THE
REMOVAL OF ORGANIC SULPHUR
FROM
TOWN'S GAS

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BY

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SUMMARY.

This work consists of a study of the removal of organic sulphur compounds to synthesis purity limits, from vertical retort coal gases and similar gases.

A survey of the existing processes was made and catalytic hydrogenation of the organic sulphur was chosen as a feasible process. Catalysts available commercially for this purpose were reviewed and Peter Spence 3.5/10 Nimox was chosen for further investigations. Peter Spence Luxmasse was used as the absorbent.

A suitable six-stage apparatus was constructed to study the conversion of organic sulphur.

Synthetic mixtures containing carbon monoxide, hydrogen and individual organic sulphur compounds were purified by giving single and multiple stage treatment. Conversion of carbonyl sulphide, by using single-stage, was 94 - 95% at 350 °C and atmospheric pressure. Thiophene conversion was 50% at 350 °C and atmospheric pressure, while at 350 psia and 400 °C, conversion rose to 97%. Conversion of carbon disulphide was complete at less than 350 °C, and conversion of Butyl mercaptan was 99% at this temperature.

Purification of coal gas containing 15 - 20% carbon monoxide was carried out at atmospheric and higher pressure, by providing single and multiple stage treatment. While removal of total organic sulphur depended upon the extent of thiophene present, it was found that conversion of organic sulphur was about 97% on a single conversion stage, at 350 °C. Conversion rate fell gradually with the passage of time.

With six-stage treatment, an outlet gas containing 0.2 p.p.m. of

organic sulphur was obtained. Higher pressure and 5% of water vapour were found beneficial. High space velocity could be used when the catalyst was comparatively fresh, but with the passage of time lower space velocity was needed for maintaining the same rate of conversion.

The Luxmasse at a higher temperature also helped the conversion of organic sulphur. Blockage of the Luxmasse bed above 350 °C was noted with gas free from sulphur, but at a lower temperature of 300 °C this difficulty was obviated.

Results of conversion by using another type of Nimox (4.5/12); and I.C.I. Comox and zinc oxide were obtained. It was found that zinc oxide alone would remove 90% of total organic sulphur both by conversion and simultaneous absorption at 400 °C.

A preliminary design for a small scale package unit has been worked out.

INTRODUCTION

Town's gas prepared from conventional raw materials like coal and heavy oil contains hydrogen sulphide and organic sulphur before final purification. Hydrogen sulphide is removed almost completely by passing the gas through specially prepared iron oxide, which leaves the bulk of organic sulphur untouched. In most countries no legal limitations exist for the complete removal of sulphur from town's gas and consequently organic sulphur ranging from 20 to 50 grains/100 cu.ft. is passed on to the consumer.

The principle compounds which constitute the bulk of organic sulphur are carbon disulphide, thiophene, carbon oxysulphide, mercaptans and other compounds occurring in traces only, such as disulphides etc. Little effort is made to remove these compounds from town's gas; however, certain applications do require a lower total sulphur content in fuel gases than is obtained by removing hydrogen sulphide only. In these instances, at least partial removal of organic sulphur compounds is necessary. Synthesis gases used in catalytic processes usually require almost complete absence of all sulphur compounds because many synthesis catalysts are extremely sensitive to sulphur poisoning. Consequently, two types of organic sulphur removal processes have been developed, depending upon the ultimate use of purified gas. In the first case, the organic sulphur content of fuel gases is reduced sufficiently to make them suitable for use in such applications as flueless heating appliances, directly fired pottery kilns, heat treating processes for non-ferrous metals and related processes. For these applications sulphur content of 3 to 10 grains/100 cu.ft. can be tolerated.

The second type of process is intended for essentially complete removal of organic sulphur compounds from industrial gases, especially synthesis gases. Because of the extremely low total sulphur concentrations required in gases used for many catalytic synthesis, sometimes less than 0.01 grain sulphur/100 cu.ft. these processes should, ideally, be capable of removing completely not only carbonyl sulphide, carbon disulphide, and mercaptans but also thiophene.

The present work concerns with the development of latter processes, i.e. complete removal of organic sulphur from town's gas so as to achieve synthesis purity limits.

Here are methods of removing organic sulphur :-

(1) Chemical absorption and disposal of spent absorbent as in lime purification.
(2) Absorption by solvents (oils) and desorption.
(3) Absorption by solids (active carbon) and desorption.
(4) Conversion to hydrogen sulphide or to sulphur dioxide at high temperatures in the presence of catalysts, and
(5) Refrigeration and condensation.

The degree of removal of organic sulphur depends a great deal on the distribution of individual compounds. Generally speaking, the more volatile sulphur compounds usually regarded as carbonyl sulphide, are, not materially altered by oil washing or active carbon absorption. On the other hand little more than 20% of the organic sulphur classified as thiophene is removed in the catalytic processes.

This work consists of a study of the removal of organic sulphur compounds to synthesis purity limits, from vertical retort coal gases and similar gases, so that these gases may undergo further reaction in catalytic processes, in which the catalysts are not tolerant of sulphur. This represents an attempt to reach a degree of purity from sulphur hitherto not attained with gases of this type, since they contain a quantity of carbon monoxide which interferes with normal purification processes.

To achieve this aim, effort shall be directed primarily towards finding a suitable catalyst, preferably available commercially, which should be able to convert all the organic sulphur compounds to hydrogen sulphide in the presence of the hydrogen content of the gas itself. Steam may be added if necessary to enhance organic sulphur conversion or to suppress undesirable side reactions.

THE SIGNIFICANCE OF THE PROBLEM.

With the use of gas for greater numbers of new processes, there is a growing interest in almost complete removal of sulphur compounds. It is becoming more important to reduce corrosion from the gas and its products of combustion so as to minimise attention and maintenance of gas appliances. Also, gas burning equipment is being made more automatic, and with sulphur-free gas this equipment will acquire a longer life and minimum maintenance. Some metallurgical uses of town's gas need lower sulphur content. The main problems arise in space and water heating where presence of products of combustion of sulphur cause annoyance to the household consumer.

Sulphur compounds in gas burn to form a mixture of sulphur dioxide and trioxide and main objections to the presence of sulphur compounds in gas arise (1) from the harmful physiological, physical and chemical effects produced by these oxides. These objections are discussed below :-

(1) PHYSIOLOGICAL EFFECTS.

These effects were discussed by Royal College of Physicians,(2) by Masterman(3), Dunning and Densham, and 1942 Committee(4) of Enquiry on Sulphur Removal. The threshold perception of sulphur trioxide is about 0.00002% and for sulphur dioxide 0.0002%, leading to a figure for the combined oxides (80% SO_2 and 20% SO_3) of about 0.0001% or 1p.p.m. If gas is being burnt in a flueless appliance, this limit should not be exceeded. It is a familiar experience that the threshold of perception can be affected by other influences such as the presence of water vapour and of cooking smell and hence few complaints are associated with gas cookers.

The Code of Practice(5) dealing with space heating in domestic premises recommends a maximum continuous consumption of 1 cu.ft. per hour in 100 cu.ft. of room space when burnt fluelessly. An hourly change of two is required with a sulphur level of 10 gr./100 cu.ft., while at higher levels of sulphur, higher air changes will be needed. The rate of air change in some buildings is lower than that recommended, particularly in winter. It will be clear from these considerations, that if a room or building is to be heated fluelessly to full comfort conditions, there is at the present time likely to be a perceptible smell due to sulphur oxides and an immediate reduction in sulphur concentrations to 10 gr./100 cu.ft. would considerably increase the scope for flueless heating.

(2) PHYSICAL EFFECTS

Sulphur oxides raise the dew point or temperature at which condensation begins. This is because the oxides can combine with water vapour in the presence of oxygen to produce sulphuric acid which has much lower vapour pressure than water. This effect has been studied by many authors.(6)(7)(8)(9)(10)

Hence the corrosion of gas flues may occur if the temperature falls below dew point of water.

(3) CHEMICAL EFFECTS

Sulphur dioxide and trioxide dissolve in water in an oxidising atmosphere to give sulphuric acid. On an actual surface the acid will be cold and dilute, but in an appliance it will be hot and also progressively become concentrated, so that under condensing conditions, corrosion of a variety of materials can be expected to occur.

(4) LIMITATION OF INDUSTRIAL USES BECAUSE OF SULPHUR IMPURITY.

In the industrial gas field, presence of sulphur can effect either the appliance or the product. If the appliance is working continuously, there are less chances of corrosion, but if the use is intermittent, then condensation may occur with the consequent attack of surface by sulphuric acid. By no chance, any appliance will work continuously and hence the damage is likely to occur at one time or the other to the appliance or the gas flue.

Sulphur, in the concentrations normally encountered in town gas, has negligible effect(1) on a large number of industrial heating processes. There are, nevertheless, processes in which presence of sulphur can be decidedly deleterious, and these constitute a valuable portion of industrial load. Three major examples are processes concerned with glass, ceramics, and heat treatment of non-ferrous metals. One of the small applications is the heating of the greenhouses. A brief discussion on these items follows :-

(1) GLASS. Gas has always been universally used for the flame working of glass, but when glass is heated in the presence of sulphur oxides, a bloom is formed on its surface. This bloom can easily be removed by wiping or washing, and its formation toughens the glass; nevertheless, it is very disadvantageous when for example, it forms on the inside surface of the television tube during the process of welding the surface to the body. Another aspect of the same problem is the "bloom" that forms on vitreous enamel during firing if sulphur is present. This spoils the appearance of the finished product; and for this reason direct gas firing is not employed in vitreous enamelling furnaces.

Another large use for gas in the glass industry is the annealing of mass produced glass-ware, which must remain free from bloom. As a result such processes must either be indirectly heated, or catalytic sulphur removal of the fuel gas be provided locally.

(2) CERAMICS. Sulphur oxides affect certain colours and glazes on ceramic bodies, and, in consequence; pottery kilns are commonly indirectly heated. In one instance(11), the availability of gas containing less than 10 gr.S/100 cu.ft. enabled the installation of a direct-fired kiln fired by town gas and consuming some 120,000 therms per annum. Had the kiln been indirectly heated, the fuel chosen would have been oil.

(3) HEAT TREATMENT OF METALS. The clean treatment of non-ferrous metals, such as silver, copper, nickel and their alloys is a very important heating load, and, if acceptable results are to be obtained, sulphur free atmospheres must be provided. This can be done by the provision of local catalytic plants, but this increases the effective price of the gas.

(4) OTHER APPLICATIONS. There are many other small applications of the town's gas where reduction in sulphur is desirable. One of them is the house plants. Sulphur dioxide can cause trouble to plants, principally by damage to foliage(12). The sensitiveness of plants varies with the species and with atmospheric and seasonal conditions, but the concentrations of the order of 1 p.p.m. can cause serious damage.

Many plant growers are, therefore, unwilling to allow products of combustion of town gas to come into contact with such plants in their greenhouses, and flueless heating of greenhouses by gas is generally excluded.

Gas can, of course, still be used indirectly, for example, by means of a hot water circulator and pipe system, but the potential advantage of cheapness and simplicity of direct heating is lost, and load generally goes to other fields.

SYNTHESIS GAS: Synthesis gas, whatever its source, must be almost completely free of sulphur and its compounds for use in the well-known Fischer Tropsch synthesis processes, about 0.1gr./100 cu.ft. being the maximum tolerable limit.(13)

For synthesis of methane the ultimate purity limit is 0.002 gr./100 cu.ft., otherwise(14) the nickel catalysts used for methane synthesis are poisoned easily.

TOWN'S GAS AS A COMPETITIVE FUEL.

It is generally recognised(15) that the domestic market is the mainstay of the gas industry, and that, of the many uses for gas, those that offer the most promising fields for expansion are for water heating and space-heating. Table No. 1 makes the point clear.

Gas sales in the West Midlands Gas Board area rose to 457.9×10^6 therms in 1965-66, 9.2% higher than in 1964-65 and an increase of 34% in the last five years. The increase in sales is due to the continued success in the domestic market in which there was a rise of 22.2%. The use of gas in the home has risen in the last two years by over 40% and domestic sales now exceed sales to industry.

At the same time great inroads have been made by distillate oils into space-heating market because of their low sulphur content. The gas industry on the other hand has to compete with electricity.

The Table No. 2 compares sulphur content per therm of town's gas from various sources with that of distillate oils.

TABLE NO. 1. Classification* of Customers and Analysis of Gas sales.

PARTICULARS	No: of Customers		Gas Sales Thousand Therms		Per Cent of total sale		Average therms sold per customer	
	March 1966	March 1965	1966	1965	1966	1965	1966	1965
Domestic	1,143,369	1,123,629	217,500	177,984	47.5	42.4	190.2	158.4
Industrial	10,604	10,502	205,359	206,619	44.8	49.3	19293.4	19674.3
Commercial	40,886	41,892	31,511	30,702	6.9	7.3	770.8	732.9
Public Admin.	2,347	2,366	3,013	3,110	0.7	0.8	1283.7	1314.5
Public Lighting	-	-	522	903	0.1	0.2	-	-

* West Midlands Gas Board, Annual Report 1965-66, P.20.

TABLE NO. 2. Sulphur Content of various(15) fuels.

FUELS	SULPHUR CONTENT	
	Usual basis of Expression	Gr.S/therm of net potential heat.
1	2	3
Town's gas	0.2 p.p.m. H_2S	0.03
–	3.0 gr.S/100 cu.ft.	6.70
–	10.0 gr.S/100 cu.ft.	22.00
–	30.0 gr.S/100 cu.ft.	67.00
Refinery gas to (N.T.G.B.)	3.0 gr.S/100 cu.ft.	2.50
Refinery gas after reforming	0.5 gr.S/100 cu.ft.	1.00
Commercial propane and butane	0.02% by wt.	7.50
Paraffin	0.05% by wt.	18.50
Light distillate (P.F.D.)	0.5% by wt.	19.00
Gas oil	0.90% by wt.	325
Fuel oil	3.50% by wt.	1400

This comparison shows that if town gas is to compete in over-all performance with paraffin, its sulphur content must not be greater than about 8 gr.S/100 cu.ft.

A still lower level of near to 3 gr /100 cu.ft. must be attained if town gas is to retain existing and gain new industrial loads (against the competition of liquid propane or butane fuels), where low sulphur content is important.

The oil companies(15) have spent considerable sums in recent years on plants to reduce the sulphur content of all their refined hydrocarbon products. In the case of paraffin, they have succeeded in reducing the sulphur impurity to a level such that it does not create a detectable odour in the products of cumbustion. Simple economics will explain the rapidly expanding sales of paraffin for domestic heating. Selling at around 24d. per gallon, it yields, when burnt in a flueless appliance, one therm of useful heat for 16d. Town gas which contains appreciably more than 10 gr S/100 cu.ft., and which therefore cannot be burnt satisfactorily in flueless appliances, will yield up to 0.65 therm of useful heat for each therm of gas when supplied to the heat type of convective fire. If the price of gas is 22d. per therm, the cost of useful heat per therm to the consumer is 34d. This comparison done on the basis of prices in 1957-58, will however, be true at all times.

It is often argued that most gas users are satisfied with the quality of existing supplies, and that the gas industry cannot afford to make any further improvements of quality and so to worsen its competitive selling price.

If, by reducing the sulphur impurity in town gas, more could be sold, the economics of the gas supply need not be prejudiced(15), for example, it can be shown that, if the cost of increased sulphur removal at the works imposed an additional cost of 1/2d. per therm on all the gas made, this could be offset in the form of useful therms sold to the public by increasing the use of gas in flueless appliances by only about 4% of the sales of gas.

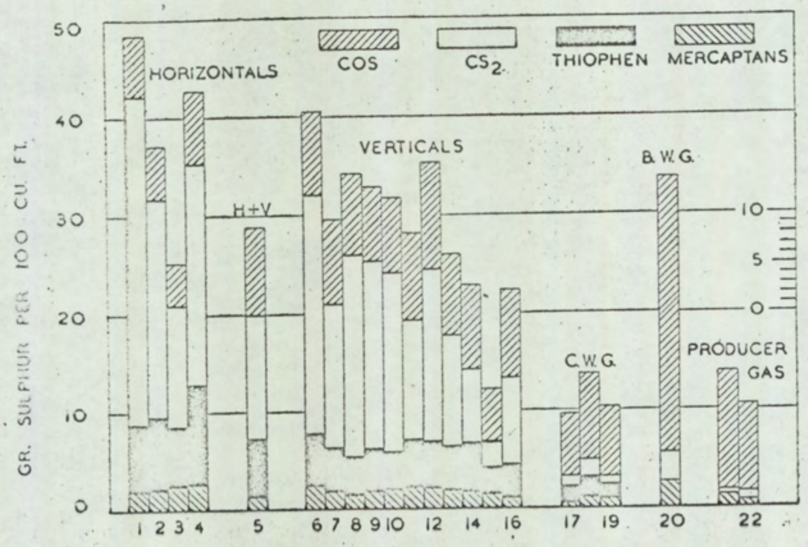


Figure I. Organic Sulphur Content of Unwashed Gases arranged according to type of gas production Plant and roughly in order of C.V.

DISTRIBUTION OF ORGANIC SULPHUR IN TOWN GAS.

Immediately before the war a sulphur content of 22-25 gr/100 cu.ft. for town gas in this country was typical. In quite a number of places the sulphur content was reduced to well below 20 gr. as the result of benzole washing.

Wood & Clayton(16) examined the distribution of organic sulphur compounds present in town gas. They reported that sulphur contents of various gases ranged from about 10 gr. to nearly 50 gr./100 cu.ft. Their findings are shown in Fig.1.

It is clear that the sulphur content of various gases ranges from about 10 gr. to nearly 50 gr./100 cu.ft.

Carbon disulphide is the chief organic sulphur compound present.

The results from gas from vertical retorts at five works, show a tendency for the total organic sulphur of the gas to fall as the calorific value of the gas is reduced; the type of retort appears to be of minor importance. While carbon disulphide still remains the chief constituent, the C O S is higher and the thiophene lower throughout than for the gas from horizontal retorts.

The carburetted water gas examined at three different works gave closely similar figures for sulphur content, which were, however, characteristically lower than those for coal gas of equal value.

The blue water gas results are characterised by a high organic sulphur content, the greater part of which is carbon oxysulphide; thiophene is absent.

The principal organic sulphur compounds in producer gas in both cases is C O S, thiophene being absent, the small amount of thiophene shown for the Trefois gas is due to the inclusion of small amounts of green coal with the coke breeze supplied to the generator.

With regard to the effect of the type of carbonizing plant upon the total organic sulphur content of the gas, it will be noted that, as they stand, the figures show a higher sulphur content for gas from horizontal retorts than for that from vertical ones, namely, an average of 37 gr/100 cu.ft. as against 30 gr/100 cu.ft. It must be borne in mind, however, that the horizontal retort gases are of higher calorific value and would require to be diluted before distribution. Final sulphur content will depend upon the amount and type of diluent and hence it should not be assumed that gas distributed will have any higher sulphur content.

It would not be unreasonable to assume that, other things being equal, the organic sulphur content of the gas would increase with increasing sulphur content of coal. This point will be taken up again in details with the origin of sulphur in gas, but in the above cases, higher sulphur contents were produced from coals containing the highest percentage of sulphur and the very low sulphur content was obtained with a coal containing only 1.02% of sulphur. The problem is more complicated than this, however, and the organic sulphur content of the gas may be expected to vary with the pyritic and organic sulphur content of the coal, and with the types of organic sulphur compounds, ring or chain, originally in coal.

SULPHUR CONTENT OF GASES AFTER BENZOLE EXTRACTION.

At the present time the removal of organic sulphur compounds from gas is usually incidental to benzole extraction rather than an end in itself. The various organic sulphur compounds are not equally affected by benzole extraction, and the sulphur content of the finished gas must in consequence depend upon the nature and quantity of the sulphur compounds originally present and the method employed for benzole recovery. Table No. 3 shows the percentage removal of individual organic sulphur compounds after benzole washing.

<u>TABLE NO. 3.</u> Percentage(16) Removal of Individual Sulphur Compounds during Benzole extraction.

TYPE OF PLANT	COS	CS_2	C_4H_4S	RSH	TOTAL
1	2	3	4	5	6
Horizontal retorts Creosote oil washing	3	37	70	41	35
	6	36	81	27	37
	5	28	79	33	33
V.R.Gas oil washing	5	26	94	52	32
V.R.Gas oil washing (Special coal	11	42	80	71	41
V.R. (New carbon)	22	89	64	40	62
V.R. (Old Carbon)	Nil	35	60	40	28

It is clear that creosote oil washing removes 33 - 37% of total sulphur, while gas oil washing produces the same results with the exception that thiophene removal is greater in this case.

As regards removal with active carbon, the efficiency of sulphur removal falls by about half, namely from 62% at the beginning to only 28% at the end of the run.

As with oil washing, the carbon oxysulphide escaped absorption except when the carbon was very new. The carbon disulphide recovery was very good at first but falls to a value similar to that obtained with oil washing as time elapses. It may be seen that with active carbon washing, carbon disulphide goes up while thiophene removal becomes less.

On the whole, removal of sulphur compounds by active carbon is more efficient than by oil washing as usually practiced for benzole recovery, but the removal is by no means complete.

TABLE NO. 4. Distribution of Organic(16) Sulphur Compounds in Town Gas.

Sulphur in gr. per 100 cu.ft.

PLANT	C V	COS	CS_2	C_4H_4S	RSH	TOTAL	
1	2	3	4	5	6	7	
Horizontal coal gas debenzolized plus producer gas.	470	7.1	12.0	1.1	1.1	21.3	(1)
Vertical coal gas partially debenzolized plus C.W.G.	470	8.0	13.7	2.4	1.2	25.3	(2)
Do	450	8.3	12.9	0.5	1.0	22.7	(3)
V.R. gas debenzolized	450	9.0	9.3	0.3	1.4	20.0	(4)
V.R. gas debenzolized with new carbon	450	7.6	1.8	1.9	1.5	12.8	(5)
V.R. gas debenzolized with old carbon	450	8.4	6.8	2.0	1.2	18.4	(6)
Mixed horizontal and V.R. gas, debenzolized, plus C.W.G.	450	9.8	8.2	2.4	1.3	21.7	(7)

It is clear from the preceding table that the average sulphur content is slightly above 20 gr. per 100 cu.ft., and that of this rather more than half is carbon disulphide, and one third COS, with the remainder divided between thiophene and mercaptans.

OCCURRENCE OF SULPHUR IN THE ORIGINAL FUEL.

There are three important raw materials from which town gas is manufactured. These are coal, coke and oil. Both hydrogen sulphide and organic sulphur in crude fuel gases are produced from the sulphur present in these raw materials. Below we discuss the occurrence of sulphur in each of these raw materials.

1. COAL

Sulphur is present in coal in three forms :-

(a) As iron pyrites or marcasites ($Fe\ S_2$),

(b) As sulphates, mainly gypsum or calcium sulphate ($Ca\ SO_4\ 2\ H_2O$),

(c) As complex compounds of sulphur and carbon in the coal substance itself.

Pyrites(17) loses part of its sulphur by decomposition in strongly heating, hence becoming iron-monosulphide,

$$Fe\ S_2 \ \_\_\_\_ \ Fe\ S + S$$

Calcium sulphate may be reduced by contact with the hot carbon to the sulphide,

$$Ca\ SO_4 + C \ \_\_\_\_ \ Ca\ S + 4CO$$

In the majority of cases the coke will still contain over 80% of the original sulphur of the coal.

Yancy and Fraser(18) published details of work carried out on 39 different samples of coal of world-wide origin, showing the relative proportions of these three groups as follows :-

Pyrites Sulphur : 0.02 to 2.61% Average 1.00%
Sulphate Sulphur: 0.01 to 0.32% Average 0.05%
Organic Sulphur : 0.23 to 7.90% Average 1.21%
Total Sulphur : 0.44 to 9.01% Average 2.29%

The "organic sulphur", expressed as a percentage of the total, varied from 11.7% to 97.1%, average 52.8%

(A) Carbonization of coal

When coal is carbonised, as in normal gas works, or coke oven practice, roughly half the total sulphur is evolved in the gas and tar vapours, the other half being retained by the coke. Hydrogen sulphide is a low temperature product, appearing in the gas for the first time, when the temperature of the coal reaches the zone 200 - 300 °C when it ceases or falls to a very small amount. Some organic sulphur compounds, notably mercaptans and thio-ethers also appear at this latter stage. According to Powell(19) the primary reactions are :

(1) The complete decomposition of iron pyrites to ferrous sulphide, pyrrohtite and hydrogen sulphide, below 600°C but in the range of 400 - 500°C,

(2) The reduction of sulphates to sulphides below 500°C,

(3) The decomposition of the organic sulphur compounds of the coal below 500°C, with the liberation of one fourth to one third of the sulphur as hydrogen sulphide, simultaneously with a pronounced chemical change in the state of carbonisation of the organic sulphur remaining in the solid. Although, little is known of the actual structure of the carbon-sulphur complexes, they are extremely stable, even at very high temperatures.

It may be similar to that of benzene, part of the general high temperature of aromatisation, either by dehyrogenation of hydroaromatic rings or olefin condensation. On the other hand it may be formed by the high temperature decomposition of organic sulphides, or by the inter-action of acetylene with pyrites.(22)(23(24)

(B) GASIFICATION OF COAL AND COKE.

In gasification of coal, the mechanism of production of hydrogen sulphide is generally similar to that of carbonisation. In coke gasification, the residual sulphur present is attacked by the hydrogen or steam(20). Unpublished results showed that steam itself was not quite so effective as hydrogen for stripping the residual sulphur our of the coke. Hydrogen is, however, produced during the reaction; and also the opening up of the coke structure by gasification of the carbon would go on simultaneously with any attack on the sulphur complexes. The hydrogen sulphide content of gases produced by gasification (B.W.G., C.W.G. or Producer) is less than that of carbonisation gases because the average sulphur content of the original fuel tends to be less, and the volume of gas in which it is eventually distributed is greater.

The organic sulphur content of these gases is usually lower, as well, but in B.W.G., it may be higher. In C.W.G., the three main compounds, CS_2, COS, C_4H_4S are all present, COS accounting for up to 75% of the whole. In B.W.G., and producer gas, thiophene is absent and carbon disulphide present only in small amounts, the bulk again being carbon oxysulphide. This is, no doubt, due to synthesis from hydrogen sulphide and carbon monoxide.

$$CO + H_2S \rightleftharpoons COS + H_2$$

The effect of ash constituents and gaseous atmospheres on the evolution of hydrogen sulphide were studied by Priestly and Cobb(20). Inorganic constituents were added to the coal prior to carbonisation which was carried out in stages up to 1,000°C in nitrogen or hydrogen. It was shown that the addition of lime resulted in the retention by coke of over 95% of the original sulphur in coal. The addition of iron oxide caused a retention of 90% of the coal sulphur in a nitrogen atmosphere, but when hydrogen was used, an initial retention to about 600°C was followed by a marked breakdown, so that at 1,000°C, the total hydrogen sulphide evolved compared with that from the untreated coal. Sodium carbonate reduced the sulphur retention in nitrogen, but increased it in hydrogen. Comparing the results from the point of view of the atmosphere used, using "pure" coal, the results were nearly the same up to 500°C when about 30% of the coal sulphur had been evolved. Beyond this temperature however, was a marked difference. Comparing the sulphur evolution up to 1000°C, only a further 13% (total 42.4%) were noted in nitrogen, but a further 40% (total 70.9%) in hydrogen; which indicated a vigorous attack by hydrogen in the high temperature ranges on the stable sulphur compounds formed at 500°C.

Evans(21) concluded that the organic sulphur occurring in coal gas is not directly related to the total sulphur in the coal although the tendency is for higher sulphur coals to produce higher sulphur containing gas. So far only mercaptans and thio-ethers have been mentioned. In carbonisation gases, however, carbon disulphide thiophene (or a thiophene type compound) and carbon oxysulphide are also present. Two of these are essentially high temperature products formed by secondary reactions, as is well brought out by the following Table No. 5 taken from Evan's paper, giving results of carbonising 30-lb. charges of coal in a test retort.

The retort was heated empty to the desired temperature and then the coal charged. The temperature was maintained at the chosen value until gas making ceased.

TABLE NO. 5. Organic Sulphur Compounds present in the gas evolved during test run.

TEMP. °C	ORGANIC SULPHUR				H_2S
	TOTAL	As COS	As CS_2	As C_4H_4S	
700	13.0	7.8	3.2	2.1	920
800	22.6	9.7	8.3	4.6	684
900	39.4	8.6	25.4	5.4	660
900 - 1,000	45.0	7.8	-	-	700

(All results expressed in gr. S/100 cu.ft.)

From these, carbon oxysulphide would appear to be a primary product of distillation, formed by the inter-action of carbon, carbon dioxide, or carbon monoxide with hydrogen sulphide, with the possible effect of catalysis by the ash constituent or the charge container.

Carbon disulphide and thiophene are shown to be high temperature products. Carbon disulphide is strongly endothermic (-25.4 K CAL) and its formation is favoured by high temperatures, either by the direct reaction between carbon and sulphur, or between carbon and hydrogen sulphide. Thiophene is a five-membered ring compound of great stability, and is chemically very similar to benzene. The high temperature conditions which favour the formation of one, also favour the formation of the other. No information is available on the likely mode of formation of thiophene during carbonisation.

Sands, Wainwright and Eglesen(25) have reported their results obtained in model gasifiers. The results are summarized in the Table No. 6.

<u>TABLE NO. 6.</u> Sulphur in Gas from 50-lb. gasifier.

Coal used.	S in coal %	Steam/coal ratio	H_2 in gas %	Generating temp. °F	Gr.S/100 cu.ft.	
					H_2S	Org. S
West Virginia	2.9	0.23	33.3	1997	310	43.9
Bituminous	2.9	0.08	35.0	1927	330	50.6
Colorado Sub-bituminous	0.4	0.18	33.8	1810	60	5.3
Pennsylvania	0.9	0.17	31.0	1820	110	23.8
Anthracite	0.9	0.29	34.9	1800	100	21.2

The relation between organic sulphur concentration in the gas and sulphur content of the coal appears to be affected by the steam/coal ratio and the type of coal gasified. It will be noted that, with a given coal, generally lower organic sulphur concentration result from higher steam/coal ratios. This undoubtedly due to hydrolysis and destructive hydrogeneration of the organic sulphur compounds, in the presence of steam and hydrogen content.

On the basis of two runs with anthracite, it would appear that this coal gives higher concentration of organic sulphur in proportion to the sulphur content of the coal when due consideration is given to the steam to coal ratios employed.

It is important to note from the foregoing that the organic sulphur concentration in the case is not necessarily proportional to the sulphur content of the coal. It is especially important to observe the decreased concentration of organic sulphur in the gas when the steam/coal ratio is increased.

In another experiment, hydrated lime was added to the coal feed in the above 50-lb. gasifier. The experiment was carried out primarily to investigate the possibility of lowering the slagging temperature of the ash, as it was planned to operate the Bureau's pressure gasifier with the ash slagging. A laboratory experiment had shown that a ratio of 0.35 lb. lime per lb. of ash (0.038 lb. lime per lb. of coal) gave the greatest lowering of the ash fusion temperature. Use of this lime/coal ratio in the gasifier had no effect on the hydrogen-sulphide content but did apparently lower the organic sulphur content of the gas. Doubling this lime/coal ratio resulted in much lower hydrogen-sulphide and organic sulphur concentrations in the gas, as will be clear from Table No. 7.

TABLE NO. 7. Sulphur in Gas from coal/lime runs.
50-lb. gasifier.

Coal used : West Virginia Bituminous
S in Coal = 2.8%
Steam/coal ratio + .01%

Generator temp. °F	Lime/Ash ratio	H_2 in gas %	Gr.S/100 cu.ft.	
			H_2S	Org. S.
1891	-	32.2	275	43.4
1853	0.35	32.8	295	25.7
1845	0.70	31.9	80	5.1

In passing, it may be noted that this would not ordinarily be an economical method of gas purification, addition of lime to the coal feed would be of interest only where it would be desired to operate a slagging gas generator with a coal of high ash-fusion temperature.

2. SULPHUR CONTENT OF OILS AND OTHER PETROLEUM DISTILLATES.

The sulphur content of oils and other petroleum(26) distillates which are cracked during oil gasification depends to a large extent on the nature of the original crude oil and the treatment it received prior to gasification. Usually the sulphur content of the crude oil fractions increases as the boiling range increases as is clear from Table No. 8.

TABLE NO. 8. Sulphur Content of Fractions of Crude:

SAMPLE	AMERICAN	CANADIAN (PRETORIA)	
S in Crude	0.72%	0.98 ---- 1.01%	
S in fraction °C	%	°C	%
to 90	0.02		
110 - 115	0.10	115 - 150	0.28
150 - 220	0.38	150 - 200	0.42
220 - 257	0.41	200 - 250	0.50
257 - 300	0.37	250 - 300	0.51
300 - 350	0.37	300 - 350	0.86
Residue	0.54	Residue	0.70

The sulphur compounds present in straight products belong to various classes, including hydrogen sulphide, mercaptans, mono and disulphides and thiophenes. Resinous and asphaltic ingredients which are compounds of oxygen and sulphur tend to concentrate in the higher boiling fractions and residues.

