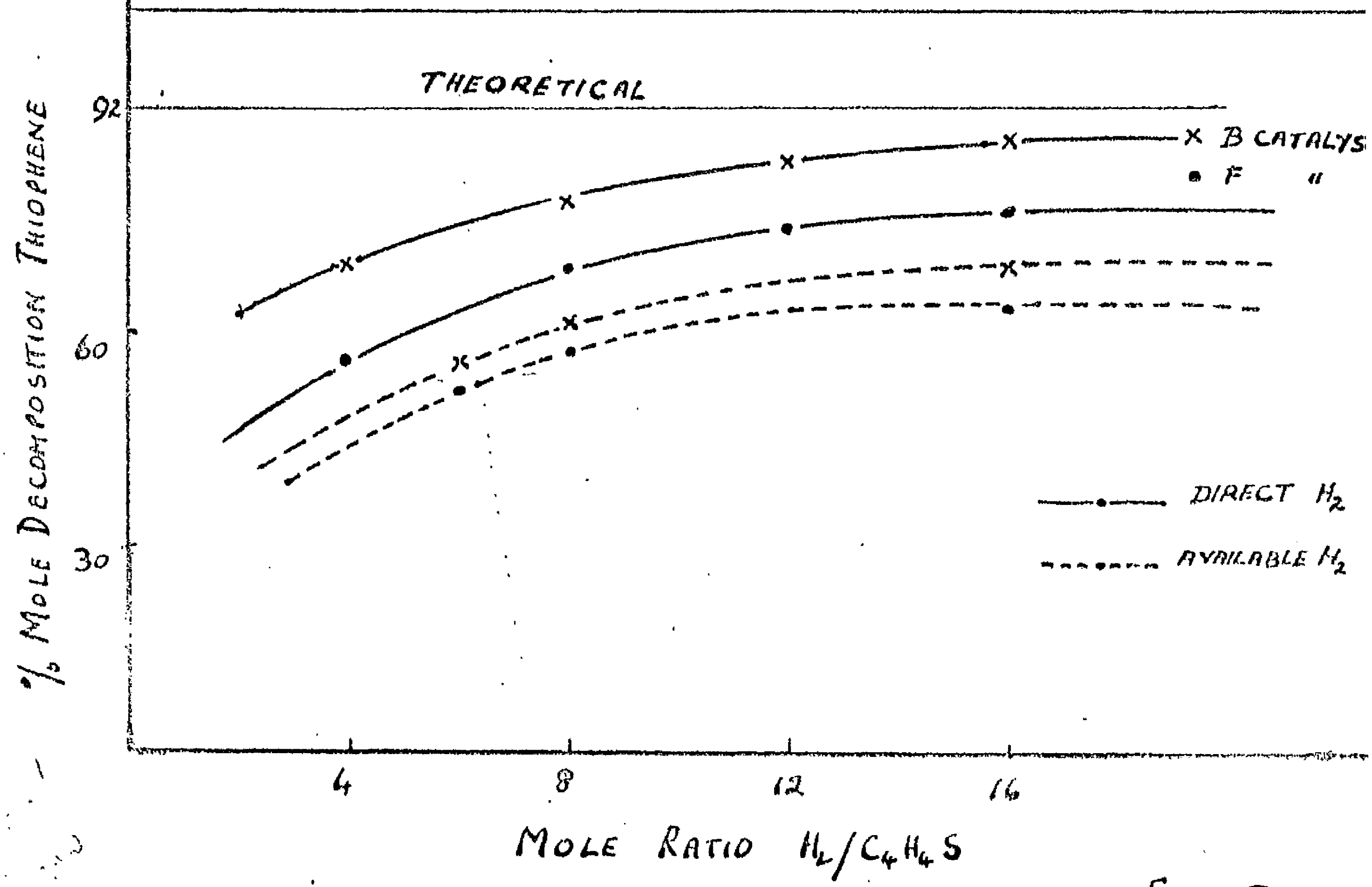

THEORETICAL
92
60
30
% MOLE DECOMPOSITION THIOPHENE
× B CATALYS
• F "
DIRECT H_2
AVAILABLE H_2
4
8
12
16
MOLE RATIO H_2/C_4H_4S

FIG 5·8

seen from the Table 5.2(ii) that the extent of hydrogenation obtained for the catalyst "B" at 400°C and a residence time of 12.0 seconds was 78.5 percent. It is thus likely that this catalyst will approach to equilibrium at a relatively lower residence time than with catalyst "F".

It was possible that the effect of hydrogen in the reaction could be stated in the form:-

$$\%D = A(pH)^{n}$$

where pH is hydrogen partial pressure and %D is the percentage decomposition in a given apparatus at a particular mean residence time and temperature. The value from Table 5.3(i) and 5.3(ii) and Figure 5.8 were put into the above formula.

In Figure 5.9 $\log_{10}(pH)$ is plotted against $\log_{10}\%D$ and the linear relation was obtained.

$$\log_{10}\%D = \log A + n \log(pH)$$

The value of n was obtained from the slope of the line and was found to be -0.799.

It was shown earlier that the best catalyst of the series under test for dehydrogenation was "C". In this series of hydrogenation experiments catalyst "B" proved best. Thus it was felt that a composite catalyst made up of equal volumes of pellet of catalysts "B" and "C" would be a first approximation to an autofining catalyst which would be expected to carry out efficiently hydrogen transfer from naphthene to thiophenes.

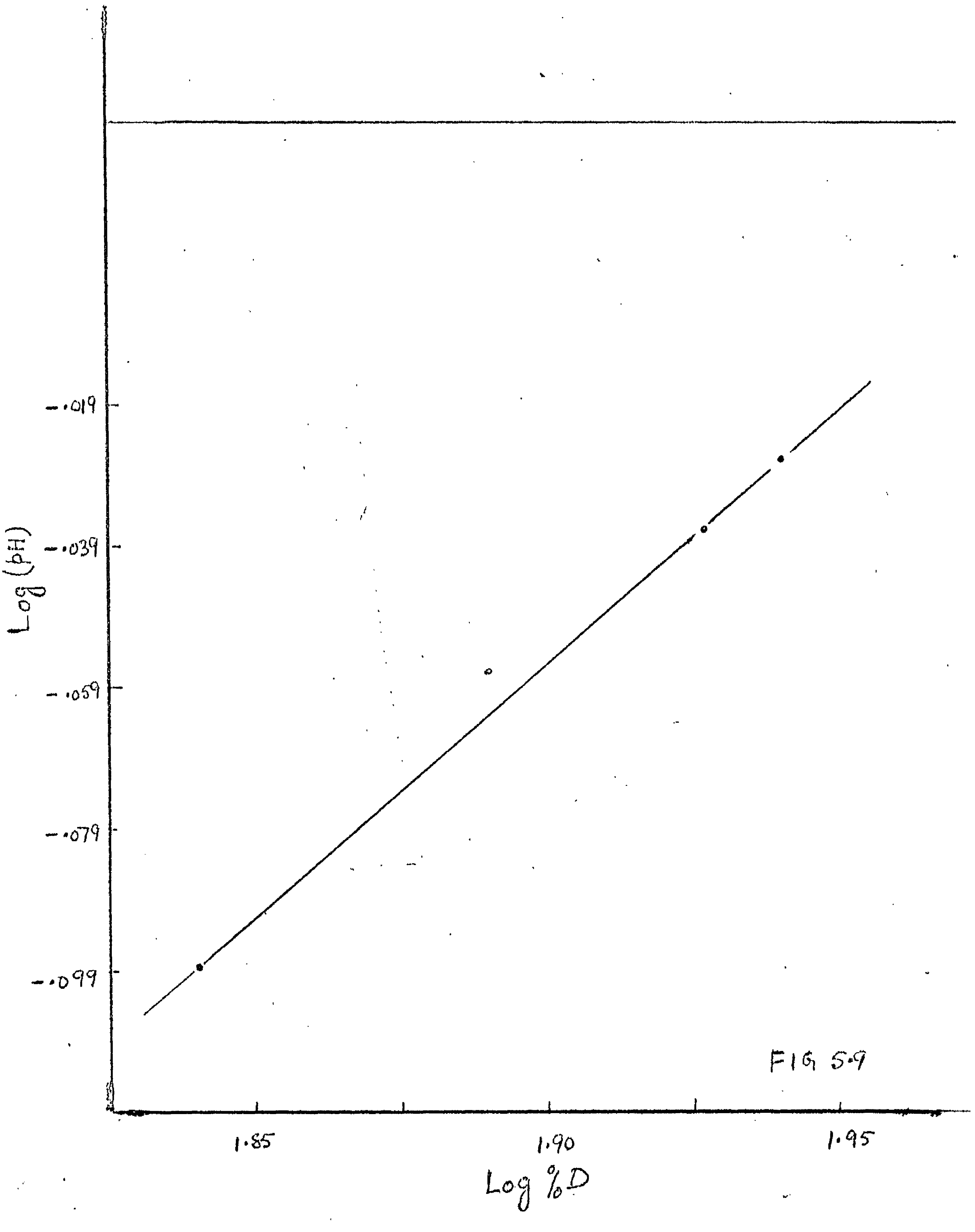


FIG 5.9

The reaction rate constants for the hydrogenation of thiophene in this apparatus were determined in the usual way at the various temperatures and for the three catalysts viz., A, B and C. The activation energy was then calculated and is shown below. Full details of these calculations are included in the Appendix. (as shown in Chapter 4.)

Catalyst	Temperature				Activation Energy K cal/mole
	300	350	400	450	
	k (Rate Constants in sec^{-1})				
A	1.0×10^{-3}	3.5×10^{-3}	13.0×10^{-3}	16.0×10^{-3}	16.1
B	7.4×10^{-3}	28.0×10^{-3}	52.0×10^{-3}	89.0×10^{-3}	12.1
C	8.0×10^{-3}	17.0×10^{-3}	49.0×10^{-3}	54.0×10^{-3}	12.3

The value of the activation energy obtained here agrees well, with that for a general hydrogen hydrocarbon exchange reaction. The value normally quoted in 13 ± 2 K cals. It should be noted, of course, that the hydrogenation of thiophene is exothermic while dehydrogenation of naphthene is endothermic. Thus under suitable conditions a system in which both reactions are occurring will be thermally neutral.

From a comparison of the relative values of Activation Energy of the dehydrogenation of cyclohexane and of the hydrogenation of thiophene, it would appear that the former reaction rate is more sensitive to reactor temperatures than is the latter. Thus in an Autofining process the overall reaction rate may well be controlled by the availability of hydrogen rather than its efficiency of utilisation.

6. HYDROGEN TRANSFER (AUTOFINING) STUDIES WITH CYCLOHEXANE AND THIOPHENE.

Having determined that it was possible to dehydrogenate cyclohexane effectively with catalysts under tests and that the same catalyst could act in the hydrogenation of thiophene, the next step was to carry out hydrogen transfer reaction from cyclohexane to thiophene.

The results of hydrogen transfer runs would possibly indicate the suitability of the catalyst in an autofining process for residual fuel oil.

6.1 Raw Materials Used.

All materials used were of Analar grade. The benzene and cyclohexane and thiophene used to calibrate the gas chromatograph showed no other peak.

6.2 Analysis of Products.

The procedure for hydrogen and hydrogen sulphide determination were the same as described in 4.3.3 and 5.2 respectively. The liquid condensed from the exit gases was analysed by gas chromatograph. It was found to consist of cyclohexane, benzene, thiophene and traces of cyclohexene. A reference curve for use with the gas chromatograph was prepared from different standard mixtures of cyclohexane and benzene in a two percent v/v of thiophene.

6.3 Reaction Procedure and Results.

The sulphided-oxide pellets were left in the reactor at the required temperature in a current of purified nitrogen for one hour at a steady flow rate of 0.0061 ft^3/min at N.T.P. A two percent v/v solution of thiophene in cyclohexane was fed into the reactor at a rate of 0.50 ml/min. The hydrogen-transfer run was continued for two hours; and during this time six samples each of twenty minutes duration for the hydrogen sulphide determination and for the hydrogen content in the off gases were obtained. The total liquid product was analysed after the run. The hydrogen-transfer runs were carried out with catalysts A, B, C and F. The first three were studied at different temperatures and bed depths of catalyst. The results are shown in the Tables 6.2(i) to 6.2(iii). Catalysts D and E were not studied here due to their earlier poor performance. Catalysts B and F were also studied at different mole ratios of available hydrogen to thiophene. This was achieved by diluting the cyclohexane with benzene before mixing with thiophene.

In computing the proportion of the mixtures of cyclohexane, thiophene and benzene the amount of hydrogen assumed to be available was that already found in the corresponding dehydrogenation study on cyclohexane alone under the same conditions of flow rate and temperature. Using this approach, mixtures were prepared which had mole ratios of available hydrogen to thiophene of 6:1, 8:1, and 16:1 for use with catalyst B and 6:1, 8:1, 16:1 and 32:1 for use with catalyst F.

The proportions of the mixtures calculated to be required to provide the above ratios are given in Table 6.1

Table 6.1

Catalyst	Components	%v/v mixture to give 6:1 H_2 to thiophene	%v/v mixture to give 8:1 H_2 to thiophene	%v/v mixture to give 16:1 H_2 to thiophene	%v/v mixture to give 32:1 H_2 to thiophene
B	cyclohexane	18.10	36.20	72.40	-
	benzene	79.90	61.80	25.60	-
	thiophene	2.00	2.00	2.00	-
F	cyclohexane	7.50	15.00	30.00	60.00
	benzene	90.50	83.00	68.00	38.00
	thiophene	2.00	2.00	2.00	2.00

The catalyst F was studied over a range of input flow rate of 2% v/v cyclohexane in thiophene. The result is shown in the Table 6.4.

A typical set of experimental values for a hydrogen-transfer run is shown in the Table 6.2.

In the left hand column of each table the letters signify the following:-

(a) signifies the mean residence time (seconds)

(g) signifies percentage decomposition of thiophene by H_2S determination.

(h) signifies percentage decomposition of thiophene by gas chromatography.

(k) signifies total hydrogen (gm mole) in off gases.

(l) signifies mole hydrogen utilised per mole of thiophene.

(e) signifies mole of available H_2/100 mole C_6H_{12}.

Table 6.2

"Autofining" of Thiophene by Catalyst "F" at 400°C.

Liquid Flow Rate = 0.5 ml/min (2% v/v of thiophene in cyclohexane)

Nitrogen Flow Rate = 0.0061 ft^3/min at N.T.P

Volume of Catalyst = 48.8 ml.

Time of Run = 120 mins.

Time	Input sulphur wt. (gm)	Output sulphur As H_2S (gm)	% decomposition of thiophene (wt)	Gas chromatograph decomposition of thiophene (wt)
0-20'	0.0805	0.0605	75.0	
20-40'	"	0.0614	76.1	76.6
40-60'	"	0.0613	76.2	
60-80'	"	0.0618	76.8	
80-100'	"	0.0624	77.3	
100-120'	"	0.0613	76.1	

Hydrogen Analysis

Measured outlet gas volume = 1.126 ft^3 at N.T.PZ

Snap gas sample volume = 250 mls at 20°C = 0.0079 ft^{3}at N.T.P

Time	%H_2 in outlet gas	Volume H_2 in snap samples	Total outlet Hydrogen	Total outlet gas
		←——ft^3	at N.T.P——→	
0-20'	35.50	0.0028	0.069	
20-40'	36.40	0.0029	0.071	
40-60'	39.40	0.0031	0.077	
60-80'	37.40	0.0030	0.073	
80-100'	38.50	0.0031	0.075	
100-120'	37.70	0.0030	0.074	

Total 1.126 + 6 x .0079

= 1.173 ft^3.

Table 6.2(i)

"Autofining" of Thiophene using Cyclohexene with Catalyst "A" at different temperatures and bed volumes.

Temperature °C	300	350	400	450
Run No.	1	2	3	4
Catalyst Volume (ml)	16.5			
(a)	2.63	2.43	2.18	2.09
(g)	0.50	1.90	19.20	24.10
(h)	0.60	2.10	19.20	24.40
(k)	0.031	0.073	0.169	0.231
(l)	-	-	4.1:1	4.0:1
(e)	5.76	13.95	31.90	43.00

Temperature °C	300	350	400	450
Run No.	5	6	7	8
Catalyst Volume (ml)	33.00			
(a)	5.13	4.74	4.29	4.07
(g)	0.80	7.10	26.20	32.40
(h)	0.95	-	26.40	32.40
(k)	0.077	0.159	0.276	0.361
(l)	-	5.7:1	7.4:1	4.1:1
(e)	13.90	29.70	51.30	68.30

Temperature °C	300	350	400	450
Run No.	9	10	11	12
Catalyst Volume (ml)	49.5			
(a)	7.70	7.13	6.39	6.13
(g)	1.20	8.60	39.60	42.80
(h)	1.20	8.40	39.70	42.90
(k)	0.102	0.228	0.360	0.428
(l)	-	8:1	4.0:1	5.2:1
(e)	18.40	41.30	69.30	81.50

Table 6.2(i) continued.

Temperature °C	300	350	400	450
Run No.	13	14	15	16
Catalyst Volume (ml)	66.00			
(a)	10.25	9.50	8.58	8.18
(g)	4.60	9.40	44.80	48.80
(h)	-	9.40	44.80	48.60
(k)	0.134	0.271	0.422	0.492
(l)	-	11.3:1	5.05:1	4.1:1
(e)	24.10	50.20	80.50	94.20

Table 6.2(ii)

"Autofining" of Thiophene using Cyclohexane with Catalyst "B" at different temperatures and bed volumes.

Temperature °C	300	350	400	450
Run No.	17	18	19	20
Catalyst Volume (ml)	12.20			
(a)	3.71	3.46	3.06	2.94
(g)	6.10	21.10	59.20	63.40
(h)	6.30	21.40	59.20	63.80
(k)	0.081	0.119	0.196	0.258
(l)	-	4.0:1	4.1:1	4.1:1
(e)	14.60	23.70	41.80	53.00

Temperature °C	300	350	400	450
Run No.	21	22	23	24
Catalyst Volume (ml)	24.40			
(a)	7.24	6.70	6.00	5.74
(g)	10.80	38.40	66.40	71.80
(h)	10.90	38.40	66.70	71.90
(k)	0.113	0.192	0.288	0.378
(l)	4.0:1	4.1:1	9.2:1	4.3:1
(e)	21.40	38.90	58.40	75.80

Table 6.2(ii) continued.

Temperature °C	300	350	400	450
Run No.	25	26	27	28
Catalyst Volume (ml)	36.60			
(a)	10.04	9.20	8.70	8.33
(g)	12.80	41.40	69.80	73.60
(h)	13.10	41.60	69.90	73.60
(k)	0.154	0.259	0.390	0.492
(l)	4.0:1	4.2:1	4.7:1	4.7:1
(e)	28.90	51.00	77.90	96.20

Temperature °C	300	350	400	450
Run No.	29	30	31	32
Catalyst Volume (ml)	48.80			
(a)	14.45	13.40	12.00	11.50
(g)	14.20	43.40	70.40	74.00
(h)	14.30	43.50	70.60	74.20
(k)	0.251	0.365	0.450	0.596
(l)	4.0:1	4.6:1	4.4:1	4.9:1
(e)	46.30	70.00	88.70	114.00

Table 6.2(iii)

"Autofining" of Thiophene using Cyclohexane with Catalyst "C" at different temperatures and bed volumes.

Temperature °C	300	350	400	450
Run No.	33	34	35	36
Catalyst Volume (ml)	7.05			
(a)	1.96	1.80	1.67	1.57
(g)	4.50	11.20	42.10	49.60
(h)	5.10	11.30	42.40	49.80
(k)	0.06	0.101	0.150	0.220
(l)	4.1:1	4.0:1	4.1:1	4.0:1
(e)	10.82	19.30	32.80	45.00

Table 6.2(iii) continued.

Temperature °C	300	350	400	450
Run No.	37	38	39	40
Catalyst Volume (ml)		14.10		
(a)	3.92	3.62	3.35	3.14
(g)	7.40	24.80	49.40	56.70
(h)	7.60	24.90	49.80	56.70
(k)	0.031	0.116	0.276	0.336
(l)	-	$4.5_{8}1$	$4.1_{8}1$	$4.4_{8}1$
(o)		32.10	55.20	67.00

Temperature °C	300	350	400	450
Run No.	41	42	43	44
Catalyst Volume (ml)		28.20		
(a)	7.84	7.24	6.69	6.28
(g)	9.70	26.40	56.20	61.40
(h)	9.80	26.50	56.40	61.40
(k)	0.138	0.294	0.408	0.560
(l)				
(o)	25.90	54.20	79.00	107.00

Temperature °C	300	350	400	450
Run No.	45	46	47	48
Catalyst Volume (ml)		42.30		
(a)	11.75	10.85	10.05	9.43
(g)	11.20	28.80	61.20	66.20
(h)	11.30	28.90	61.40	66.50
(k)	0.164	0.342	0.496	0.712
(l)	$5.9_{8}1$	$4.1_{8}1$	$4.2_{8}1$	$4.4_{8}1$
(o)	30.60	63.40	95.70	135.50

Table 6.3

"Autofining" of Thiophene using Cyclohexane with Catalyst "F" at different temperatures.

Temperature °C	300	350	400	450
Run No.	49	50	51	52
Catalyst Volume (ml)	48.80			
(a)	13.15	12.10	10.85	10.40
(g)	18.20	46.40	76.40	82.80
(h)	18.20	46.70	76.60	82.80
(k)	0.121	0.311	0.566	0.704
(l)	10.6:1	6.95:1	4.9:1	5.4:1
(e)	23.90	61.30	109.50	135.00

Table 6.4

"Autofining" of Thiophene using Cyclohexane with Catalyst "F" at different flow rates at 400°C.

Flow Rate ml/min	0.4	0.3	0.2	0.1
Run No.	53	54	55	56
Catalyst Volume (ml)	48.80			
(a)	14.35	19.65	28.50	59.30
(g)	78.10	84.80	86.20	86.20
(h)	78.40	84.80	86.30	86.20
(k)	0.621	0.594	0.426	0.226
(l)	5.07:1	6.4:1	7.9:1	5.1:1
(e)				

Table 6.5

"Autofining" of Thiophene using Cyclohexane with Catalyst "B" at 400°C, at different mole ratios of hydrogen availability to Thiophene.

Mole ratio, H_2:thiophene	6:1	8:1	16:1
Run No.	57	58	59
Catalyst Volume (ml)	48.8		
(a)	12.00		
(g)	56.20	61.70	68.30
(h)	56.00	61.70	68.20
(k)	0.042	0.074	0.194
(l)	5.34:1	5.07:1	4.75:1

Table 6.6

"Autofining" of Thiophene using Cyclohexane with Catalyst "F" at 400°C, at different mole ratios of hydrogen availability to Thiophene.

Mole ratio, H_2:thiophene	6:1	8:1	16:1	32:1
Run No.	60	61	62	63
Catalyst Volume (ml)	48.80			
(a)	10.85			
(g)	52.30	58.40	63.40	68.70
(h)	52.40	59.20	63.40	68.60
(k)	0.058	0.079	0.196	0.421
(l)	5.6:1	4.6:1	5.7:1	5.9:1

6.4 Discussion.

The hydrogen-transfer studies with the test catalysts A, B, C and F showed considerable decomposition of thiophene, and that the catalysts differed in their relative efficiencies. Catalyst "A" had a poor efficiency as may be seen from the Figures 6.1A to 6.2B; however the nature of its curves indicate that a longer residence time would have given an adequate reaction.

It should be noted that with only two percent of thiophene in the feed mixture the hydrogen available for reaction was at least four times the stoichiometric requirement and in many cases much larger than this. Thus the operation of the catalyst was not being limited by hydrogen partial pressure. Catalyst "C" on the other hand tended towards a constant efficiency in about twelve seconds of residence time at all temperatures.

Referring to the dehydrogenation studies Table 4A(iii), this catalyst gave the maximum hydrogen production. Thus if the hydrogen-transfer reaction was only dependent on hydrogen partial pressure, this catalyst should have shown a maximum reaction at a given residence time. The experimental results for this catalyst indicating low hydrogenation of thiophene seem however to indicate that the extent of the reaction is not dependent on hydrogen partial pressure alone. Again if one compares the calculated moles of available hydrogen per hundred moles of cyclohexane determined from the dehydrogenation studies for this