When low and medium molecular weight sulphur compounds are subjected to cracking conditions, it has been shown that the mercaptans and thiophenes are the most stable. Sulphides and disulphides form mostly elemental sulphur, hydrogen sulphide and mercaptans. The mercaptans in the further stages of cracking yield hydrogen sulphide (26) and olefins.

$$C_4H_9SH \longrightarrow C_4H_8 + H_2S$$

In all gasification processes of the cyclic type, not all the sulphur in the original fuel is to be accounted for in the fuel gas produced (apart from the small amount remaining in the ash and clinker). In solid fuel gasification considerable amounts leave the system in the "blow" gases as sulphur dioxide. In oil gasification, in such processes as the Onia-Gegi, some sulphur is fixed by the active material of the catalyst during the cracking portion of the cycle, and is subsequently driven out as sulphur dioxide in the other part of the cycle or "blow" in which the catalyst is reheated and the carbon deposit burned off.

In the reforming of high calorific value crude refinery gas some hydrogen sulphide is converted to organic sulphur compounds.

Removal of Hydrogen Sulphide and Organic Sulphur from Town Gas at ordinary temperature.

Of all the impurities present in crude coal gas manufactured for public supply, hydrogen sulphide is unique in that its removal is demanded by law. Tests are carried out by Gas Examiners in a manner described in their general directions (43). The degree of sensitivity of this test has been investigated by Hollings and Hutchinson(44), who found that the critical concentration of hydrogen sulphide at which it was possible to detect discoloration was 1.5 p.p.m. by volume or 0.09 gr.S/100 cu.ft. More recently Hopton(45) has quoted the figure of 0.7 p.p.m. by volume or 0.043 gr.S/100 cu.ft. With a modern turbidity meter it is possible to detect H_2S by volume much below this figure.

The removal of H_2S has been practiced since the very early days of the industry, over 150 years ago. Marsden(46) records that in 1804, Henry suggested the use of lime as a purifying medium, an idea which was developed by Clegg. In his washer, gas was made to bubble through a lime and water sludge, the lime being kept in suspension by a paddle. The difficulties of the disposal of the evil-smelling spent lime sludge were great.

In 1817(26) Phillips patented the first dry lime purifier, in which the gas passed through a series of trays filled with slaked lime. Although this was an improvement in technique, the problem of disposing of the spent lime remained unsolved and dumping on the wasteland was the only practical solution. In spite of elaborate precautions, the nuisance created by transporting and unloading became much worse than that caused by burning untreated gas.

In 1849, Hill patented the use of iron oxide as a purifying medium, but it was not immediately adopted in place of the objectionable lime process(39). The answer is that the gas engineers of the time were concerned not only with the hydrogen sulphide content of the treated gas, but also with the organic sulphur content and the illuminating value, all of which were subject to legal restrictions. The use of lime reduced the carbon disulphide(40)(41) content as well as reduced the candle-power of the gas. Until the sulphur clauses were repealed, the iron oxide process could not be used alone. Frequently, lime was added to the trays of the last purifier(47) or extra lime purifiers were used. It was not until about 1905, that the restrictions on organic sulphur were finally abolished and along with the lime purification process.

From that time onward, that is, for over half a century the iron oxide process has been the standard method of removing hydrogen sulphide from gas. Plant design and operating techniques have changed, as prevailing conditions and our understanding of the processes have changed, but the process has remained the same and has not been seriously challenged by any alternative method. It is responsible in Britain today for the purification of over 5,000 million cu.ft. of gas per annum.

COMMON METHODS OF REMOVAL OF ORGANIC SULPHUR COMPOUNDS FROM TOWN'S GAS.

There are three very common methods of removing organic sulphur from town gas. They are as follows :-

(1) Oil washing
(2) Active Carbon adsorption.
(3) Catalytic conversion to hydrogen sulphide or sulphur dioxides.

The degree of removal of organic sulphur depends a great deal on the distribution of the individual compounds(26). Generally speaking, the more volatile sulphur compounds usually regarded as carbon oxysulphide COS, are not materially altered by oil washing or active carbon adsorption. On the other hand little more than 20% of the organic sulphur classified as thiophene is removed in the catalytic process. Table No. 9 makes it clear(27)(28)(29).

TABLE NO. 9. Percentage Removal of Organic sulphur compounds.

COMPOUND	OIL WASHING	ACTIVE CARBON	CATALYSIS.
Mercaptans	70%	40 - 80%	92%
Thiophene	87%		23%
Carbon disulphide	90%		96%
Volatile Compounds	Nil	Nil	93%
Over-all reduction	73%	40 - 80%	87%

The oil washing and active carbon processes are seldom, if ever, operated for the sole purpose of sulphur removal, but rather for benzole recovery. With the latter the degree of desulphurisation is incidental although the former may be operated with a higher oil flow than is required solely for benzole removal, with the intention of removing carbon disulphide and improving the overall removal of sulphur compounds.

(1) OIL WASHING.

A preliminary examination(28) of the possibility of removing sulphur compounds was begun in 1927 and the results of this were described by Hollings and Hay(30). The theoretical treatment followed from a simplified application of Raoult's Law to a counter-current washing operation, in which a number of solutes might be absorbed simultaneously. It was suggested that the quantity of solvent required to wash a given solute from the gas would be proportional to the vapour pressure of that solute in the pure liquid form. Since the vapour pressure of carbon disulphide is four times as great as that of benzene at the normal washing temperatures, the quantity of wash oil required should be four times as great as that required for complete extraction of benzole. Conversely, in a normal benzole plant the quantity of oil used is only sufficient to remove about one quarter of the carbon disulphide in the gas.

In 1928, Dawson(31), published an account of a theoretical analysis of the absorption problem, based on the same assumption as to the validity of the Raoult's Law, and curves were given showing the minimum quantities of oil which would have to be circulated in order to effect complete removal of carbon disulphide and of thiophene respectively, at different temperatures; and with oils of different molecular weights. The minimum circulation of oil required at a normal washing temperature of 70°F was given as between 24 - 36 gallons per 1,000 cu.ft. of gas, according to the molecular weight of oil, but in practice Dawson was able to circulate a maximum of only 11 gallons per 1,000 cu.ft. Under these circumstances it proved impossible to test the theory, and as might be expected, the efficiency of sulphur removal was not high, 35 gr. of sulphur/ 100 cu.ft. being left in the gas.

In one process developed in the Laboratory (B.P. 452,162)(32) gas is washed with a relatively large volume of oil in order to remove carbon disulphide from the gas. The oil is then regenerated by treating it with a solution of alcoholic caustic soda. As a preliminary step, however, it is necessary to remove carbon dioxide which is dissolved in the oil in order to avoid an excessive loss of the alcoholic caustic soda. In this process carbon disulphide is removed from the gas without any substantial removal of benzole as the wash oil becomes saturated with hydrocarbons. It appears, however, that the process would be rather expensive in large scale operation and there might be the difficulty in avoiding the formation of unpleasant by-products.

(2) ACTIVE CARBON PROCESS.

The active carbon adsorption process as installed in this country, was designed to yield benzole of the highest purity, and sulphur removal was an incidental feature(28)(33)(30)

The early experimental work of the Gas Light and Coke Co. in connection with the active carbon process has been described by Pexton and Chaplin(37). The benzole yield commenced at 20% by weight of the carbon and gradually fell to 4% after 1500 saturations. The steam consumption started at 2.2 lb. per lb. of benzole but steadily increased, so that the average was 3.32 lb. per lb. of benzole for the whole period. The efficiency of benzole extraction varied between 93% and 95%. The carbon was replaced at the end of this period, so that the equivalent consumption of carbon was 6.8 lb. per 1,000 lb. of benzole.

In respect of removal of organic sulphur(30) from gas, the active carbon process is much more efficient than the oil-washing process. In the early part of the absorption period practically the whole of both the thiophene and the carbon disulphide are removed, but as saturation of carbon is approached, the more volatile compounds are displaced. In one of the runs described by Hollings and Hay(30), the inlet gas contained 28 gr. of S/100 cu.ft. All this was removed during the first five hours, but towards the end of the run the sulphur content at the outlet rose sharply, and finally just exceeded that at the inlet. The average sulphur content of the treated gas for the whole period was 7.0 gr/100 cu.ft., giving an extraction extraction efficiency of 75%.

COMPARISON OF PRECEDING TWO PROCESSES.

Considering together the preceding two processes, a considerable number of plants of these types were installed between the years 1930 - 42, but since that time, few new plants have been commissioned due to the continuing downward trend of benzole recovery profits, since the end of the second World War.

Existing plants(15) are mostly capable of removing between 85 - 90% of the thiophene and carbon disulphide. Unfortunately benzole plants have an intermittent record of service, being bypassed whenever maximum thermal output is required or when benzole recovery becomes excessively non-profitable. Also many plants have been out of action for years because some post-war coals, when carbonized in certain types of vertical retorts and with maximum steaming rates, yield gas of insufficiently high calorific value above the level of 500 B.T.U./cu.ft. to permit full extraction of benzole. The operation of carburetted water gas plant to make high calorific value gas to enrich the fully extracted coal gas is possible, but generally is not applied either because of the greater cost of C.W.G. per therm or because of the restriction that would be imposed on the flexibility of operating the plants independently. A method by which some degree of sulphur removal can be maintained through active carbon or oil washing plants when calorific value limitations exist, involves returning a large proportion of the benzole to the gas after fractional distillation to remove the bulk of carbon disulphide. Because, however, the thiophene cannot be completely separated from the benzole returned to the gas, the overall reduction of sulphur achieved is not likely to exceed about 50%. A more attractive method to restore or even increase further, the calorific value of the stripped gas is to replace the benzole by butane/propane or by another rich gas produced from a low sulphur content oil.

By this method, the sulphur content of the stripped gas, assessed in terms of its heat content, may be further reduced.

Although, as already stated, the efficiencies of sulphur removal achieved by the active carbon and intensive oil washing processes when operated normally, are the same, the fundamental physical principles that determine these performances are completely different. The oil absorption and stripping process is such that, if it were desired to reduce the sulphur slip below 30%, when treating a normally constituted gas, this would add considerably to the capital cost of the plant, and the expenditure of steam will be greatly increased. In the case of the active carbon adsorption process, the consumption of steam for heating and for stripping does not increase very much with increase in extraction efficiency. For this reason, it is possible to employ the active carbon process to reduce the sulphur content of a normally constituted gas to around 20%. This can be achieved by shortening the adsorption cycle time so that gas does not continue to flow through the carbon bed after the beginning of the sulphur break point. This possibility was proved on a large plant at Beckton(15), when an extraction efficiency of 80% was obtained.

(3) CATALYTIC CONVERSION.

Catalytic processes(34) used in sulphur removal from gases differ from previously discussed processes of oil washing and active carbon adsorption in that the organic sulphur compounds are not physically removed from the gas stream but rather, converted to compounds which are either not objectionable and, therefore may remain in the gas stream or which can subsequently be removed with greater ease than the compounds originally present.

While, in the first case, the catalytic conversion step constitutes the entire purification operation, additional steps such as absorption or adsorption are required in the alternative case.

When a fuel gas is passed through a bed of catalyst of a suitable type at a higher temperature (say 300 - 400°C), the organic sulphur compounds may be decomposed by one or more of three separate reaction mechanism given below :

(1) Oxidation
(2) Hydrogenation
(3) Hydrolysis.

(1) <u>OXIDATION.</u>

Oxidation(35)(36) can happen on a nickel-subsulphide catalyst as follows:

$CS_2 + 3O_2 \qquad 2SO_2 + CO_2$ ------- (1)

SO_2 may undergo hydrogenation as below :

$SO_2 + 3H_2 \qquad H_2S + 2H_2O$ ------- (2)

Reaction (1) takes place in the presence of oxygen which is either present in the gas being treated, or is bled in from outside. Reaction (2) takes place when oxygen concentration is very low.

(2) <u>HYDROGENATION.</u>

Some catalysts based on copper-chromium(14) and molybdenum etc. hydrogenate the organic sulphur compounds to hydrogen sulphide. Following reactions take place :

Mercaptans $RCH_2SH + H_2 = RCH_3 + H_2S$ ....(3)
Thiophene $C_4H_4S + 4H_2 = C_4H_{10} + H_2S$ ....(4)
Carbon disulphide $CS_2 + 2H_2 = C + 2H_2S$ ....(5)
Carbon oxysulphide $COS + H_2 = CO + H_2S$ ....(6)

(3) HYDROLYSIS.

Copper-chromium and molybdenum type catalysts, when operating on average fuel gases to which water vapour has been added, promote the hydrolysis of two major constituents CS_2 and COS, as below :

$$CS_2 + 2H_2O = CO_2 + 2H_2S \quad \text{....(7)}$$
$$COS + H_2O = CO_2 + H_2S \quad \text{....(8)}$$

Catalytic processes came into prominence on commercial scales in the 1930's only, but the first catalytic process was described by Carpenter(38) in 1914 and is called the Carpenter Evans process. In this process broken fire-brick impregnated with nickel chloride was used as the catalyst. The active catalyst was - $Ni_3 S_2$ nickel sub-sulphide.

A detailed discussion of catalytic methods will be given later on, but at this stage it should suffice to say that each method discussed above has its own merits. While active carbon adsorption and oil washing are done primarily with a view to winning benzole from town gas, catalytic decomposition is employed solely for the removal of organic sulphur, especially where the aim is to purify gas to very fine limits. There appears to be a lot of scope in using catalytic decomposition techniques, where debenzolisation is of secondary importance.

It is common experience that during hydrogenation on a suitable catalytic surface, mercaptans and carbon disulphide are quantitatively decomposed to hydrogen sulphide and other products, while carbon oxysulphide rapidly establishes the following equilibrium in the presence of carbon monoxide :

$$COS + H_2 \quad = \quad CO + H_2S \; ..... \quad (6)$$

Decomposition of COS in the presence of hydrogen is quite high between a temperature range of 350 - 400 °C. A single-stage treatment will eliminate about 95% of COS. If complete elimination of COS is the goal, then removal of H_2S from the sphere of action, and treatment of the remainder of COS on another catalytic stage will almost completely eliminate this compound.

Thiophene is known to be quite stable towards catalytic hydrogenation, but modern catalysts which possess very high hydrogenating potential, can be used for breaking thiophene molecule as shown in equation No. 4.

Above is given a comparison between the three important methods of sulphur removal. Each method has been taken to commercial scale and proved successful. The tendency, nowadays, is to find out selective and powerful catalysts for the complete elimination of organic sulphur so as to reach synthesis purity limits and the next chapter is devoted to discussion on the historical development of catalytic removal of organic sulphur.

A Survey of the Catalytic Processes.

High temperature processes for the elimination of organic sulphur compounds from gas have a long history of 150 years. According to Carpenter(38), it was Heath, who in 1806 patented the first proposal for the purification of gas by heat. In the first place, he proposed to add alkalis or alkaline earths to the coal in retort and distil both together. His second suggestion was to pass the crude gas over alkaline earths or certain metals or their oxides, previously laid in an iron tube or other vessel and exposed to a furnace.

In 1818, one G. Palmer took patents on a process in which he passed crude coal gas through heated tubes containing iron, oxides of iron or iron-stone. He claimed that the gas thus treated affords no disagreeable smell during combustion.

Lowe, used iron turnings in the secondary retorts and S. Palmer used a simple arrangement of horizontal iron pipes heated in a furnace. Palmer's method was referred to by Peckston in 1819 as working on a small scale at Macclesfield.

It was first pointed out in 1820 by Brande, that sulphur in purified coal gas existed probably as bisulphide of carbon, and he also predicted that Palmer's process could not succeed because of deposition of carbon and the consequent loss of illuminating power.

In 1832 Mathews referred very fully to the proposals of Palmer and others.

In 1842 Faraday and Brande investigated the damage to the Library of the Athenaeum Club and reported that sulphur combustion products were responsible for the damage.

In 1852 Letheby reported on the desirability of purifying coal gas from sulphur so that it could be employed to any extent as a source of light or heat. Thompson at the same time passed the gas free from hydrogen sulphide over lime heated to a dull red heat or lower, or a small piece of brick or pumice stone previously steeped in a solution of the chloride of platinum. He also considered that it was not even requisite to remove the sulphuretted hydrogen.

In 1860 Bowditch took a patent on his process, in which he proposed to pass the gas, (first purified in the cold in the ordinary manner), through heated clay, oxide of iron or lime, the temperature found most efficient being between 140 - 215°C. By these means the sulphur compound found in the ordinary purified gas decomposed to hydrogen sulphide, which was then removed in the ordinary way. On increase in cost due to this extra purification he reflected that it could be included in the price and expected that consumers would pay 4s.2d. extra a year, rather than have sulphur. He also expected that sulphur free gas would be used more freely, and the extra consumption would in the long run more than counterbalance the extra cost, a belief which is shared even today. Unfortunately, his belief was not shared by many of his contemporaries. Kitt, in 1861, reported that heating a gas of 14 candle power at 150°C in contact with broken fire brick reduced the C.P. to 8.5, while two subsequent heatings brought it down to 5.75. C.P.

Conclusions of the same character were arrived at by Barlow and Ellisen in 1863. Ellison concluded that the remedy was to be found in the careful selection of coal.

Eveleigh, in 1869, proposed to carbonize coal at a low heat and afterwards effect a second distillation of the product in another retort. A make of 11,000 cu.ft. of gas per ton was claimed with a sulphur content of 7 gr./100 cu.ft. This process was taken to commercial scale but results were not promising.

In 1870 Harcourt proposed to decompose the sulphur compounds other than hydrogen sulphide by placing a mass of iron turnings or wire in the mouth-piece of each retort, or, alternatively, conducting the gas before reaching the purifiers through a system of tubes heated to redness and partially filled with suitable surface presenting material. A year later Evans suggested admitting a jet of super-heated steam to the ascension pipes. These processes were taken to a large scale, but abandoned because of the expense, danger, cost, loss of gas or loss of illuminating power.

In 1878, Quaglio and Vessmann, of Stockholm, proposed the use of clay balls impregnated with chlorides of different metals or the metals themselves. They proposed practically all the catalytic metals and specified 216 - 288°C as working temperatures. Wear and tear of the catalytic tubes made of cast iron were the cause of the failure of these processes.

Williams in 1883 made long series of experiments to find better catalysts.

In the same year, the so called "Cooper" process of mixing lime with coal before carbonizing was tried but later on discontinued. A little earlier, Lugo and Less in Germany, and Wright in England proposed the admixture of 2½% air prior to heating to between 200 - 260°C, but the idea did not progress further than the experimental stage.

Carpenter(38) in his paper also makes mention of another contemporary process called Guillet's process. Guillets process is based upon the well-known reaction, that in the presence of water carbon disulphide yields H_2S as below :

$$CS_2 + 2H_2O = CO_2 + 2H_2S$$

This reaction, hardly perceptible when iron is not present and at ordinary temperature, assumes greater importance and technical rapidity when temperature is raised. For the reaction to be complete it is necessary that the sulphuretted hydrogen is continually absorbed and for this purpose iron oxide can be used. Tests in the laboratory made by Guillet show that gas of 16 gr./100 cu.ft. can be purified to the extent of 4.3 gr.S/100 cu.ft. The temperature of reaction is 130°C and thus seems to be less heavy on fuel costs.

Mechanical and chemical engineering problems prevented commercial application of such processes at these early days, and the more recent developments(39) of commercial processes have been the work of engineers, rather than of chemists. Pabast(48) applied the principles of blast-furnace stove operation for supplying heat to the gas, and a commercial plant treating about 4 million cu.ft. of gas per day was built and operated in 1908.

In this system two checker-brick packed stoves were used. During this time the gas was being heated by passing through one of the stoves, the other stove was off the line and was being heated by producer gas. By passing the gas alternatively through one stove and then through the other, it was heated to about 650°C and was then passed through purifier boxes to remove the hydrogen sulphide formed. The process reduced the organic sulphur from 59 grains to 17 gr./100 cu.ft., a reduction of about 71%.

Recent Catalytic Conversion Processes.

The Carpenter-Evans Process.

The first catalytic process used commercially for the removal of organic sulphur compounds from manufactured gas was developed in England by Carpenter and Evans(49)(50)(51). The catalyst used in this process is a sulphide of nickel, shown by Evans and Stanier(52) to be nickel subsulphide of the formula Ni_3S_2. This catalyst is prepared by soaking broken fire-brick in a solution of nickel chloride and then heating the fire-brick to 930 °F. The Nickel oxide thus obtained is subsequently sulphided with the hydrogen sulphide contained in crude coal gas. The catalyst is most active at 800 - 850 °F and loses its effectiveness quite rapidly at lower temperatures. The basic reaction occurring in the process is hydrogenation of the organic sulphur compounds, primarily carbon disulphide, to hydrogen sulphide.

$$CS_2 + 2H_2 \quad = \quad 2H_2S + C$$

Since the above reaction yields carbon, which is deposited on the catalyst surface, periodic regeneration of the catalyst is required. The presence of appreciable quantities of hydrogen sulphide in the inlet gas decreases the efficiency of organic sulphur conversion(51).

The process operates at essentially atmospheric pressure and temperatures between 790 - 840 °F (420 - 450 °C). The operation begins with preheating the gas, first by heat-exchange with product gas and then in a coke-fired heater, almost to reaction temperature before admission to the catalyst chamber.

After passing through the catalyst contained in steel tubes, the gas is heat-exchanged with the inlet gas and cooled, and the hydrogen sulphide formed in the converter is removed in iron oxide purifiers. Regeneration of the catalyst is accomplished by contact with air at a temperature somewhat below that used during conversion. Operating data given by Evans(51) indicate a typical organic-sulphur removal efficiency of about 80% (from 35 to 7.5 gr.S/100 cu.ft.), and a catalyst life (between regeneration) of 30 - 35 days. No appreciable change in gas properties after the treatment takes place. Cost of removal figure was about 0.3d. per 1,000 cu.ft. per day until 1939. Experience with this process showed that certain modifications were desirable, for example carbon deposition could be reduced by operating the catalyst bed at a lower reaction temperature, with a catalyst of increased activity. The process, however, has not been accepted widely, primarily because of its high fuel and maintenance cost.

A modification of Carpenter Evans process, used for the removal of small amounts of organic sulphur compounds (8 gr.S/100 cu.ft.), from coal gas is described by Trutnovski(53). In this process nickel turnings are used as the catalyst. Approximately, 90% conversion of carbon disulphide to hydrogen sulphide is claimed at operating temperature of about 860 °F (460 °C) and a space-velocity of 2,000 v/v/hr. The catalyst is regenerated periodically by air blowing.

GAS LIGHT AND COKE COMPANY'S PROCESS.

This was the next process to be tried in England on a commercial scale. This process dates from 1938(28)(35)(54).

The catalyst employed is again nickel subsulphide, but on a china clay base. The catalyst operates at a temperature between 230 - 360°C. The inlet gas is preheated by heat exchange with treated gas and additional heat is produced by combustion, on the catalyst, of hydrogen and oxygen in the gas. Regeneration of the catalyst is necessary after 90 - 120 days. The organic sulphur compounds are oxidized in this process into sulphur oxides, although small amounts of hydrogen sulphide are also produced. After purification of the gas involves washing with soda solution to remove sulphur oxides, followed by either iron oxide secondary purifier or a liquid washing process based on alkaline(55) Zinc reagent to remove the trace of hydrogen sulphide. This process was operated on a scale of 1.5 million cu.ft. per day at Harrow for several years and gave results as shown below :

TABLE NO. 10. Removal of Individual Sulphur Compounds by G.L. C.C. Catalytic Process.

1	2	3	4
IMPURITY	INLET S	OUTLET S	REMOVAL
	gr.S/100 cu.ft.	gr.S/100 cu.ft.	%
Thiophene	10.2	10.2	0
Carbon disulphide	16.3	0.9	95
Carbon Oxysulphide	7.2	2.5	65
TOTAL	33.7	13.6	60

Thus it is clear that thiophene is not at all touched, while the overall removal is only 60%,

The catalyst consists of nickel subsulphide supported on $\frac{1}{4}$ x $\frac{1}{4}$ in. china pellets fired at 1650°F (900°C). The pellets are impregnated by boiling in a solution of nickel sulphate, followed by drying at 750°F (420°C), and sulphiding with hydrogen sulphide contained in the coal gas. This method of preparation gives a catalyst of large surface area containing approximately 8% nickel subsulphide.

The kinetics of oxidation of carbon disulphide and carbon oxysulphide was investigated by Crawley and Griffith(36) who found that carbon disulphide is chemisorbed and oxidized by impact with oxygen, while carbonyl sulphide reacts by collision with chemisorbed oxygen. The following two reactions are also catalyzed by nickel subsulphide :

$$2H_2 + O_2 = 2H_2O$$

$$SO_2 + 3H_2 = H_2S + 2H_2O$$

The first of these reactions is strongly exothermic and provides heat for internal temperature control of the process. At normal operating temperatures the rate of reaction is proportional to the oxygen concentration of the gas. The oxidation of organic sulphur compounds occurs in spite of the presence of high concentrations of hydrogen which would tend to reduce sulphur dioxide. This reaction only takes place to an appreciable extent at very low oxygen concentrations.

The catalyst is fouled by[(56)] deposition of gummy and carbonaceous material, the rate depending on the operating temperature. Fouling of the catalyst inhibits the reaction of hydrogen sulphide with oxygen, and when the carbon content of the catalyst reaches approximately 6% at operating temperature of about 700°F (370°C) or 2% at an operating temperature of 480°C, regeneration becomes necessary. At the higher temperatures the deposits are carbonized materials, which are less objectionable. It is, therefore, desirable to operate the process at the highest possible temperature. Fouling is caused by picrates, acetylene, diolefins, and cyclopentadiene, while hydrogen cyanide and nitric oxide are not objectionable.

Thiophene is not decomposed over the nickel subsulphide catalyst although free nickel catalyzes oxidation. However, the formation of free nickel from the catalyst is inhibited by certain compounds present in coal gas.

THE PEOPLES GAS COMPANY PROCESS.

This process was developed by the Peoples Gas Company of Glassboro, New Jersey for removing a sufficient amount of organic sulphur compounds from town gas to make it suitable for use in a glass-annealing furnace at a New Jersey glass factory. The process which is described by Menerey(57) and Darlington(58), employs a catalyst consisting of magnesium sulphate and zinc oxide and is stated to be capable of reducing the organic sulphur content of town gas from 15 grains to less than 3 grains/100 cu.ft.

In the installation described, the gas to be purified is first preheated to about 800°F in a preheater which is located in the annealing furnace. It then passes downwards through four layers of catalysts, each 1ft.thick. The catalyst vessel consists of brick-lined, 24 in. standard steel pipe insulated on the outside. The gas, which emerges from the bottom of the catalyst vessel at about 650°F, is cooled to 100 - 150°F in an air-cooled heat-exchanger and finally freed of H_2S in an iron-oxide box. The catalyst is regenerated weekly by circulating air through the vessel for 12 hours at the rate of 8 cfm. Replacement of catalyst is usually required after six months of operation. The plant operates at a pressure of 10 psig and has an average capacity of 2,500 cu.ft. per hour, with a maximum of about 4,000 cu.ft. per hour. The entire plant is constructed of carbon steel, with the exception of stainless steel catalyst trays and supports.

THE HOLME'S MAXTED PROCESS.

This is the most extensively used commercial process for removing organic sulphur compounds from coal-derived fuel gases and was invented by W.C.Holmes and Company, of Huddersfield.

This process(29)(59-65) employs a catalyst consisting of a metal thiomolybdate which promotes conversion of organic sulphur compounds to hydrogen sulphide by hydrogenation. At present the process is used in more than 50 installations ranging in capacity from 5,000 to 4 million cu.ft. gas per day(34).

The catalyst used in the Holmes-Maxted process consists of a normal thiomolybdate. Its normal composition in the case of a bivalent metal, M, can be represented by the formula $MMoS_4$. The composition of this compound, especially its sulphur content, is subject to variation in the presence of gaseous sulphur compounds, and other constituents of coal gas at high temperatures and its ability to establish a kinetic sulphur balance under these conditions is presumed to be a major factor in determining its catalytic activity.(60).

A commercial catalyst, e.g. copper thiomolybdate, is prepared by disolving molybdenum trioxide in a 25% aqueous ammonia solution to which copper sulphate has been added. The pale blue precipitate of copper-molybdate is re-disolved by addition of a slight excess of ammonia, and this solution is then used for the impregnation of the catalyst support. Granular bauxite of 1/8 - 1/4 in. diamter is used as the carrier materials. After impregnation, the bauxite is heated to approximately 750°F in order to drive off excess ammonia and to decompose ammonium sulphate.

The catalyst is subsequently converted to copper thiomolybdate by treatment with hydrogen sulphide containing gas at temperature between 570 and 750° F(60).

The conversion efficiency of the catalyst is unaffected by fairly large variations in space-velocity. Maxted and Priestley(60) investigated space velocities ranging from 1,000 to 20,000 volumes per volume of catalyst per hour (V/V/H), with copper, tin, zinc and cobalt.thiomolybdate catalysts. The organic sulphur content of the treated gas was found to be the same during initial operation for all space velocities and to increase after passage of a given volume of gas. This indicates that the activity of the catalyst within this range of space velocities is entirely a function of the amount of carbon deposited on the surface. Space-velocities of 2,000 V/V/H are practical for large plants and up to 5,000 for small installations.

The process operates at essentially atmospheric pressure (1 - 2 psig) and within a temperature range of 580 - 720°F (300 - 385°C) with an optimum around 650°F (350°C). No benefit is obtained from operating at high pressures. The reaction temperature is maintained either by an external heat supply, or if the gas contains sufficient oxygen, by the heat of reaction liberated during conversion.

The operation of the process is unaffected by the presence of water vapour (up to 50% pf the gas volume) and ammonia (up to 700 gr./100 cu.ft.) in the outlet gas. Hydrogen sulphide in concentrations up to 200 gr./100 cu.ft. reportedly has no detrimental effect on the efficiency of the catalyst.

However, at higher H_2S concentrations and at temperatures above 700°F (370°C), carbon oxysulphide is synthesised from carbon monoxide and H_2S, resulting in less complete organic sulphur conversion.(59).

Results from the continuous operation of a plant treating about 500,000 cu.ft. per day of coal gas with a copper thiomolybdate catalyst were reported by Priestley(63) and are shown in the table given below. Also, a table is given showing the removal efficiency for individual sulphur compounds in the same installation. The plant has been operated with gas containing as much as 100 gr. H_2S per 100 cu.ft. without noticeable effect on the organic sulphur removal efficiency. Table No. 11 shows the typical removal of individual organic sulphur compounds.

Table No. 11. Typical Operating results of Holmes Maxted Process.(63)

Operating variables.	Results.
Total gas volume treated cu.ft.	198,105,000
Average daily gas volume treated cu.ft.	542,000
Fuel gas used for heating converter cu.ft.	755,000
Fuel gas used for Catalyst regeneration cu.ft.	126,000
Catalyst regenerated lbs.	10,800
Catalyst discharged from Converter lbs.	12,310
Catalyst temp. °F	680 - 725
Space velocity V/V/H	1,300 - 2,000
Pressure Drop through Catalyst in H_2O	2.8

Table No. 11. contd..

Operating variables	Results
Organic Sulphur, gr.S/100 SCF	
Inlet (average)	23.1
Outlet (average)	6.7
Oxygen %	
Inlet	1.1
Outlet	0.0
Carbon on spent Catalyst %	7.5

Table No. 12. Typical Removal of Individual Organic Sulphur Compounds.

Compound	S gr./100 cu.ft.		Removal
	Inlet	Outlet	%
Thiophene	4.5	3.6	20
Carbon disulphide	14.5	1.3	91
Carbonyl sulphide	4.1	1.8	56
Total organic sulphur	23.1	6.7	71

Wedgwood(29) reports some operating data from a plant treating 4 million cu.ft. per day of coal gas in two parallel units of equal capacity. In this installation, either the gas was heated to the reaction temperature of 590 - 680°F (310 - 360°C) by the use of external heat in a preheater, or sufficient air or oxygen was added to the gas to maintain proper converter temperature. Total sulphur removal was to the extent of 85 - 89%. An interesting result of this work is the discovery that significant amounts of ammonia are formed during conversion, presumably by direct synthesis from nitrogen and hydrogen as well as by reduction of nitric oxide. The ammonia present in the converter-outlet gas was found to promote the growth of hydrogen Sulphide generating bacteria in the iron oxide boxes and thus led to slippage of hydrogen sulphide through the beds. Removal of ammonia from the gas stream ahead of the iron oxide boxes resulted in proper functioning of these units. This experience is contrary to normal operating practices with iron oxide boxes, where a small amount of ammonia is often deliberately maintained in the feed gas to ensure proper pH of the iron oxide.

No expensive construction materials are required in a Holmes-Maxted plant. Carbon steel is satisfactory for all components with the exception of the catalyst baskets; these are constructed from either cast iron or aluminized carbon steel.