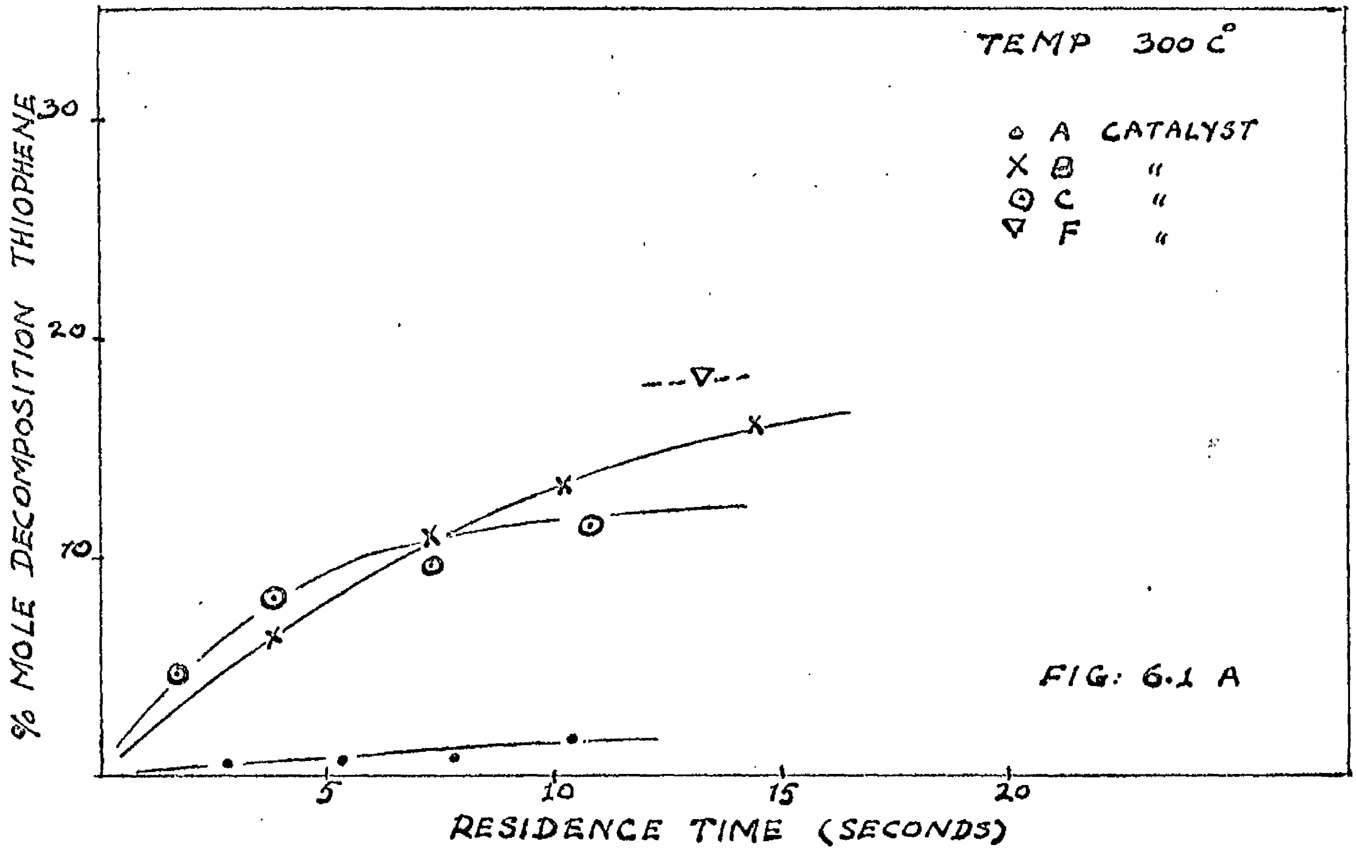


FIG: 6.1 A

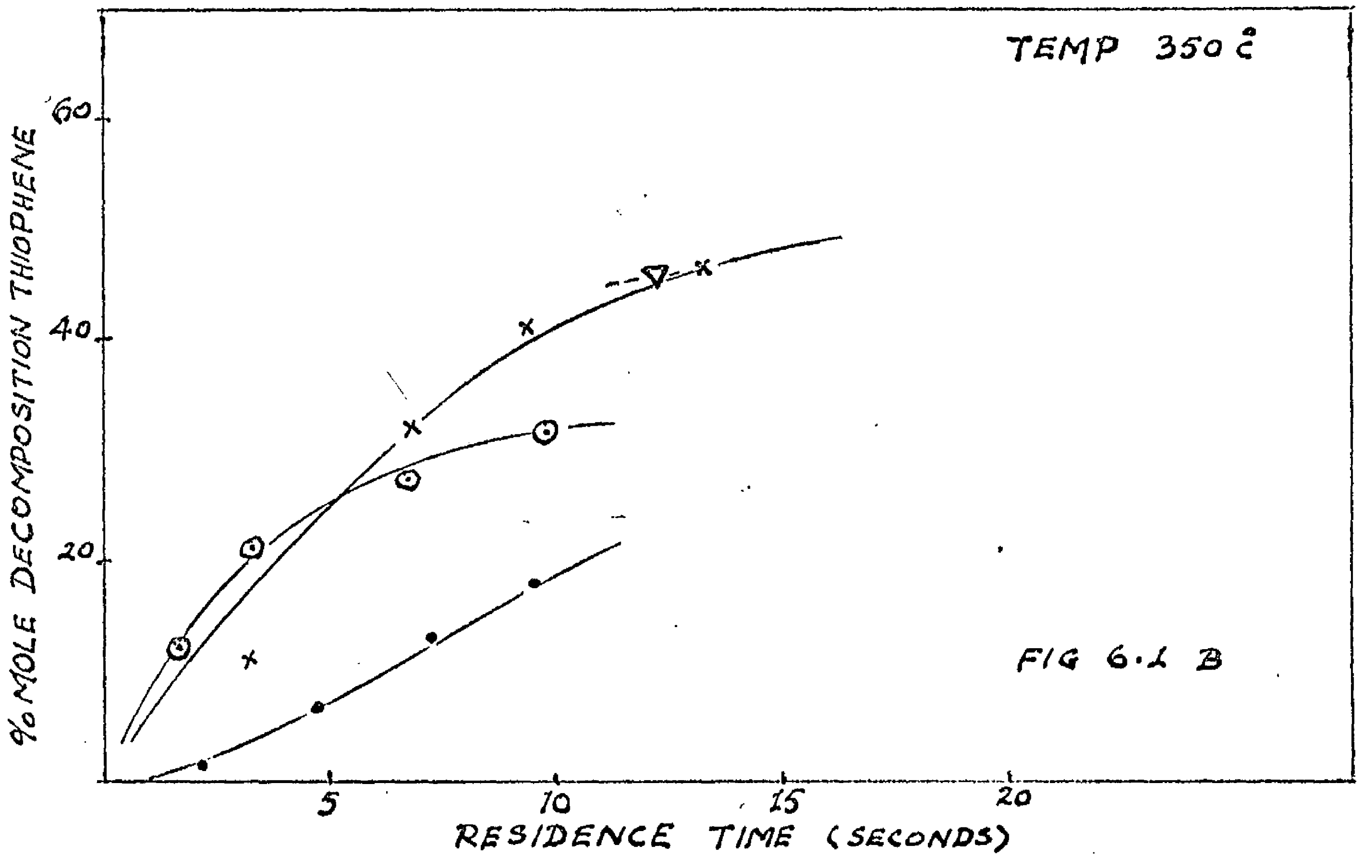


FIG 6.1 B

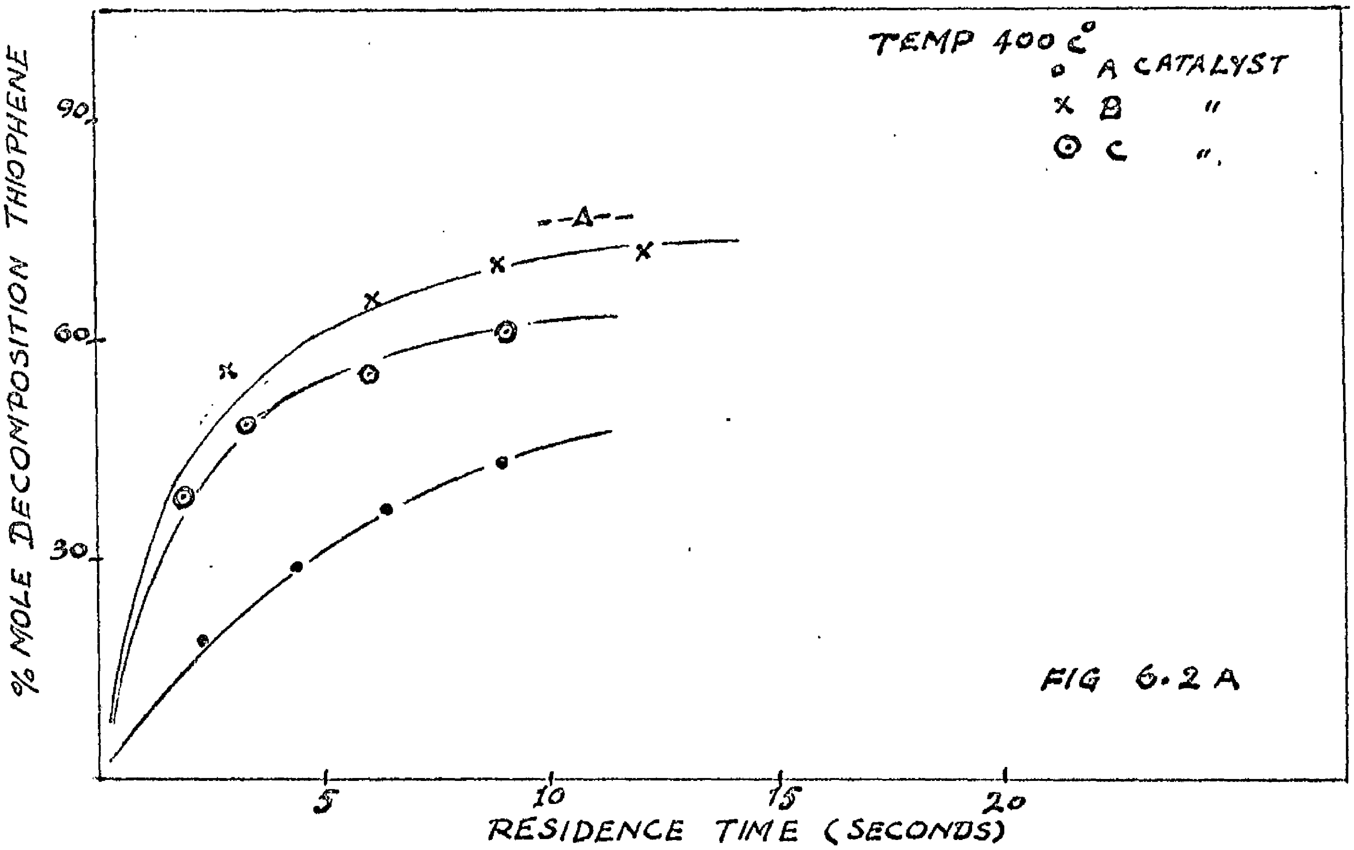


FIG 6.2 A

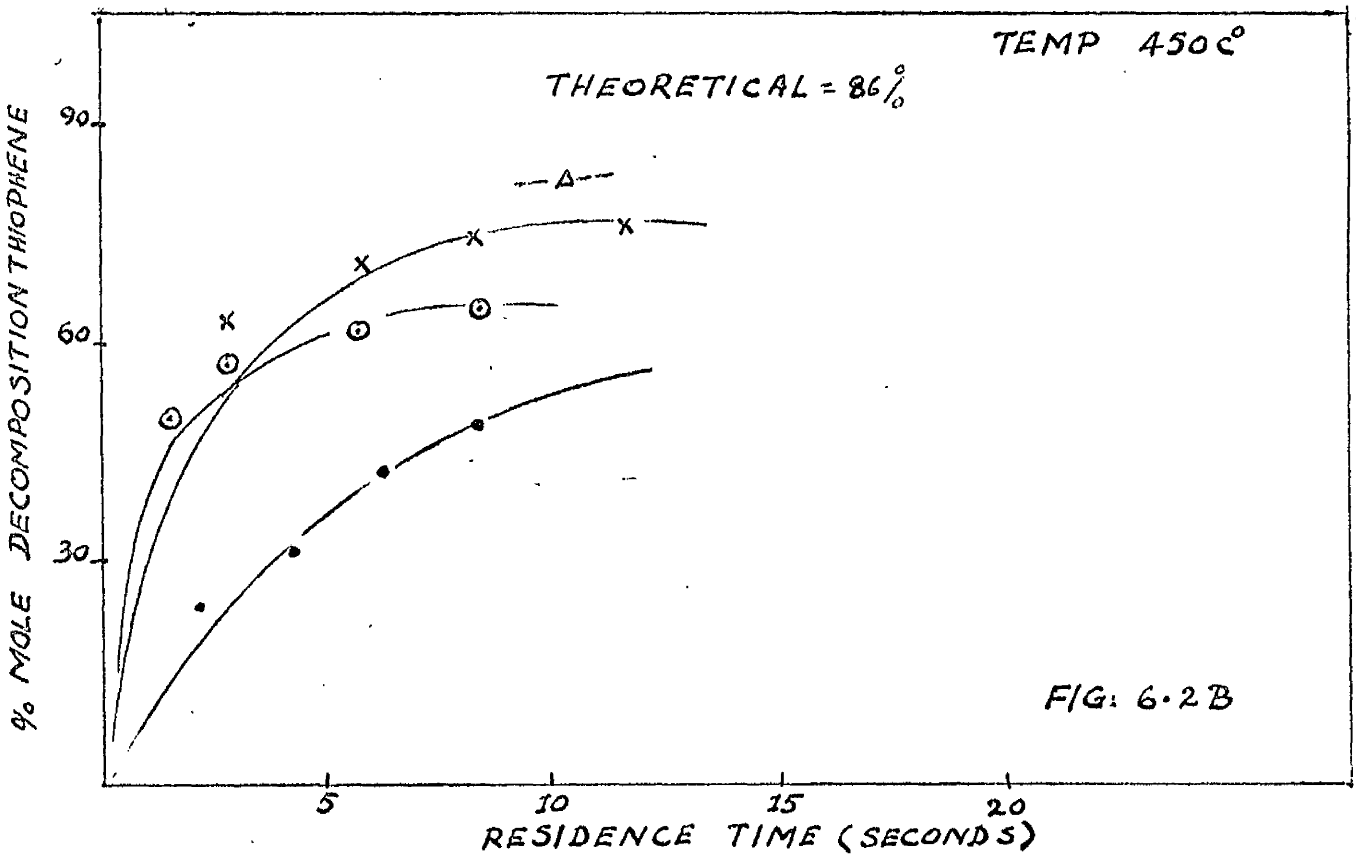


FIG: 6.2B

catalyst "C" (Table 4.4(iii), column "e") and the hydrogen actually found in the off gases from the corresponding hydrogen-transfer runs plus the hydrogen taken up to hydrogenate the thiophene to the determined extent (Table 6.2(iii), column "e"), it may seen that there is a small but significant difference between them. This inhibition of the dehydrogenation of cyclohexane may be due to the fact that thiophene molecules are competing for the active sites on the catalyst surface. This effect is similar to the effect described by Hoog[29] who found, in a small-scale autofining plant, that the oil partial pressure influenced the reaction rate.

Catalyst "B" on the other hand showed quite excellent hydrogen-transfer and its efficiency approached constancy at 400 and 450°C and a residence time of twelve seconds.

Catalyst "F" provided the best results. A decomposition of thiophene to an extent of 82.8 percent was obtained at 450°C, with a mean residence time of 10.40 seconds.

It will be recalled that catalyst "C" was the best dehydrogenation catalyst while catalyst "B" was the best for hydrogenation of thiophene. It was therefore decided that a combined catalyst of "C" and "B" might well be appropriate for optimum hydrogen-transfer. Catalyst "F" was accordingly prepared by simply mixing equal volumes of pellets of Catalyst "C" and catalyst "B" and using the mixture in the reactor. It may be seen that for hydrogen-transfer catalyst "F" is much better than "C" and a little better than "B" (Figure 6.3).

The Figure 6.4A and the Table 6.4 in which the effect of inlet flow rate with catalyst "F" was studied showed that the reaction reached equilibrium in about 29 seconds of residence time. A decomposition of 86.2 mole percent of thiophene was obtained at 400°C with this catalyst.

The Figure 6.4B shows the effect of different mole ratios of available hydrogen to thiophene and the efficiency of catalysts "B" and "F". This comparison shows that at any value of available mole ratio of hydrogen to thiophene catalyst "B" was more effective than "F". This agrees with the earlier finding that in hydrogenation with catalyst "B" and with "F" (Table 5.3(i) and 5.3(ii)) at constant hydrogen partial pressure, catalyst "B" was more effective. This is in contrast to the results in Figure 6.1Ato 6.2B which shows catalyst "F" to be better on a basis of residence time

The effect of hydrogen partial pressure on the decomposition of thiophene with direct hydrogen and with available hydrogen may be seen by comparing Table 5.3(i) and 5.3(iii) and Table 6.5 and 6.6 and from Figure 5.8. It may be seen that the lower decomposition of thiophene achieved in the hydrogen-transfer runs was due to a lower hydrogen partial pressure.

It is to be concluded from the above that with the system under test a partial pressure of hydrogen equivalent to at least a mole ratio of hydrogen to thiophene of 16:1 is required to

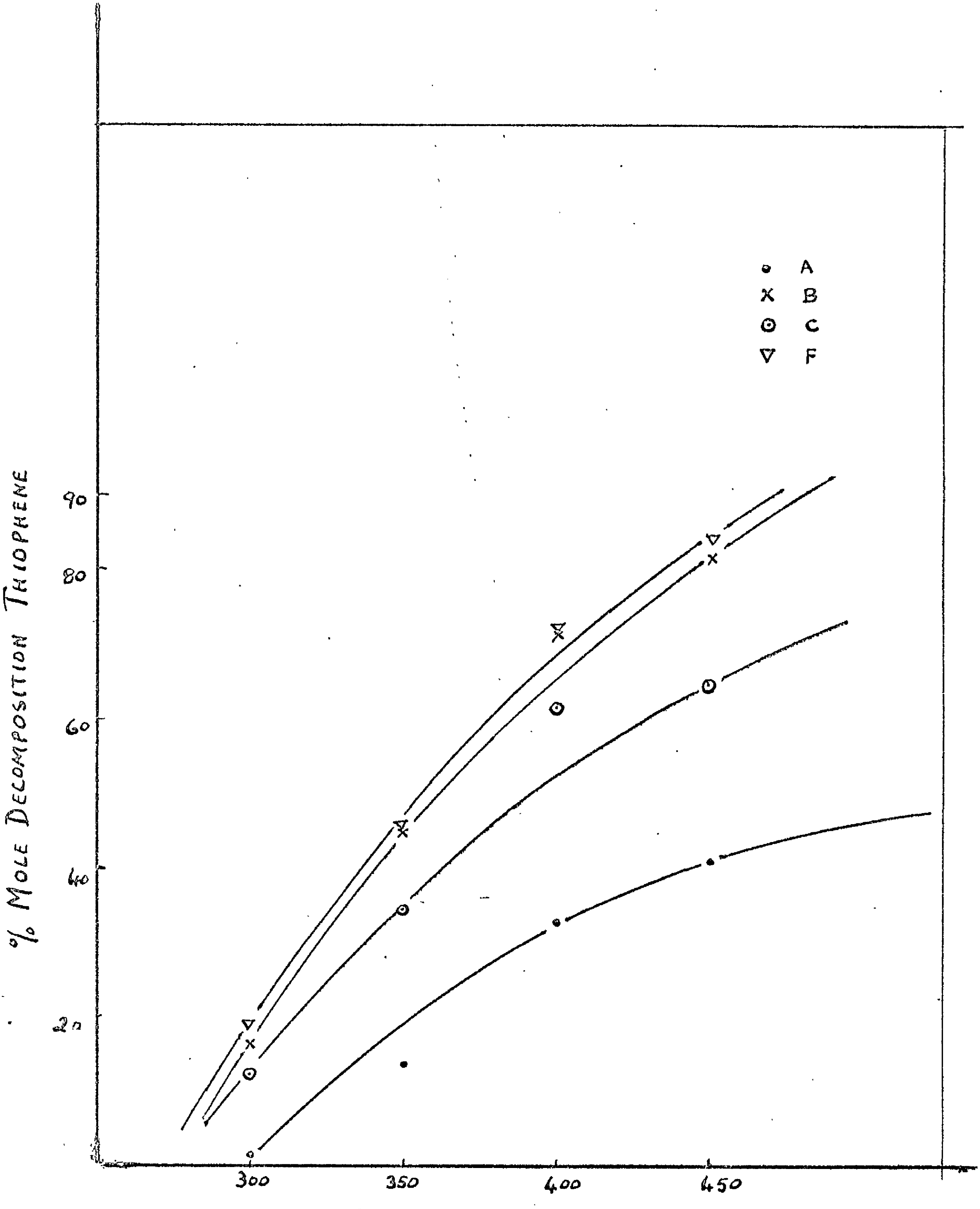

• A
× B
⊙ C
▽ F
% Mole Decomposition Thiophene
90
80
60
40
20
300
350
400
450
Temperature °C

Fig 6·3

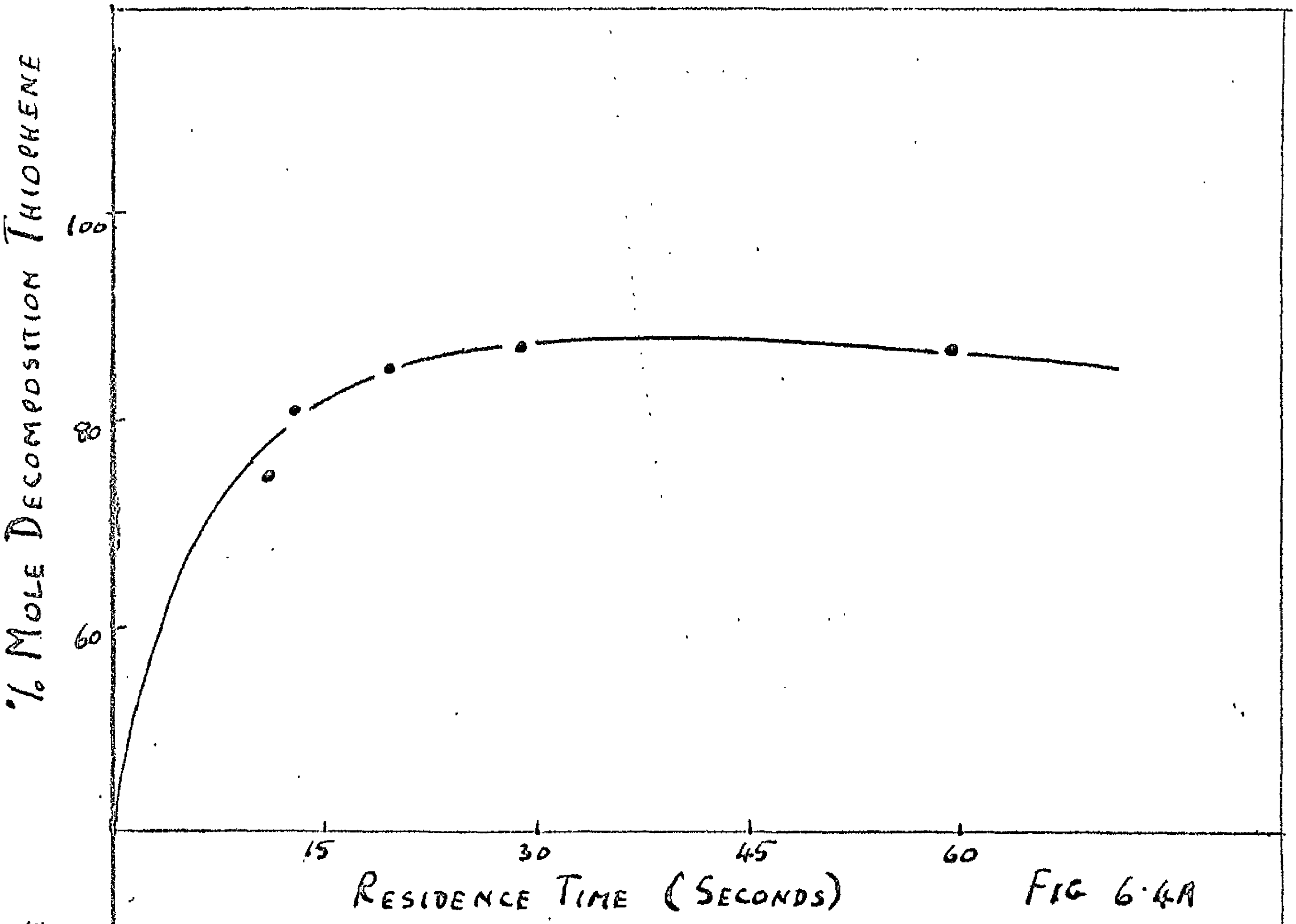


Fig 6·4A

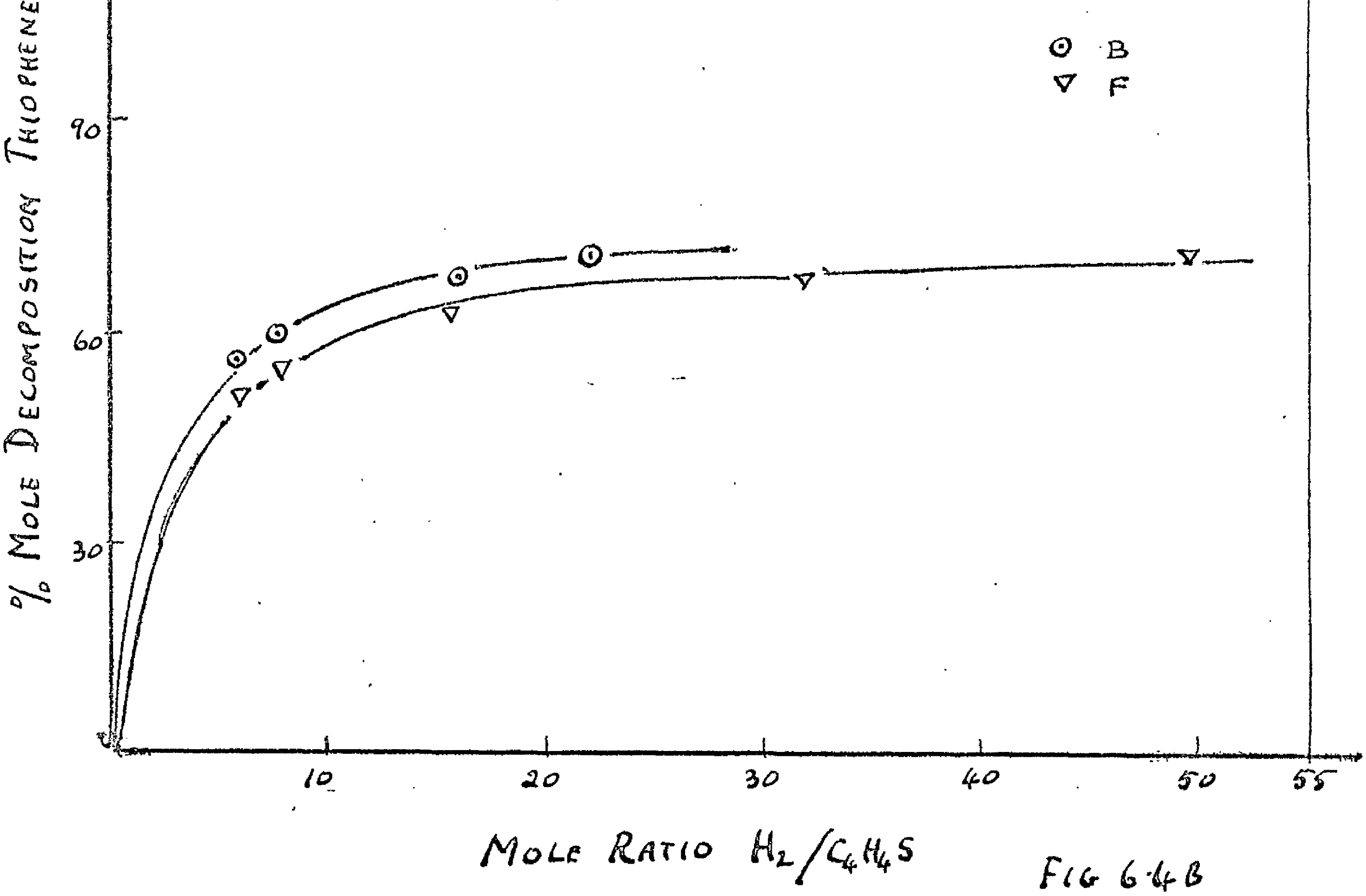


Fig 6·4B

achieve maximum reaction. With a longer residence time a lower partial pressure would suffice.

7. HYDROGEN-TRANSFER (AUTOFINING) STUDIES WITH NAPHTHA AND THIOPHENE.

If one assumes that in any hydrogen-transfer process adequate quantities of the hydrogen producing material will be present, the "bottle-neck" to the hydrogenation process is more likely to be the reactivity of the hydrogenation catalyst than hydrogen partial pressure. Thus the most suitable catalyst will be that which gives the maximum hydrogenation of thiophene in the minimum residence time.

For this reason in subsequent hydrogen-transfer runs only catalyst "F" was employed.

7.1 Raw Materials.

The naphtha used in the dehydrogenation studies (4) was utilised here and as before the thiophene and benzene were of Analar grade.

7.2 Analysis of Products.

The procedure for hydrogen and hydrogen sulphide determinations were the same as described in 4.3.3 and 5.2 respectively. It was however not possible in these runs to analyse the condensed liquid product, since the original naphtha was shown on the gas chromatograph to be a mixture of a large number of hydrocarbons covering a molecular weight range from C_5 to C_{10}.

7.3 Reaction Procedure and Results.

The reaction procedure was as described in 6.3. Catalyst "F" was studied first at different temperatures and then at different inlet flow rates. The results are included in the Table 7.1 and 7.2 respectively.

The effect of catalyst "F" was also studied at different mole ratios of available hydrogen to thiophene. The necessary mole ratios were obtained by diluting the naphtha with Analar benzene. The various proportions required are shown below, while the results are shown in Table 7.4.

Table 7.1

Component	%v/v mixture 6:1 H_2 to thiophene	%v/v mixture 8:1 H_2 to thiophene	%v/v mixture 16:1 H_2 to thiophene	%v/v mixture 32:1 H_2 to thiophene
Naphtha	6.20	12.40	24.80	49.60
Benzene	91.80	85.60	73.20	48.40
Thiophene	2.00	2.00	2.00	2.00

Table 7.2

"Autofining" of Thiophene using Naphtha with Catalyst "F" at different temperatures.

Temperature °C	300	350	400	450
Run No.	1	2	3	4
Catalyst Volume (ml)	48.80			
(a)	13.15	12.10	10.85	10.40
(g)	21.40	57.60	81.20	85.80
(k)	0.189	0.458	0.576	0.729
(l)	4.9:1	4.6:1	9.85:1	6.5:1
(e)	42.10	103.10	130.05	163.50

Table 7.3

"Autofining" of Thiophene using Naphtha with Catalyst "F" at different flow rates at 400°C.

Flow rate ml/min.	0.4	0.3	0.2	0.1
Run No.	5	6	7	8
Catalyst Volume (ml)	48.80			
(a)	14.35	19.65	28.50	59.30
(g)	82.10	87.40	89.20	89.20
(k)	0.672	0.678	0.510	0.245
(l)	5.76:1	4.7:1	5.3:1	9.8:1
(e)	186.50	251.10	285.00	270.10

Table 7.4

"Autofining" of Thiophene using Naphtha with Catalyst "F" at 400°C at different mole ratio of hydrogen available to thiophene.

Mole ratio, H_2:thiophene	6:1	8:1	16:1	32:1
Run No.	9	10	11	12
Catalyst Volume (ml)	48.80			
(a)	10.85			
(g)	39.20	64.70	72.80	78.40
(k)	0.042	0.069	0.186	0.424
(l)	8:1	5.4:1	4.8:1	5.1:1

7.4 Discussion.

The hydrogen-transfer studies with naphtha-thiophene mixtures over catalyst "F" gave results parallel to those given by cyclohexane-thiophene mixture (6). The Figure 7.1A and the Table 7.2 show the extent of thiophene decomposition at various temperatures. While Figure 7.1B shows the effect of longer residence time. When one compares the extent of thiophene hydrogenation produced by the two sources of hydrogen, i.e. cyclohexane and naphtha at the same mole ratios of available hydrogen to thiophene, it is found as shown in Figure 7.2B that naphtha is a better material with catalyst "F".

The shape of the curves in Figure 7.2A suggests that even greater decomposition of thiophene could be obtained at still higher hydrogen partial pressures. The final decision as to the most suitable hydrogen partial pressure to employ would depend on whether it was necessary to remove the last traces of thiophenic material, and on the economic degree of dehydrogenation of the naphtha.

The results of these tests indicate as in the case of cyclohexane that a residence time of at least twenty-nine seconds and a mole ratio of at least 16:1, hydrogen:thiophene would be required for significant thiophene decomposition.