BRITISH GAS RESEARCH BOARD PROCESS.

Key and Eastwood(14) describe two catalysts for organic sulphur removal from water and coal gases, which were developed jointly by the British Gas Research Board and the University of Leeds. A composition consisting of a mixture of copper sulphide and chromium oxide, supported on active carbon was found to be quite effective for practically complete removal of organic sulphur compounds (carbonyl sulphide and carbon disulphide) from water gas.

This catalyst, which promotes primarily the hydrolysis of carbonyl sulphide, is reported to be capable of removing 98% of the organic sulphur with the concentration dropping from 15 to 0.3 gr./100 cu.ft. at a temperature of 250°C (482°F) and space velocities up to 6,000 V/V/Hr. The activity of the catalyst appears to be unimpaired by the presence of relatively large amounts of hydrogen sulphide in the inlet gas (250 gr./100 cu.ft.) and is definitely increased by the addition of steam. Removal of about 95% of organic sulphur compounds present in gas streams containing appreciable amounts of H_2S and 30% (by volume) of space velocity of 2,000 V/V/H. Multistage treatment of water gas, with hydrogen sulphide removal after each stage, results in much more complete removal of organic sulphur compounds. It is claimed that a three stage process yields a purified gas containing less than 0.002 gr.S/100 cu.ft.

The copper sulphide-chromium oxide catalyst is unfortunately poisoned by acetylenic compounds and, therefore, is not usable for treatment of coal gas, which always contains small amounts of such compounds. A process modification, applicable to coal gas treatment, consists of pretreatment of the gas with a nickel-sulphide or molylidenum sulphide hydrogenation catalyst, supported on activated alumina, for conversion of acetylenic copper-sulphide-chromium oxide preparation. This double treatment is claimed to be effective for quite complete conversion of organic sulphur compounds present in coal gas, with the exception of thiophene, which is hardly effected. The molylidenum sulphide hydrogenation catalyst alone is reportedly capable of promoting 85 - 90% conversion of organic sulphur compounds, besides hydrogenation of acetylene, at a temperature of 300° C (572°F) provided a space-velocity of 2000 V/V/H is not exceeded.

Although somewhat lower final sulphur contents in the treated gas are obtainable with the two-stage treatment, the ineffectiveness of both catalysts in removing thiophene makes the economic justification of two stage process doubtful.

THE APPLEBY FRODINGHAM PROCESS.

This process has been described by Reeve(66) of the Appleby Frodingham Steel Company. In this process, hydrogen sulphide and organic sulphur compounds are removed from coke-oven gas by absorption on iron oxide in a continuous fluidized system at a temperature of approximately 660°F (350°C). The fouled iron oxide which contains about 10% by weight of sulphur (as iron sulphide) is regenerated with air at 1110 - 1470°F (600 - 800°C) and recycled to the absorption stage. The sulphur dioxide leaving the generator is used for the manufacture of sulphuric acid. A pilot plant treating a daily volume of 2.5 million cu.ft. of gas containing 600 grains H_2S and 20 grains organic sulphur per 100 cu.ft. is described. Total sulphur removal efficiencies of 80% and 98% are obtained by use of one and two-stage absorbers respectively. The main advantages claimed for this process are low labour cost and excellent heat economy, because $\frac{2}{3}$ of the heat required is obtained by heat-exchange between the inlet and outlet gas and the remaining $\frac{1}{3}$ is provided by the hot regenerated iron oxide.

SYNTHESIS GAS PURIFICATION PROCESSES.

The processes discussed above have been mainly devised for treatment of coal based gases. But there is practically no difference between the processes peculiar to coal based gases and processes applied generally to desulphurize synthesis gases. Following is a brief description of processes which have been mainly invented for synthesis gas purification.

Iron oxide Catalysts.

Typical catalysts used in the purification of ammonia synthesis gases, for simultaneous shift conversion and conversion of carbonyl sulphide to hydrogen sulphide, contain 5 - 15% chromic oxide, besides iron oxide and a small percent of inert binder material. These catalysts promote both hydrogenation and hydrolysis of carbonyl sulphide. The extent to which carbonyl sulphide is either hydrogenated or hydrolyzed is largely determined by the simultaneously occurring water-gas reaction. If the water gas reaction is not at equilibrium, hydrogenation is predominent, while both reactions take place to about an equal extent, if the water-gas reaction is at equilibrium.

Under typical operating conditions, involving temperatures between 650 - 950°F (345 - 510°C), pressures from near atmospheric to 450 psig and space velocities from 400 - 4000 V/V/H, a shift converted outlet gas containing only a few p.p.m. of carbonyl sulphide is obtained(34). Moderate quantities of H_2S present in the inlet gas have no detrimental effect on the activity of the catalyst.

Use of iron oxide catalyst containing 6 - 7% chromic oxide, for the purification of essentially H_2S -free ammonia synthesis gas in a German installation, has been reported by Holroyd(67). It is stated that the treated gas was suitable for ammonia synthesis, indicating a residual sulphur content of only a few p.p.m.

Sands, Wainwright and Eglesen of the U.S.B.M.$^{(25)}$ investigated the suitability of an iron-oxide catalyst for the removal of organic sulphur from gases containing large amounts of carbon monoxide and hydrogen sulphide. The results from this study were quite disappointing, as it was found that the catalyst promotes the synthesis of organic sulphur compounds from CO and H_2S and that the organic sulphur content of the outlet gas is primarily determined by the CO content of the inlet gas.

Chromia-Alumina and Copper-Chromia-Alumina Catalysts.

The chromia-alumina catalyst is used for the removal of carbonyl sulphide and carbon disulphide from synthesis gases containing large amounts of carbon monoxide. The catalyst promotes selective hydrolysis of the sulphur compounds with essentially no conversion of carbon monoxide and is unaffected by the presence of H_2S in the inlet gas. Practically complete conversion of organic sulphur compounds is obtained at temperatures of 600 - 800°F (318 - 425°C), elevated pressures and space velocities of 250 - 1000 V/V/H.$^{(34)(68)}$.

A catalyst containing copper-chromia-alumina is useful for the same applications as the chromia-alumina catalyst. However, its activity is reported to be much higher, permitting operation at higher space-velocity and low temperature$^{(34)}$.

Both the chromia-alumina and copper-chromia-alumina catalysts are also effective for removing organic sulphur compounds, mainly carbonyl sulphide, from CO_2 gas streams used for dry-ice manufacture or Urea - synthesis$^{(34)}$.

Huff Catalysts. (Copper-chromium-vanadium oxides).

Huff catalysts were developed by Huff & Logan(69)(70), to promote conversion of organic sulphur compounds to hydrogen sulphide which is retained on the catalyst as metal sulphide, together with any hydrogen sulphide originally present in the gas. Thus, conversion and actual removal of sulphur compounds from the gas are effected in one operation. The catalyst has to be regenerated with air periodically to convert the metal sulphide back to the oxide.

Removal of several organic sulphur compounds from synthesis gas with Huff catalysts have been studied by Sands and Coworker(25). The catalysts consist of mixtures of copper, chromium and vanadium oxides; in some cases the vanadium is replaced by uranium. The catalysts are of four types :- fused, precipitated, precipitated on a carrier, and simple mixed oxides. A typical composition, based on the pure metal content, consists of 80 parts copper, 10 parts chromium, and 10 parts vanadium. The preparation of the various catalyst forms is described by Sands, Wainwright and Eglesen(25).

The catalysts appear to be very effective for the removal of organic sulphur compounds, especially carbon disulphide and mercaptans, from synthesis gas in the presence of hydrogen sulphide. However, thiophene is not decomposed and, if present in appreciable amounts causes catalyst poisoning. Removal of 13 - 35 gr. of organic sulphur (present as CS_2) and 150 - 300 grains of H_2S per 100 cu.ft. to yield a concentration less than 0.1 grain of total sulphur per 100 cu.ft. is reported at two operating temperatures 570 and 840°F (300 - 450°C) and a space velocity of 2000 V/V/H(25). Under these conditions, the capacity of the catalyst for sulphur is about 6 - 14% of its weight, depending upon the degree of regeneration.

The catalyst is regenerated by contact with air at approximately 850°F (450°C) and subsequent reduction with raw synthesis gas at a space velocity of 2000 V/V/H.

A commercial process using the Huff catalysts would have the obvious advantage of simultaneous removal of H_2S and organic sulphur in one step. However, the cyclic operation and the consumption of synthesis gas required for reduction of the regenerated catalyst are definite disadvantages. In addition the catalyst is ineffective for the removal of thiophene.

WORK ON PURE COMPOUNDS.

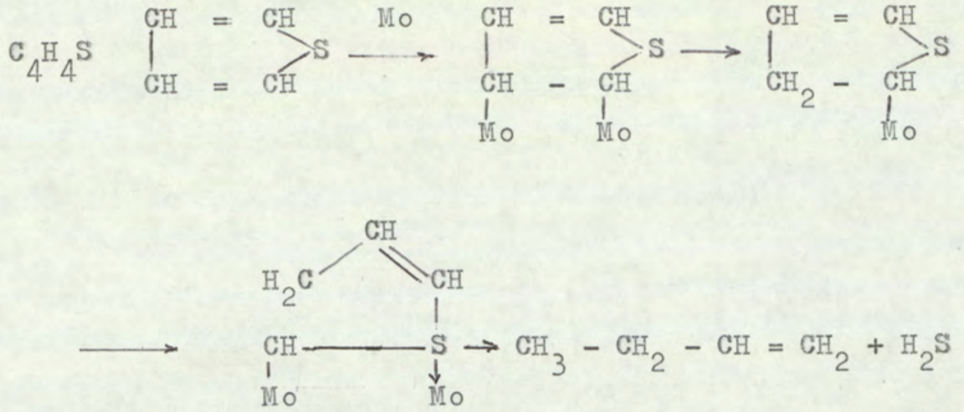
Griffiths and Coworkers(77)(78)(36), have studied the atmospheric hydrogenation of carbonyl sulphide, carbon disulphide and methyl mercaptans over nickel subsulphide catalyst. Carbon disulphide was hydrogenated over the temperature range 100 - 250 °C, the concentration of sulphur compound in hydrogen was varied between 8.0 and 48.5 mg/ft^3. At the lowest concentration in hydrogen employed, the reaction with respect to carbon disulphide approached first order. As the concentration of the sulphur compound was increased, its decomposition became less than would be predicted for a first order reaction, and, at the intermediate concentrations employed, passed through an apparent zero order stage. At higher concentrations the rate of carbon disulphide decomposition became inversely proportional to its concentration, and at the highest concentration studied, retardation was quite pronounced. Methanethiol was observed as an intermediate and probably the primary hydrogenation product.

The hydrogenation of carbonyl sulphide(77) in excess of hydrogen was found to be first order with respect to this sulphur compound between 150 - 200 °C but there was retardation at lower temperatures.

The reaction of methanethiol(77) in large excess of hydrogen was shown to be first order with respect to the sulphur compound, and to proceed at an appreciable rate in the temperature range 200 - 250 °C, where activated adsorption of methanethiol takes place. The rate of methanethiol hydrogenation was found to be slower than the rate of carbon disulphide reaction, which makes possible the isolation of methanethiol from the products of the mild hydrogenation of CS_2.

Cawley & Hall(80) found that benzenethiol was more easily desulphurized than carbon disulphide, which in turn was more easily desulphurized than thiophene in experiments at 20 atmospheric pressure, and elevated temperatures, using molybdenum disulphide as the catalyst and a high hydrogen concentration. At a contact time of about two minutes, the temperatures required for complete desulphurization were 200 °C for benzenethiol, 250 °C for carbon disulphide, and 300 °C for thiophene. It was concluded that the relative ease of desulphurization could be predicted on the basis of the nature of the reaction involved. Benzenethiol was pictured to desulphurize in one step. Carbon disulphide was thought probably to hydrogenate to methanethiol before removal of the sulphur atom, and, as described above, thiophene probably undergoes hydrogenation to thiacyclopentane followed by ring opening to form a mercaptan before desulphurization takes place. Thus it was thought; in these particular instances, that the relative ease of desulphurization was tied up with the number of steps involved in the process.

Griffith, Marsh and Newling(81) observed that thiacyclopentane could be hydrogenated more rapidly than thiophene. In the atmospheric pressure runs which were made at 200 °C with 260 p.p.m. of sulphur compound in the hydrogen, the former was 80% converted over molybdenum disulphide catalyst, while the latter was only 60% converted. Over a nickel subsulphide catalyst, a mixture of hydrogen and 280 p.p.m. of sulphur compound gave conversions of thiacyclopentane of 41% and 100% at 200 and 350 °C respectively, /o
and corresponding conversions of thiophene of 0 - 15% respectively. It was thought(81) that the more rapid decomposition of thiacyclopentane over the molybdenum disulphide catalyst might be /o
the result of only single-point adsorption on the molybdenum surface being necessary in comparison with the stated requirement of two point adsorption in the case of thiophene as follows :-



Griffith and Coworkers(81) obtained additional information on the atmospheric pressure hydrogenation of thiophene. Data obtained with the nickel subsulphide catalyst, in the temperature range 350 - 500 °C and three concentrations (206 p.p.m., 378 p.p.m. and 550 p.p.m.) of thiophene in hydrogen showed the conversion to be nearly first order with respect to thiophene. With molybdenum oxide/molybdenum disulphide catalyst, at temperatures in the range 200 - 300 °C and also three concentrations (155 p.p.m., 275 p.p.m., and 500 p.p.m.) of thiophene in hydrogen, the reaction order with respect to sulphur compound concentration was stated to be between 0.2 and 0.6. Data obtained with molybdenum disulphide catalyst, at 200 °C at thiophene concentration between 162 p.p.m. and 690 p.p.m. indicated that the reaction was approximately zero order with respect to thiophene. Griffith and Coworker(81), in their work on molybdenum catalysts concluded that the rate determining step was the activated adsorption of hydrogen on the molybdenum sulphide surface.

Key and Eastwood(14) found that significant amounts of mercaptans may be formed from hydrogen sulphide and unsaturated hydrocarbon, depending upon the temperature and catalyst used. Wedgwood(29) presents a detailed study of the side reactions occurring in a plant using the Holmes-Maxted process.

He also mentions[(29)] the unpredictable production of ammonia (reaction 14) in heat exchangers, and also production of bacteria which generate hydrogen sulphide by fouling iron oxide. Side reactions which result in the deposition of gummy matter on the catalyst are especially undesirable, because they cover the active centres of the catalyst.

From the previous discussion it is clear that organic sulphur compounds in the presence of hydrogen will be converted to hydrogen sulphide. While carbon disulphide and mercaptans are completely converted to hydrogen sulphide, carbon oxysulphide forms an equilibrium mixture. Thiophene though resistant to breakdown, can be decomposed on a molybdenum sulphide catalyst.

Thus the overall reduction of organic sulphur in coal gas, in which all the organic sulphur compounds are present, will be a function of the following variables :-

(1) Concentrations of individual sulphur compounds, and unsaturated compounds.
(2) Presence of water vapour
(3) Condition of temperature, pressure and space velocity selected and
(4) The nature of the catalyst used.

It is also evident that while carbon disulphide and mercaptans most probably will be decomposed by using one conversion stage, carbonyl sulphide and thiophene will require more than one conversion stage with intermediary absorption stages to remove hydrogen sulphide from the sphere of reaction.

Hence in work of this kind it was necessary to use a number of reactors packed alternately with conversion catalyst and a suitable absorbent which could stand the same conditions of temperature and pressure as the conversion catalyst.

For this particular work where it was decided to hydrodesulphurize the organic sulphur content of the gas to hydrogen-sulphide, it became necessary to construct an apparatus in which multistage treatment could be given. A survey of commercially available catalysts and absorbents was then made.

A SURVEY OF RECENTLY DEVELOPED CATALYSTS.

A SURVEY OF RECENTLY DEVELOPED COMMERCIAL CATALYSTS.

Modern catalysts have been developed for the hydrodesulphurization of petroleum fractions. The feed stock is vaporised at pressure, mixed with hydrogenating gas, and passed over a suitable conversion catalyst at 350 - 400 °C to convert the organic sulphur to hydrogen sulphide, which is absorbed in specially prepared absorbents like iron oxide, zinc oxide or oxides of other suitable metals.

Hydrogenating gas may be pure hydrogen stream or a recycle stream having suitable hydrogen partial pressure.

As hydrogen forms one of the most important constituents of town gas distributed at present in this country, any commercially available and suitable hydrogenating catalyst may be employed for the desulphurization of town gases. Such catalysts are often classified broadly on the basis of the Periodic Table. Suitable(72) compositions contain oxides or sulphides of Groups II to Vll, preferably in conjunction with metals of Group Vlll or with heavy metals of Groups I and II or their oxides or sulphides. Typical carriers for such catalysts are indicated to be active charcoal, fullers earth, silica gel, alumina gel, pumice, bauxite and burnt fire clay. Typical commercial catalysts of modern origin contain molybdenum, tungsten, chromium and uranium with iron, nickel, cobalt etc. and mostly supported on highly porous alumina.

Nickel subsulphide Ni_3S_2 has been used both as a hydrogenating and oxidation catalyst. But catalysts known as Nimox, containing molybdenum promoted by nickel; Comox, containing molybdenum promoted by cobalt; and other catalysts containing tungsten and nickel are rather promising for this work.

These catalysts developed by various manufacturers at home and abroad are supported on highly porous alumina and have extensively proved their usefulness in the hydrodesulphurization of petroleum distillates. A brief description of these catalysts, with their physical properties and acclaimed uses is given in the Appendix No. 3.

For the absorbents to remove the hydrogen sulphide produced over the conversion catalyst, it is necessary that they remove hydrogen sulphide quantitively at the process temperature and pressure. Compounds of metals like copper, iron, nickel, cobalt, manganese and zinc are suitable for this purpose. (Commercially available absorbents are chiefly compounds of iron and zinc.) Luxmasse containing iron oxide, and zinc oxide are freely available in the market.

In this particular work emphasis has been laid on hydrodesulphurization with a combination of Nimox/Luxmasse both manufactured in this country. This combination has been found very suitable for the purification of petroleum feed stocks and the intention was to try this combindation on town gas containing 15 - 20% carbon monoxides along with 2 - 3% unsaturated compounds. This particular brand of Nimox contained 3.5% and 10% wt./wt. of nickel and molybdenum oxides supported on alumina.

The Luxmasse which was used as an absorbent contained about 50% Fe_2O_3, the rest being silica, alumina, titania, lime and sodium oxide. It was claimed that this particular product was capable of absorbing 20% wt./wt. of sulphur.

Other conversion catalysts tried on town gas in this work were Comox, manufactured by I.C.I.; another Nimox containing 4.5% and 12% as nickel and molybdenum oxides, and a zinc oxide catalyst, again manufactured by I.C.I. and claimed to contain 93% zinc oxide.

Zinc oxide was claimed to contain more than 20% S wt./wt. when discharged after use. Zinc oxide was available in commercial form as 3/16 in. spheres. The Luxmasse is preferred over the zinc oxide for being less expensive and zinc oxide is mostly used as a catch after the Luxmasse. Zinc oxide was also claimed to be a conversion catalyst and its conversion properties were also tested.

STATE OF EQUILIBRIUM CATALYSTS.

In the case of catalysts used for hydrodesulphurization, only the hydrogen reduction equilibrium of the sulphides need to be considered in as much as these are the final equilibrium states whether metals, oxides or sulphides are the starting points. Emmet(72) has summarized these results. The hydrogen reduction equilibrium for several pertinent sulphides is given. Diagrams from Emmet(72) have been reproduced in Figure No. 9 The results are presented as the logarithm of the ratio of hydrogen sulphide to hydrogen necessary to maintain various sulphide states as a function of temperature. Results on sulphides of nickel, cobalt, iron, molybdenum and tungsten are shown. The figures indicate that, in the hydrodesulphurization temperature range, only a small fraction of 1% of hydrogen sulphide in hydrogen is necessary to convert the metals to the lowest indicated sulphides. Thus, the conversion of nickel to Ni_3S_2, cobalt to Co_9S_8, iron to Fe S, molybdenum to $Mo\ S_2$ and tungsten to WS_2 is expected, even when relatively sulphur poor stocks are hydrodesulphurized.

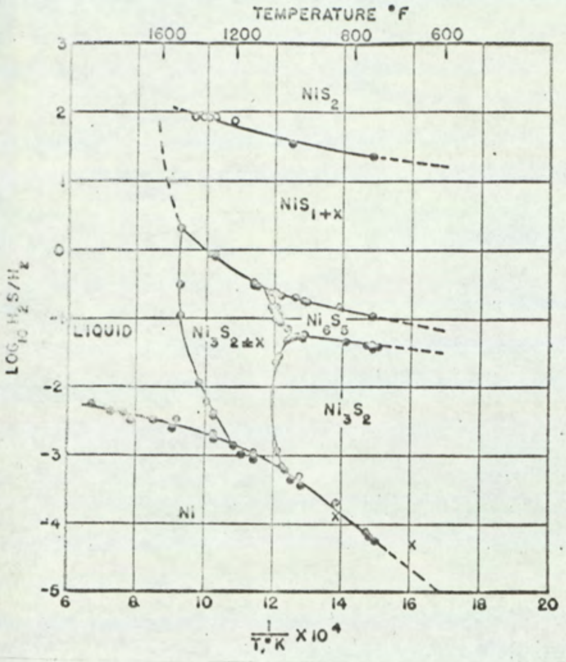
The Nimox catalysts containing nickel and molybdenum oxides would normally be sulphides as shown below :-

$$3\ Ni\ O + H_2 + 2\ H_2S = Ni_3S_2 + 3\ H_2O$$

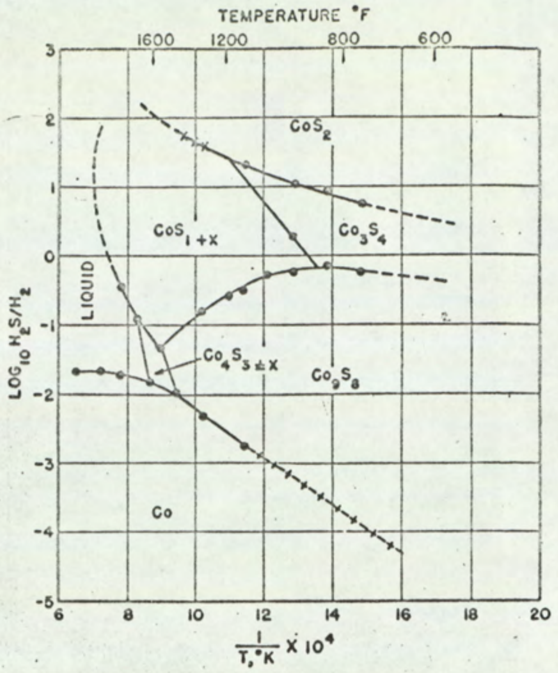
$$Mo\ O_3 + H_2 + 2\ H_2S = Mo\ S_2 + 3\ H_2O$$

The stability of the sulphided catalyst is determined by the logarithm of the ratio of H_2S to H_2, expressed as partial pressures,

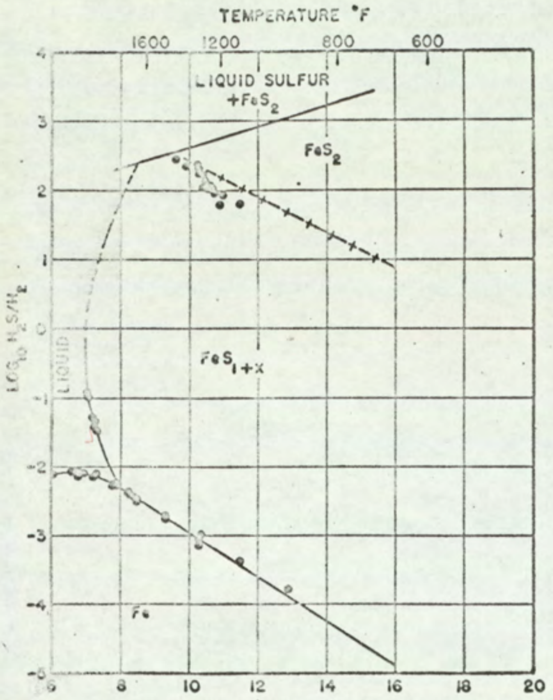
i.e. $$\frac{[H_2S]}{[H_2]}.$$



NICKEL SULPHIDES

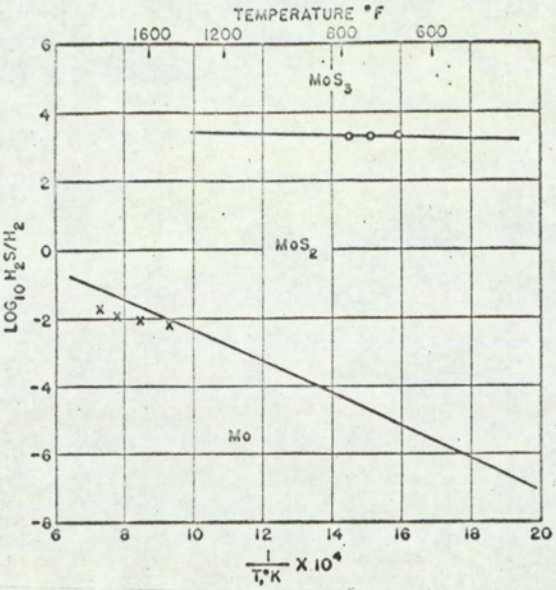


COBALT SULPHIDES



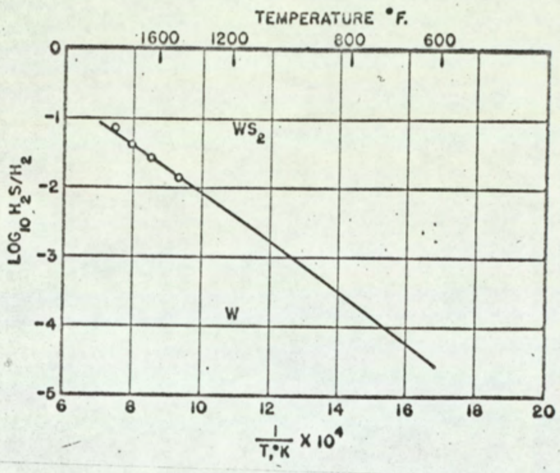
IRON SULPHIDES.

FIGURE 9. HYDROGEN REDUCTION EQUILIBRIA OF VARIOUS SULPHIDES. (REPRODUCED FROM REFERENCE 72.



MOLYBDENUM SULPHIDES

FIGURE 9. CONTINUED



TUNGSTEN SULPHIDES.

At an operating temperature of 350 °C or 600 °F (approximately) Ni_3S_2 and $Mo\ S_2$ are the stable phases for ratios from -4.3 to -1.3 and from -5.0 to +3 respectively. But in this work, where H_2S concentrations of 500 p.p.m. to 0.05 p.p.m. (i.e. -7 to -3) may be encountered, it is quite possible that only metalic states can exist at the lower limit, and as nickel is known as a synthesis catalyst, methanation may take place with the development of hot spots in the reactor bed. In that case it will be advisable to work at lower temperatures. It is also clear that at 350 °C, with H_2S concentration of 0.5 p.p.m. nickel would exist in pure metalic state, while molybdenum would be still as $Mo\ S_2$ and this would be converting organic sulphur to H_2S. Among the conversion catalysts, thus catalysts containing molybdenum, have the advantage that they can be used for very fine purification, for other catalysts it will be desirable to lower the reaction temperature.

Considering Luxmasse now, its iron content would exist as $Fe\ S_{1+x}$ only at 350 °C if the H_2S concentration is more than 5 p.p.m Hence to obtain very fine purification, either the temperature has to be lowered or hydrogen concentration has to be lowered. As in town gas, 50% of hydrogen content is normally encountered, evidently for fine purification iron oxide would give better results if a lower temperature is used.

When we consider a multistage process, in which a conversion stage is followed by an absorbent stage, then as the gas passes through the latter stages, its H_2S content is likely to fall below the critical concentration, with the consequent danger of the pure metal being formed. Hence no advantage of the process can be taken by increasing the number of stages, beyond those absolutely required.

Another aspect of absorption of H_2S in Luxmasse at higher temperature is the presence of water vapour in the gas stream.

Hydrogen sulphide reacts with magnetite to form ferrous sulphide as shown below :-

$$Fe_3O_4 + H_2 + 3\ H_2S \quad = \quad 3\ FeS + 4\ H_2O$$

The absorption reaction is reversed by water vapour, causing a slip of hydrogen sulphide. The logarithm of the equilibrium constant for this reaction are :-

at 300 °C = 10.85 and
at 400 °C = 9.62

Assuming H_2S slip = 1 p.p.m. and
H_2 = 50%

then the equilibrium concentration of water vapour between 300 - 400 °C is approximately 1%. Evidently a concentration of water vapour of more than 1% in the gas stream will cause a slip of H_2S from the partly sulphided Luxmasse. Hence presence of water vapour from this point of view is undesirable.

EXPERIMENTAL STUDY OF THE REMOVAL OF ORGANIC SULPHUR COMPOUNDS FROM TOWN'S GAS.

Experimental study of the Removal of Organic Sulphur from Town's Gas.

The final removal of organic sulphur from town gas depends upon the following factors :

1. The nature of the conversion catalyst.
2. The efficiency of the absorbing material.
3. The concentration of individual and total organic sulphur compounds.
4. Concentration of hydrogen, carbon-monoxide and carbon dioxide
5. H_2/CO Ratio.
6. Concentration of the water vapour in the gas.
7. Pressure.
8. Temperature.
9. Space-velocity
10. The number of stages.

In the succeeding pages a detailed account of the experimental results is given.

Note 1. Concentration of total and individual organic sulphur compounds is given in p.p.m. equivalent to H_2S.

Note 2. H_2S out means H_2S coming out of a converter.

Note 3. H_2S slip means H_2S slipping from the absorber.

APPARATUS.

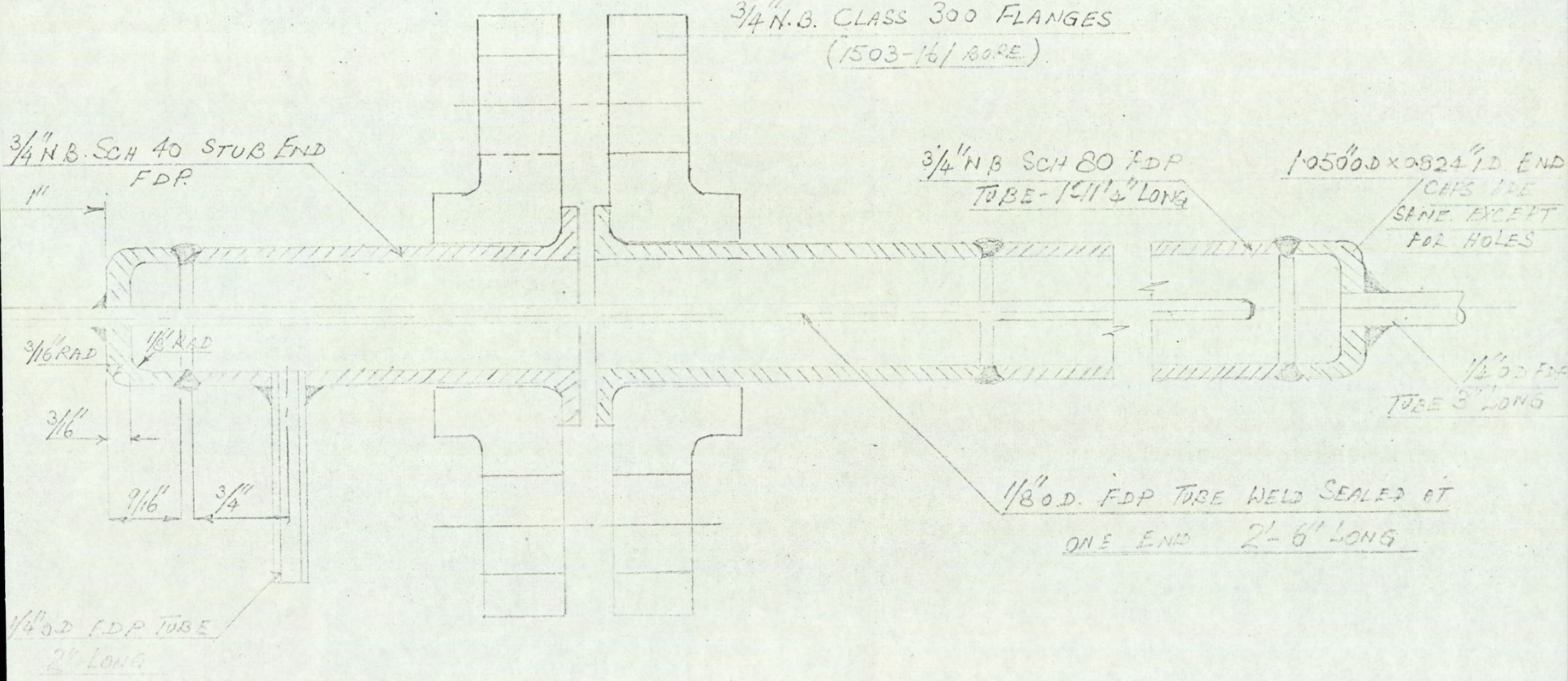


Figure 2. REACTOR SECTIONAL DIAGRAM

WELD PREP - 1/32" ROOT 37½° CHAMFERS
3/32" TO 1/8" GAP
ALLOW 1/64" CLEARANCE ON TUBE CONNECTION

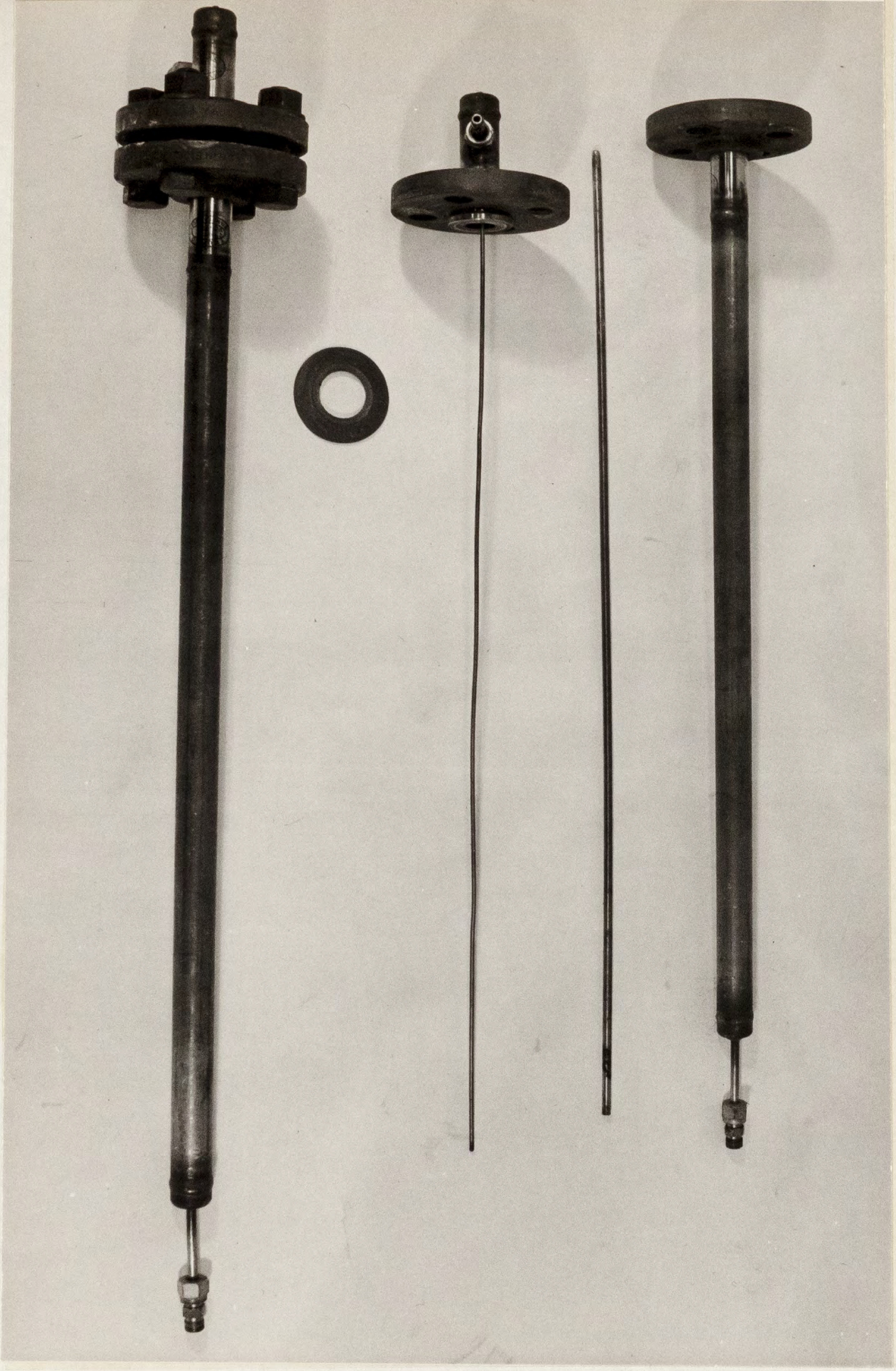


Figure 3. Photograph of the Reactor showing its Components.

Apparatus.

To study these variables a six-stage plant was constructed. It consisted of six reactors, which could be alternately packed with conversion catalyst and iron oxide, both suitably graded. These reactors were $26\frac{1}{2}$" approximately in length and 0.742" i.d., made of stainless steel (F.D.P.) pipe of 0.154" thickness. In these reactors, treatment of town gas could be carried out conveniently at 300 - 500 °C and up to a pressure of 350 psig. A thermowell was provided in each reactor, made of 1/8" o.d. stainless steel tube and running along the axis of the reactor tube. In the thermowell a 1/16" NC/NA thermocouple could be inserted. This thermocouple could be adjusted at any position along the axis of the reactor. A 1/4" o.d. S.S. tube sealed at one end, was placed in the reactor, just before it was packed. Its function was to house the thermowell in the packed reactor. (See figures 2 and 3).

These reactors were placed in individual furnaces, heated electrically. Each furnace had three elements wound on a silica tube. These three elements consisted of one central winding running along the whole length of the silica tube and two end windings for compensating the heat losses at the two ends of the furnace. All these windings were separately controlled by variac transformers.

Temperatures were measured separately with a temperature indicator fitted with a 6-point multiple switch and also recorded on an Electroflo Recorder.

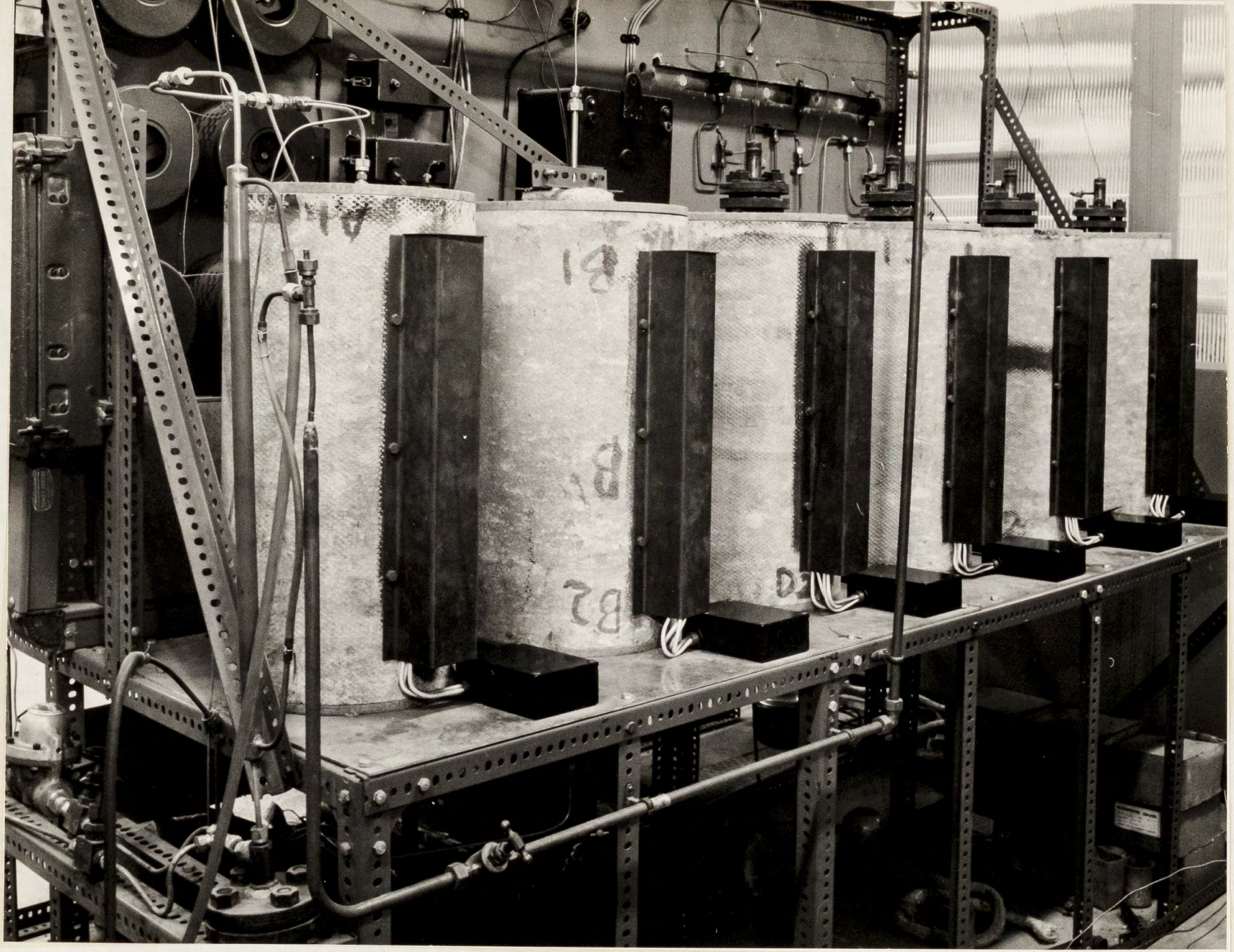


Figure 4. Photograph showing Furnaces.

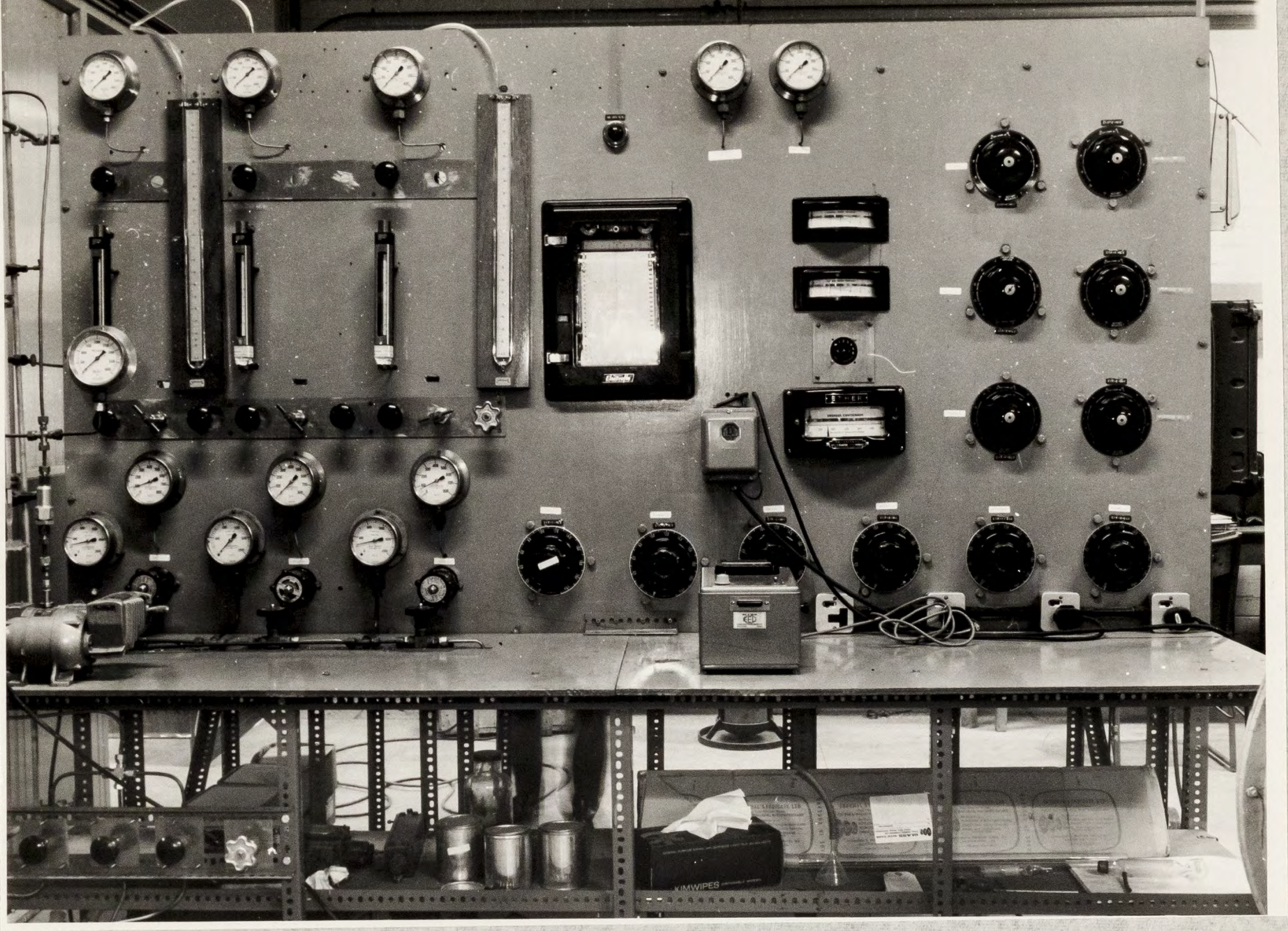


Figure 5. Main Instuments Panel.

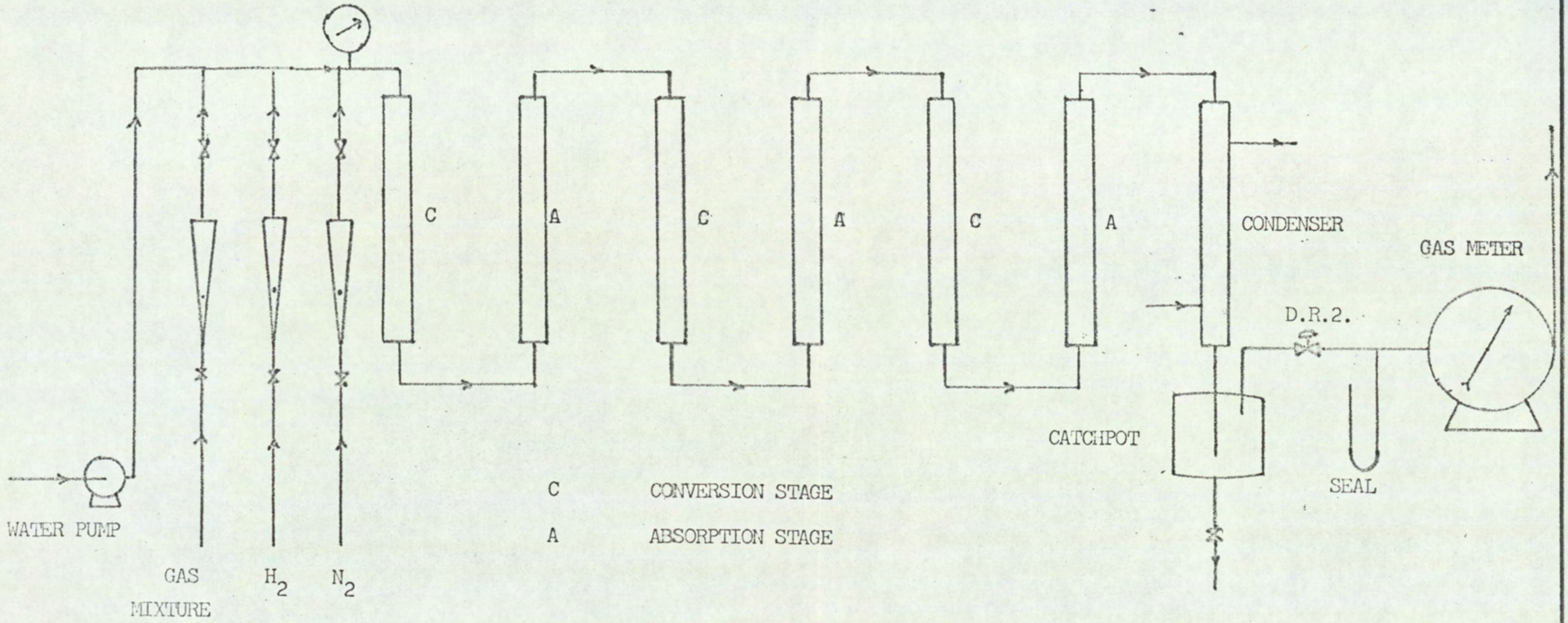


Figure 6. PROCESS FLOW DIAGRAM

Three flo-rators were provided, capable of being independently connected to three different sources of supply. Pressure on the inlet side is governed by Hale Hamilton L15 or L16 type pressure controller, while the pressure on the outlet side is controlled by Hale Hamilton D.R.2 type outlet pressure controller. The outlet gas was reduced to ambient pressure and could be metered with a wet type gas meter. Figures 4 and 5 show respectively the furnace with reactor in, and the main panel on which instruments were placed.

A D.C.L. metering pump was used for metering requisite amount of water going through the reactor. Figure No. 6 shows the process flow diagram.

All connections were made in stainless steel tube.

Sometimes, when higher flows were required, then lengths of 1/4" o.d. or 3/8" o.d. tubes were used in place of the main reactor.

Experimental Techniques.

(A) Experiments were to be carried out on (a) synthetic mixtures containing CO, H_2, N_2 and one organic sulphur compound at one time, and (b) on town gas.

All gases were procured from the British Oxygen Company in their high pressure stock cylinders. Samples of COS were obtained from Matheson Company.

(B) For preparing synthetic mixtures, a suitable rig was prepared. The stock cylinder in which the mixture was to be prepared was evacuated first and then pressurized to calculated pressures with individual gases to prepare the wanted mixture.

(C) Packing of the Reactors:

Catalyst or absorbent (Luxmasse) was first graded in size, and the requisite quantity of the sample weighed. A 1/4" o.d. tube was then placed in position and the annular space of the reactor was then packed with alumina/catalyst/alumina in such a way that the catalyst bed was in the middle of the furnace.

Normally, catalyst was crushed in a ball-mill and graded between 1/16" - 1/32" particle size. A six-inch bed was usually packed.

Analytical Techniques.

It was necessary to know the composition of the inlet and outlet gases as regards their permanent constituents like H_2, O_2, N_2, CO, CH_4, CO_2 etc. and their hydrocarbon constituents like C_2H_4, C_2H_6 and C_3H_8 etc. For this purpose a Beckman GC - 2 Gas Chromatograph was procured. Permanent constituents were analysed on 13 X molecular sieve column and CO_2, C_2H_4, C_2H_6 etc. on silica gel column to find out CO_2, unsaturated compounds and oxygen.

Total sulphur in the gas was analysed by mixing the gas with excess of hydrogen and passing it over a hot platinum spiral at 800 - 900 °C. H_2S thus produced was analysed in two ways.

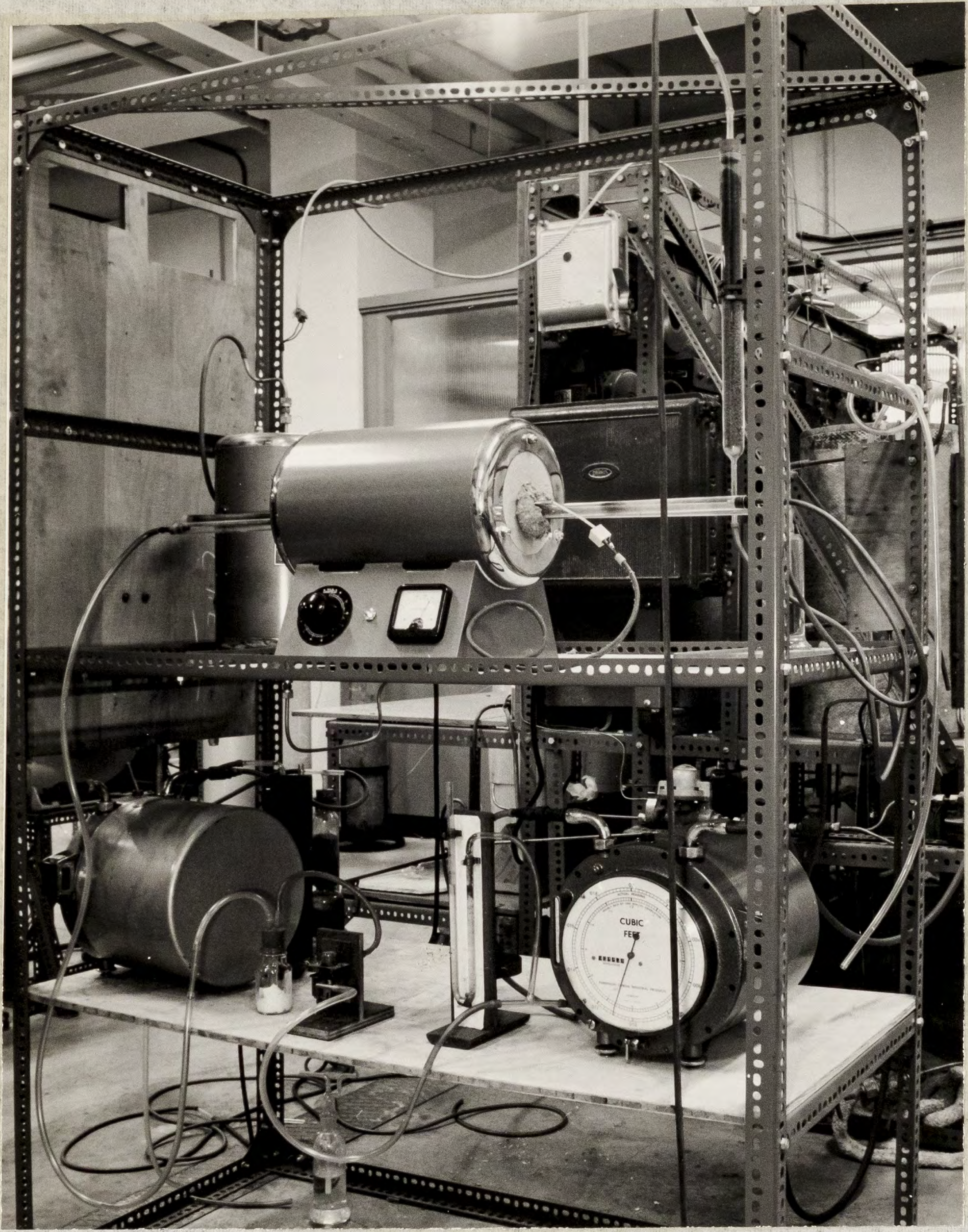


Figure 7. Platinum Spiral Arrangement.

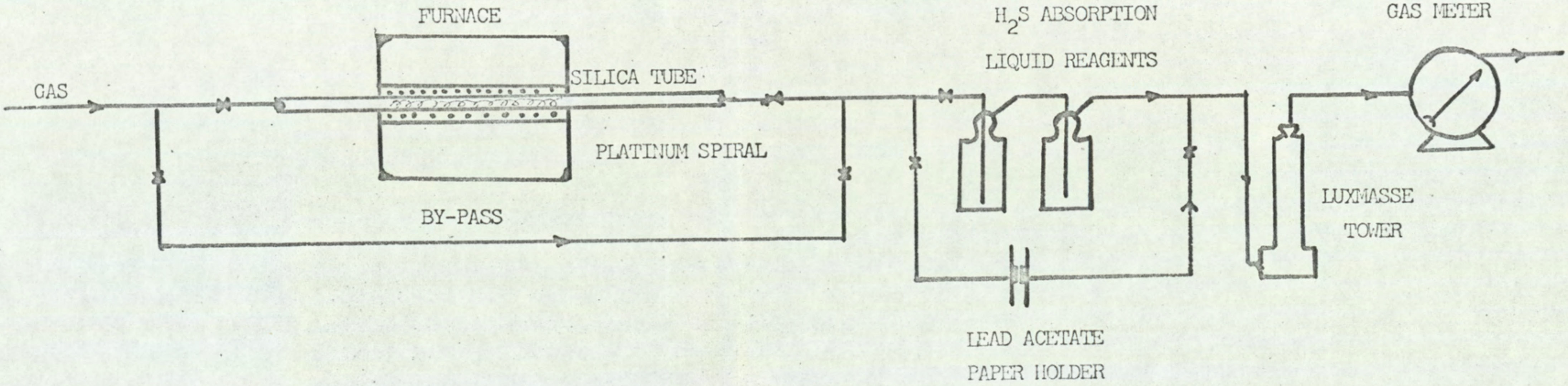


Figure 8. FLOW ARRANGEMENT OF PLATINUM SPIRAL METHOD.

If the concentration was 100 p.p.m. or above, then idiometric methods were used. Liquid absorbing reagents were 10% Cadmium chloride or Ammoniacal zinc sulphate prepared according to B.S. No. 3156, 1959. If the concentration was 25 p.p.m. or below, then the lead sulphide stain method was used. An E.E.L. H_2S meter was procured for this purpose. (See Figs. 7 and 8).

For a concentration of 25 - 100 p.p.m. both the methods were used.

Individual organic sulphur compounds were determined by using the selective reagents described by Hakewill and Rueck(71).

DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS.

A. Results obtained on Synthetic Mixtures containing individual Sulphur Compounds.

1. Mixtures containing carbonyl sulphide : (Experiment Nos. 1 and 2, Table Nos. 13 - 25).

A synthetic mixture containing 271 p.p.m. COS and having H_2/CO ratio 9.7, was passed through the reactor at 370 °C for 104 hrs. This was a preliminary investigation to find out the suitability of the Nimox as a conversion catalyst.

It was found that at low space-velocity (140 - 370 v/v/h) all the organic sulphur was absorbed on the catalyst. After the catalyst bed absorbed about 8 grains of sulphur (i.e. 1.5% approx. of its weight, or 16% of theoretical sulphur content), it started passing out sulphur (Table 15).

This catalyst bed was then sulphided further with H_2S rich mixture (Table 16) and a gas mixture containing 130 p.p.m. COS and having H_2/CO ratio of 11.4, was treated. Reactor temperature was maintained at 370 °C and space velocity at 630 v/v/h. Although total sulphur coming out was not constant over time, the catalyst was passing out 3.92 - 5.8 p.p.m. of COS. Value of

$$K = \frac{(CO)(H_2S)}{(H_2)(COS)} \quad \text{is 13 theoretically,}$$

while experimental value of K was found = 2.3. Thus it was clear that equilibrium was not established.

To find out the effect of temperature and space velocity a smaller reactor (Table 19) was used. The catalyst was presulphided and a mixture containing 397 p.p.m. COS and having an H_2/CO ratio of 3.9 was treated. Conversion at 250 °C was found higher at higher space velocity, i.e. 11,000 v/v/h. (Table 21); while increased temperature, i.e. 400 °C, did not show increased conversion. Theoretical value of K at 250 °C is 8.3 and thus theoretical decomposition should be 97.3%, while experimental value was only 93.6%. Theoretically, conversion should be better at 400 °C than at 250 °C. Conversion figures were repeated at 400 °C (Tables 22,23) and it was found that with COS in a mixture containing COS = 120.8 p.p.m., conversion was better. Higher space velocity again produced better results.

Before the conclusion of this series of experiments, another mixture containing 445 p.p.m. COS and having H_2/CO ratio of 4.26 was treated at different space velocities and temperatures. At S.V. = 500 v/v/h., conversion was found almost similar at 250 and 350 °C (Table 25), while higher temperature (485 °C) showed a decline in conversion. Conversion also fell with increase in space velocity.

As this experiment was more or less of a probing nature, no absorbent was placed after the converter. Organic sulphur coming out undecomposed was measured by finding out the H_2S concentration that was coming out and subtracting it from the inlet sulphur concentration i.e. -

COS undecomposed = Total S in - H_2S out

all figures expressed in p.p.m. H_2S

On this basis it was found that conversion figure fell with increased temperature (Table 25). It was afterwards realised that a kinetic balance is set up as given below :

[Inlet Sulphur] = [Outlet Sulphur] + [Sulphur —retained by the catalyst]. Hence it is possible that at higher temperature if catalyst is not given enough time to sulphide completely, the H_2S coming out figure is bound to fall, and thus if % conversion is calculated on the basis of actual H_2S out then the resultant figure is likely to be smaller than the actual one.

From these preliminary investigations, it became clear that,

(1) Nimox had a good conversion capacity.
(2) Nimox did not need to be pre-sulphided.
(3) Conversion was good at a temperature range of 250 - 350 °C. Higher temperature for COS conversion was not necessary.
(4) Higher space velocity on a fresh catalyst gave better results.

Hence it was decided to try further experiments by using 3.5/10 Nimox.

2. Absorption of H_2S on Peter Spence Luxmasse at higher temperatures : (Experiment No. 3, Tables 26 - 31)

Absorption was conducted at 370 °C with a mixture containing 410 p.p.m. H_2S and having H_2/CO ratio = 3.85.

Absorption was very good as only 0.8 - 1.00 p.p.m. H_2S slipped at S.V. = 585 v/v/h., but reactor very soon developed back pressure. On opening the reactor it was found that carbon deposition had taken place. In fact the increase in weight of Luxmasse was found to be 11.3 gms. and at this stage it had not absorbed much sulphur. It was found (Table 29) that most of CO disappeared. Some 8.4% of carbon disappeared altogether. Hydrogen disappeared to the extent of 15%. CO_2 and CH_4 formation was found. A possible explanation could be that at 370 °C, all the H_2S is being taken up by the Luxmasse at the top, while the rest of the Luxmasse bed is reduced and thus started promoting methanation, with the consequent development of hot spots and lay down of carbon. Hence the reactor was opened and packed fresh. Tables 30 and 31 show results obtained at 300 °C. i.e. at a reduced temperature. At S.V. = 610 v/v/h. and 300°C no major change in the composition of the gas was noticed. CO_2 which was formed originally in the first few hours, disappeared afterwards. This proved that CO_2 came from this reaction $CO + H_2O = CO_2 + H_2$.

As the formation of water ceased, CO_2 disappeared. H_2S slip was only 0.13 p.p.m., while about 3 p.p.m. COS was coming out, thus showing that Luxmasse at 300 °C also promoted the following reaction -

$$CO + H_2S \quad = \quad COS \; + H_2$$

The above experiments proved that at low space velocity and temperature = 370 °C, there is a danger of carbon deposition in the reactor freshly packed with Luxmasse.

Hence in case of putting on a fresh Luxmasse reactor on stream, care may have to be taken that temperature increase is gradual. A lower temperature at the start up should avoid methanation.

3. Decomposition of thiophene on Nimox in the presence of CO and H_2. (Experiment Nos. 4,5, Tables 32-39).

(1) In this run thiophene was hydrogenated on a presulphided Nimox catalyst at different temperatures, at atmospheric pressure and in the presence of CO. Results are given in Tables 34,35. It was noticed that almost fresh catalyst decomposed 66.2% of thiophene at 300 °C but decomposition fell afterwards. Conversion at 200 °C was only 2% but rose to 91% when temperature was 450 °C and above. These results are also plotted as Decomposition vs Temperature in Figure No. 9.

(2) Decomposition of C_4H_4S in pure Hydrogen Atmosphere (Tables 36,37,38,39).

In this series, thiophene was hydrogenated in a pure atmosphere of hydrogen. Temperature, space velocity and pressure were varied. Concentration of thiophene in the mixture was 600 p.p.m. as H_2S (Table 37).

At a pressure of 345 psia, and a temperature range of 280 - 490 °C, decomposition was 95.8 - 98.7%, while decomposition at a lower temperature of 240 °C, the decomposition was 73.3%. This shows that pressure had a pronounced influence on decomposition. These results are also plotted in Figure No.   for comparison.

Conversion was also favoured by high space velocity (Table 38). A space velocity of 40,000 - 50,000 is definitely advantageous towards reduction of thiophene. It was clear that the diffusional resistance was playing the part. As the space velocity increased from 800 to 50,000 v/v/h, the decomposition improved, till at exceedingly high space velocity the slip of undecomposed thiophene increased again.

(3) Decomposition of C_4H_4S in pure hydrogen after treating coal gas on the same bed. (Table 39).

In Table 39, in the first block of this table, decomposition temperature was maintained around 400 °C and space velocity was varied. Decomposition was carried out at atmospheric pressure. It is clear that high space velocity is not an advantage, although decomposition to the extent of 65 - 86% was obtained. However, in the second block, at 350 psia, decomposition increased with increasing space velocity.

In the third block decomposition is shown at 185 psia. Decomposition was better at higher space velocity. In the last block reduction was carried out again at atmospheric pressure and conversion figures again fell.

From the above it is clear that decomposition of thiophene is better at high pressure. The equation -

$$C_4H_4S + 4\,H_2 = C_4H_{10} + H_2S$$

shows reduction in the number of molecules to the right hand side and according to Le Chatlier's law, thus hydrogenation of thiophene should be favoured by high pressure.

4. Decomposition of Butyl mercaptan (C_4H_9 SH) in pure Hydrogen on Nimox, at atmospheric pressure. (Experiment No. 6, Table 40).

In this run, the Nimox bed from the previous experiment was retained and decomposition of Butyl mercaptan was studied against space velocity and temperature. It is clear from the upper block of Table No. 40, that decomposition moved towards completion, at higher space velocities.