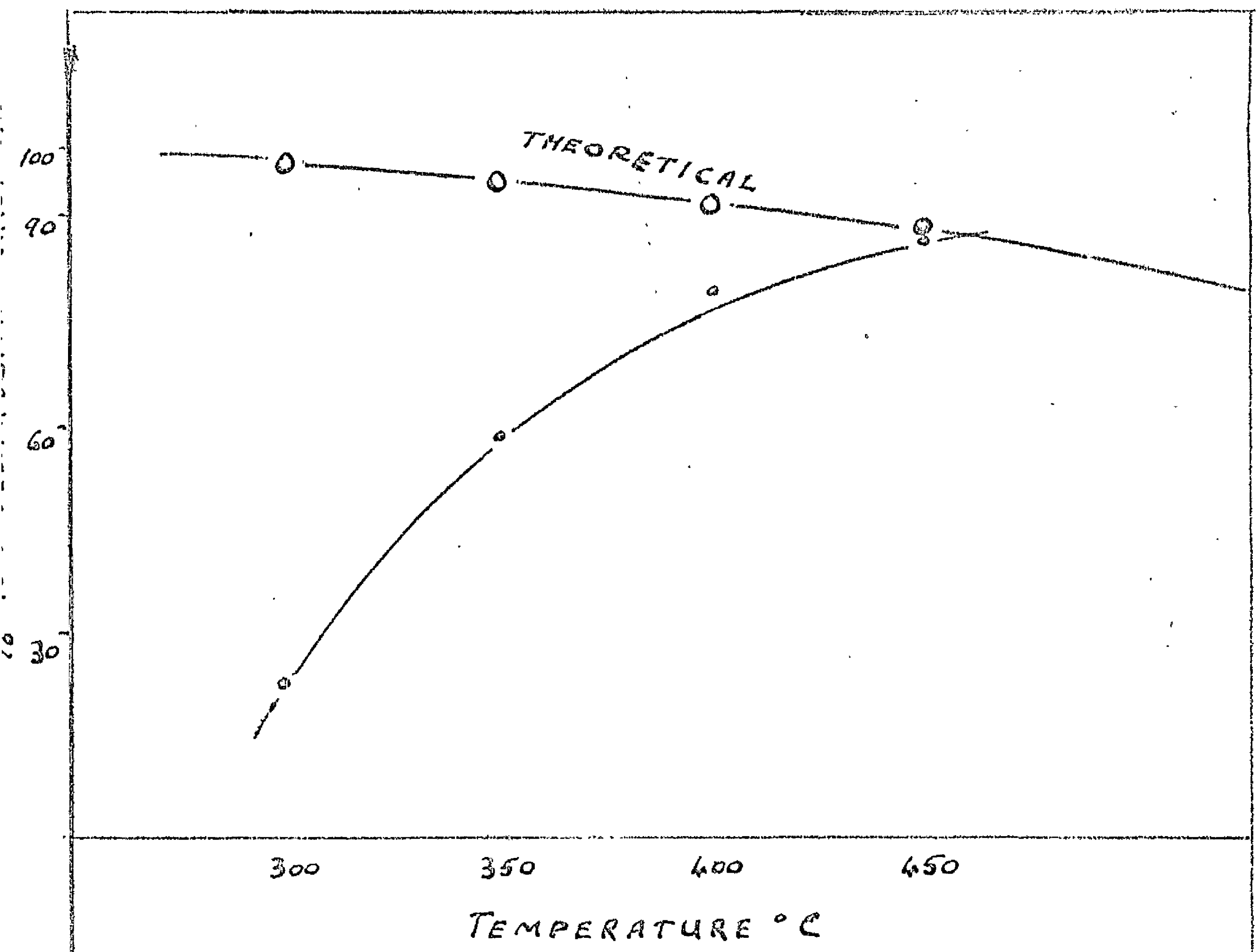


FIG 7·1A

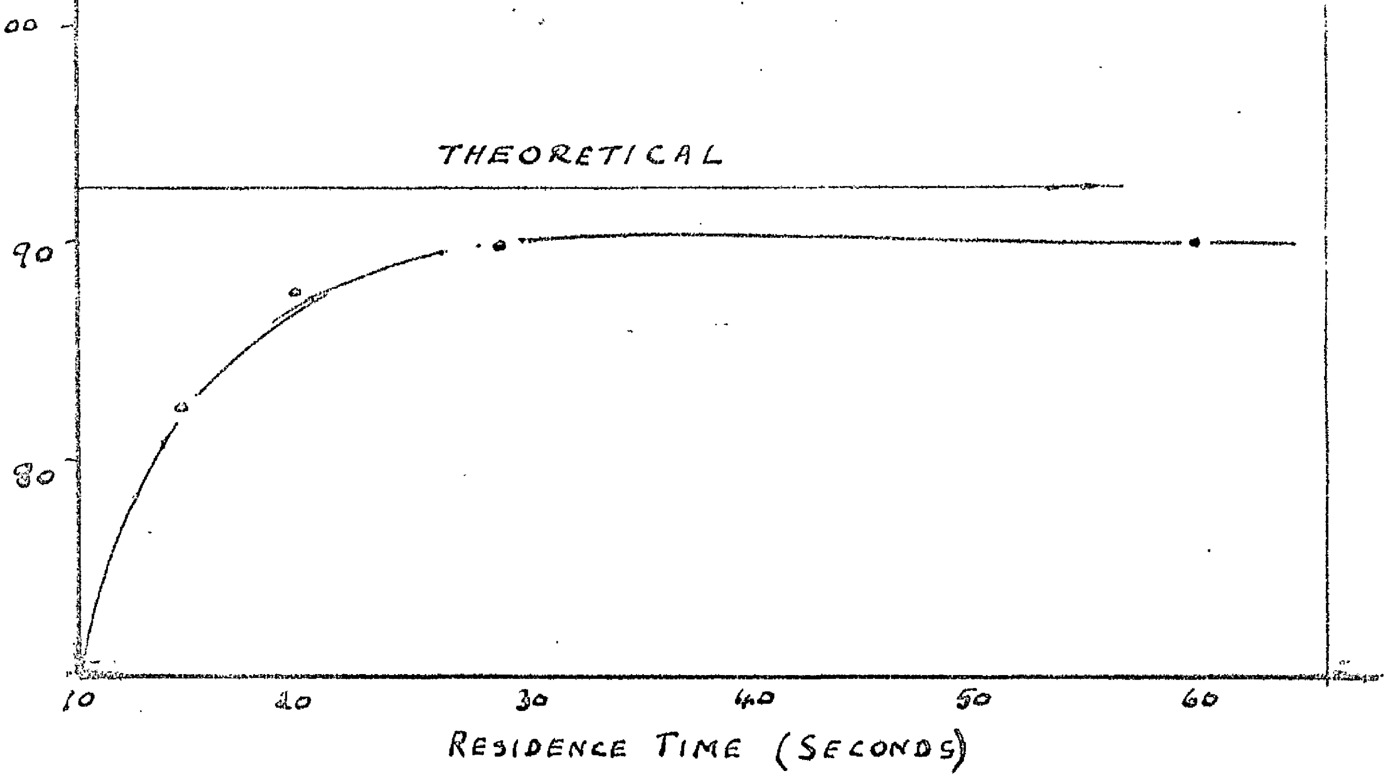


FIG 7·1B

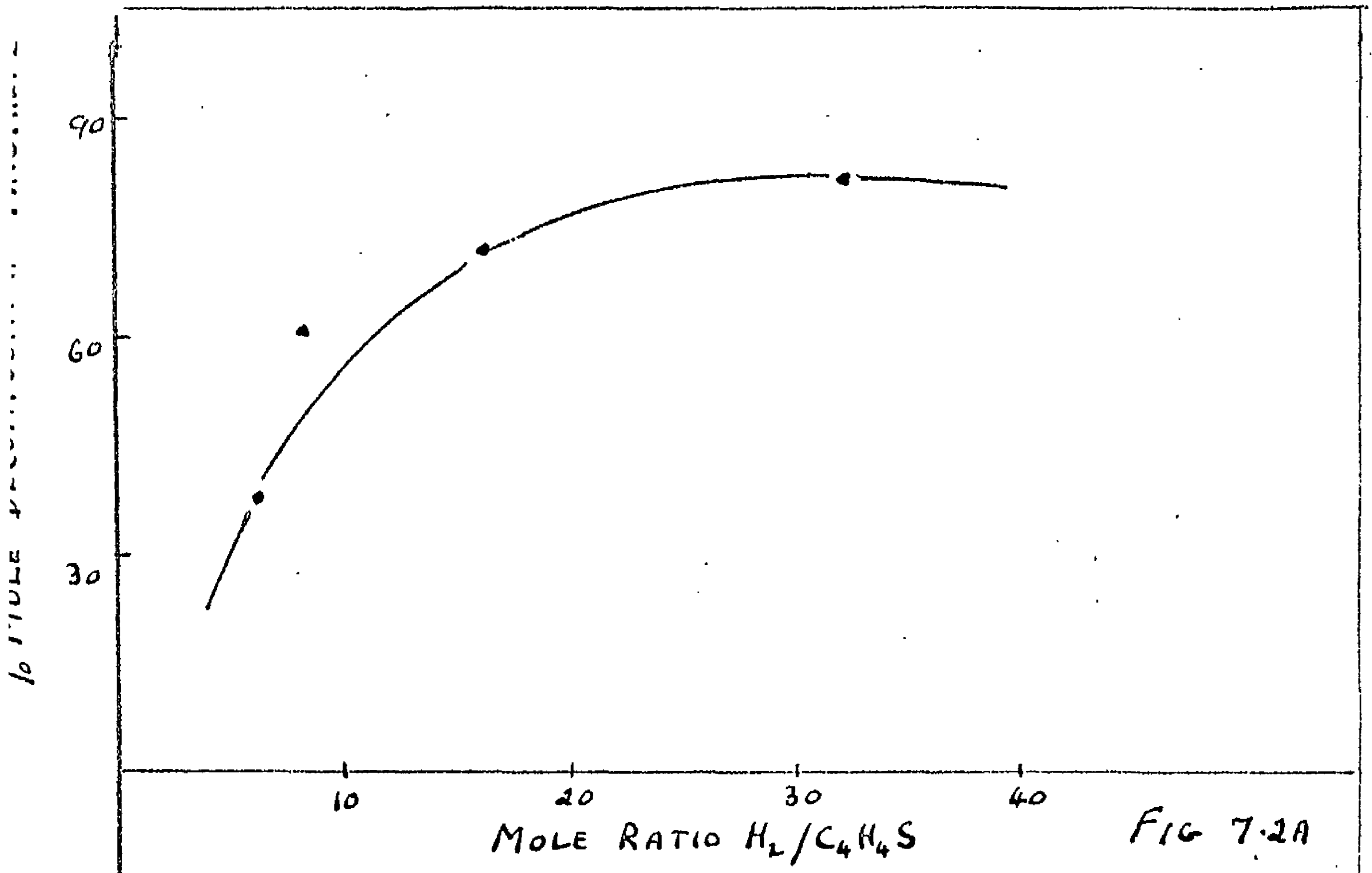
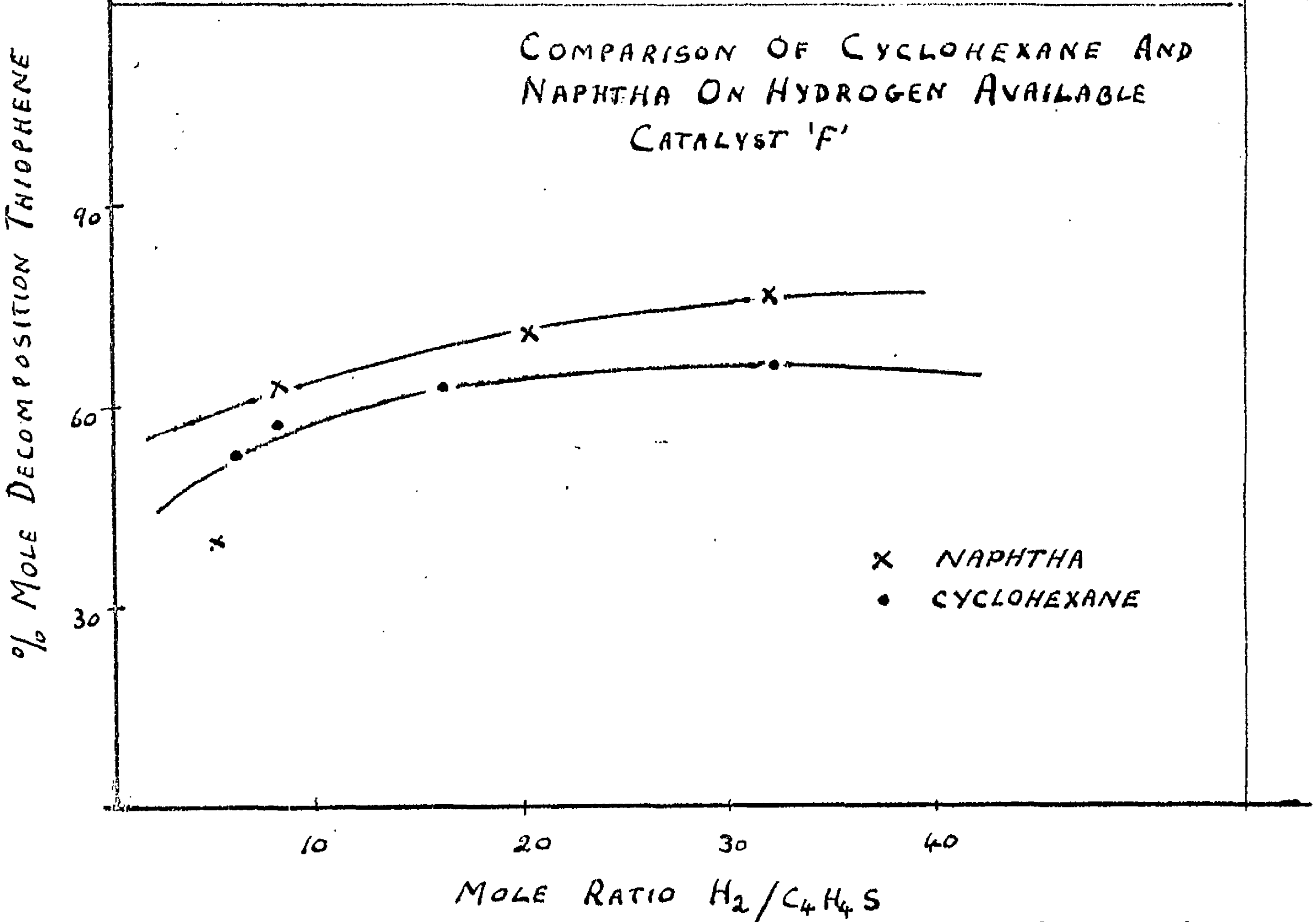


FIG 7·2A



COMPARISON OF CYCLOHEXANE AND NAPHTHA ON HYDROGEN AVAILABLE CATALYST 'F'

FIG 7·2B

8. HYDROGEN TRANSFER (AUTOFINING) STUDIES WITH MIXTURES OF NAPHTHA AND RESIDUAL FUEL OILS.

It was established in the last two chapters that catalyst "F" promoted adequate hydrogen transfer at minimum residence time under the test conditions. Attention was now turned to the possibility of utilising catalyst "F" with mixtures of naphtha and residual fuel oil containing sulphur. It was realised that the viscous fuel oil might well cause difficulties of operation and moreover lead to deposition of carbon on the catalyst. It was necessary to determine the optimum flow rate of the mixture through the reactor and the most suitable ratio of naphtha to oil. Accordingly two series of runs were carried out as follows:-

(a) A 50% naphtha 50% oil (by weight) mixture was fed at five different flow rates.

(b) The different mixtures of naphtha and oil were fed at 0.3 ml/min.

Thereafter at selected test conditions, the three residual oils were subjected in turn to an extended hydrogen-transfer run in the presence of naphtha.

8.1 Raw Materials.

The three residual oils A, B, and C whose characteristics were determined in Chapter 2 were used here. The naphtha as used in Chapter 4 and 7 was employed as the source of hydrogen.

8.2 Analysis of Products.

The procedures used for hydrogen and hydrogen sulphide determination were the same as described in 4.3.3 and 5.2 respectively.

It was not possible to analyse the desulphurised oil by chromatograph, since both the oil and naphtha consisted of a large numbers of hydrocarbons. The liquid product from each of the ten runs in which the effect of flow rate and of naphtha:oil was studied. This was not analysed directly due to the fact that it was diluted with an indeterminate volume of dehydrogenated naphtha. In the case of the three extended runs the liquid product was redistilled to remove dehydrogenated naphtha and the residual oil analysed for sulphur content in the usual way.

The distillation range of the feed naphtha was determined by I.P 123/64; and the distillation curve is shown in Figure 8.1. The corresponding curve for dehydrogenated naphtha, dehydrogenated under the same conditions as in the three extended tests is given in the same Figure. It was hoped by this means to determine the amount of desulphurised oil in the liquid product.

8.3 Reaction Procedure and Results.

A bed of 48.8 mls of catalyst "F" was activated in the reactor at 400°C as described in 4.3.4. At the end of the activation period the hydrogen was replaced by a flow of nitrogen (0.0061 ft^3 at N.T.P) and an appropriate mixture of oil

"C" and naphtha was fed into the reactor at the required flow rate. The run was carried out for two hours and samples of the exit gas were collected as before to enable hydrogen sulphide and hydrogen to be determined.

Tabulated below are the feed flow rates of 50:50 mixture of naphtha to oil used in the first series of runs and the latter includes the expected mole ratio of available hydrogen to sulphur in the reactor. The amount of hydrogen was calculated from the already determined dehydrogenation characteristic of the feed naphtha and the sulphur from the analysis of the residual oil.

In the second series of tests the ratio of oil to naphtha fed was varied and the ratios used are tabulated in Table 8.2. The table includes the expected mole ratio of available hydrogen to sulphur in the reactor.

Table 8.1

Flow rate ml/min	Oil ml/min	Naphtha ml/min	Expected Mole ratio $H_2 : S$
0.5	0.204	0.296	20.1 : 1
0.4	0.163	0.237	27.1 : 1
0.3	0.122	0.178	27.5 : 1
0.2	0.082	0.118	27.4 : 1
0.1	0.042	0.058	27.4 : 1

Table 8.2

Percentage w/w oil - naphtha.					
	60/40	50/50	40/60	30/70	20/80
Mole ratio H_2:S (theoretical)	16.3:1	27.5:1	38.7:1	50.6:1	90.5:1
Flow of naphtha ml/min	0.146	0.178	0.205	0.232	0.256
Flow of oil "C" ml/min	0.156	0.121	0.095	0.069	0.045

Table 8.3

The Effect of Flow Rate with Catalyst "F" at 400°C.

(Feed material 50/50 w/w oil - naphtha)

Catalyst Volume (ml)	48.8			
Run No.	1.	2.	3.	4.
Flow rate ml/min	0.5	0.4	0.3	0.2
% S removed	29.4%	36.5%	38.4%	38.4%
Mole H_2 in off gases	0.594	0.621	0.462	0.297

The catalyst activity during these two hour runs proved very constant as was indicated by the hydrogen sulphide content of the exit gas determined every twenty minutes of run time.

After the completion of each run about a hundred millilitres of benzene were run through the hot reactor to flush out any soluble material. Nothing however was found appart from traces of feed oil. The results are shown in Table 8.3. It may be seen that a steady percentage decomposition was obtained at a rate of 0.3 ml/min flow of oil-naphtha mixture. Hence further runs on the above mixtures shown in Table 8.4 were carried out exactly on the same pattern at the fixed flow rate of 0.3 ml/min.

From a stoichiometric point of view only one mole of hydrogen is required per mole of sulphur to form hydrogen sulphide and hence from an economic point of view high input of hydrogen should be avoided. Since however, the studies with thiophene had shown that a considerable excess of hydrogen was necessary with the test reactor, oil:naphtha ratio used in the extended tests (30/70) was selected to provide an adequate amount of hydrogen.

For the extended runs a fresh bed of the catalyst volume (48.8 ml) "F" was taken and activated as described before. A large quantity of oil:naphtha mixture (30/70 w/w) was prepared and the test runs carried out under the conditions described already at 400°C. The determination of hydrogen sulphide and that of the hydrogen in the exit gases was carried out after every half an hour. These extended test runs were continued as long as the analysis of the exit gas was constant and for two hours beyond the time at which the catalyst began to show loss of activity. Thus the period of run extended to 17½–24 hours as shown in the table. From the analysis of the products the percentage removal of the sulphur was then calculated. The calculation is shown in the Appendix while the results are shown in Tables 8.5 to 8.7 ~~and Figures 8.1~~.

At the end of each extended run the reactor was allowed to cool in a current of purified nitrogen. A total of about 200 mls of benzene were then run through the cooled reactor from the dozing pump at a rate of 0.5 ml/min to wash benzene soluble material from the catalyst bed. The washed reactor was freed from benzene by a current of nitrogen and then weighed to determine the amount of carbon deposited on the bed. The benzene solution was evaporated on a water bath and the residue weighed.

Prior to the subsequent extended run the reactor and catalyst were heated to about 480°C in a slow current of air to burn carbon from the catalyst. The catalyst was then reactivated in the usual way with hydrogen sulphide and hydrogen, and the next run carried out with nitrogen and oil : naphtha mixture. In this way the three residual oils C, B, and A were subjected to desulphurisation.

Owing to the difficulty of running the reactor for

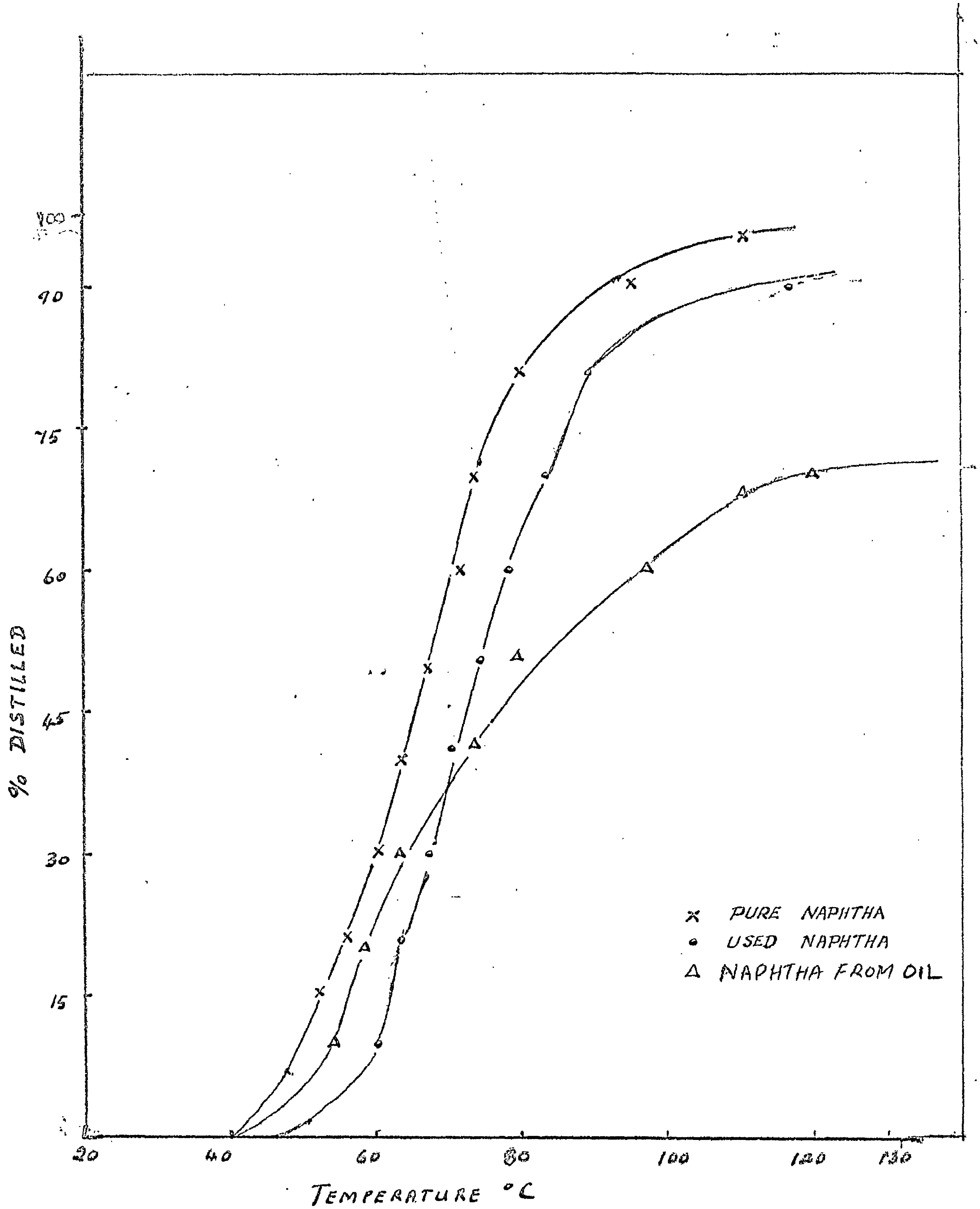

100
90
75
60
45
30
15
% DISTILLED
20
40
60
80
100
120
130
TEMPERATURE °C
× PURE NAPHTHA
● USED NAPHTHA
Δ NAPHTHA FROM OIL

FIG 8·1

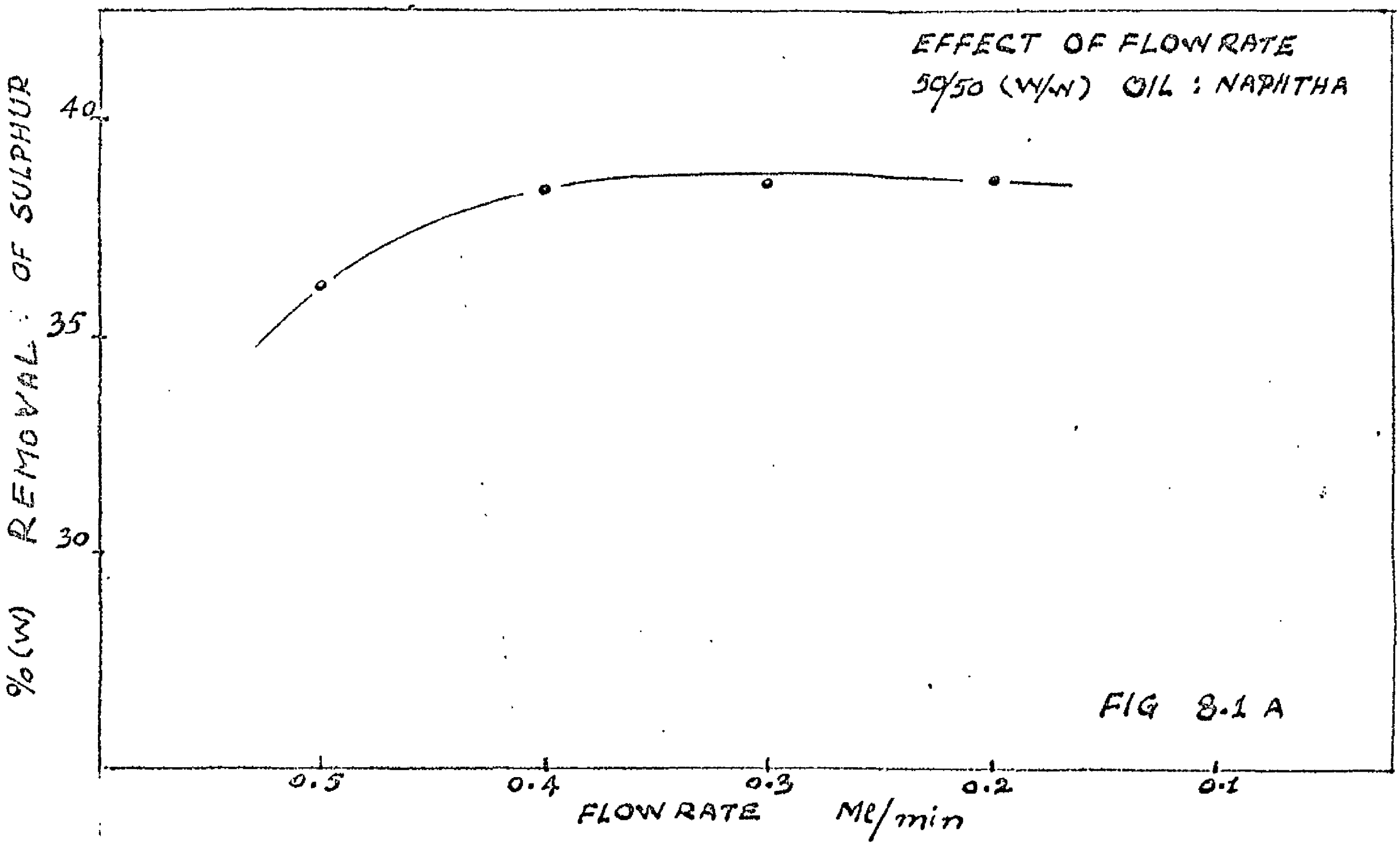


FIG 8.1 A

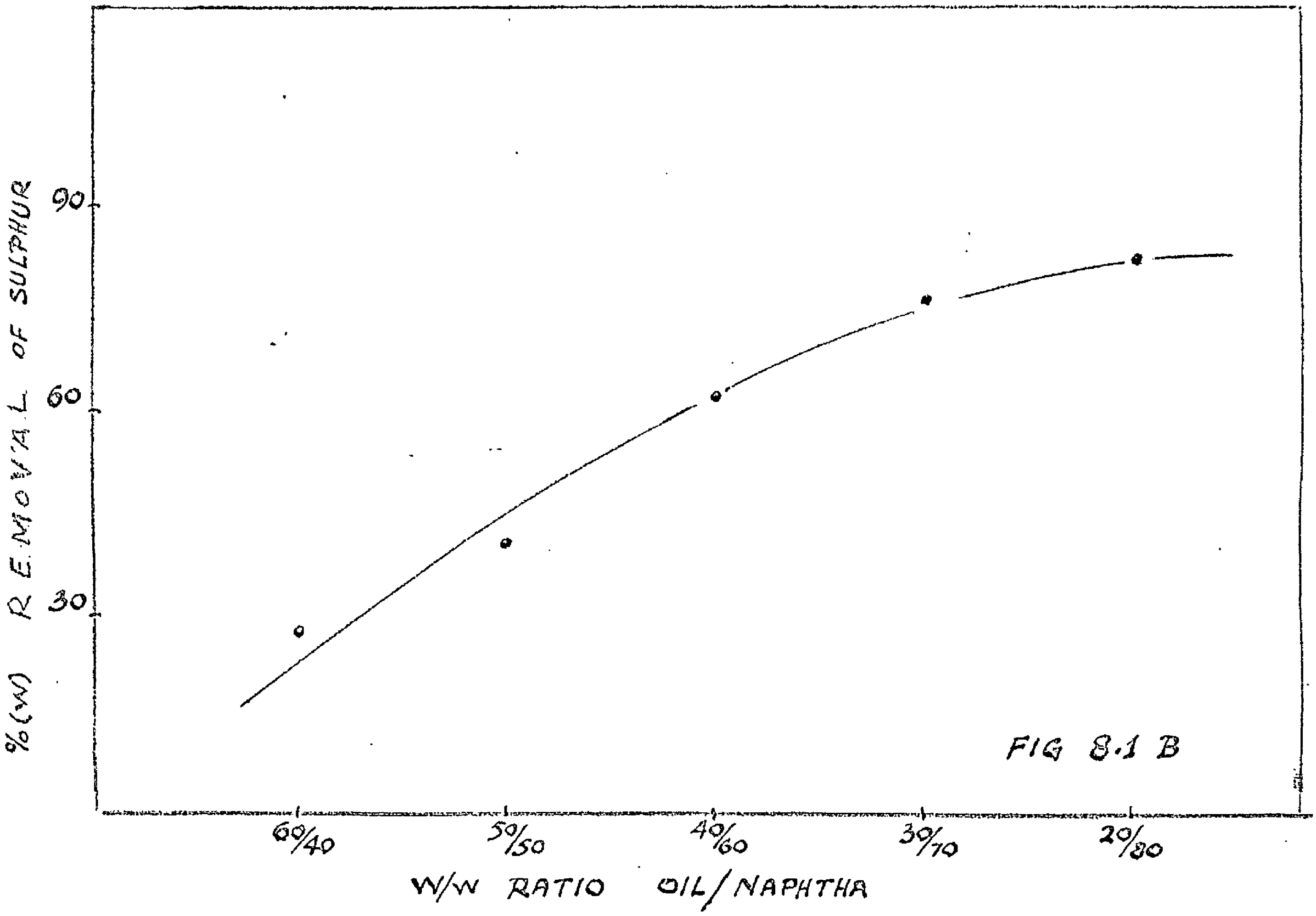


FIG 8.1 B

extended periods into the night, the flow of oil : naphtha had to be shut off at the end of a working day. At that time the flow of nitrogen was continued into the hot reactor until the following morning when the flow of oil : naphtha was restarted. The first few analysis readings after restart generally showed slight loss of activity of the catalyst but after about two hours the catalyst was back to the activity it had shown the previous evening.

The test results are shown in Table 8.5 . to 8.7.

Table 8.4

The Effect of Mixture Ratio of oil : naphtha, with Catalyst "F" at 400°C.

Catalyst Volume (ml)	48.8				
Run No.	5	6	7	8	9
Flow rate ml/min		0.3			
Ratio oil/naphtha w/w	60/40	50/50	40/60	30/70	20/80
% S removed	28.4%	38.4%	63.6%	72.2%	79.1%
Mole H_2 in off gases	0.291	0.462	0.520	0.560	0.595

Table 8.5

Analysis Data from Continuous Run with Oil "C", 30/70 w/w oil : naphtha ratio.