In the lower block it is clear that Butyl mercaptan was 94.4% decomposed at as low a temperature as 220 °C.

On the whole it is clear that a lower temperature and higher space velocity should obtain a reduction of Butyl mercaptan (90 -98%).

5. Decomposition of CS_2 in the presence of CO and H_2 on 3.5/10 Nimox at atmospheric pressure. (Experiment No.7 Tables 41 - 45).

(1) In this run decomposition of CS_2 in a mixture (Table 41) containing 180 p.p.m. of CS_2 (equivalent to 360 p.p.m. H_2S) and having H_2/CO ratio = 4.8 was studied on a presulphided Nimox bed.

$$CS_2 + 2\,H_2 \quad = \quad 2\,H_2S + C$$

CS_2 decomposes according to above equation depositing carbon on the catalyst bed. The run lasted for 200 hours and no back-pressure developed.(Table 43).

These results were re-arranged in Table No. 44. The decomposition was 98.3% at a temperature of 175 °C. Higher temperature and higher space velocity both contributed towards increased decomposition of CS_2.

In some cases (Table 43), it was seen that total sulphur coming out was greater than the total sulphur going in. There are two reasons for it, (a) it is possible that the catalyst is partly desulphiding or (b) the platinum spiral method was showing the inlet sulphur figures slightly less than the actual.

Another point worth mentioning is that due to the presence of CO in the gas, there may be some COS formed at every temperature, and taking that into account, it may be said that in those cases where decomposition of sulphur is about 97.5%, 2.5% unconverted organic sulphur may be actually COS being produced.

Hence it can easily be surmised that decomposition of CS_2 on Nimox is almost complete. H_2O formation was not noticed.

(2) Two stage (Nimox/Lux.) study of the decomposition of CS_2 in a mixture containing CS_2 equivalent to 382 p.p.m. H_2S. Tables 46 - 47.

Space velocity was kept constant at 2300 v/v/h. while temperatures of Nimox and Lux. were varied individually. Slip of H_2S through lux remained 0.4 - 0.6 p.p.m. at temperatures between 100 - 246 °C.

Decomposition of CS_2 increased with rise in temperature of both stages.

It may be seen that the decomposition of CS_2 in the presence of CO over two stages is almost complete.

When lux temperature reached 400 °C, the reactor was blocked. This observation was already made when H_2S alone was absorbed on Luxmasse at 370 °C (Table 28).

Consequently, fresh lux was packed and gas containing CS_2 equal to 395 p.p.m. CS_2 or 790 p.p.m. as H_2S was treated. From Table 50 it is found that at 250/250 °C on Nimox/Lux. respectively and at S.V. = 2500 v/v/h, total sulphur out was only 0.3 p.p.m. When S.V. was increased to 8,000, H_2S slip decreased, while organic sulphur out increased slightly (Table 50).

When temperature was increased to 350 °C, the Lux. reactor blocked again. Table 51 shows that methane formation took place.

Hence the Lux. reactor was packed a third time and results were obtained by keeping Nimox/Lux. at 250/300 °C.

It was found that at increased space velocity, conversion was better. Total S coming out was 1.6 - 3.4 p.p.m. only. Minimum H_2S slip was 0.06 p.p.m.

From the perusal of the above discussion it was found that Luxmasse may not stand temperatures above 300 °C. At a space velocity of 10,000 - 25,000, slip of H_2S is insignificant.

It was also found that 9 gms. of catalyst took about 12 grains of sulphur or about 8% of its original weight.

B. Decomposition of Organic Sulphur in Town's gas, on Nimox.

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1. Decomposition of organic sulphur in coal gas over a pre-sulphided Nimox at atmospheric pressure and at 370 °C

(Experiment No. 9, Tables 53 - 55)

In this run, temperature was maintained at 370 °C and coal gas obtained from B.O.C. was treated on a pre-sulphided Nimox bed. From Table 54, it was clear that Nimox which was sulphided with a higher concentration of sulphur, started desulphiding. The run lasted for 300 hours and in the end a steady rate of decomposition was maintained. Pressure increase due to carbon deposition was only 4.1 in.Hg. after 300 hours. This run was of a preliminary nature only and it was proved that Nimox was suitable for treating coal gas also.

In Table No.55 Inlet and Outlet composition are compared. CO_2 increased slightly, while unsaturated compounds were also hydrogenated to some extent. O_2 disappeared altogether. There was an increase in CO and CH_4 constituents. Hydrogen was partly used.

Calorific value of the gas also increased.

Considering the $\frac{(CO)(H_2S)}{(H_2)(COS)}$ equilibrium, the theoretical amount of COS out should have been 4.92 p.p.m., while a figure of 5.7 - 6 p.p.m. was obtained. This proved that this particular equilibrium is satisfied. Also it was proved that thiophene as present in this gas was almost completely hydrogenated.

2. Decomposition of Organic sulphur in coal gas on Nimox/Lux. system at atmospheric pressure. (Experiment No.10, Tables 56,57,58).

Nimox and Lux. were packed in separate reactors (Table 56) and Nimox was pre-sulphided. The run lasted for nearly 700 hours and no back-pressure developed. Temperature over Nimox was varied from 250 - 350 °C. Space velocity over Nimox was varied and the maximum value was 10,000, while the maximum value of S.V. on Lux. was 1530. While in the beginning 80.5% of the total organic sulphur was decomposed, afterwards, decomposition remained steady. Slip of H_2S remained at about 0.2 p.p.m. in the first + 300 hours, but H_2S started slipping when 300 $ft.^3$ of coal gas was treated. Increase in slippage of un-decomposed organic sulphur took place, when H_2S started slipping, thus proving that Lux. not only absorbs H_2S but helped in the decomposition of organic sulphur. Also from the rate of slippage of H_2S from Lux., it may be inferred that the absorption of H_2S was complete on the first one or two inches of the bed. But as the Lux. became sulphided, the zone of absorption moved forward, till the absorption was impaired.

It was also found that temperature up to 300 °C should be capable of removing about 95 - 97% of total Sulphur (Column 10, Table 57).

From Table 58, it is clear that unsaturated compounds were partly hydrogenated. O_2 disappeared completely. No drastic change in the composition of the gas took place. Calorific value of the gas did not change materially. No loss of carbon was experienced. Lux. also helped in the decomposition of organic sulphur as the experimental value of outlet sulphur was less than the theoretical value of sulphur out from the equilibrium

$$K = \frac{(CO)(H_2S)}{(H_2)(COS)}$$

High temperatures were not needed. Also it was found that if the temperature on Luxmasse was gradually increased, no carbon deposition should take place. A high percentage of CO in the gas did not impair the efficiency of decomposition and absorption.

From Table 59, it was clear that 15 - 16% of S was absorbed on the original weight of the Luxmasse charged, but actually H_2S started slipping earlier. As it was noticed that with the increase in H_2S slippage, organic sulphur figure also increased in the outlet gas, it was inferred that Luxmasse bed would have to be replaced, when about 7 - 8% weight of sulphur had been taken up.

Summarizing the above inferences, it was clear that Nimox/Lux. system should be able to remove 97% of sulphur. It was also clear that a practical limit to refining existed if only one combination of Nimox/Lux. was used. For further purification another combination of Nimox/Lux. would be needed.

3. Decomposition of organic sulphur in coal gas under pressure at 350 °C. (Experiment No. 11, Tables 60 - 61)

At a pressure of 100 psig, decomposition was 90.7% at S.V. = 1500 v/v/h but it fell to 80.8% when space velocity was increased, to 10,500 v/v/h. (Table 60).

This run had to be called off after 300 hours, but it was restarted and pressure kept atmospheric. At this pressure and S.V. = 2100 v/v/h, conversion was between 83.6 - 87.5%

At a pressure of 100 psig and S.V. = 10,000 conversion fell again to 66.6% and at S.V. = 22,000 conversion was only 45.5%. When pressure was increased to 170 psig, conversion became slightly better, i.e. 77.4 - 85.5%.

Few things became evident. On a fresh catalyst, reaction is diffusion controlled and very high space velocities can be tolerated, but with the passage of time, the reactive surface area diminishes due to carbon deposition or gum formation and then the reaction depends upon the active surface available, and thus the decomposition becomes inversely proportional to space velocity. This point has to be considered when designing an actual unit, which is supposed to run for 2,000 - 3,000 hours to leave a manageable time interval between repeated regeneration of catalyst.

From Table 60, once again it is clear that increased pressure was favourably disposed towards higher conversion.

From Table 61 it was clear that composition of the gas being treated is not affected but % conversion fell with increased space velocity. Calorific value of the gas did not change materially. Apparently, no carbon loss occurred.

4. The decomposition of organic sulphur in Town's gas on a regenerated catalyst bed at atmospheric pressure.

(Experiment No. 12, Tables 62 - 67)

From the discussion on the previous experiment, the logical step was to test a regenerated catalyst.

Hence the catalyst bed already used was regenerated (Table 62). Steam was passed till no H_2S stain appeared. Then coal gas was treated with this catalyst (Table 63). Conversion efficiency at 350 °C remained 95.5 97.0% for about 200 hours.

In Table 64 conversion of individual sulphur compound is given. Overall decomposition was best at 350 °C and higher temperatures were not necessary with the increase in temperature RSH increased in the outlet gas. Conversion of thiophene remained the same, while COS + CS_2 figure also increased with increase in temperature (Table 64B, rows 1 and 3, compared).

In Table 65, the effect of water vapour on conversion of organic sulphur is given. 40 - 46% of water in the gas actually showed no advantage at all as far as conversion was concerned.

In Table 66 a comparison between the composition of inlet and outlet gas is given. Calorific value did not change. Theoretical values of three pertinent equilibrium constants were compared. The COS hydrolysis equilibrium and shift conversion equilibrium were not satisfied but in the case of COS hydrogenation equilibrium experimental value higher than the theoretical was obtained. No carbon disappeared as was clear from the C/N_2 ratios.

In Table 67 results are shown when a partly sulphided Luxmasse bed was connected after the Nimox stage. At 46% water content, conversion of organic sulphur was 97.5 at 400/400 °C, while H_2S was coming out at the rate of 205 - 227 p.p.m. This showed that Fe S in the lux. was reacting with water vapour and H_2S instead of being absorbed was being released; hence when H_2O going in was reduced to 4.5%, H_2S slip decreased to 7 p.p.m. Conversion of organic sulphur increased to 98.5%. Increased temperatures of 450/450 °C did not help, and conversion of organic sulphur fell and slip of H_2S increased. Reduction of water content to 3% did not help in conversion. Hence it was surmised that 4.5% of water content is helpful and assists in the decomposition of organic sulphur. Increase in temperature above 400 °C was not necessary.

Also it was proved that regeneration of the used or inactive catalyst could be carried out with steam, without impairing the quality of the catalyst.

5. Decomposition of organic sulphur in coal gas by using four stages (i.e. Nimox/Lux/Nimox/Lux), at atmospheric pressure. (Experiment No. 13, Tables 68 - 74).

In this run, four reactors were packed (Table 68). Two Nimox reactors were connected together and sulphided with $CS_2/CO/H_2$ mixture containing CS_2 = 756 p.p.m. H_2S. Then these two reactors were treated with coal gas,(Table 69). Afterwards two fresh Lux reactors were interposed to give Nim/Lux/Nim/Lux system,while Nimox reactors were kept at 350 °C, Lux reactors were kept at ambient temperature. Decomposition of coal gas was 81.2% and 95.3% with two different types of coal gas, one containing less sulphur than the other. When the fresh Lux was also at 350 °C, then the decomposition increased to 96 - 96.7%. The same gas doped with additional thiophene showed decrease in conversion of overall organic sulphur. Conversion was 64.3 - 66.0%, but when the second Nimox was brought to 450 °C, then the conversion of organic sulphur in coal gas containing excess of thiophene increased to 82.7%. By cooling the second Nimox to ambient temperature, conversion fell to 71.4% (i.e. conversion on two stages), but when only the first Nimox stage and Luxmasse was operative, the conversion was 40.6% only.

In Table 71, these results are summarized. It will be clear that with higher temperature, i.e. 450 °C on the second Nimox stage, thiophene was increasingly decomposed. First Lux reactor at 350 °C also contributed towards decomposition of organic sulphur.

Table 72 shows the decomposition of individual organic sulphur compounds. At 350/350/350/20 °C, the overall decomposition is 94.7 - 96.0%, while thiophene is left mostly untouched. Almost similar results were obtained on coal gas fortified with thiophene, but when the temperature on the second Nimox was increased to 450 °C, the quantity of $COS + CS_2$ rose, but thiophene was increasingly decomposed. When the second Nimox was taken out, then thiophene again increased in the outlet gas. By using single stage only, overall decomposition suffered tremendously as it was only 40.6%.

Table 73 shows the individual sulphur compounds coming out with the outlet gas, when temperatures were 350/350/450/20 °C. It may be seen that mercaptans persisted. Thiophene was removed to sufficient extent while $COS + CS_2$ were removed by the first two stages and in the third stage COS most probably was again regenerated.

This run lasted for 1,000 hours. It became clear that if thiophene was present in sufficient quantity, then four stages would be needed to reduce the overall sulphur content. If thiophene was present in small quantities, two stages may give enough purification.

It was also noticed that the catalyst was somewhat deactivated after 1,000 hours. The reason could be that Nimox beds were heavily presulphided with a mixture comparatively rich in CS_2 and thus even to start with, enough carbon was deposited on the catalyst.

6. Decomposition of organic sulphur in Town's gas by using six stages at atmospheric pressure. (Experiment No.14, Tables 75 - 79)

Reactors were packed as shown in Table 79. The arrangement used was Nimox/Lux/Nimox/Lux/Nimox/Lux.

A nominal temperature of 350 °C was maintained on the first five stages, while the sixth stage was kept at ambient temperature. Results obtained are shown in Table 76A. Reactor 4 containing the second lux bed was blocked twice, and repacked twice, and the third time, when back pressure started developing, its temperature was lowered initially. This effect has already been seen. When a lux bed above 350 °C received a supply of gas free from sulphur, then methanation took place, but if the initial temperature was kept low, till the lux bed had received some sulphur, then afterwards this methanation reaction was suppressed.

Table 76B shows the % removal after each combination of Nimox/Lux. It would be clear that maximum % removal after 500 hours was 99.48%.

Table 77 shows the effect of the temperature maintained in reactor 4 (2nd. lux.). Organic sulphur figure in the outlet gas was down to .09 p.p.m. when Lux was at 410 °C.

At the end of Table 76A inlet and outlet sulphur figures are given. The total removal although not up to synthesis purity limits was fairly complete.

In Table 78A, decomposition of COS in COS/H_2 mixture in six-stage treatment is given. It was clear that decomposition was almost complete.

In Table 78B, decomposition of thiophene in pure hydrogen is given at six stages. Decomposition was 82.4% but when T5, i.e. 3rd. Nimox was raised to 410 °C, the decomposition figure rose to 93%.

Table No. 79 shows the comparison between inlet and outlet gas. Oxygen disappeared as usual. CO_2 rose to 7.07%, but the calorific value did not change. Shift reaction did not reach equilibrium, as is clear from Table 79.

It is thus clear that six stage treatment should produce outlet gas comparatively free from organic sulphur. To get better results it would be imperative that first lux. bed should be replaced as soon as H_2S slip started, because this bed is holding almost all the H_2S produced in the whole system. As the H_2S slipped from 1st. lux., the sulphur content of outlet gas increased.

In fact to achieve complete purity, it will be necessary to limit thiophene in the gas being treated. If the amount of thiophene can be limited, then a number of stages can be correspondingly reduced.

It has been found that lux. not only absorbed H_2S but also converted organic sulphur to some extent. A luxmasse bed can easily be blocked by carbon deposition and the best treatment to avoid this is to use initial temperatures less than 300 °C. Once the lux. bed has a trace of sulphur absorbed, its methanation activity is lost and then its temperature can be raised.

Very fine purification can be achieved, if the first lux is taken out as soon as it starts slipping H_2S. It is this H_2S which subsequently may help in the regeneration of COS in the presence of carbon monoxide. Water vapour up to 4.5% is advantageous. More than this causes the slip of H_2S and less than this has no pronounced effect.

7. Decomposition of organic sulphur in coal gas at pressure, by using six stages. (Experiment No.15, Tables 80 - 84).

Reactors were packed alternately with Nimox and Luxmasse (Table 80). The sixth stage consisting of 3rd. lux bed was actually used on the decompressed gas. Results are given in Table 81. Nominal pressure was 300 psig, although pressure to start with was 260 psig. A consistent water rate was maintained but the percentage of water in the outlet gas was calculated on the basis of the condensate collected. Nominal temperature in all the reactors was maintained around 350 °C. The gas being treated had inlet sulphur equal to 274/300 p.p.m. H_2S.

In the first 500 hours, at a nominal temperature of 350 and nominal pressure of 260 - 290 psig, H_2S slip was .03 - 0.3 p.p.m. It was found that H_2S slip was 0.27 p.p.m. when the fresh lux was initially exposed to the atmosphere. If the coal gas was passing through it continuously, H_2S slip fell to 0.03 p.p.m. Organic sulphur slip at the beginning was 0.21 p.p.m. (H_2S) but gradually increased to 0.93 when at low space velocity. At higher space velocity, in between, it was 2.4 p.p.m. at a space velocity of 14,500 v/v/hr.

When the temperature was increased to 400 °C nominal, the organic sulphur content fell to 0.5 p.p.m. When the temperature of the third Nimox was increased, the organic sulphur content again increased. When in the end water was not fed in with the inlet gas, the organic sulphur content increased further in the outlet gas.

In Table 82 the effect of space velocity on the decomposition of organic sulphur is shown. With increasing space velocity more undecomposed organic sulphur escaped. Space velocity seemed to have no effect on H_2S slip.

In Table 83, comparison between the inlet and outlet gas is given. In the first 100 hours, there was increased methanation with loss in CO content and rise in methane and CO_2. After 300 hours, CO loss became less, also methanation went down slightly. There was an increase in the calorific value of the gas. The shift reaction did not approach equilibrium.

In Table 84, analysis of the Nimox and Lux beds is given. The sulphur content of the Nimox was 1.54 and 1.05 % respectively wt/wt. on the first and third stages. Carbon deposition was 3.81% and 0.31% respectively.

In the case of Luxmasse, both stages 4 and 6 were sulphided to almost equal extent and carbon deposition was 7.36% and 6.32% respectively.

Comparing the results of decomposition at six stages both at atmospheric and high pressure, it was noted that pressure did not make much difference on the efficiency of removal, but higher space-velocity could be used when working under pressure.

8. Decomposition of organic sulphur in coal gas with (higher) 4.5/12 Nimox in conjunction with I.C.I. zinc oxide absorbent. (Experiment No. 16, Tables 85 - 90).

Reactors were packed as shown in Table 85. Town gas at atmospheric pressure was treated. To start with zinc oxide bed was not connected. Organic sulphur removal (Table 88) was 93.3% at a temperature of 220 °C, 96.7% at a temperature of 298 °C., and 95 - 98% at 400 °C. At 500 °C it was 97.8%, so a very high temperature is not advantageous.

When gas was treated with zinc oxide only, it was found that (Table 86) at temperatures 370 - 400 °C the slip of unconverted organic sulphur was comparable with that obtained on 4.5/12 Nimox. The slip was 2.8 to 6.0 p.p.m. At a higher temperature of 460 °C, slip was 5.5 p.p.m. and hence no advantage seemed to have accrued by working at a higher temperature.

Also, both the reactors did not develop any back pressure, even when the conversion and absorption was carried out at 400 - 500 °C.

H_2S slip (Table 86) over zinc oxide was measured. At a temperature of 20 °C it was 1.06 p.p.m. to start with, but was only 0.3 afterwards. The slip remained around 0.2 - 0.3 p.p.m. even at higher temperature. No water was pumped in, hence the effect of water vapour on the Zn S was not found.

At a pressure of 355 psia higher space velocities were used. It was found that higher space velocity of 8700 v/v/h had no deleterious effect on H_2S absorption capacity. In fact under pressure absorption was much better.

In Table 87 results of conversion of organic sulphur over zinc oxide are given. A synthetic mixture containing COS in pure hydrogen and having a concentration of 686 p.p.m. COS was treated. Decomposition of COS was 98.5 - 99.1% at 400 °C. H_2S slip was subsequently 0.05 p.p.m. When the mixture containing thiophene in pure hydrogen (C_4H_4S = 238 p.p.m. as H_2S) was treated at 400 °C over zinc oxide, the decomposition was only 10 - 15.3%. Thus it did not show much activity towards decomposition of thiophene.

Temperature profile was measured by passing respectively O.F.N., H_2 and the coal gas in. It was clear that hydrogenation of the reaction is accompanied by the rise in temperature. When coal gas was passed, it was found that the temperature increased at a position 1 in. below the top of the catalyst bed. The temperature increase is due to consumption of oxygen by the reaction

$$H_2 + 1/2\ O_2 = H_2O$$

A higher temperature is then maintained throughout the reactor.

Hence it may be inferred that both 4.5/12 Nimox and zinc oxide were good conversion catalysts. Zinc oxide was capable of converting organic sulphur compounds excepting thiophene. H_2S slip through zinc oxide was comparable with that of Luxmasse. 4.5/12 Nimox has better metal content than 3.5/10 Nimox and hence correspondingly its utility vis-a-vis 3.5/10 Nimox can be compared only on a pilot-scale plant.

In Table 89 comparison between the inlet and outlet gas composition has been carried out. As usual oxygen disappeared, ethylene was partly or totally hydrogenated to ethane. The calorific value did not change materially.

In Table 90 temperature profile in the reactor containing Nimox is given. Curve No. shows the temperature along the length of the reactor.

9. Decomposition of organic sulphur on I.C.I. Comox (Cobalt/Molybdenum) catalyst. (Experiment No. 17, Tables 91 - 95).

Reactor was packed as shown. Treatment of the coal gas was carried out at atmospheric pressure. Only one-stage treatment was given. H_2S was absorbed over Luxmasse at ambient temperature.

After 650 hours coal gas from the tap was switched on. Nominal temperature was kept around 400 °C. Results are given in Table No. 92A and 92B.

At moderate space velocity (1,000 v/v/h nominal) decomposition of organic sulphur in compressed town's gas (Tables 92A, 93) varied between 96.6 - 97.8%. At 200 °C there was no significant decomposition. Temperatures higher than 400 °C did not show any advantage.

Decomposition of organic sulphur in the ordinary coal gas on tap was 76.5% at 272 °C, but increased to 95.9% at 370 °C. There was no significant advantage in carrying out decomposition at temperatures higher than this.

Temperature profile in the reactor is given in Table 94. Reduction of fresh catalyst with hydrogen produced a temperature rise and when coal gas was switched on, more heat was generated probably from the oxidation of hydrogen.

In Table 95 composition of the inlet and outlet gas is compared. No significant change in the calorific value took place. Density of the gas did not change.

On the whole the catalyst showed promise. Hydrogenation of organic sulphur was comparable with that of Nimox.

10. Decomposition of organic sulphur in coal gas with added carbonyl sulphide and hydrogen, on 3.5/10 Nimox and at high pressure. (Experiment No. 18, Tables 96 - 99)

This run was carried out to find out the effect of increased concentration of COS. Nominal temperature during the run was 400 °C in the middle and pressure was maintained at 355 psia. In Table 97 results are given. Slip of undecomposed organic sulphur is given against the space velocity which was varied. 6 - 9 p.p.m. of undecomposed sulphur in a gas containing about 600 p.p.m. (as H_2S) of total sulphur was noticed. Increased space velocity brought the reaction zone forward and space velocity of 50,000 - 60,000 was found rather better, but as it has already been found, fresh catalyst behaves differently from one slightly used. Overall removal at single stage was 98 - 99%. This was probably due to a small concentration of thiophene which is about 10 - 20 p.p.m. in this gas. A comparison of the inlet and outlet gas shows the usual disappearance of the oxygen and ethylene contents. An increase in ethane. CO_2 was less, rather unusual. Calorific value increased by 4% but gas density did not change materially.

Experimental concentration of outlet gas was almost equal to the theoretical concentration of COS considered from the COS hydrogenation equilibrium constant.

In Table 99 decomposition of organic sulphur was carried out at atmospheric pressure and nominal temperature of 400 °C. Decomposition was 98.5% which is equivalent to that obtained at 355 psia. Higher space velocity shows an advantage up to a certain extent, but above 41,000 v/v/h, decomposition showed a decline.

CONCLUSIONS.

CONCLUSIONS.

From preliminary experiments carried out on P.S. 3.5/10 Nimox, it was found that this catalyst had a good conversion capacity.

Synthetic mixtures containing carbon monoxide, hydrogen and individual organic sulphur compounds were purified by giving single and multistage treatment. Conversion of carbonyl sulphide, by using single stage was 94 - 95% at 370 °C and atmospheric pressure. Thiophene conversion was 50% at 350 °C and atmospheric pressure, while at 350 psia and 400 °C, conversion rose to 97%. Conversion of carbon disulphide was almost complete at 350 °C. Conversion of Butyl mercaptan was 99% at 350 °C.

Purification of coal gas containing 15 - 20% carbon monoxide has been carried out both at atmospheric and higher pressure, by providing single and multistage treatment. While removal of total organic sulphur depended upon the extent of thiophene present, it was found that conversion of organic sulphur was about 97% on a single stage conversion at 350 °C. Conversion rate fell with the passage of time.

With six-stage treatment, an outlet coal gas containing 0.2 p.p.m. of organic sulphur was obtained. Higher pressure and the presence of 5% water vapour were found to be beneficial. It was also found that high space velocity could be used at the start, when the catalyst was fresh, but with the passage of time, for the same conversion rate low space velocity would be required.

It was also found that Luxmasse at a higher temperature helped in the conversion of organic sulphur. Blockage of Luxmasse reactor due to carbon deposition was often noticed, when gas purified from sulphur on previous stages was passed through it at 350 °C. With a lower temperature to start with, (300 °C) no carbon deposition was observed.

Results of conversion by using another type of Nimox (4.5/12 - NiO/MoO_3), and I.C.I. Comox and zinc oxide have been obtained. It was found that 4.5/12 Nimox was suitable for conversion of organic sulphur but it was recommended that tests be carried out on a pilot plant. It was found that Comox was also a suitable catalyst for conversion purposes. It was also found that zinc oxide alone would remove about 90% of the total organic sulphur by conversion and simultaneous absorption at 400 °C.

The calorific value of the gas did not change materially and unsaturated compounds were hydrogenated at a lower space velocity. Oxygen disappeared completely on the first stage.

A preliminary design for a small scale package unit has been worked out. The cost of sulphur removal by using Nimox/Luxmasse system is very much influenced by the cost of Luxmasse as the absorbent. Ultimately the cost will be proportional to the amount of organic sulphur present in the gas. At a sulphur concentration of 25 gr./100 cu.ft., the cost of sulphur removal will be 1d./therm approximately. The cost of Luxmasse alone will be 0.4 - 0.5d/therm. If a customer is getting only 10 gr.S/100 cu.ft. in his gas, the cost of Luxmasse will be 0.2d/therm only, and the cost of removal will be roughly 0.7d/therm. If a cheaper grade of iron-oxide can be found, the cost figure will still go down.

A tentative design for a package unit is suggested in Appendix 2.

Suggestions for future work:

A tentative design for a 1,000 cu.ft/hr. desulphurization unit is given in Appendix 2. This design is based on the assumption that gas contains 25 gr.S/100 cu.ft. and on this basis the cost of complete removal of sulphur works out roughly equal to 1d/therm. It is suggested that a search be made for a cheaper variety of iron-oxide. It is also suggested that zinc oxide be used as the first stage replacing the first combination of Nimox/ Luxmasse. Carbon-disulphide is decomposed as shown below :

$$CS_2 + 2H_2 \quad = \quad C + 2H_2S$$

If zinc oxide is used as the first stage, very little deactivation of Nimox reactors should occur. It should be possible then to use increased space velocities, and also thiophene decomposition will improve. It may be possible to reduce the number of stages. Also it should increase the working life of various beds. However, it depends upon the cost of the zinc oxide available. At present this chemical is definitely dearer than the iron-oxide available.

It is suggested that this package unit be built as a trial unit and developed further, so that it can be placed on the user's site. The unit is supposed to work without much supervision and should be appreciated by those customers who like to have sulphur-free gas and thus can offset the price of sulphur removal against some other factor which comes into play because of the presence of sulphur in the gas.

EXPERIMENTAL WORK.

Experiment No. 1.

To study the decomposition of COS in a $CO/H_2/N_2/COS$ mixture over 3.5/10 Peter Spence Nimox catalyst.

Table No. 13. Packing of the reactor.

No.	PARTICULARS	INFORMATION.
1	Reactor ID	0.742 in.
2	Cross-section of the annular bed	0.383 in.^{2}
3	Volume of the annular bed	2.300 in.^{3}
4	Weight of catalyst packed	35.500 grm.
5	Size of catalyst particles	1/16 - 1/32 in.
6	Bed height (approximately)	6.00 in.
7	Temperature of the bed	370°C
8	Flow rate for 1000 v/v/h s.v.	1.33 ft.^{3}/hr.

Table No. 14. Composition of the Synthetic mixture No.1.

No.	CONSTITUENTS	%
1	CO	4.88
2	H_2	47.30
3	N_2	46.85
4	O_2	.90
5	Total	99.93
6	COS as grains $H_2S/100$ ft.^{3}	16.84
7	COS as p.p.m. H_2S	271.00

Table No. 15. Conversion and absorption of COS on Un-sulphide Nimox.

No.	Time from Start Hrs.	Flow rate of gas Ft^3/hr.	S.V. v/v/hr.	H_2S out p.p.m.	COS out p.p.m.
1	1.5	0.183	140	0.100	Nil
2	3.5	0.183	140	1.000	3.30
3	7.0	0.183	140	1.200	0.70
4	24.0	0.218	160	0.145	0.04
5	31.0	0.673	500	0.143	0.06
6	100.0	0.500	370	0.400	0.72
7	104.0	0.500	370	200 *	0.30

* Doubtful

Note 1. COS is expressed as p.p.m. H_2S

Note 2. H_2S is measured by the lead acetate paper method by using E.E.L. H_2S meter.

Note 3. COS = Total H_2S out through Platinum Spiral - H_2S out as such, (i.e. without passing the gas through Platinum Spiral).

Table No. 16. Composition of the H_2S rich gas used for part-sulphiding of Nimox bed used in this experiment. Synthetic Mixture No. 2.

Constituents	%
H_2S	1.42
N_2	74.21
H_2	24.37
Total	100.00

Table No. 17. Composition of the Synthetic Mixture No. 3.

Constituent	%
H_2	69.70
CO	6.10
N_2	24.20
COS (approximately)	130 p.p.m.(H_2S)

Table No. 18. Conversion of COS in above mixture over the partly sulphided Nimox bed.

Reactor temperature = 370°C

Approximate space velocity = 630 v/v/h.

1	2	3	4	5	6
No.	Time from start	Total COS in inlet gas	H_2S out	COS out	Total S out
	Hrs.	p.p.m. H_2S	p.p.m.H_2S	p.p.m.H_2S	p.p.m.H_2S
1	24	130	-	-	100.20
2	25	130	101.8	3.92	105.72
3	48	121	121	Nil	121.00
4	120	120	-	-	98.20
5	144	126	100.2	4.5	104.70
6	168	126	93.5	5.8	99.30

Note 1. Total sulphur in the inlet and outlet gas measured with Platinum Spiral method, and E.E.L. H_2S meter.

Note 2. Column 5 = Column 6 - Column 4

Experiment No. 2.

To study the decomposition of COS in a $CO/H_2/N_2/COS$ mixture at different temperatures and different space velocities, over pre-sulphided Nimox.

Table No. 19. Packing of the Reactor.

No.	PARTICULARS	INFORMATION.
1	Reactor I D	3/16 in.
2	Cross-section of the bed	.0276 $in.^2$
3	Height of the bed	4.5 in.
4	Volume of the bed	.1242 $in.^3$
5	Weight of the catalyst (3.5/10 Nimox)	1.39 gms.
6	Size of the catalyst	1/32 - 1/86 in.
7	Flow rate for 10,000 s.v.	0.7185 $ft.^3$/hr.

Table No. 20. Composition of the Synthetic mixture No.4.

Constituent	%
CO	12.50
N_2	38.30
H_2	49.20
Total	100.00
COS	397 p.p.m.

Table No. 21. Results:

Space-velocity.	S.V. = 5,500		S.V. = 11,000	
Temperature	H_2S out	Conversion	H_2S out	Conversion
°C	p.p.m.	%	p.p.m.	%
250	358.4	90.2	371.5	93.6
400	331.5	83.5	337	84.9

Table No. 22. Composition of the Synthetic Mixture No. 5.

Constituent	%
CO	9.0
N_2	40.4
H_2	50.6
Total	100.0
COS	120.8 p.p.m.

Table No. 23. Results:

Temp. °C	S.V. v/v/hr.	H_2S out p.p.m.	Conversion %	Expected Conv. %
400	5,800	105.1	86.95	98.5
400	15,000	112.4	93.10	98.5

Table No. 24. Composition of the Synthetic Mixture No. 6.

Constituent	%
CO	10.16
H_2	43.30
N_2	46.50
Total	99.96
COS	445 p.p.m.

Table No. 25. Results:

No.	S.V.	Temperature °C					
		250 °C		350°C		485°C	
	v/v/h.	H_2S out p.p.m.	Conv. %	H_2S out p.p.m.	Conv. %	H_2S out p.p.m.	Conv. %
1	500	403	90.5	403	90.5	345	77.5
2	1000	396	89.0	–	–	–	–
3	1500	387	87.0	384	85.7	–	–

Note: Expected conversions are as below :-

at 250 °C = 97.2%

at 350 °C = 98.0%

at 485 °C = 95.0% 98.5

Experiment No. 3

To study the absorption of H_2S on Peter Spence Luxmasse in the presence of CO and H_2.

Table No. 26. Packing of the Reactor.

No.	PARTICULARS	INFORMATION
1	Reactor I D	0.742 in.
2	Cross-section of the annular bed	0.383 $in.^2$
3	Volume of the annular bed	0.2145 $in.^3$
4	Weight of Luxmasse packed	41.6 gms.
5	Size of Luxmasse particles	1/16 - 1/32 in.
6	Height of the bed	5.6 in.
7	Temperature of the bed	370 °C
8	Flow rate for 500 s.v.	0.622 $ft.^3$/hr.

Table No. 27. Composition of the Synthetic Mixture No. 7

Component	%
CO	12.45
N_2	39.45
H_2	48.10
H_2S	410 p.p.m.

Table No. 28. Results:

Time of Start	Details of results.
At start	H_2S out = 0.8 - 1.00 p.p.m.
	Total S out = 1.04 - 1.36 p.p.m.
	Temperature = 370 °C
	Flow of gas = 0.272 $ft.^3$/hr.
	S.V. = 585 v/v/hr.
After 20 hrs.	Back pressure developed = 35 psi
	Flow =0.27 $ft.^3$/hr.
	H_2S out = 0.76 p.p.m.
	Total S out = 1.134 - 1.83 p.p.m.
	Temperature = 370 °C
	S.V. = 200 v/v/hr.
	Total H_2O collected = 4 mb. from 14.2 $ft.^3$ of gas
After 44 hrs.	Back pressure developed to 100 psi and run was discontinued. On opening the reactor, carbon deposition was evident, and the increase in luxmasse was 11.3 gms. This could be carbon produced from 27.56 $ft.^3$ of gas.

Table No. 29. Composition of the Inlet and Outlet gas after 20 hours.

Particulars	Inlet Gas	Outlet Gas
H_2	48.10%	41.60%
N_2	39.45%	47.38%
CO	12.45%	1.39%
CO_2		5.15%
CH_4		4.40
Total	100.00	100.00
C/N_2 (%)	31.55	23.10
H_2/N_2 (%)	121.8	106.5
O_2/N_2 (%)	15.76	12.34
O/H_2 (%)	25.9	20.4

Results obtained after cleaning the reactor and repacking it with 48.7 Luxmasse. Reactor temperature maintained at 300 °C.

Table No. 30. % Composition of the Inlet and Outlet gas.

Particulars	Inlet	Outlet after 6 hrs.	Outlet after 26 hrs.
CO	12.45	8.00	11.80
CO_2	–	2.80	0.00
CH_4	–	0.40	0.10
H_2	48.10	47.80	48.30
N_2	39.45	41.00	39.80
Total	100.00	100.00	100.00

Table No. 31. Other observations.

No.	After 6 hours	No.	After 26 hours
1	No change in reactor pressure	1	No change in reactor pressure
2	Part CO changes to $CO_2 + CH_4$	2	CO_2 formation suppressed, but 0.1% CH_4 formed
3	1.5 ml H_2O formed from 4.54 $ft.^3$ gas	3	No H_2O formed
4	Total S out = 4.48 p.p.m.	4	Total S out = 3.1 p.p.m.
5	H_2S out = 0.18 p.p.m.	5	H_2S out = 0.13 p.p.m.
6	COS out = 4.3 p.p.m.	6	COS out = 2.97 p.p.m.
7	S.V. = 545	7	S.V. = 610

Experiment No. 4.

To study the decomposition of thiophene in $CO/H_2/C_4H_4S$ mixture over 3.5/10 Nimox, at atmospheric pressure.

Table No. 32. Packing of the Reactor.

No.	PARTICULARS	INFORMATION
1	Reactor I D	3/16 in.
2	Cross-section of the bed	.0276 in.^{2}
3	Height of the bed	6.4 in.
4	Volume of the bed	.177 in.^{3}
5	Weight of the catalyst	2.1 gm.
6	Size of the catalyst	1/32 - 1/86 in.
7	Flow rate for 10,000 S.V. (approx.)	1 ft.^{3}/hr.

Table No. 33. Composition of the Synthetic Mixture No. 8

Composition	%
CO	16.66
H_2	83.34
C_4H_4S	194 p.p.m. (as H_2S)

Table No. 34. Results:

No.	Time from start	Temp.	S in Inlet gas	H_2S in outlet gas	Conv.
	Hrs.	°C	p.p.m. as H_2S	p.p.m.	%
1	28	300	230	152.3	66.2
2	52	450	268	246.0	91.85
3	80	381	285	192.2	67.4
4	101	382	277.4	194.3	70.1
5	121	200	-	5.5	2.0
6	127	250	293.4	34.0	11.58
7	146	270	274	52.1	19.00
8	170	405	298	238	79.8
9	176	320	283	103	36.4
10	192	350	342	171.4	50.1
11	198	500	481	437	90.8

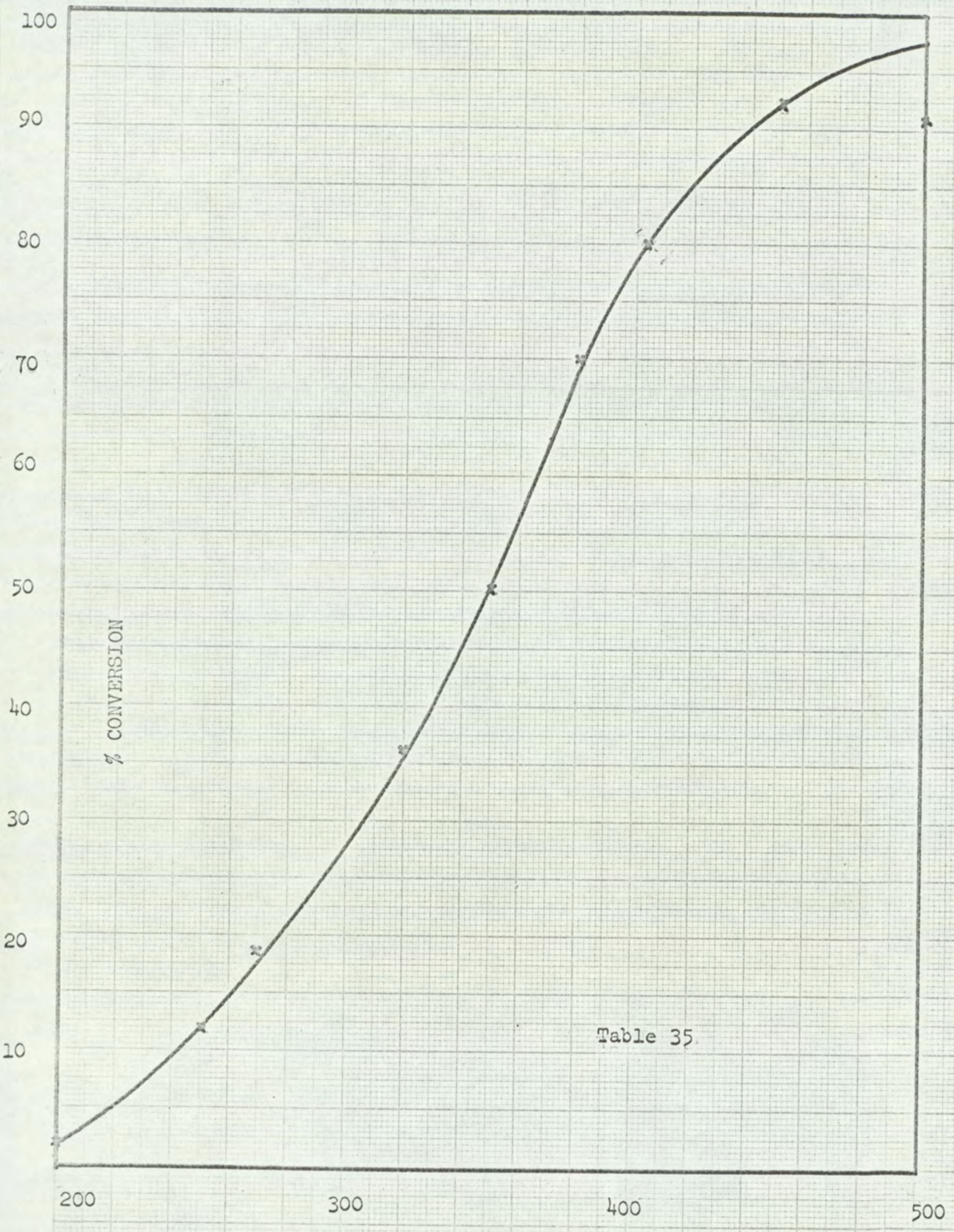


Figure 10 % CONVERSION OF THIOPRENE VS. TEMPERATURE

Table No. 35. Table No.34 conversion rearranged in order of temperature.

Temperature °C	Conversion %
200	2.00
250	11.58
270	19.00
300	66.20
320	36.40
350	50.10
380	70.10
405	79.80
450	91.85
500	90.80

SEE FIG. NO. 10 OPPOSITE.

Experiment No. 5.

To study the decomposition of thiophene in C_4H_4S/H_2 mixture on 3.5/10 Nimox, at pressure.

(Thiophene in Pure Hydrogen).

Table No. 36.

No.	PARTICULARS		INFORMATION
1	Reactor ID.	(in)	15/64
2	Cross-section of the reactor	($in.^2$)	.0431
3	Height of the bed	(in.)	6
4	Volume of the bed	($in.^3$)	.2586
5	Weight of the catalyst	(gm.)	4.909
6	Size of the Catalyst	(in.)	1/16 - 1/32
7	Flow for 10,000 S.V.	($ft.^3$/hr.)	1.498.

Table No. 37. Results obtained on the decomposition of thiophene in C_4H_4S/H_2 mixture, on a fresh un-sulphided 3.5/10 Nimox bed, (containing C_4H_4S = 600 p.p.m. H_2S app.)

1	2	3	4	5	6	7	8	9	10	11
No.	Pressure	Flow	S.V.	T_1	T_2	T_3	H_2S out	C_4H_4S out	Total S out	Decomposition
	psia	$ft.^3/hr$	v/v/h	°C	°C	°C	p.p.m.	p.p.m.	p.p.m.	%
1	345	0.23	1534	482	464	428	338.6	8.4	347	97.5
2	345	0.23	1534	482	464	428	-	-	-	-
3	345	0.23	1534	482	464	428	-	-	-	-
4	345	0.23	1534	482	464	428	--	-	-	-
5	290	0.36	2400	490	475	440	552	24	576	95.8
6	290	0.36	2400	490	475	440	480	10	490	97.8
7	345	0.36	2400	490	475	440	455	12	467	97.3
8	345	0.55	3670	432	420	392	448	14	462	97.0
9	345	0.37	2470	432	420	392	-	12.4	-	-
10	345	0.71	4740	388	378	354	457	11.2	468.2	97.5
11	340	0.60	4000	330	325	305	619	8.0	627	98.7
12	340	0.60	4000	330	325	305	-	-	-	-
13	340	0.60	4000	330	325	305	-	-	-	-
14	340	0.60	4000	282	279	264	563	10	573	98.1
15	340	0.60	4000	240	240	230	452	163.4	615.4	73.3

Note 1. % decomposition is based on the total S out figure.

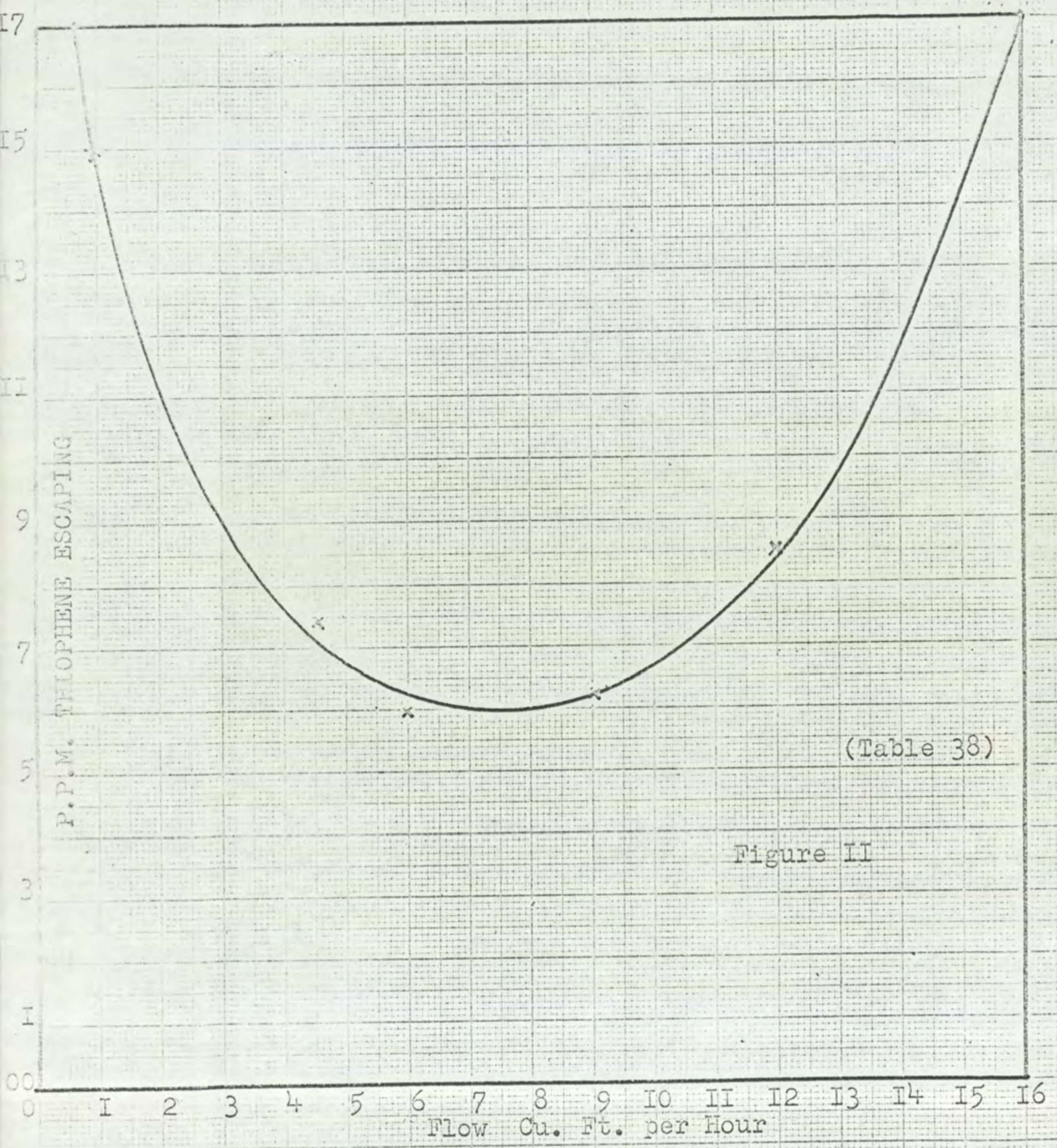
Note 2. Decomposition studied in order of decreasing temperature.

Note 3. T_1 = temperature at the beginning of the catalyst bed

T_2 = temperature at the middle of the catalyst bed

T_3 = temperature at the end of the column.

Note 4. C_4H_4S out measured by passing the outlet gas through fresh Lux, and then over the hot platinum spiral.



(Table 38)

Figure II

FIG. 11. P.P.M. THIOPHENE ESCAPING VS. FLOW

Table No.38 The decomposition of thiophene in C_4H_4S/H_2 mixture, at high space velocities.

Pressure = 345 psia

C_4H_4S = 600 p.p.m. H_2S app.

1	2	3	4	5	6	7
No.	Flow	S.V.	T_1	T_2	T_3	C_4H_4S out
	$ft.^3/hr.$	v/v/hr.	°C	°C	°C	p.p.m.
1	0.120	800	380	360	320	75
2	0.525	3500	380	360	320	90
3	0.710	4750	380	355	320	32.5
4	1.000	6700	380	355	320	15
5	4.640	31000	375	362	340	7.5
6	6.000	40000	380	380	355	6.0
7	9.000	60000	386	395	385	6.3
8	12.000	80000	386	395	385	8.5
9	12.000	80000	340	370	370	21.5
10	16.000	107000	385	395	388	17.0

Note 1. T_1, T_2, T_3 are temperatures respectively at the beginning, middle and the end of the 6 in. catalyst bed.

Note 2. H_2S out was not measured.

Note 3. C_4H_4S measured by passing the gas through fresh Luxmasse and then on the hot platinum spiral.

SEE FIG. 11. OPPOSITE.

Table No.39 Decomposition of thiophene in C_4H_4S/H_2 mixture after treating coal gas on the same catalyst bed.

1	2	3	4	5	6	7	8	9
Flow	S.V.	T_1	T_2	T_3	Org. S. out	H_2S out	Total S out	Decomposition
ft.^{3}/hr.	v/v/h.	^oC	^oC	^oC	p.p.m.	p.p.m.	p.p.m.	%
Pressure = 14.7 psia								
0.99	6600	412	412	398	71	448	519	86.3
1.74	11620	405	405	395	151.4	280	431.4	65.0
2.88	19220	405	405	398	66.3	260	326.3	79.6
2.88	19220	422	425	420	43.4	240	283.4	84.7
8.00	53400	-	-	-	131.0	-	-	-
Pressure = 350 psia								
0.43	2870	418	400	415	107	405	512	79.1
2.00	13350	415	415	410	6.5	-	-	-
5.49	36650	405	415	415	18.4	627	645.4	97.2
5.49	36650	-	-	-	-	650	-	-
5.49	36650	-	-	-	-	650	-	-
Pressure = 185 psia								
2.44	16300	426	426	415	10	643	653	98.5
7.00	46700	390	410	412	23	-	-	-
Pressure - atmospheric = 14.7 psia								
2.76	18430	405	408	400	173.4	285	458.4	62.1

<u>Experiment No. 6.</u> Decomposition of Butyl mercaptan (C_4H_9 SH) in C_4H_9 SH/H_2 mixture, on 3.5/10 Nimox, (already used.).

<u>Table No. 40.</u>

(1) Reactor bed - Same as used before (Table No. 36) with C_4H_4S/H_2 mixture etc.

(2) C_4H_9 SH = 550 p.p.m. (as H_2S) approximately in the synthetic mixture.

<u>Results:</u> Pressure atmospheric.

A. Decomposition vs S.V.

1	2	3	4	5	6	7	8	9
Flow	S.V.	T_1	T_2	T_3	C_4H_9SH out	H_2S out	Total S out	Decomp.
ft^3/hr.	v/v/h.	°C	°C	°C	p.p.m.	p.p.m.	p.p.m.	%
0.206	1370	382	380	365	68.5	554	612.5	88.7
0.740	4950	382	380	365	66.0	495	561	88.2
1.530	10200	402	402	392	4.4	549	553.4	99.3
2.800	18700	396	399	390	5.4	562	567.4	99.0
4.400	29400	390	398	395	4.3	564	568.3	99.2
B. Decomposition vs Temperature.								
0.740	4950	462	458	440	8.8	473	481.8	98.2
0.780	5200	399	396	382	6.0	585	591	98.9
0.720	4800	348	344	332	6.4	607	613.4	98.9
0.785	5250	245	245	240	7.0	563	570	98.7
0.750	5000	220	220	215	35.0	597	632	94.4

Experiment No. 7

To study the decomposition of CS_2 in the presence of CO and H_2, on 3.5/10 Nimox.

Table No. 41. Composition of the Synthetic Mixture No. 9.

Constituent	%
CO	17.30
H_2	82.70
CS_2	180 p.p.m. as CS_2 or 360 p.p.m. as H_2S

Table No. 42. Packing of the Reactor:

No.	PARTICULARS	DATA
1	Reactor ID.	9/32 in.
2	Cross-section of the annular bed	0.0622 $in.^2$
3	Volume of the bed	0.3732 $in.^3$
4	Weight of the catalyst	5.5 gms.
5	Size of catalyst particles	1/16 - 1/32 in.
6	Height of bed	6 in.
7	Flow for 10,000 S.V.	2.16 $ft.^3$/hr.

Table No. 43. Results obtained on pre-sulphided catalyst.

No.	Time from zero hr.	Temp.	SV	H_2S out	Total S out	Conversion
	Hrs.	°C	v/v/h.	p.p.m.	p.p.m.	%
1	26	260	2180	332	326	100
2	50	323	2380	326	324	100
3	97	320	2380	332	332	100
4	119	315	5760	335	338	99
5	127	305	9620	314	332	94.6
6	152	220	2100	342	351	97.5
7	170	220	8630	355	363	97.7
8	192	460	2140	336	353	95.1
9	195	465	8400	381	374	100

Note: Where H_2S out $\geq$ Total S out, conversion has been shown as 100%.

Table No. 44. Results obtained above (Table No.43) re-arranged.

Temp. °C	S.V. =2200	S.V. = 6000	S.V. = 9000
	Conv. %	Conv. %	Conv. %
175	98.30	-	-
220	97.50	-	97.7
260	100.0	-	-
305	-	-	94.6
315	-	99	-
320	100.0	-	-
323	100.0	-	-
460	95.1	-	-
465	-	-	100

Note: Where H_2S out $\geq$ Total S out, their conversion has been shown as 100%

Experiment No. 8

Two-stage study of the decomposition of CS_2 in a $CO/H_2/CS_2$ mixture, at atmospheric pressure.

Stage 1. Peter Spence 3.5/10 Nimox.

Stage 2. Peter Spence Luxmasse.

Table No. 45. Packing of Reactors.

No.	PARTICULARS	STAGE 1	STAGE 2
1	Catalyst or absorbent	3.5/10 Nimox	P.S. Luxmasse
2	Reactor ID, (in.)	9/32	7/32
3	Cross-section of the bed (in.^{2})	.0622	.0376
4	Height of the bed (in.)	6	9.8
5	Volume of the bed (in.^{3})	0.3732	0.3685
6	Weight of the bed (gms.)	5.5	8.8
7	Particle size of the material (in.)	1/16 - 1/32	1/16 - 1/32
8	Flow rate for 10,000 s.v. (ft.^{3}/hr.)	2.16	2.13

Note: Stage 1 is the Nimox bed already packed and used - see Table No. 42.

Table No. 46. Composition of the Synthetic Mixture No.10.

Constituent	%
CO	17.30
H_2	82.70
Total	100.00
CS_2	191 p.p.m. as CS_2 382 p.p.m. as H_2S

Table No. 47. Results:

S.V = 2300 V/V/H

1	2	3	4	5	6	7	8
Time from zero hour	Nimox temp.	Lux. temp.	Org. S out	H_2S out	Total S out	Conv. efficiency.	Slip of H_2S
Hrs.	°C	°C	p.p.m.	p.p.m.	p.p.m.	%	%
20	175	100	17.53	0.47	18	95.2	0.13
21	175	105	2.00	0.56	2.56	99.2	0.15
22	175	110	2.00	0.50	2.50	99.2	0.13
24	175	130	3.40	0.60	4.00	98.9	0.16
40	210	170	1.16	0.34	1.50	99.5	0.09
44	210	215	0.60	0.40	1.00	99.7	0.09
46	210	230	0.60	0.40	1.00	99.7	0.09
48	210	246	0.60	0.40	1.00	99.7	0.09
69	210	400	-	-	-	-	-

Note: When the temperature on Luxmasse reached 400 °C, the reactor was blocked. Hence the reactor containing Luxmasse was cleaned and repacked.

Table No. 48. Repacking of Stage 2.

No.	PARTICULARS	STAGE 2
1	Absorbent	P.S. Luxmasse
2	Reactor ID. (in.)	7/32
3	Cross-section of the bed ($in.^2$)	.0376
4	Height of the bed (in.)	10.5
5	Volume of the bed ($in.^3$)	0.394
6	Weight of the bed (gms.)	9
7	Particle size of the material (in.)	1/16 - 1/32
8	Flow rate for 10,000 s.v. ($ft.^3$/hr.)	2.285

Table No. 49. Composition of the Synthetic Mixture No. 11.

Constituent	%
CO	19.30
H_2	80.70
Total	100.00
CS_2	395 p.p.m. as CS_2 790 p.p.m. as H_2S

Table No. 50. Results.

1	2	3	4	5	6	7	8
S.V.	Nimox temp.	Lux. temp.	Org. S out	H_2S out	Total S out	Conv. eff.	Slip of H_2S
v/v/hr.	$^{\circ}$C	$^{\circ}$C	p.p.m.	p.p.m.	p.p.m.	%	%
2500	250	250	0.1	0.2	0.3	99.99	.025
8000	235	235	0.4	0.1	0.5	99.95	.012

Note : Stage 2 blocked again, when its temperature was raised to 350 °C. Methane formation was noticed as would be clear from the table below:

Table No. 51. Comparison of the composition of the inlet and outlet gases.

Constituent	Inlet gas	Outlet gas before blockage	Outlet gas after blockage
CO	19.3	12.90	2.5
H_2	80.7	87.10	87.2
CH_4	-	Traces	10.3
CO_2	-	not determined	not determined
Total	100.00	100.00	100.00

Table No. 52. Results obtained after packing Stage 2 third time.

Table No. 52.A. Weight of Luxmasse packed = 9 gms.
Height of Luxmasse bed = 10.3 in.

Table No. 52.B Results obtained with the previous gas (see Table No. 49)

Time from zero hr. Hrs.	S.V. v/v/h	Nimox temp. °C	Lux. temp. °C	Org. S out p.p.m.	H_2S out p.p.m.	Total S out p.p.m.	Conv. eff. %	Slip %
22	2800	250	300	7.85	0.15	8.0	99.02	0.02
23	10000	250	300	3.34	0.06	3.4	99.58	0.01
24	25000	250	300	1.54	0.06	1.6	99.75	0.01
25	25000	280	300	1.76	0.14	1.9	99.70	0.02

Note: Last two results obtained on gas containing 300 p.p.m. CS_2 (H_2S = 600 p.p.m.).

Experiment No. 9.

To study the decomposition of organic sulphur in coal gas, on a pre-sulphided 3.5/10 Nimox catalyst bed. (A single stage study at atmospheric pressure).

Table No. 53. Packing of the reactor.

No.	PARTICULARS	INFORMATION
1	Reactor ID. (in.)	0.742
2	Cross-section of the annular bed (in.^{2})	0.383
3	Height of the catalyst bed (in.)	6.000
4	Volume of the bed (in.^{3})	2.300
5	Weight of catalyst packed (gms.)	35.500
6	Size of catalyst particles (in.)	1/16 - 1/32
7	Temperature of the bed (^{o}C)	370
8	Flow rate for 1000 v/v/h S.V. ft.^{3}/hr.	1.33

Table No.54. Results obtained on coal gas by using pre-sulphide catalyst.

1	2	3	4	5	6	7	8	9	10
No.	Hrs. from start	Flow	S.V.	Total S in	H_2S out	Org. S out	Total S out	Conv-sion	Pressure diff. developed across the reactor.
	Hrs.	ft^3/hr.	v/v/h.	p.p.m	p.p.m	p.p.m	p.p.m	p.p.m	
1	0	0.516	390	166	-	-	239	-	
2	16	0.516	390	"	247	-	-	-	
3	36	0.564	420	"	203.5	-	-	-	
4	37	0.270	200	"	194.5	-	-	-	
5	42	0.576	430	"	-	-	-	-	
6	46	0.576	430	"	189	5.7	194.7	-	
7	68	0.610	460	"	203.5	6.0	194.6	-	7" w.g.
8	114	0.610	460	"	158	-	-	95.1	
9	160	0.610	460	"	-	-	-	-	1.0" hg.
10	164	0.610	460	"	140	-	185.2	84.3	1.8 "
11	188	0.671	500	"	-	-	-	-	2.3 "
12	212	0.671	500	"	153	-	152	92.1	2.9 "
13	216	0.671	500	"	148.2	-	-	89.2	
14	240	0.748	560	"	156.4	-	-	94.1	3.7 "
15	281	0.748	560	"	125.3	-	-	-	3.8 "
16	304	0.748	560	"	157.2	-	-	94.6	4.1 "

Note 1: In columns 5 to 8, S means sulphur out and is expressed on p.p.m. H_2S.

Note 2: Conversion of organic sulphur becomes steady after about 100 hrs.

Note 3: Org. S in column 7 has been obtained by passing the outlet gas through fresh lux and measuring the remaining sulphur through platinum spiral.

Table No. 55. Comparison of the inlet and outlet coal gas.

PARTICULARS	INLET GAS	OUTLET GAS
1. Composition %		
CO_2	2.60	3.70
Unsat.	2.50	2.30
O_2	0.90	0.00
H_2	52.52	46.40
CH_4	11.54	15.12
CO	13.14	17.66
N_2	16.80	14.82
Total	100.00	100.00
2. C.V.(gross) Dry gas - at $0^\circ C$ and 760 mm. BTU/ft^3.	403	431
3. $K = \frac{(CO)(H_2S)}{(H_2)(COS)}$ at 370°C = 12.2		
4. Theoretical value of COS out		4.92 p.p.m.
5. Total organic sulphur actually out		5.7 - 6 p.p.m.

Experiment No. 10

To study the decomposition of organic sulphur in coal gas, using two stages, at atmospheric pressure.

Table No.56 Packing of the Reactors.

No.	PARTICULARS	INFORMATION	
		Stage 1	Stage 2
		3.5/10 Nimox	P.S. Luxmasse
1	Reactor ID. (in.)	9/32	0.742
2	Cross-section of the bed (in.^{2})	0.0621	0.383
3	Height of the bed (in.)	6	6.35
4	Volume of the bed (in.^{3})	0.3726	2.434
5	Weight of the material (gms.)	5.8	50.0
6	Size of the material (in.)	1/16 - 1/32	1/16 - 1/32
7	Flow-rate for 1000 v/v/h S.V. ft.^{3}/hr.	0.2155	1.498
8	Temperature varied		

Table No. 57

Decomposition and absorption of organic sulphur in coal gas over Nimox and Lux respectively.

1 Time Hrs.	2 Temp on Nimox $^\circ C$	3 Temp on Lux $^\circ C$	4 S.V. on Nim. v/v/hr.	5 S.V. on Lux. v/v/hr.	6 Total S in. H_2S ppm	7 Total S out H_2S ppm	8 H_2S only out H_2S ppm	9 Org.S. out H_2S ppm	10 Nimox effcy. % Conv.	11 Lux effcy. % Slip of H_2S	12 Total gas in Cu.Ft.
16	250	220	1800	277	136	27.20	0.63	26.6	80.5	0.58	-
23	260	260	6200	950	-	2.50	0.75	1.78	98.7	0.56	-
46	250	250	7000	1070	-	-	0.42	-	-	-	-
70	250	250	6400	980	220	2.67	0.56	2.11	98.9	0.26	100
140	300	260	10000	1530	-	1.6	0.14	1.46	99.3	0.06	-
162	300	250	2600	400	-	14.6	0.23	14.37	93.4	0.11	-
167	300	250	6700	1025	326	5.6	0.20	5.40	98.3	0.06	200
186	300	250	6100	935	-	4.9	0.22	4.69	98.5	-	-
214	350	250	6700	1025	-	3.0	0.20	2.80	99.0	0.07	-
234	350	250	6300	965	258	3.14	0.16	3.00	98.8	0.06	300
258	350	250	2800	430	-	5.60	0.21	5.40	97.8	0.06	-
282	350	350	2400	370	-	5.75	0.78	5.00	98.0	0.31	-
312	350	350	2600	400	-	7.80	1.10	6.70	97.3	0.44	-
336	350	350	3800	582	-	8.45	1.5	7.00	97.2	0.62	-
354	350	350	6000	920	258	6.50	4.4	2.10	99.1	1.72	400
379	350	350	6000	920	-	-	5.0	-	-	-	-
428	350	350	6000	920	-	13.60	8.0	5.60	97.7	3.17	-
448	350	350	2500	380	-	13.20	3.7	9.50	96.2	1.49	-
472	350	350	2700	410	220	14.00	5.0	9.00	95.8	2.37	500
496	350	350	6200	950	-	14.60	9.5	5.00	97.6	4.41	-
520	350	350	8000	1220	-	26	20	6.00	97.2	9.35	-
522	350	350	6200	950	-	35	21	14.00	93.6	10.20	-
598	350	350	6500	1000	220	173	166	7.00	96.8	77.90	660
621	350	350	6500	1000	-	176	170	5.90	97.3	79.40	-
644	350	350	6500	1000	-	182	176	6.50	97.0	82.40	-
666	415	Room Temp.	6200	950	-	-	-	10.7	95.2	-	750

Table No. 58 The comparison of the composition of inlet and outlet gases.