Flow rate ml/min	0.3				
Catalyst Volume	48.8				
Time (hrs)	% S removal	Mole H_2 in off gases	Time (hrs)	% S removal	Mole H_2 in off gases
0.0 - 0.5	68.6	0.142	9.0 - 9.5	72.8	0.145
0.5 - 1.0	68.6	0.138	9.5 - 10.0	71.7	0.146
1.0 - 1.5	70.4	0.141	10.0 - 10.5	72.4	0.143
1.5 - 2.0	71.1	0.146	10.5 - 11.0	72.4	0.141
2.0 - 2.5	72.4	0.142	11.0 - 11.5	68.4	0.139
2.5 - 3.0	72.6	0.146	11.5 - 12.0	69.4	0.141
3.0 - 3.5	72.8	0.146	12.0 - 12.5	69.8	0.142
3.5 - 4.0	72.4	0.145	12.5 - 13.0	72.4	0.146
4.0 - 4.5	72.4	0.140	13.0 - 13.5	72.6	0.146
4.5 - 5.0	72.8	0.140	13.5 - 14.0	74.1	0.143
5.0 - 5.5	73.1	0.146	14.0 - 14.5	72.4	0.142
5.5 - 6.0	72.4	0.142	14.5 - 15.0	72.6	0.145
6.0 - 6.5	72.6	0.145	15.0 - 15.5	72.4	0.146
6.5 - 7.0	72.4	0.146	15.5 - 16.0	72.1	0.134
7.0 - 7.5	72.1	0.143	16.0 - 16.5	69.4	0.128
7.5 - 8.0	72.5	0.140	16.5 - 17.0	66.2	0.124
8.0 - 8.5	72.5	0.143	17.0 - 17.5	66.	[illegible]

Table 8.6

Analysis Data from Continuous Run with Oil "B" 30/70 w/w Oil : Naphtha Ratio.

Flow rate ml/min		0.3			
Catalyst Volume (ml)		48.8			
Time (hrs)	%S removal	Mole H_2 in off gases	Time (hrs)	%S removal	Mole H_2 in off gases
0.0 - 0.5	68.4	0.153	10.0 - 10.5	73.8	0.156
0.5 - 1.0	68.6	0.153	10.5 - 11.0	74.4	0.154
1.0 - 1.5	69.2	0.151	11.0 - 11.5	69.8	0.139
1.5 - 2.0	70.4	0.158	11.5 - 12.0	69.4	0.142
2.0 - 2.5	74.8	0.158	12.0 - 12.5	66.8	0.138
2.5 - 3.0	76.4	0.156	12.5 - 13.0	64.9	0.148
3.0 - 3.5	76.8	0.160	13.0 - 13.5	69.8	0.152
3.5 - 4.0	76.8	0.154	13.5 - 14.0	71.6	0.15 3
4.0 - 4.5	76.4	0.158	14.0 - 14.5	74.4	0.156
4.5 - 5.0	76.7	0.158	14.5 - 15.0	76.8	0.156
5.0 - 5.5	76.4	0.156	15.0 - 15.5	76.4	0.154
5.5 - 6.0	74.8	0.158	15.5 - 16.0	76.4	0.158
6.0 - 6.5	75.2	0.158	16.0 - 16.5	74.4	0.151
6.5 - 7.0	76.1	0.156	16.5 - 17.0	72.2	0.144
7.0 - 7.5	76.4	0.156	17.0 - 17.5	71.8	0.139
7.5 - 8.0	76.2	0.154	17.5 - 18.0	71.1	0.148
8.0 - 8.5	76.2	0.156	18.0 - 18.5	69.8	0.124
8.5 - 9.0	76.8	0.158	18.5 - 19.0	69.8	0.121
9.5 - 10.0	76.4	0.156			
9.0 - 9.5	76.4	0.156			

——— indicates shut down due to intervention of night.

Table 8.7

Analysis Data from Continuous Run with Oil "A" (30/70 w/w oil : naphtha ratio).

Time (hrs)	%S removal	Mole H_2 in off gases	Time (hrs)	%S removal	Mole H_2 in off gases
0.0 - 0.5	76.8	0.163	12.0 - 12.5	74.6	0.176
0.5 - 1.0	79.2	0.161	12.5 - 13.0	75.2	0.174
1.0 - 1.5	83.1	0.159	13.0 - 13.5	76.8	0.173
1.5 - 2.0	83.4	0.164	13.5 - 14.0	81.4	0.179
2.0 - 2.5	83.4	0.169	14.0 - 14.5	83.4	0.176
2.5 - 3.0	83.4	0.172	14.5 - 15.0	83.1	0.174
3.0 - 3.5	83.4	0.171	15.0 - 15.5	83.7	0.171
3.5 - 4.0	83.8	0.172	15.5 - 16.0	83.6	0.176
4.0 - 4.5	83.4	0.173	16.0 - 16.5	83.2	0.174
4.5 - 5.0	83.1	0.174	16.5 - 17.0	83.2	0.169
5.0 - 5.5	83.6	0.171	17.0 - 17.5	83.4	0.172
5.5 - 6.0	83.4	0.171	17.5 - 18.0	83.2	0.174
6.0 - 6.5	83.1	0.172	18.0 - 18.5	83.4	0.173
6.5 - 7.0	83.7	0.176	18.5 - 19.0	83.1	0.174
7.0 - 7.5	83.1	0.174	19.0 - 19.5	83.6	0.176
7.5 - 8.0	83.4	0.164	19.5 - 20.0	83.4	0.176
8.0 - 8.5	83.6	0.168	20.0 - 20.5	83.1	0.174
8.5 - 9.0	79.4	0.171	20.5 - 21.0	81.8	0.169
9.0 - 9.5	83.1	0.174	21.0 - 21.5	81.4	0.168
9.5 - 10.0	81.8	0.175	21.5 - 22.0	79.4	0.163
10.0 - 10.5	83.6	0.174	22.0 - 22.5	79.4	0.154
10.5 - 11.0	83.8	0.168	22.5 - 23.0	76.1	0.158
11.0 - 11.5	81.4	0.173	23.0 - 23.5	73.4	0.153
11.5 - 12.0	74.8	0.172	23.5 - 24.0	73.4	0.153

——— indicates shut down due to intervention of night.

8.4 Discussion.

The results show a significant desulphurisation of the order of 70 to 80 percent with these residual fuel oils.

Referring to Table ~~8.[illegible] and~~ 8.3 it may be seen that at a 50/50 oil : naphtha ratio , a desulphurisation of not more than 38.4 percent could be achieved at the minimum flow rate of 0.2 ml/min. This was equivalent to a relatively low space velocity in the reactor of 0.25 vol/vol/hr.

The total hydrogen produced during the desulphurisation runs was also recorded in Table~~s~~ ~~8.[illegible] and~~ 8.3. To obtain however a strict comparison, one must record this hydrogen to a basis of rate of production per unit weight of naphtha fed to the reactor. This is shown in the Tables 8.8 and 8.9 given below.

Table 8.8

Run No.	Flow Rate (ml/min)	Available mole H_2/min lb naphtha
	0.5	0.0950
	0.4	0.1270
	0.3	0.1265
	0.2	0.1245

Table 8.9

Run No.	Feed Ratio (w/w) oil : naphtha	Available mole H_2/min lb naphtha
	60/40	0.0925
	50/50	0.1260
	40/60	0.1160
	30/70	0.1330
	20/80	0.1280

It may be seen that the rate of production of hydrogen was virtually constant in both series of experiments, indicating that the primary influences on desulphurisation were contact time and hydrogen partial pressure.

The total amount of hydrogen produced in these desulphurisation runs was somewhat less (about 19%) than the amount of hydrogen obtained from naphtha alone (Table 4.5) when dehydrogenated under the same experimental conditions. It is possible that the oil partial pressure was reducing the amount of active surface on the catalyst.

It should be noted (Table 8.9) that the lower values of oil: naphtha correspond to very high mole ratio of available hydrogen to sulphur (i.e up to 90.5 :1). Only a relatively small amount of this hydrogen input is utilised to hydrogenate the sulphur compounds and if not recycled would pass to waste. Even at such a high ratio of available hydrogen about twenty percent of the sulphur compounds in the oil remained unhydrogenated. Better results may be expected with longer contact time and recirculation of hydrogen.

In the case of the extended desulphurisation runs with the three oils the hydrogen production figures have the same relative values as the extent of desulphurisation achieved. This again indicates the influence of hydrogen partial pressure.

From the structural group analysis at 70°C (Table 2.7) it had been found that oil A was the least aromatic of the three oils.

It is possible that its sulphur compounds are more reactive than those of the other two oils.

At the temperature used in the extended tests (400°C) only a relatively small extent of pyrolysis of the oil seems to occur. This may be judged by the small amounts of carbon and benzene - soluble residue found in the reactor at the end of a run. This may be seen in Table 8.10 given below.

Table 8.10

	%W sulphur input oil	%W sulphur in product oil	%W sulphur reduction	%W carbon in 100 gm oil	%W benzene soluble in 100 gm oil
Oil A	3.34	1.76	48.20	4.6	0.9
Oil B	4.08	2.24	45.40	6.2	0.9
Oil C	4.14	2.41	41.50	7.4	1.3

It is likely that these values may be reduced by running the reactor under pressure to further increase the hydrogen partial pressure.

It was somewhat difficult to obtain a true sulphur balance in these extended runs. The total liquid product contained dehydrogenated naphtha and hydrogenated oil. The latter was likely to have an extended boiling range and might well include spirit of the same boiling range as the naphtha. Thus it was possible to separate accurately the treated oil and naphtha by distillation.

The sulphur contents of the test oils could be obtained in two ways.

1. By calculation:-

The total sulphur removal found in the exit gases was calculated, and subtracted from the total sulphur in the fuel oil. This gave a residual sulphur content per 100 grams of feed oil. This is shown in Table 8.11 given below.

Table 8.11

Sulphur Balance.

Oil	Extended Run	
A	Total Input sulphur in 24 hrs 97.0 x 3.34 = 3.20 gms	Output sulphur Total sulphur as hydrogen sulphide = 2.410 gms Difference = 0.790 3.200
B	Total Input sulphur in 19 hrs 77.2 x 4.08 = 3.15 gms	Output sulphur Total sulphur as hydrogen sulphide = 2.210 Difference = 0.940 3.150
C	Total Input sulphur in 17.5 hrs 71.0 x 4.14 = 2.94 gms	Output sulphur Total sulphur as hydrogen sulphide = 2.06 Difference = 0.88 2.94

2. By direct determination :-

The tested oil was separated by distillation from the dehydrogenated naphtha and its sulphur content determined in the usual way[37]. The results are given in Table 8.10.

The difference between these two sets of results would appear to be due to the change in the boiling range of the residual oil on hydrogenation.

The characteristics of the oils after "autofining" treatment and separation of the dehydrogenated naphtha by distillation are recorded in the Table 8.12 below

Table 8.12

Desulphurised oils	n_{20}	d^{20}	V_K cs	C_A	C_N	C_P	Molecular weight
A	1.522	0.913	3.53	15.5	50.5	24	280
B	1.510	0.892	2.62	21.5	52.5	26	295
C	1.525	0.921	3.99	15.6	34.4	40	282

It is apparent that considerable change has been produced in the overall molecular make-up of the three oils by passage through the hydrogen-transfer reactor. There is a very large drop in viscosity by a factor of 200 to 300 times and a considerable drop in the content of aromatics in the oils with an accompanying increase in the amount of naphthenic carbon. Some change in the amount of carbon atoms in paraffinic structure is also noteable

The average molecular weight of the desulphurised oils is about one half of the original oils.

These facts all point to hydrogenation and hydrocracking of the oils in the hydrogen-transfer reactor. Aromatics have been hydrogenated to naphthenes and paraffinic side chains have been split off to give light spirit and an overall lowering of the molecular weight.

These changes show that a certain amount of the available hydrogen has been absorbed by the oil and gives another explanation of the seemingly low available hydrogen found when only the amount of hydrogen sulphide formed and percentage of hydrogen in the exit gas were taken into consideration.

9. GENERAL DISCUSSION AND CONCLUSION.

The work described here, developed into a study of the feasibility of utilising the "autofining" process at atmospheric pressure to desulphurise residual fuel oil. The "autofining" process was originally developed to desulphurise middle distillates and the few studies of the process which have been made are confined to the desulphurisation of such materials, which are in themselves easier to desulphurise due to their relatively low sulphur content and the less complicated nature of the sulphur compounds present.

Szobony[53] has published the results of "batch autofining" with gas oil using naphthenes as a source of hydrogen, but there is no accurate information available on the feasibility of this process with residual fuel oil.

The Union Oil Company of California[54] have claimed that ninety-nine percent of the sulphur in any fraction, irrespective of the type of sulphur compound , can be removed by their direct hydrodesulphurisation process using a cobalt-molybdate catalyst. Assuming that such hydrogen could be made available cheaply from light naphtha, there is every reason to expect that an autofining process could perform quite as well as this.

A hydrogen production of 52.6 cubic feet at N.T.P per gallon of naphtha was achieved from the naphtha used in this work with catalyst "F" at 400°C, and a residence time of thirty seconds. It has been reported[30] that a commercial hydrofining unit requires seventy cubic feet of hydrogen per barrel of oil to remove one percent of sulphur. On the basis of these figures an oil : naphtha ratio of 10 : 1 would be required to remove three percent sulphur from a residual fuel oil.

The work reported here however has indicated that a much higher proportion of naphtha would be required to achieve the necessary hydrogen partial pressure for an adequate reaction rate. The small percentage of hydrogen utilised indicates that before such a process would be commercially feasible , recirculation of hydrogen might be necessary.

Amberg[55] who studied the hydrodesulphurisation of thiophene over a chromium oxide-sulphide catalyst has concluded that the reaction rate is dependent on the adsorption of hydrogen and the reaction at the surface. Our findings agree with this, in that a first order change indicating a heterogenous reaction was evident in our studies of thiophene hydrogenation, and that the rate of reaction is thus very dependent on hydrogen partial pressure. It also appeared however that adsorption of the thiophene itself might prevent hydrogen reaching the active sites on the catalyst.

It has been concluded by Griffith[56] that thiophene hydrogenation with nickel oxide-sulphide follows a strictly chemical cycle of changes in which the solid does not function as a true catalyst. The first step is supposed to be the production of nickel metal by the reduction of its sulphide;

this is followed by a heterogenous reaction of the thiophene with the metal to give again the metallic sulphide which subsequently again undergoes reduction. If such a mechanism applied when the oxide is present water would appear in the exit stream. Since we found no water in our work, it would appear that if a chemical reaction does take place it only involves the metallic sulphide and not the oxide.

In our work a constant catalyst activity over periods of up to twenty-four hours has been achieved. It is likely that this may be improved by a better design of the catalyst bed. In any event the catalyst is readily reactivated by burning off carbon deposited and by treating again with hydrogen sulphide and hydrogen.

The transition-metal oxide catalysts tested here have all shown themselves to be very active, the most active oxide proving to be WO_3, and that for hydrogenation of thiophene, V_2O_5. A very simple mixture of pellets of these oxides proved a useful combined catalyst and it is likely that such materials perhaps diluted with alumina or with some neutral binding material would be superior on the industrial scale to the cobalt molybdate catalyst popular at the present time.

It is suggested that a future programme of work should study the development of a commercial catalyst for autofining based on these two oxides.

The limitations of the laboratory results could well be reduced by operation under pressure conditions. The effect of pressure would be no doubt to increase the extent of hydrogenation and reduce carbon deposition on the catalyst thus giving a longer on-stream period which is important from a commercial point of view. It is therefore suggested that future experimental work should be carried out at the moderate pressures (5 to 15 atm.) used in the commercial "autofining" process.

Under such conditions it is likely that a lower proportion of naphtha would be required.

It has been shown that considerable change has taken place in the molecular make-up of the parent reisdual oil when it passed through the autofining reactor. From a commercial point of view there is probable some advantages to this as the lower viscosity oil produced may well have a ready market. However it should be noted that the treated oil still contains a significant proportion of sulphur and thus requires further treatment.

The extensive hydrogenation of the parent oil suggests that future extension of the work should include a careful determination of hydrogen balance in the autofining process, to determine the relative proportion of hydrogen as exit gas, as hydrogen sulphide and as hydrogenated oil, resulting under a variety of experimental conditions.