Cylinder No.	1		2		3		4		5	
Hrs. from start	70		140		234		354		496	
GAS	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT
(1) Constituents										
CO_2	2.8	3.4	3.8	4.4	4.4	4.2	3.8	4.3	4.1	4.6
Unsat.	2.2	2.0	2.6	2.4	3.1	3.0	2.9	3.0	2.9	2.9
O_2	0.2	Nil	1.0	Nil	1.0	Nil	1.1	Nil	1.1	Nil
CO	19.5	19.3	20.3	19.6	20.3	20.7	20.3	20.2	20.5	20.7
H_2	51.1	50.7	48.6	49.2	48.7	48.6	47.4	47.7	47.3	47.6
CH_4	12.9	12.8	11.5	12.4	11.2	11.7	11.7	11.8	11.6	11.8
N_2	11.3	11.8	12.2	12.0	11.7	11.8	12.8	13.0	12.5	12.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
(2) Total S (p.p.m)	136	2.5	220	1.6	326	3.14	258	6.45	221	14.7
(3) S.V.										
On Nimox	-	6400	-	10000	-	6000	-	6000	-	6200
On Lux.	-	900	-	1430	-	860	-	860	-	890
(4) Bed temp. °C										
Nimox	-	250	-	300	-	300	-	350	-	350
Lux.	-	250	-	250	-	250	-	350	-	350
(5) C.V.	428	420	416	421	424	428	420	424	420	424
(6) $K = \frac{(CO)(H_2S)}{(H_2)(COS)}$	-	9.3	-	9.3	-	9.3	-	12.4	-	12.4
(7) COS theoretically out	-	5.6	-	9.3	-	14.90	-	8.8	-	7.8
(8) $\frac{C}{N_2}$ Ratio *	3.55	3.345	3.345	3.43	3.60	3.61	3.25	3.26	3.26	3.46

* Unsaturated compounds considered as C_2H_4

Table No. 59. Results obtained on Luxmasse charged.

No.	PARTICULARS	LUXMASSE IN	LUXMASSE OUT
1	Weight of Lux. (gms.)	50.00	76.0 (A)
2	% H_2O	3.65	Not determined
3	% Fe	34.82	22 - 16.6
4	% S	–	10.56
5	Total Fe (gms.)	17.41	16.84
6	Total S	–	8.02
7	Sulphur absorbed %	-	-
	(basis original wt.)	-	16.4 (B)
8	Formula of $FeS_{1 \pm x}$	–	$FeS_{0.83}$

(A) Luxmasse mixed with alumina

(B) Sulphur slip started earlier

(C) Atomic wts.

Fe = 56

S = 32

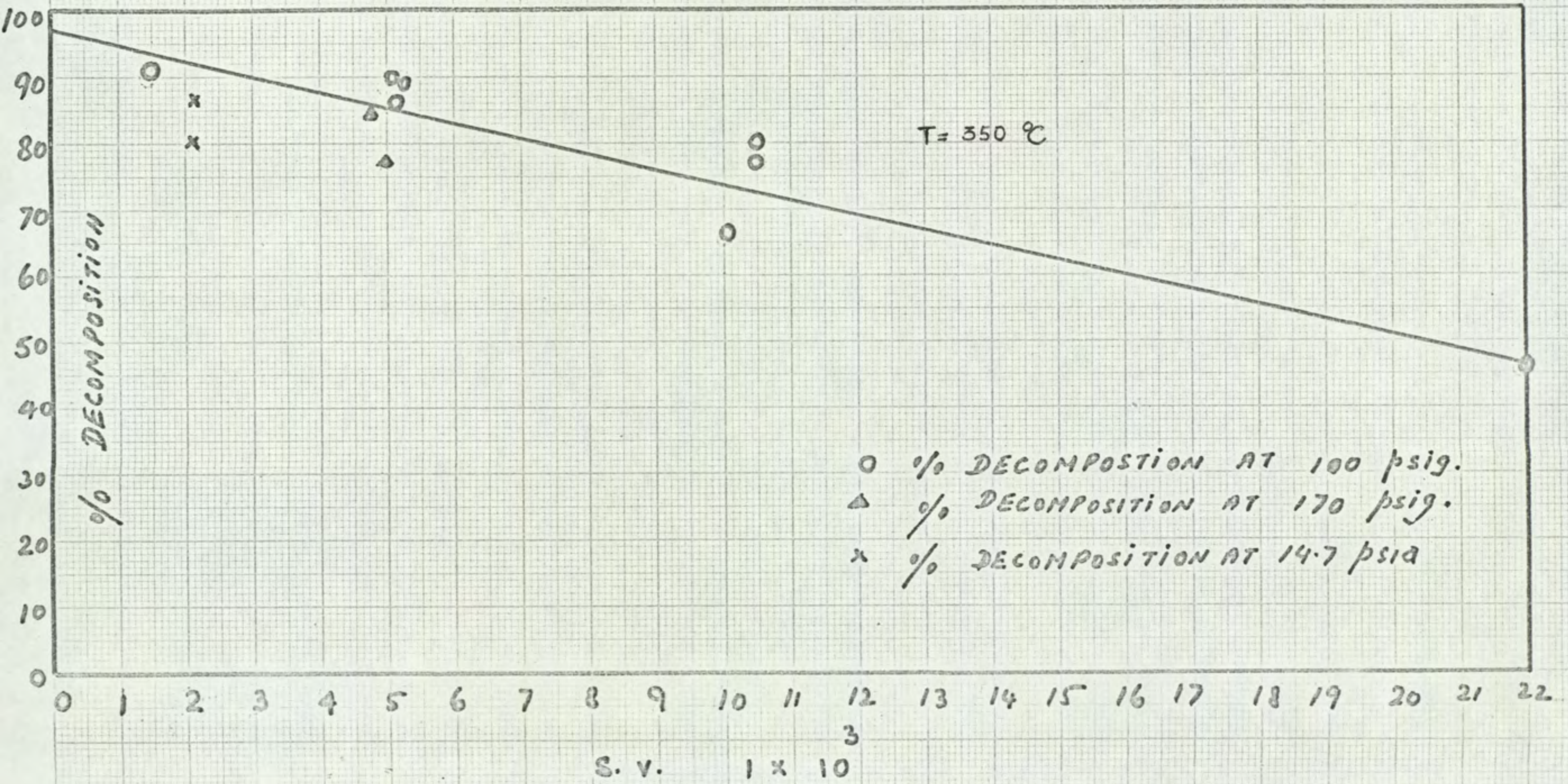


Figure I2. % Decomposition of Organic Sulphur in Town Gas at various Pressures.

Experiment No. 11.

To study the decomposition of organic sulphur in coal gas under pressure, (by using one stage only).

Packing of the reactor: Same as in Table No. 56.

No Luxmasse reactor used, but instead outlet gas passed through fresh luxmasse at ambient temperature and pressure.

Table No. 60. Results. (Temperature maintained at 350°C)

No.	Time from start	Pressure	S.V.	H_2S out	Org. S out	Total S out	Decomposition
	Hrs.	psig	v/v/hr	p.p.m.	p.p.m.	p.p.m.	%
1	90	100	1500	230.0	23.7	253.7	90.7
2	140	100	5100	179.6	26.4	206.0	87.2
3	230	100	5100	179.2	22.4	201.6	88.8
4	260	100	10500	131.0	38.2	169.2	77.4
5	280	100	10500	126.2	31.2	157.4	80.3
6	330	ATM.	2100	279.4	41.0	320.4	87.5
7	354	ATM.	2100	303.0	75.3	378.3	80.0
8	420	ATM.	2100	148.4	29.0	177.4	83.6
9	445	100	10000	-	-	-	-
10	470	100	10000	102.0	51.6	153.6	66.6
11	494	100	22100	85.7	102.7	188.4	45.5
12	510	170	-	-	-	-	-
13	584	170	4850	48.3	8.2	56.5	85.5
14	650	170	4850	60.4	17.7	78.1	77.4

SEE FIG. 12. OPPOSITE

Table No. 61.

Comparison between inlet and outlet gas.

No.	PARTICULARS	1		2		3		4	
		IN	OUT	IN	OUT	IN	OUT	IN	OUT
1	Temp. °C	-	350	-	350	-	350	-	350
2	Pressure psig	-	100	-	100	-	100	-	170
3	S.V. v/v/hr.	-	1550	-	5080	-	10500	-	6000
4	Constituents								
	CO_2 %	4.2	5.2	3.7	4.8	3.7	4.5	5.2	5.7
	Unsat.	3.0	1.8	2.6	2.4	2.6	2.3	3.0	2.7
	O_2	0.5	0.0	0.9	0.0	0.9	0.0	0.5	0.0
	CO	20.3	20.3	20.1	19.7	20.1	20.9	15.7	15.8
	H_2	47.9	47.9	48.7	48.2	48.7	48.2	51.4	50.4
	CH_4	11.5	12.1	11.1	11.6	11.1	11.7	13.7	14.4
	N_2	12.6	13.1	12.9	13.3	12.9	12.4	10.5	11.0
	Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
5	Total S out (p.p.m.)	-	253.7	-	206	-	169.2	-	78.1
6	H_2S out (p.p.m.)	-	230	-	179.6	-	131.0	-	60.4
7	Org. S out (p.p.m.)	-	23.7	-	26.4	-	38.2	-	17.7
8	% Conversion	-	90.7	-	87.2	-	77.4	-	77.3

Table No. 61 contd.....

		1		2		3		4	
		IN	OUT	IN	OUT	IN	OUT	IN	OUT
9	$K = \frac{(CO)(H_2S)}{(H)(COS)}$	-	11.65	-	11.65	-	11.65	-	11.65
10	COS (theoretically out)	-	8.4	-	6.3	-	4.9	-	1.6
11	C.V.	422	402	411	409	411	412	442	440
12	$C/_{N_2}$ Ratio *	3.33	3.15	3.11	3.08	3.11	3.36	3.86	3.75

* Unsaturated taken as C_2H_4

Note: C.V. for unsaturated compounds = 2200 BTU/ft^3.

Experiment No. 12.

To study the decomposition of organic sulphur in town's gas on a regenerated catalyst bed.

Table No. 62. History of the catalyst bed.

No.	PARTICULARS	INFORMATION
1	Reactor ID (in.)	9/32
2	Height of the bed (in.)	6
3	Volume of the bed ($in.^3$)	0.372
4	Wt. of Nimox (gms.)	5.8
5	Flow required for 10000 S.V. ft^3/hr.	2.152
6	Medium of regeneration	Steam
7	Temperature of regeneration	600 - 700 °C
8	Duration of regeneration (hrs.)	90
9	Medium of activation	Hydrogen
10	Duration of activation (hrs.)	72
11	Pressure during regeneration and activation	Atmospheric

Table No. 63 Sulphiding of the regenerated catalyst.

Medium of sulphiding	-	Coal gas
Organic S. in coal gas	-	200 p.p.m. as H_2S
Flow maintained	-	0.58 ft^3/hr.
S.V.	-	2700 v/v/hr.
Temp. for sulphiding	-	350 °C

Results:

1	2	3	4	5	6	7
Hrs. from start	Total gas in	Total S in	H_2S out	Org. S out	Total S out	Conv.
Hrs.	ft^3.	grains H_2S	p.p.m.	p.p.m.	p.p.m.	%
0.00	-	-	0.172	-	-	-
2.50	1.45	0.18	-	-	4.2	-
4.00	2.32	0.29	-	-	-	-
7.00	4.06	0.51	-	-	4.5	-
22.00	12.76	1.60	4.9	4.5	9.4	-
23.00	13.34	1.67	4.9	-	-	-
24.00	13.90	1.74	-	-	25.6	-
26.00	15.10	1.89	-	-	-	-
26.50	15.36	1.92	42.0	4.0	46.0	-
27.00	15.62	1.95	49.7	4.3	54.0	-
28.00	16.24	2.03	-	6.4	-	-
30.00	17.40	2.18	-	4.5	-	-
96.00	55.60	6.96	186.4	5.9	192.3	97.0
120.00	69.60	8.70	-	7.2	-	-
150.00	87.00	10.90	164.0	7.4	171.4	95.5
168.00	97.50	12.20	-	6.0	-	-

Table No. 64. Individual Sulphur Compounds in outlet gas at different temperatures.

(64.A) Individual Sulphur Compounds in the inlet gas:

RSH + C_4H_4S = 20 p.p.m. as H_2S

COS + CS_2 = 165 p.p.m. as H_2S

Total = 185 p.p.m. as H_2S

(64.B) Results:

1	2	3	4	5	6	7	8	9	10
Temp.	S.V.	COS + CS_2	C_4H_4S	RSH	Total Org. S.	H_2S only	Total S out	Conv.	See note
°C	v/v/h	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	%	No.
350	2700	3.9	2.4	1.1	7.4	164	171.4	95.5	1
400	2700	7.9	3.4	1.3	12.6	185	197.6	93.6	2
450	2700	4.8	2.5	2.7	10.0	210	220.0	95.5	3

Note 1. Cylinder pressure above 400 psig.

Note 2. Cylinder pressure below 300 psig.

Note 3. New cylinder in.

Table No. 65. Effect of water vapour on conversion of organic sulphur in town's gas.

1	2	3	4	5	6	7	8	9	10
Temp.	S.V.	% H_2O	H_2S out	COS + CS_2 out	C_4H_4S out	RSH out	Total Org.S out	Total S out	Conv.
°C	v/v/hr.	%	p.p.m	p.p.m	p.p.m.	p.p.m	p.p.m	p.p.m.	%
400	5760	46.10	176.4	5.0	3.3	1.7	10.0	186.4	94.7
400	5540	46.10	192.3	4.7	9.1	1.3	15.1	207.4	92.8
400	5650	46.20	205.8	2.3	4.7	1.2	8.2	214	96.1
400	5650	44.20	205.5	-	-	-	8.5	214	96.0
400	5920	40.70	209.0	-	-	-	10	219	95.5
400	5920	40.7	208.0	-	-	-	10	218	95.5

Table No. 66. Comparison of the composition of inlet and outlet gas.

No.	PARTICULARS	INLET GAS	OUTLET GAS	OUTLET GAS
1	Composition		Dry	Wet
	CO_2	2.47	3.35	1.91
	C_2H_4	0.56	0.62	0.33
	C_2H_6	0.59	0.46	0.25
	CO	19.90	19.50	10.52
	CH_4	12.87	13.20	7.14
	O_2	1.61	0.00	0.00
	N_2	9.02	9.17	4.95
	H_2	52.98	53.70	28.90
	H_2O	–	–	46.00
	Total	100.00	100.00	100.00
2	$COS + CS_2$	188	2.3	1.24
	C_4H_4S	22	4.7	2.54
	RSH	4	1.2	0.65
	H_2S	–	205.8	111.20
	Total	214	214.0	115.63
3	Equilibrium Constants			
(A)	$\frac{(H_2S)(CO_2)}{(COS)(H_2O)}$			
	Theoretical (400 °C)	–	–	1.85×10^2
	Experimental	–	–	3.72
(B)	$\frac{(H_2S)(CO)}{(COS)(H_2)}$			
	Theoretical	–	–	13.1
	Experimental	–	–	32.65
(C)	$\frac{(CO_2)(H_2)}{(C))(H_2O)}$			
	Theoretical	–	–	13.0

Table No. 66 contd.....

NO	PARTICULARS	INLET GAS	OUTLET GAS	
			DRY	WET
	Experimental	-	-	0.114
4	C.V.	408	411	-
5	$C/_{N_2}$ Ratio	4.16	4.16	-

Table No. 67. Decomposition of Organic Sulphur over Nimox/Luxmasse system in the presence of water vapour.

S.V. comb. v/v/hr	H_2O %	Nim. temp. °C	Lux. temp. °C	H_2S out (slip) p.p.m	Org.S out p.p.m.	COS + CS_2 out p.p.m.	C_4H_4S out p.p.m	RSH out p.p.m	Total S out p.p.m	Conv. %
5900	46	400	400	227	5.6	-	-	-	232.6	97.5
5900	46	400	400	205	4.6	-	-	-	209.6	97.8
3340	4.5	425	400	7.0	3.3	-	-	-	10.3	98.5
3340	4.5	440	400	7.0	3.0	-	-	-	10.0	98.5
3340	4.5	450	450	11.5	5.3	-	-	-	16.8	97.5
3285	3.0	450	450	21.5	15.3	2.9	2.9	9.5	36.8	93.0

Note: Luxmasse was partly sulphided.

Experiment No. 13.

To study the decomposition of coal gas, at atmospheric pressure by using four stages - i.e. Nimox/Lux/Nimox/Lux.

Table No. 68

PARTICULARS	NIMOX Stage 1	LUX Stage 2	NIMOX Stage 3	LUX Stage 4
(1) Reactor ID. (in.)	3/16	0.742	3/16	0.742
(2) Height of bed (in.)	6.5	6.1	6.5	6.1
(3) Volume of bed (in.^{3})	0.1792	2.395	.1792	2.395
(4) Wt. of the material (gm.)	2.234	50	2.117	50
(5) Size of the material (in.)	.0336 -.0116	1/16 - 1/32	.0336 - .0116	1/16 - 1/32
(6) Flow of gas for 1000 v/v/h S.V. (ft.^{3}/hr.	.104	1.386	.104	1.386

Table No. 69. Conversion of organic sulphur over two Nimox reactors (only) connected together.

Temperature = 350°C
Pressure = Atmospheric
S.V. = 2000 - 2500

1	2	3	4	5
Time from start	H_2S out	Org. S out	Conv.	Remarks
Hrs.	p.p.m.	p.p.m.	%	
5	19	-	-	$CO/H_2/CS_2$ mixture in for
120	196.4	.048	100	1st. 30 hrs.
192	99	4.83	95.3	CS_2 = 756 p.p.m. as H_2S.
216	97.5	9.20	91.3	Then coal gas in.
384	57.5	11.30	83.5	
480	224.5	61.00	78.6	
490	-	-	-	Four stages together now.

Table No. 70 Four stages together now.

T_1 = 350 °C - Nimox 1
T_2 = ambient - Lux 1
T_3 = 350 °C - Nimox 2
T_4 = ambient - Lux 2

Results after 4th stage:

1	2	3	4	5	6
Time from start	H_2S out	Total S out	Total S in	Conv.	Nature of inlet gas
Hrs.	p.p.m.	p.p.m.	p.p.m.	%	
504	0.20	8.2	42.5	81.2	Coal gas
552	0.06	11.0	232.0	95.3	Coal gas

Table No. 70 contd...

	Temperature	350/350/350/20 °C			
1	2	3	4	5	6
648	traces	11.6	303	96	Coal gas
696	traces	15.6	303	94.7	Coal gas
700	traces	95	266	64.3	Coal gas *
792	traces	5.8	184	96.7	Coal gas
840	traces	90.5	266	66.0	Coal gas *
	Temperature	350/350/450/20 °C			
960	traces	46	266	82.7	Coal gas *
	Temperature	Nimox 350/ out /20 °C			
984	traces	76.1	266	71.4	Coal gas *
	Temperature	350/out/out/20 °C			
-	traces	158	266	40.6	Coal gas *

* Coal gas with excess thiophene

Table No. 71. Summary of results:

(A) Conversion of ordinary coal gas.

State of reactors	Conversion %
(1) 350/out/350/out °C	78.6
(2) 350/20/350/20 °C	81 - 95.3
(3) 350/350/350/20 °C	95 - 96

(B) Conversion of coal gas (with additional thiophene)

(1) Conversion after 1st. stage (at 350 °C)	40.6
(2) Conversion after 1st. and 2nd. stages (at 350°C)	71.4
(3) Conversion after 1, 2 and 3rd. stages (at 350°C)	66.0
(4) Conversion after 1, 2 and 3 stages - temperatures as 350/350/450 °C	82.7
(5) Decomposition by Lux 1 at 350°C	30.8
(6) A rise of 100 °C on reactor 3 raises conversion by	16.7

Table No. 72

Decomposition of Individual Sulphur Compounds.

	p.p.m. S in				p.p.m. S out				
Hrs. from start	RSH	Thiophene	COS + CS_2	Total	RSH	Thiophene	COS + CS_2	Total	Conv.
Hrs.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	%
		350/350/350/20 °C		Coal gas					
648	33.5	10	231.5	275	2	8	1.6	11.6	96.0
696	48	26	257	331	nil	9.6	6.0	15.6	94.7
		(A) 350/350/350/20 °C		Coal gas with excess Thiophene					
720	20	84	162	266	7	86.5	1.5	95	64.3
840	"	"	"	"	nil	88.5	2	90.5	66
		(B) 350/350/450/20 °C							
960	"	"	"	"	10	31.5	4.5	46	82.7
		(C) 350/350/out/20 °C							
984	"	"	"	"	10	64.5	1.6	76.1	71.4
		(D) 350/out/out/20 °C							
	"	"	"	"	12	71.5	74.5	158	40.6

Table No. 73. Composition of the Sulphur Compounds present after each stage.

Inlet gas consists of synthetic mixture containing excess of Thiophene.

S Compd.	Inlet before Stage 1	After S.1.		After S.2	After S.3	After S.4.
		350 °C		350 °C	450 °C	20 °C
H_2S	Nil	108	4.0	4.0 *	34.1	Nil
RSH	20	12	45.1	10.0	10.0	10
C_4H_4S	84	71.5	29.4	64.5	31.5	31.5
COS + CS_2	162	74.5	1.6	1.6	4.5	4.5
Total	266	266	80.1	80.1	80.1	46.0

Note 1. Elimination of Total Organic S

By Stage 1 + 2 = 70%

By Stage 3 + 4 = 82.7 - 70 = 12.7%

Note 2. Efficiency of Conversion

By Stage NIM 1 = 70%

By Stage NIM 2 = 57.4%

Table No. 74 Composition of the typical outlet gas.

Constituent	%
CO_2	5.9
Unsat.	2.5
O_2	0.0
CO	16.3
H_2	51.0
CH_4	13.6
N_2	10.7
Total	100.0
Individual Sulphur Compounds *	
RSH	20 p.p.m.
C_4H_4S	84 p.p.m.
$COS + CS_2$	162 p.p.m.
Total S	266 p.p.m.

* IN COAL GAS WITH EXCESS THIOPHENE.

Experiment No. 14.

To study the decomposition of organic sulphur in town gas, by using six-stages, at atmospheric pressure.

P.S. 3.5/10 Nimox was the conversion catalyst and P.S. Lux. was the absorbent.

Table No. 75. Packing of the reactors.

		Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
No.	PARTICULARS	Nim.	Lux.	Nim.	Lux.	Nim.	Lux.
1	Size of catalyst (in.)	1/16 - 1/32	1/8 and less	1/16 - 1/32	1/8 - and less	1/16- 1/32	1/8 and less
2	Wt. of Catalyst (gm.)	35.2	130.6	35.2	130.6	35.2	135.1
3	Bed height (in.)	6.8	18.1	6.55	17.9	6.4	18.9
4	Bed volume (in.^{3})	2.57	7.22	2.57	7.22	2.57	7.22
5	S.V. for 1 ft.^{3}/hr	672	240	672	240	672	240

Table No. 75 A.

Results.

(S as H_2S p.p.m.)

1	2	3	4	5	6	7	8	9
HRS.	PARTICULARS	REACTOR 1	2	3	4	5	6	REMARKS
		NIMOX	LUX	NIMOX	LUX	NIMOX	LUX	
24	Bed temp. °C	355	358	355	370	370	20	
	S.V. v/v/hr.	1400	500	1400	500	1400	500	
	% H_2O = 14.54	-	-	-	-	-	-	
	H_2S out	-	-	-	-	-	.085	
	Org. Sulphur out	-	-	-	-	-	.652	
	Total Sulphur out	-	-	-	-	-	.737	
48	-	-	-	-	-	-	-	Reactor 4 blocked
96	Bed temp. °C	360	350	340	340	350	25	Lux renewed
	S.V. v/v/hr.	1000	350	1000	350	1000	350	
	% H_2O in 10.85							
	H_2S out p.p.m.	253	0.134	-	0.150	-	0.20	
	Org. S out p.p.m. H_2S	8.5	1.116	-	1.145	-	1.314	
	Total S out p.p.m. H_2S	261.5	1.250	-	2.295	-	1.514	
120	Bed temp. °C	354	353	350	350	350	25	
	S.V. v/v/hr.	1000	350	1000	350	1000	350	
	% H_2O in = 4.4	-	-	-	-	-	-	
	H_2S out p.p.m.	230	-	-	-	-	-	
	Org. S. out p.p.m.	6.8	-	-	-	-	-	
	Total S. out p.p.m.	236.8	1.36	-	0.66	-	0.48	

Table No. 75A contd.....

150	-	-	-	-	-	-	-	Reactor 4 blocked again Lux renewed.
200	Bed temp. ^oC	355	350	360	120	350	25	
	S.V. v/v/hr.	1000	350	1000	350	1000	350	
	% H_2O in = 3.1	-	-	-	-	-	-	
	H_2S out p.p.m.	254.5	2.33	3.35	0.25	0.94	0.18	Reactor 4 kept at low temp. because it was developing back pressure again
	Org. S out p.p.m.	5.5	1.67	1.85	2.27	1.46	2.42	
	Total S out p.p.m.	260	4.00	5.20	2.52	2.40	2.60	
360	Bed temp. ^oC	350	350	350	360	355	25	
	S.V. v/v/hr.	2200	800	2200	800	2200	800	
	% H_2O in = 3.5%	-	-	-	-	-	-	
	H_2S out p.p.m.	-	-	-	0.2	-	0.25	
	Org. S. out p.p.m.	-	-	-	2.48	-	2.39	
	Total S out p.p.m.	-	-	-	2.68	-	2.64	
500	Bed temp. ^oC	355	350	350	355	465	25	Temp. in 3rd. Nim. = 465 ^oC.
	S.V. v/v/hr	1000	350	1000	350	1000	350	
	% H_2O = 5.6%	-	-	-	-	-	-	
	H_2out p.p.m.	291.5	29.4	76.48	2.58	-	1.00	
	Org. S. out p.p.m.	7.0	3.6	35.20	2.52	-	1.56	
	Total S out p.p.m.	298.5	33.0	80.00	5.00	-	2.56	
	Individual S compounds							
	RSH	-	-	-	-	-	0.06	
	C_4H_4S	2.60	2.53	2.32	1.96	-	0.90	
	$COS + CS_2$	4.40	1.07	1.07	0.56	-	0.60	

Table No. 75^A contd.....

Individual S compound in inlet gas

RSH	=	22 p.p.m.
C_4H_4S	=	10 p.p.m.
CS_2	=	157
COS	=	128
Total	=	317 p.p.m.

Table No. 76. Percentage removal of the organic sulphur after different stages.

Hrs. from start	Total Org. S in	% Removal after		
		2nd. reactor	4th.reactor	6th.reactor
Hrs.	p.p.m.	%	%	%
96	261.5	99.57	99.56	99.5
200	260	99.36	99.15	99.07
500	298.5	98.90	99.15	99.48

Table No. 77. Organic sulphur after the six stages, when the temperature of the 4th reactor (2nd. lux.) was raised.

S	$T_4 = 110^\circ C$	$T_4 = 300^\circ C$	$T_4 = 410\ ^\circ C$
p.p.m.	p.p.m.	p.p.m.	p.p.m.
H_2S only	0.176	0.178	0.210
Organic S only	2.420	0.289	0.090
Total	2.600	0.467	0.300

Table No. 78.

(A) Decomposition of COS in COS/H_2 mixture by six-stage treatment.

COS = 756 p.p.m.

Reactors were respectively at -

350/350/360/330/350/25 °C

Results:

H_2S slip = 0.07 p.p.m.

Org. S out = 0.37 p.p.m.

Total S out = 0.44 p.p.m.

(B) Decomposition of C_4H_4S in C_4H_4S/H_2 mixture by six-stage treatment.

C_4H_4S = 220 p.p.m. as H_2S

Reactors 350 °C

Results:

	Sulphur (as p.p.m. H_2S) out after stage					
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Org. S	95	57	167	72.0	43.5	38.7
H_2S slip	235	7	43	0.5	1.5	0.1
Total S	330	64	210	72.5	45.0	38.8
Conv. %	71.2	82.7	-	78.2	86.8	88.2

Note 1. When T_5 was raised from 350 to 410 °C, the total sulphur was 22.8 p.p.m. and conversion = 93%

Note 2. % conversion done on the basis of total inlet sulphur = 330 p.p.m.

Table No. 79. Comparison of the inlet and outlet gas.

	Inlet gas	Outlet gas	
		Dry	Wet
Composition			
H_2 %	54.36	52.69	48.33
O_2	1.30	0.00	0.00
N_2	7.72	7.85	7.20
CO	17.33	15.20	13.95
CH_4	15.09	15.74	14.45
CO_2	3.04	7.07	6.48
C_2H_4	0.42	0.12	0.11
C_2H_6	0.74	1.33	1.22
H_2O	–	–	8.26
Total	100.00	100.00	100.00
T_1 °C			352
T_2			350
T_3			358
T_4			330
T_5			352
T_6			22
C.V. (BTU/ft.^{3})	427	427	–
$\frac{(CO_2)(H_2)}{(CO)(H_2O)}$ at 350 °C			
Theoretical			22.000
Experimental			2.715

Experiment No.15

To study the decomposition of organic sulphur in coal gas at pressure, by using six stages.

Table No. 80. Packing of the reactors.

No.	PARTICULARS	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
		Nim.1	Lux 1	Nim.2	Lux 2	Nim.3
1	Reactor ID (in.)	0.742	0.742	0.742	0.742	0.742
2	Bed height (in.)	6.55	18	6.4	17	5.7
3	Bed volume (in.^{3})	2.57	7.22	2.57	7.22	2.57
4	Wt. of catalyst (gm)	35.2	130	35.2	130	35.2
5	Size of catalyst (in.)	1/16 - 1/32	+ 1/8	1/16 - 1/32	+ 1/8	1/16 - 1/32
6	S.V. for 1 ft.^{3}/hr v/v/hr.	670	240	670	240	670
7	Flow for 1000 v/v/h S.V. ft.^{3}/hr	1.486	4.17	1.486	4.17	1.486

Notes: Stage 6 was fresh lux and decompressed gas was passed.

Stage 1 was presulphided and was from the previous run; was stage 3

Stage 3 was presulphided and was from the previous run; was stage 5.

Stage 5 was freshly packed Nimox

Stage 2, 4, were freshly packed Lux.

Conversion catalyst was Peter Spence 3.5/10 Nimox

Absorbent was Peter Spence Lux.

Table No. 81. Results:

1 Time from start Hrs.	2 Plant pressure psig	3 S.V. Nim. (Gas out) v/v/h	4 S.V. Lux (Gas out) v/v/h	5 T_1 °C	6 T_2 °C	7 T_3 °C	8 T_4 °C	9 T_5 °C	10 T_6 °C	11 % H_2O out %	12 Total S in p.p.m.	13 Org. S out p.p.m.	14 H_2S slip p.p.m.	15 Total S out p.p.m.
125	260	1080	386	350	345	360	380	350	20	12.2	274	0.21	0.27	0.48
155	260	830	300	350	345	360	380	350	20	17.3	274	0.13	0.11	0.24
170	280	830	300	360	345	350	365	350	20	17.3	274	0.164	0.07	0.234
195	280	865	310	360	345	345	365	350	20	13.4	274	0.172	0.043	0.215
270	290	1075	384	365	350	355	356	356	20	9.1	274	0.300	0.06	0.360
288	290	2100	750	350	350	350	360	358	20	7.2	274	0.210	0.03	0.240
312	300	2060	735	350	350	350	350	350	20	7.3	300	0.621	0.064	0.685
340	300	2200	785	352	350	350	350	350	20	1.6	300	1.000	0.100	1.100
360	290	4750	1700	360	350	350	350	360	20	1.4	300	1.470	0.130	1.600
435	290	6500	2330	350	350	350	350	350	20	1.0	300	1.580	0.020	1.600
460	290	8100	2900	370	385	440	310	385	20	0.8	300	2.150	0.050	2.200
485	290	11300	4060	355	330	215	280	320	20	0.6	300	2.000	0.300	2.300
488	290	14500	5200	355	330	215	280	320	20	0.3	300	2.36	0.200	2.560
504	290	1490	530	350	350	350	350	350	20	2.7	300	0.93	0.170	1.100
535				400	400	400	400	400	20		330.5 (A)			

CONTD....

Table No. 81 contd.....