Ideally, a process which uses hydrogen-transfer from naphtha to residual oil to desulphurise the latter should provide the following products:-

(a) a naphtha fraction, high in aromatics,

(b) a light fuel oil of low sulphur content,

(c) excess hydrogen and (d) hydrogen sulphide for sulphur manufacture.

APPENDIX

The index number refers to the chapters in the main part of this work.

2.1 Determination of Sulphur Content of Residual Oil[37].

Solutions required:-

1. 0.005M barium perchlorate. 2.0 gms of barium perchlorate is dissolved in 200 mls of distilled water and to this is added 800 mls of ethanol. The pH is adjusted to 3.5 (as measured on a pH meter) by adding a few drops of dilute perchloric acid to the solution.

2. Thoron indicator. 0.2 gms of thoron is dissolved in 100 mls of water.

3. N/10 sodium carbonate. 5.30 gms of anhydrous sodium carbonate is dissolved in water and made up to a litre.

Procedure:-

The barium perchlorate solution is standardised with 0.005M sulphuric acid solution using the thoron indicator. 0.3 to 0.5 gms of oil are accurately weighed into the crucible of a bomb calorimeter. 10 mls of N/10 sodium carbonate solution are placed in the body of the bomb and the crucible fitted in place in the bomb and a fine nylon fuse thread connected from the oil to the firing system. The bomb is filled with oxygen to a pressure of 35 lb/in^2 gauge and fired. After about 15 minutes, the pressure in the bomb is reduced to atmospheric and the bomb is opened. The contents of the bomb are washed into a flask and the washings made up to 250 mls with water.

A cation exchange column containing about 5.0 gms of Permutit resin is prepared and activated by N/50 hydrochloric acid solution. 10 mls of the diluted bomb washings are passed through the ion exchange column and collected. The column is washed with 5.0 mls of water and the washing added to the collected sample. To this solution 40 mls of ethanol and two drops of thoron indicator are added and titrated with standard barium perchlorate solution. The end point is when the solution changes form yellow to pink.

With the concentrations used -

1.0 ml of 0.005M barium perchlorate solution = 0.0038 gms of sulphur.

2.2 Chromatographic Separation of Oils[39].

Procedure:-

40 gms of silica gel (about 50 mesh) is heated for three hours at 160°C. This is put into a 30 inches long, 12 mm I.D glass tube, one end of this tube is narrowed to 2 mm diameter. This end is packed with cotton wool. The dried silica gel is then poured into the tube which is arranged in a vertical position so that the bed of silica rests on the cotton wool pad.

1.0 gm of the oil is dissolved in 100 mls of 60/80 petroleum ether and is then passed through the silica column.

Owing to differences in the rates of adsorption the non-aromatic fraction comes through the column while the aromatics are retained.

The addition of the petroleum ether is continued for some time and a check is made from time to time at the end of the tube by means of filter paper to determine the point at which the naphtha fraction ceases to appear. An oily stain, after the ether has evaporated from the filter paper, indicates the presence of naphtha. Thus addition is continued till clear petroleum ether comes from the outlet. The collected naphtha solution is heated to evaporate the petroleum ether and the residue weighed.

Solvent ether is now passed into the column and the procedure described above is continued. Thus the aromatic fraction is also obtained. The difference between the weight of oil fed and the total weight of the two fractions is recorded as material retained on the column.

2.5 Structural Group Analysis.

V_k, n, d at 20°C.

From the results obtained on Table 2.6 . The values were put into the standard graph[41] and by taking the logarithm of kinematic viscosity log V_k and refractive index a density d' was obtained. The change in density is related as

$$\Delta d = d' - d \quad \ldots\ldots(1)$$

where d is the observed density.

The graph for determining the value d' was limited to a refractive index of 1.500 and the refractive indices of the three oils were between 1.634 and 1.644. Hence the graph was extrapolated to obtain the value d' at the above refractive indices. Result from the extrapolated graph:-

d' for A, B, and C oil were
1.043, 1.051, 1.054 respectively.

Calculation for V_k, n, d at 20°C

Oil A .... $d = d' - d \ \ldots\ldots(1)$

$= 1.043 - 0.978 = 0.065$

$$\% \text{ Aromatic Carbon } C_A = 600\Delta d - (40\Delta d)^2 \quad \ldots\ldots\ldots(2)$$

Substituting the value of Δd from equation (1)

$$:.\quad C_A = 600 \times 0.065 - (40 \times 0.065)^2$$

$$= 39 - 6.74 = \underline{32.24}$$

From the graph of the molecular weight, total carbon in ring structure and total number of ring contents were read out.

M = 480; C_R = 49.0; R_T = 3.3

Since the relation Aromatic ring content was given by

$$2R_A + 1 = \frac{M \times C_A}{2800} \quad \ldots\ldots\ldots(3)$$

$$= \frac{480 \times 32.2}{2800} = 5.5$$

$$\therefore \quad 2R_A + 1 = 5.5 \quad \therefore \quad R_A = 2.25$$

Since $R_N = R_T - R_A$

$$= 3.3 - 2.25 = 1.05$$

Again since $C_N = C_R - C_A$

% Carbon in naphthenic structure

$$= 49 - 32.24 = 16.76$$

$$C_P = 100 - C_R$$

$$\therefore 100 - 49.0 = 51.0$$

Hence total result for the Shell Oil (Oil A) was obtained

% Carbon in Aromatic C_A = 32.24

% Carbon in ring structure C_R = 49.00

% Carbon in paraffinic C_P = 51.00

% Carbon in naphthenic = 16.76

Total ring content = 3.30

Total naphthenic ring content = 1.05

Total aromatic ring content = 2.25

Thus similarily the result was calculated for other oils.

n, d, M at 70°C

The following equations as reported by Van Westen[57] were used in calculating the percentage aromatic carbon (C_A), percentage naphthenic carbon (C_N), percentage paraffinic carbon (C_P) and percentage carbon in ring structure. Similarily the aromatic and naphthenic rings and total number of rings were also calculated.

General equation for $\% C_A = 410x + \frac{3660}{M}$ ……(1)

where x is related with refractive index and density

$$x = 2.42\,(n^{70} - 1.4600) - (d^{70} - 0.8280)$$

Substituting the values of refractive index (n^{70}) and density (d^{70}) for the Oil A from the Table 2.6

$$x = 2.24\,(1.541 - 1.4600) - (0.965 - 0.8280)$$

$$= + 0.059 \quad \text{………}(1a)$$

Thus $\% C_A = 410 \times 0.059 + \frac{3660}{463} = \underline{32.09}$.

Similarily the percentage cyclic carbon (Aromatics + Naphthenics)

$\% C_R = 775y - 3S + \frac{11500}{M}$ ………(2)

where y is related with refractive index and density

$$y = (d^{70} - 0.8280) - 1.11(n^{70} - 1.4600)$$

Substituting the values of refractive index and density of Oil A, the value of y comes out to be

$$y = (0.965 - 0.8280) - 1.11\,(1.541 - 1.4600)$$

$$= + 0.047 \quad \text{…………}(3)$$

Thus substituting the values of y and the values of percentage sulphur content and molecular weight from the Table 2.6 the value of % C_R was obtained.

$$\% C_R = 775 \times 0.047 - 3 \times 3.34 + \frac{11500}{463}$$

Percentage cyclic carbon % C_R = 51.3

Hence percentage naphthenic carbon % C_N = $C_R - C_A$

$$\therefore \% C_N = 51.3 - 32.09 = 19.21$$

Thus percentage paraffinic carbon % C_P = 100 − C_R

$$\therefore 100 - 51.3 = 48.7$$

Ring Contents:-

The total number of ring content (R_T) is given by

$$R_T = 1.55 + 0.146 M (y - 0.005S) \quad \ldots\ldots\ldots (4)$$

where S is the sulphur content of the oil

Substituting the values of molecular weight , and the value of y from equation (3)

$$R_T = 1.55 + 0.146 \times 463 (0.047 - 0.0167) = \underline{3.56}$$

Aromatic ring content R_A is given by

$$R_A = 0.41 + 0.055Mx$$

Substituting the value of x from the equation (1a)

$$R_A = 0.41 + 0.055 \times 463 \times 0.059$$

$$= 0.41 + 1.50 = 1.91$$

Naphthenic ring (R_N) = $R_T - R_A$

$$= 3.56 - 1.91 = \underline{1.65}$$

Calculation to assign a formula for a hypothetical average molecule.

Test Oil A (Specimen Calculation)

From the Table 2.6 Molecular weight is 463 and again from Table 2.10 Percentage carbon is 85.08, percentage hydrogen is 11.68. From Table 2.2 percentage sulphur is 3.34

Thus $\frac{85.08}{12} = 7.1$ for carbon

$\frac{11.68}{1} = 16.68$ for hydrogen

$\frac{3.34}{32} = 0.104$ for sulphur

Hence a molecule with 100 molecular weight will have 7.1 carbon

C. $\frac{7.1}{100} \times 463 = 33.5$

For hydrogen $\frac{11.68}{100} \times 463 = 55$

For sulphur $\frac{0.104}{100} \times 463 = 0.491$

The molecule may be assigned the formula

$$C_{33.5}H_{55}S_{0.491}$$

Calculation for Molecular Weight.

The ebullioscopic method was used for determination of molecular weight.

The ebullioscopic constant K_1 was determined from the equation

$$K_1 = \frac{M_1 \times W_1 \times R}{W_2 \times 1000}$$

where W_1 = weight of solvent

W_2 = weight of substance

R = resistance

M = molecular weight.

10.0 mls of benzene were used and K_1 was determined by using pure 2:6 Dimethyl naphthalene.

$$\text{Thus } M = \frac{K_1 \times W_2 \times 1000}{W_1 \times R}$$

Molecular weight of Oil A

1. $$\frac{931 \times 0.025 \times 1000}{8.76 \times 6} = 445$$

2. $$\frac{931 \times 0.031 \times 1000}{8.76 \times 6} = 457$$

3. $$\frac{931 \times 0.0234 \times 1000}{8.76 \times 5} = 492$$

Mean Value = 463

The instrument used in these determinations was a modified form of Heitlers ebulliometer[58]

3.4 Determination of Sulphur in the used Copper Foil.

Procedure:-

A 5.0 gms sample of the blackened copper foil is put into a boiling tube fitted with a B 24 glass socket joint and 10 mls of concentrated hydrochloric acid added. The tube is closed by a ground glass cone fitted with an extension arm. This latter arm is joined to a gas absorption bottle containing 40 mls of 10% aqueous cadmium chloride solution. The tube is kept vertical and gently heated. The hydrogen sulphide evolved is absorbed into the solution in the bottle and heating is continued until no more hydrogen sulphide is evolved. The hydrogen sulphide is then determined by the standard method described by Shaw[59] which involves an idiometric titration.

The calculation for the weight percentage of sulphur is as follows:-

From the standard formula given in I.P

$$\% \text{ weight of } H_2S = \frac{N(a - b) \times 0.017}{W} \times 100 \quad \ldots\ldots(1)$$

where N = normality of sodium thiosulphate

a = obserservation with iodine only (blank)

b = observation with hydrogen sulphide

W = weight of the substance taken.

Multiplication of the result of equation (1) by $\frac{32}{34}$ gives the percentage weight of sulphur.

3.5 Calculation for Residence Time.

The residence time of a static system may be given as $\frac{Vo}{U}$ where Vo is the total free volume or bed voidage. It is given here in litres. "U" is the flow rate in litre/min.

If it is assumed that the vapours obey the ideal gas law $PV = nRT$,

The flow of the liquid "U" is given by $\frac{T}{273} \times Q \times 22.4$ where Q is the gm mole of liquid feed to the reactor per minute, while T is the experimental reactor temperature (°K).

Pressure changes are neglected here since the present studies were carried out at atmospheric pressure, and bed pressure drop was negligible.

Thus residence time $R = \frac{273 \times Vo}{T \times Q \times 22.4}$ minutes.

Calculation :-

Total volume of copper obtained from its superfacial density for 150 gms = 17.42 mls

Actual total volume occupied by the 150 gms of copper = 142.0 mls.

Bed voidage or free space available for reaction = 142.0 − 17.42 = 124.58 or 0.124 litres.

Residence time for a flow of oil A 1.0 gm/min

Mole oil input/min = 0.0021 = $\frac{273 \times .124 \times 60}{703 \times .0021 \times 22.4}$ = 62 seconds

For flow rate 2.0 gm/min or .0042 mole/min

$$= \frac{273 \times .124 \times 60}{703 \times .0042 \times 22.4} = 31 \text{ seconds.}$$

Experiment temperature in these two calculations is 430°C.

4.4 Activation Energy Calculation (Catalyst A).

C_6H_{12} C_6H_6 + $3H_2$

Calculation on basis of mole/100 mole.

Inlet rate of flow of cyclohexane = 0.5 ml/min

Density of cyclohexane = 0.776

Inlet rate of nitrogen = 0.0061 ft^3 at N.T.P/min

Taking an experimental result of run (1) of Table 4.4(i)

Inlet mole C_6H_{12}/sec. $= \dfrac{0.5\ (0.776)}{84 \times 60} = 7.69 \times 10^{-5}$ .....(1)

Nitrogen inlet mole $= \dfrac{0.0061 \times 28.3}{22.4}$ ....(2)

Inlet concentration = (1) + (2) = 769/77829

Inlet concentration mole/100 mole = 0.988 ....(W)

Out let liquid = 98 ml C_6H_{12} + 2.0 ml C_6H_6 per 100 ml

$$= \left(\frac{98 \times .776}{84} + \frac{2.0 \times .886}{78} \right)$$

$= 0.905 + 0.0227 = 0.928$ mol/100 mole

Mole fraction $= \dfrac{0.905}{0.928} = 0.976$

Outlet rate of C_6H_{12} $= 7.69 \times 10^{-5} \times 0.976$ ....(X)

$= \underline{7.5 \times 10^{-5}}$

Exit mole of C_6H_6 $= 7.69 \times 10^{-5} \times 0.0245$

= or 1.88×10^{-6}

Total exit mole $= 7.69 \times 10^{-5} + 3(1.88 \times 10^{-6})$

$= 8.25 \times 10^{-5}$

∴ Outlet mole $= 8.25 \times 10^{-5} + 0.0077$ ....(4)

Outlet concentration = $\frac{(X)}{(4)}$ = 0.964 ....(Y)

Thus when logarithm of ratio of initial concentration to change in concentration (Log $\frac{(X)}{(Y)}$) was calculated at different residence time.

Run No.	Catalyst Volume	Temperature	Residence time	x/y	K	Activation Energy K cal /mol
1.	16.5	300	2.63	1.031	3.2×10^{-3}	8.05
2.	33.0		5.13	1.085		
3.	49.5		7.70	1.180		
4.	66.0		10.25	1.230		
9.	16.5	350	2.43	1.065	6.4×10^{-3}	
10.	33.0		4.74	1.134		
11.	49.5		7.13	1.270		
12.	66.0		9.50	1.480		
17.	16.5	400	2.18	1.115	12.0×10^{-3}	
18.	33.0		4.27	1.230		
19	49.5		6.39	1.520		
20.	66.0		8.58	1.665		
25.	16.5	450	2.09	1.150	20.1×10^{-3}	
26.	33.0		4.07	1.280		
27.	49.5		6.13	1.510		
28.	66.0		8.18	1.630		

The value of Log K when plotted against $1/T^{\circ}K$ and the slope was put into Arehenius equation the activation energy was obtained.

5.2

See 3.4

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