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
600	300	1090	390	400	400	400	400	400	20	4.4	330.5	0.502	0.115	0.617
630	300	1090	390	400	400	400	400	400	20	4.4	330.5	0.460	0.19	0.650
653	300	955	342	400	410	410	400	470	20	7.2	330.5	0.78	0.14	0.92
675	300	1220	437	400	405	408	395	472	20	5.2	330.5	0.50	0.14	0.64
700	300	1220	437	400	408	410	398	475	20	5.2	330.5	-	-	0.96
744	300	1275	455	403	410	410	400	480	20	4.5	330.5	1.30	0.20	1.50
795	300	1360	486	400	400	400	400	400	20	4.0	326	1.232	0.13	1.362
800 *	300	1300	467	402	400	400	400	400	20	2.6	326	-	-	2.4
816	300	1300	467	402	400	400	400	400	20	2.6	326	3.36	.04	3.4
864	300	950	339	430	430	430	430	430	20	3.9	326	3.35	.05	3.4
936	300	795	285	430	435	435	435	435	20	4.5	326	8.46	.04	8.5

* No water going in with the inlet gas.

Table No. 82. Effect of space velocity on organic sulphur decomposition and hydrogen sulphide absorption.

(1) Average temp. = 350°C (2) Average pressure = 290 psig

(3) Inlet S = 300 p.p.m. app.

Space velocity over		Sulphur out			Water out
Nimox	Lux	H_2S	Organic	Total	%
v/v/h.	v/v/h.	p.p.m.	p.p.m.	p.p.m.	
830	300	0.110	0.130	0.240	17.3
830	300	0.070	0.164	0.234	17.3
865	310	0.043	0.172	0.215	13.4
1075	384	0.060	0.300	0.360	9.1
1080	386	0.270	0.210	0.480	12.2
2060	735	0.064	0.621	0.685	7.3
2100	750	0.030	0.210	0.240	7.2
2200	785	0.100	1.000	1.100	1.6
4750	1700	0.130	1.470	1.600	1.4
6500	2330	0.020	1.580	1.600	1.0
8100	2900	0.050	2.150	2.200	0.8
11300	4060	0.300	2.000	2.300	0.6
14500	5200	0.200	2.360	2.560	0.3
1490	530	0.170	0.930	1.100	2.7

Average temperature = 400°C

1090	390	0.115	0.502	0.617	4.4
1090	390	0.190	0.460	0.650	4.4

$T_1 = T_2 = T_3 = T_4 = 400°C$ but $T_5 = 480°C$

955	342	0.140	0.780	0.920	7.2
1220	437	0.140	0.500	0.640	5.2
1220	437	-	-	0.960	5.2
1275	455	0.200	1.300	1.500	4.5
1360	486	0.130	1.232	1.362	4.0

Table No. 83. Comparison between inlet and outlet gas.

Time after start	96 Hrs.		312 Hrs.	
	IN	OUT	IN	OUT
Composition (Dry) %				
CO_2	3.09	8.07	2.85	5.21
C_2H_4	0.68	0.00	0.56	0.00
C_2H_6	0.29	1.80	0.98	2.28
H_2	53.80	53.42	51.95	48.87
O_2	1.47	0.00	1.76	0.00
CO	16.27	9.00	17.32	15.54
CH_4	17.05	20.00	14.60	16.60
N_2	7.35	7.71	9.98	11.50
Total	100.00	100.00	100.00	100.00
% H_2O out (Wet)	-	10.50	-	7.30
T_1 °C	-	350	-	350
T_2	-	400	-	350
T_3	-	340	-	350
T_4	-	330	-	350
T_5	-	350	-	350
T_6	-	20	-	20
S.V. v/v/hr.				
Nimox		1036		2060
Lux		370		735
Total S in (p.p.m.)	200	-	300	
Total S out (p.p.m.	-	2.4	-	0.69
C.V. BTU/ft.^{3}	429	461	421	440
$K = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$				
Experimental	-	4.07		2.08
Theoretical at 350°C		22		22

Table No. 84. % analysis of the Nimox and Luxmasse beds before and after use.

Constituent Elements	P. Spence Nimox 3.5/10			P. Spence Luxmasse		
	Fresh	Used Stage 1	Used Stage 3	Fresh	Used Stage 2	Used Stage 4
Iron	-	-	-	33.2	35.5	33.2
Nickel	2.6	1.90	2.50		-	-
Molybdenum	2.0	1.95	1.97		-	-
Sulphur	-	1.54	1.05	-	7.70	7.30
Carbon	-	3.81	0.31	-	7.36	6.32

Experiment No. 16.

To study the decomposition of organic sulphur in town gas on 4.5/12 Nimox in conjunction with I.C.I. Zinc oxide absorbent.

Table No. 85. Packing of Reactors.

No.	PARTICULARS	STAGE 1	STAGE 2
		4.5/12 Nimox	I.C.I. Zn 0
1	Reactor ID. (in.)	0.742	0.742
2	Bed height (in.)	6.15	6
3	Volume of the bed (in.^{3})	2.66	2.60
4	Size of the Catalyst	- 10 + 18 B.S.S.	As such (3/16 in.)
5	S.V. for 1ft.^{3}/hr.	650	665
6	Wt. of the CATALYST (gms)	38.42	40.5

Table No. 86. H_2S Slip over Zn O.

1	2	3	4	5	6	7
Pressure	Flow	S.V.	Nimox temp.	Zn O temp.	H_2S slip	Org. S out
psia	$ft.^3/hr.$	v/v/h.	°C	°C	p.p.m.	p.p.m.
ATM	0.2825	184	220	20	1.06	–
"	0.5090	330	220	20	0.84	–
"	1.0580	690	220	20	0.64	–
"	1.3580	885	220	20	0.37	8.2
"	1.8530	1200	220	20	0.29	–
"	0.8000	520	220	230	0.23	–
"	1.0580	690	220	230	0.25	–
"	1.3580	885	220	230	0.22	–
"	1.8530	1200	220	230	0.18	8.6
ATM	0.280	184	225	315	0.32	–
"	.510	330	225	315	–	–
"	.800	520	225	315	0.22	–
"	1.060	690	225	315	–	–
"	1.360	885	225	315	0.23	–
"	1.850	1200	225	315	–	–
ATM	0.280	184	220	385	–	–
"	0.510	330	220	385	–	–
"	0.800	520	220	385	0.14	–
"	1.060	690	220	385	–	–
"	1.360	855	220	385	0.13	–
"	1.853	1200	220	385	0.19	–

Table No. 86 contd.....

1	2	3	4	5	6	7
ATM	0.280	184	220	450	0.45	-
"	0.800	520	220	450	0.23	-
"	1.360	885	220	450	0.25	-
"	1.853	1200	220	450	0.12	-
ATM	0.13	90	20	460	0.36	-
"	0.80	520	20	460	0.23	-
"	1.36	885	20	460	0.19	-
"	1.85	1200	20	460	0.19	5.5
355	2.483	1650	20	400	Nil	4.80
"	4.185	2780	20	400	0.044	5.33
"	7.060	4700	20	400	0.040	3.58
"	10.000	6650	20	400	0.8 -1.44	2.60
"	13.1000	8710	20	370	Nil	-
355	2.72	1800	20	375	0.19	
"	5.70	3800	20	382	0.06	
"	8.60	5700	20	390	0.16	
"	13.00	8700	20	380	0.27	5.5
355	2.72	1800	20	380	0.26	2.8
ATM	0.747	500	20	400	0.25	6.0

Table No. 87. Treatment of Synthetic Mixture over Zn O.

1	2	3	4	5	6
Flow	S.V.	Temp.	H_2S Slip	Total Org. S out	Decomposition
$ft.^3/hr.$	v/v/h.	$^{\circ}C$	p.p.m.	p.p.m.	%
COS/H_2 mixture		COS = 686 p.p.m.			
0.37	245	400	0.30	–	–
0.50	330	400	0.28	10.00	98.5
2.40	1600	400	0.05	6.10	99.1
C_4H_4S/H_2 mixture		C_4H_4S = 238 p.p.m.			
0.28	180	400	0.12	202	15.3
0.50	330	400	0.27	214	10.0

Table No. 88. Results with town gas at atmospheric pressure.

1	2	3	4	5	6	7	8	9	10	11
Hrs. from start	S.V.	Nimox temp.	Zn O temp.	H_2S slip	Org. S out	Total S out	H_2S out	Total S in	Conv.	Differential pressure
Hrs.	v/v/h	^oC	^oC	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	%	in Hg.
0	860	-	-	-	-	-	-	-	-	-
24	845	392	Not in	Nil	4.10	4.10	78	82.1	95.0	0.4
31	850	395	"	Nil	4.30	4.3	88.5	92.8	95.4	0.6
54	850	398	"	Nil	-	-	-	-	-	0.6
96	850	396	"	Nil	5.80	5.8	148	153.8	96.2	0.6
128	850	400	"	0.26	5.54	5.8	154.8	160.6	96.4	0.6
145	850	398	"	Nil	6.60	6.6	168	174.6	96.2	0.6
195	850	399	"	0.03	4.22	4.25	167	171.3	97.4	0.5
264	875	399	"	0.05	4.65	4.70	223	227.7	98.0	0.5
312	830	395	"	0.16	4.54	4.70	153.2	157.9	97.0	0.5
340	830	390	"	0.11	4.09	4.20	185	189.2	97.7	0.5
364	845	390	"	0.10	4.30	4.40	190	194.4	97.7	0.5
393	845	390	"	0.10	4.15	4.25	-	-	-	0.5
440	845	505	"	Nil	2.90	2.90	-	-	-	0.9
460	825	490	"	Nil	3.12	3.12	138	141.12	97.8	0.7
508	825	390	"	Nil	3.60	3.60	133	136.6	97.3	0.7
531	825	492	"	Nil	-	-	-	-	-	0.7
602	350	298	"	Nil	2.93	2.93	89.7	92.63	96.7	0.2

Table No. 88 contd......

1	2	3	4	55	6	7	8	9	10	11
632	825	192	"	Nil	8.66	8.66	-	-	-	0.6
650	825	216	20	Nil	6.60	6.60	92.6	99.2	93.3	0.6
674	880	220	20	0.30	7.90	8.2	-	-	-	0.5
698	880	220	230	0.22	8.38	8.6	-	-	-	-
726	880	225	316	0.23	-	-	-	-	-	-
813	880	220	455	0.25	-	5.0	-	-	-	-
837	880	40	460	-	-	4.1	-	-	-	0.5
860	88	40	460	0.186	-	6.0	72.2	78.2	92.4	-
870 *	1610	40	400	-	-	4.8	-	-	-	-
936	880	40	-	-	-	-	77.8	-	-	-

* Pressure = 350 psig.

Note 1. Total S in = Column (7) + Column (8)

Note 2. Up to 650 hrs. absorbent used was Luxmasse.

Table No. 89. Comparison of the inlet and outlet gas.

1	2		3		4		5		6	
Time from zero hr.	145		338		458		814		930	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT
1 Temp. Nimox °C	-	398	-	390	-	490	-	220	-	20
Temp. Zn O °C										
S.V. v/v/h.		20		20		20		455		380
2 Composition %										
H_2	50.69	50.00	47.24	47.25	47.00	45.56	46.65	45.31	45.90	44.80
O_2	1.79	0.00	1.79	-	1.37	0.00	1.41	0.00	1.22	0.00
N_2	8.00	9.58	11.25	11.99	10.48	10.80	10.61	11.15	10.86	11.64
CO	14.44	15.65	12.74	12.18	7.79	10.28	8.08	9.86	7.41	7.52
CH_4	19.00	18.82	20.90	21.10	26.52	27.36	27.08	28.25	27.40	28.82
C_2H_6	0.63	1.80	0.63	1.92	0.64	1.48	0.57	0.64	0.51	0.52
C_2H_4	1.69	-	1.69	-	1.07	0.28	0.83	0.96	1.32	0.88
CO_2	3.76	4.15	3.76	5.56	5.13	4.24	4.77	3.83	5.38	5.82
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
3 C.V. Dry °C 760 mm. BTU/ft.^{3}	466	459	468	464	501	516	501	519	506	511
4 H_2S out p.p.m.	-	168.0	-	185.0	-	138.0	-	72.2	-	72.3
Org. S out p.p.m.	-	6.3	-	4.2	-	3.2	-	5.0	-	5.5
Total S out p.p.m.	-	174.3	-	189.2	-	141.2	-	77.2	-	77.8

Table No. 89 contd......

1	2		3		4		5		6	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT
5 Individual Org. S out	-	-	-	-	-	-	-	-	-	-
RSH + C_4H_4S	-	-	-	-	-	-	-	3.0	-	-
COS + CS_2	-	-	-	-	-	-	-	2.0	-	-
6 % Conversion	-	98.5	-	97.7	-	97.8	-	93.50	-	93.0

Table No. 90. Temperature profile in the reactor containing 4.5/12 Nimox.

Position of thermocouple in the bed.	N_2 in	H_2 in	Gas in
	°C	°C	°C
1 in. above the bed	375	380	360
½ in. above the bed	–	383	370
Top of the bed	381	385	378
½ in. below the top	–	388	380
1 in. " " "	382	388	390
1½ in. " " "	–	388	400
2 in. " " "	382	386	400
2½ in. " " "	–	385	400
3 in. " " "	380	385	398
3½ in. " " "	–	384	398
4 in. " " "	378	381	398
4½ in. " " "	–	380	392
5 in. " " "	370	375	390
5½ in. " " "	–	–	386
Bottom of the bed	364	–	382
1 in. below the bed	355	360	370

Experiment No.17. 17

To study the decomposition of organic sulphur on Comox, an I.C.I. Cobalt/Molybdenum catalyst. (Single stage study).

Table No. 91. Packing of the reactor.

No.	PARTICULARS	INFORMATION
1	Reactor ID (in.)	0.742
2	Catalyst particle size (in.)	1/16 - 1/32
3	Wt. of catalyst packed (gms.)	43.011
4	Height of bed (in.)	5.2

Table No. 92. (A) Results obtained on compressed coal gas.

Pressure = atmospheric.

Catalyst = unsulphided.

1	2	3	4	5	6	7	8	9	10	11
Hrs. from zero hour	Flow	S.V.	Temp.	H_2S slip from fresh Lux.	Org. S out	Total S out	H_2S out	Total S out	Decomp-osition	Potential difference across reactor
Hrs.	ft^3./hr.	v/v/h.	^oC	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	%	in. Hg.
0	1.33	1025	-	-	-	-	-	-	-	0.8
19	1.27	975	-	-	-	-	-	-	-	-
20	1.27	975	385	0.20	0.9	1.10	3.4	4.5	-	1.0
26	1.34	1025	385	0.23	2.37	2.60	20	22.6	-	1.0
96	1.34	1025	385	0.00	5.33	5.33	111	116.3	95.5	1.0
122	1.37	1025	390	0.00	3.30	3.30	109	112.3	97.1	1.4
144	1.37	1025	385	0.03	3.72	3.75	114	117.8	96.8	1.6
193	1.59	1220	385	0.17	4.33	4.5	139.3	143.8	96.9	1.7
260	1.41	1090	385	0.05	4.75	4.8	214.5	219.3	97.8	2.0
310	1.39	1070	390	0.00	4.90	4.9	153	157.9	96.9	2.4
336	1.39	1070	380	0.04	3.56	3.6	110.5	114.1	96.9	2.2
361	1.37	1055	380	0.00	3.40	3.4	96.2	99.6	96.6	2.2
388	1.37	1055	385	0.00	4.20	4.2	-	-	-	2.5
435	1.37	1055	500	0.41	3.67	4.08	-	-	-	1.5
455	1.32	1015	480	0.00	3.30	-	125	-	-	1.35
504	1.24	960	480	0.00	4.10	4.10	135	139.1	97.2	1.50

Table No. 92 contd.....

1	2	3	4	5	6	7	8	9	10	11
525	1.24	960	485	-	-	-	-	-	-	-
600	0.35	265	305	0.00	3.25	3.25	-	-	-	0.35
626	1.30	1000	210	0.00	8.60	8.6	-	-	-	0.80
645	1.30	1000	200	0.144	69.8	70.9	1.1	72.0	1.5	0.90
(B) Treatment of Laboratory Gas.										
667	1.23	945	272	.013	94.3	94.30	306	400.3	76.5	2.25
690	1.23	945	310	0.00	39.75	39.75	433	472.75	91.5	2.50
720	1.23	945	360	0.00	19.00	19.00	475	510.20	93.1	2.50
764	1.23	945	420	0.00	23.4	23.40	462	485.3	95.2	4.00
788	0.45	340	418	0.00	19.0	19.00	331	350.0	94.6	2.00
814	0.51	395	371	.074	19.2	19.20	437.5	456.7	95.9	0.50

Table No. 93. Undecomposed organic sulphur in outlet gas vs Temperature. (assuming S.V. constant).

°C	p.p.m. S	Removal %
200	69.8	1.5
210	8.6	–
305	3.25	–
380	3.40	96.6
382	3.56	96.9
385	2.37	–
386	5.33	97.8
388	4.90	96.9
390	3.30	97.1
480	3.30	–
482	4.1	97.2
500	3.67	–

Laboratory Gas

272	94.3	76.5
310	39.75	91.5
360	19.00	93.1
371	19.2	95.9
418	19.0	94.6
420	23.4	95.2

Table No. 94. Temperature profile in the reactor.

1	2	3	4	5
Position of Thermocouple	N_2 only in	H_2 only in	H_2 only in	Coal gas in
in.	°C	°C	°C	°C
2 in. above bed	354	365	350	362
1 in. above bed	362	375	364	374
Top of the bed	370	382	372	385
1 in. below top	375	390	378	393
2 in. " "	378	392	383	393
3 in. " "	378	392	383	391
4 in. " "	378	392	383	388
5 in. " "	375	390	380	382
Bottom of the bed	371	385	375	375
1 in. below bottom	365	362	368	370
2 in. below bottom	356	360	360	359

Notes:

Column 2 Only nitrogen was going in

Column 3. H_2 in, nitrogen stopped, control not adjusted.

Column 4. Heat control readjusted.

Column 5. Coal gas in, heat control not adjusted.

Table No. 95. Comparison of inlet and outlet gas.

1	2	3	4	5
PARTICULARS	INLET GAS	OUTLET GAS	INLET GAS	OUTLET GAS
Temperature °C	-	386	-	382
Flow ft.^{3}/hr.	-	1.32		1.372
S.V. v/v/h.		1015		1015
Composition %				
H_2	50.69	50.85	47.27	47.60
O_2	1.79	0.00	1.79	0.00
N_2	8.00	7.99	11.25	11.85
CO	14.44	14.96	12.74	12.22
CH_4	19.00	19.60	20.90	20.92
C_2H_6	0.63	2.17	0.63	1.90
CO_2	3.76	4.43	3.76	5.50
C_2H_4	1.69	0.00	1.69	0.00
Total	100.00	100.00	100.00	100.00
C.V.	466	475	469	463
Density (Air = 1)	0.46	0.46	0.482	0.485
H_2S out (p.p.m.)	-	111.00	-	110.5
Org. S out (p.p.m.)	-	5.33	-	3.6
Total S out (p.p.m.)	-	116.33	-	114.1
Removal %	-	99.5	-	96.7

Experiment No.18. 18

To study decomposition of organic sulphur in coal gas with added carbonyl sulphide. (Single stage study at pressure).

Table No. 96. Packing of the reactor with 3.5/10 P.S. Nimox.

No.	PARTICULARS	INFORMATION
1	Reactor ID. (in.)	15/64
2	Bed height (in.)	6
3	Wt. of the catalyst (gm.)	4.909
4	Size of the particles (in.)	1/32 - 1/86
5	Flow required for S.V. = 10,000	
	(1) Based on reactor volume ft.^{3}/hr.	1.496
	(2) Based on bulk density of the catalyst	2.196

Note: The reactor had three thermocouples soldered to the outside wall.

T_1 at the top

T_2 at the middle

T_3 at the bottom.

Table No. 97. Results:

Pressure = 355 psia.

S.V. based on reactor volume

1	2	3	4	5	6	7
S.V.	T_1	T_2	T_3	Org. S out	H_2S out	Decomposition
	°C	°C	°C	p.p.m.	p.p.m.	%
3410	395	370	330	9.1	–	–
5820	400	370	330	9.5	–	–
12580	410	385	345	7.45	–	–
21800	410	375	340	7.00	–	–
27300	400	390	353	7.50	–	–
37600	405	410	380	6.50	–	–
49600	385	415	395	7.00	–	–
54600	365	415	400	6.50	–	–
61600	350	416	408	6.60	–	–
70800	335	409	405	7.30	–	–
87400	310	402	410	7.1	–	–
2276	410	385	340	9.0	–	–
2276	406	382	340	7.5	–	–
2276	406	382	340	7.5	355	98.5
2276	406	380	340	–	–	–
5820	408	385	345	6.5 *	551	99.0

* C_4H_4S in the outlet gas = 1 - 2 p.p.m.

Notes: T_1 = T/C at the top of the bed

T_2 = T/C at the middle of the bed

T_3 = T/C at the bottom of the bed

Table No. 98 A comparison of the composition of inlet and outlet gas.

$P = 355$ psia.
$T_1 = 410\ ^{\circ}C$
$T_2 = 385\ ^{\circ}C$
$T_3 = 345\ ^{\circ}C$
Flow = 2.25 $ft.^3/hr.$
S.V. = 15,000 v/v/h.

Composition etc.	Inlet gas	Outlet gas as such	Outlet gas after Lux.
	%	%	%
CO_2	5.31	4.61	4.79
C_2H_4	1.12	0.00	0.00
C_2H_6	0.82	1.57	1.60
CH_4	17.86	20.40	19.44
CO	5.10	7.28	7.28
O_2	1.22	-	0.00
H_2	60.10	56.92	56.91
N_2	8.47	9.22	9.48
Total	100.00	100.00	100.00
C.V.	448	467	-
Density	0.39	0.40	

$$K = \frac{(CO)(H_2S)}{(H_2)(COS)} = 13$$

$(H_2S = 557)$

Theoretical COS out 5.47 p.p.m

Experimental COS out 5 - 6 p.p.m

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APPENDIX 1.

Determination of Organic Sulphur Compounds by using platinum spiral method.

The platinum spiral method was preferred to the combustion method for the ease in operation and for the rapid determination of organic sulphur present in very low concentrations with fair accuracy. The combustion method is tedious and time consuming and at the same time does not give reproducible results when organic sulphur is present in gas in the order of few parts per million.

A platinum wire, 26 B.S.W. and 36 in. long was made into a spiral and placed inside a 9/16 in. i.d. silica tube 36 in. long. The silica tube was placed in a temperature controlled tubular furnace and was heated to a temperature of about 900 °C.

H_2S was estimated iodimetrically or by producing a lead stain. For iodimetric determination H_2S produced was absorbed either in ammoniacal zinc sulphate solution as described in B.S.3156 - 1959, or in 10% Cadmium Chloride solution. At very low concentrations lead stain was produced and intensity of this stain was measured with an E.E.L.H_2S meter.

For the analysis of individual organic sulphur compounds a variation of the method Hakewill and Rueck$^{(71)}$ was used. This method is strictly applicable only to gases containing sulphur as hydrogen sulphide, mercaptans, thiophenes, carbon disulphide, carbon oxysulphide, but not to other types of sulphur compounds soluble in the selective absorbents employed.

The absorption reagents employed are given as follows :

Reagent 1. Absorption of H_2S and mercaptans - 35 ml. of 10% Cadmium chloride solution with 5 ml of normal sodium carbonate solution.

Reagent 2. Absorption of Thiophene - Sulphuric Acid of sp.gravity 1.84

Reagent 3. Absorption of carbon disulphide and carbonyl sulphide - 10 gm potassium hydroxide and 95% ethyl alcohol. Clear supernatant liquid, decanted after carbonate has settled, used at 0 °C - 5 °C.

Reagent 4. Retention of acid gases or sprays, 20% caustic soda solution.

The estimation of the concentration of the various sulphur compounds depends upon - (1) The results of determination of total sulphur in gas before and after treating the gas with selective reagents to remove specific sulphur compounds, and (2) The analysis of certain of the selective reagents for specific sulphur compounds by titration with iodine.

Absorption reagents were kept in the order as below :

Reagent (1) → Reagent (2) → Reagent (4) →
→ Reagent (3)

Procedure: As stated above Dreschel bottles containing respective reagents were connected in the above order. The gas to be analysed passed through the whole train and H_2S coming through the platinum spiral measured on an E.E.L. H_2S meter. H_2S coming out at this stage represented only unknown sulphur not falling in the general category of organic sulphur compounds. Normally the quantity of this sulphur is not significant.

Then Reagent (3) was omitted and determination repeated. H_2S

coming out of the platinum spiral represented COS + CS_2. Then Reagents (2) and (4) were omitted. H_2S out represented C_4H_4S + COS + CS_2. Then by removing Reagent (1) the total organic sulphur was found.

It is clear from the above that by suitable subtractions, it is possible to find out the individual sulphur compounds. To get limited information Reagent (3) was omitted. The COS + CS_2 was found directly.

The order of reagents given above should not be changed.

Analysis of Outlet Gas.

In practice, the outlet gas which contained H_2S along with other organic sulphur compounds was passed through a Luxmasse tower to take up H_2S and thus subsequent sulphur was of organic nature only. As organic sulphur after catalytic treatment would be of the order of a few p.p.m., no elaborate analysis would be required. Only the platinum spiral method then can be used to find out individual organic sulphur compounds.

Analysis of Inlet Gas.

Inlet gas may contain 100 - 500 p.p.m. of organic sulphur. To determine total sulphur, iodimetric analysis was used because H_2S meter was not accurate at these concentrations. 10% cadmium chloride or ammoniacal zinc sulphide as given in B.S.3156 - 1959 was used. It was found advisable to add extra hydrogen to the inlet gas. This would avoid the carbon deposition on the hot spiral. Also it would shift the equilibrium towards complete decomposition of organic sulphur compounds to H_2S.

In actual experiments it was found that carbon deposition could occur if gas was passed through the platinum spiral for a long period. Carbon deposition deactivates the platinum surface and then carbon had to be burnt out in air.

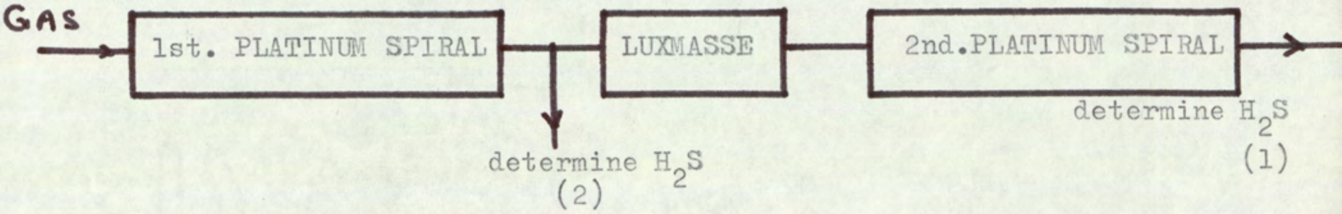
Later on it was found advisable to add more platinum wire. 5 yards of 0.0035 in. dia. platinum wire was placed in a silica tube, extra to the already placed 9 ft. of 26 B.S.W. platinum wire.

Among other things noticed was that total sulphur coming out was higher than total sulphur going in. The reason was that inlet sulphur was decomposed on the platinum spiral only and this represented single-stage treatment only. Outlet gas was treated already on Nimox, H_2S removed and then the remaining organic sulphur decomposed on the platinum spiral. This represented a two-stage decomposition, with intermediate eliminated of H_2S and hence total outlet sulphur was higher than inlet sulphur. Hence in this programme inlet sulphur figure was often taken as the sum of H_2S out and organic sulphur out.

A more positive arrangement should be as follows :

Instead of having one platinum spiral arrangement, there should be two such arrangements. Gas being analyzed for organic sulphur should be passed through the first platinum spiral and then the stream coming out should be split into two. One stream is used for determining hydrogen sulphide and the other stream passed through Luxmasse to absorb hydrogen sulphide and then through the second platinum spiral and hydrogen sulphide determined.

Sum of the two hydrogen sulphide figures obtained should give a better figure for inlet sulphur than obtained by using only one platinum spiral. This can be presented diagrammatically as follows :


GAS
1st. PLATINUM SPIRAL
LUXMASSE
2nd.PLATINUM SPIRAL
determine H_2S
(2)
determine H_2S
(1)

In one case, where a COS/H_2 mixture was tested by using one spiral only, the H_2S found was equal to 770.5 p.p.m. (H_2S). By using a second platinum spiral another 39 p.p.m. was detected. Thus an overall error was about 4.82%,

In another case, where a C_4H_4S/H_2 mixture was analysed, it was found that single spiral gave H_2S = 473 p.p.m., while another platinum spiral produced another quantity of H_2S = 55 p.p.m. Thus Thus overall error by using one spiral amounted to 10.44%.

It was also found that Luxmasse and other liquid reagents like 10% cadmium chloride etc. take up 3 - 5 % COS, and thus overall the analytical figure obtained may be short by 3 - 5%.

Among other observations made, one was that more platinum surface available gives better results. Also there is a definite time lag before the platinum spiral starts emitting constant amount of sulphur. This time lag may vary from 1 - 2 hours for pure compounds. When coal gas is being analysed, it is advisable that this much time should not be given because of the partial deactivation of the platinum surface. Two consecutive spirals should give good results.

It was thought advisable to choose the expression "p.p.m. as H_2S", as the best way of expressing the sulphur concentrations. Usual method is to express the sulphur concentrations as gr.S/100 cu.ft., which is a bit larger for expressing traces of sulphur. As the E.E.L. H_2S meter was directly calibrated in p.p.m. H_2S, this way of expressing was definitely more convenient and has been retained throughout this work.

APPENDIX 2.

A tentative design for a Town Gas Desulphurization Unit, capable of treating 1,000 cu.ft. of gas.

Process conditions selected :

1	Pressure	Atmospheric
2	Temperature at each stage °C	400
3	Flow cu.ft./hr.	1,000
4	Number of stages	6
5	Suggested conversion catalyst	P.S. Nimox (3.5/10)
6	Suggested Absorbents	P.S. Luxmasse I.C.I. Zinc Oxide
7	Suggested space velocity	
	(1) On Nimox v/v/h.	5,000
	(2) On Absorbents v/v/h.	500

Design:

1. Basic Considerations: It was clear that for complete removal of sulphur, six-stage treatment was advisable. For better temperature control all the reactors should be at one temperature i.e. 400°C. The pressure will be essentially atmospheric for the purpose of this design, although it was found that at higher pressures convertion of thiophene to hydrogen-sulphide was better. If the town gas is available at pressure, then there should not be any trouble in overcoming the back-pressure. Otherwise a booster will be essential.

In Figure No a typical layout is shown. The incoming gas is pre-heated by heat-exchange with the outlet gas. A small pre-heater and a cold by-pass will be required to control the temperature before the gas is fed to the first converter.

A pre-heater for start up will be required. Auxiliary heaters will be required to control the temperature of each reactor and absorber.

2. Heat requirements:

Suppose the gas contains 0.5% oxygen. Then according to the following equation

$$2H_2 + O_2 = 2H_2O$$

1% of Hydrogen will be consumed.

Flow = 1,000 cu.ft./hr.
% O_2 in gas = 0.5
% H_2 consumed = 1.0
Hydrogen consumed = 10 cu.ft.
Net C.V. of H_2 = 270 BTU/cu.ft.
Heat liberated = 2700 BTU/Hr.
Specific heat of gas = .02 BTU/cu.ft./ °F

Hence temperature rise of

$$\text{gas} = \frac{2700}{.02 \times 1000} = 135\ ^{\circ}F$$

$$= 75\ ^{\circ}C$$

Hence in the heat balance considerations it can be assumed that gas temperature will rise to 400 °C in the reaction zone if the inlet gas is fed at 325 °C.

Heat-balance over the Heat Exchanger.

The inlet gas enters the heat exchanger at 20 °, and is pre-heated to 325 °C. Hence, the temperature rise in the inlet gas = 305 °C.

If it is assumed that specific heat remains constant at 0.02 BTU/cu.ft./ °F, then the fall in the temperature of the outlet gas is also 305 °C.

Hence the temperature of the outgoing gas = 400 - 305 = 95 °C. So terminal temperatures over the Heat Exchanger are :

	IN	OUT
Inlet Gas °C	20	325
Outlet Gas °C	400	95

So heat exchanged = 1000 x .02 x 305 x 1.8
= 11,000 BTU/hr.

It is clear that the inlet gas is pre-heated to the required temperature without any external supply. A cold by-pass will be required to control the temperature of the inlet gas going to the first reactor.

Heat requirements for Start-up.

Temperature of the incoming gas = 20 °C
Temperature to which the gas will be pre-heated = 325 °C

Hence heat load = 305 x 1.8 x .02 x 1000 = 11,000 BTU/Hr.

If for the purpose of pre-heating, electricity is used then the capacity of the heater

$$= \frac{11,000}{3412} = 3.225 \text{ KW}$$

$$= \text{or } 4 \text{ KW}$$

So provision will be made for 4 KW heater.

Alternatively a gas burner may be used.

Design of Individual Units.

(1) Design of Converter

Space velocity in the converter = 5,000 v/v/h.

Flow/hr. = 1,000 cu.ft.

Catalyst volume = $\frac{1000}{5000}$ = 0.2 cu.ft.

Assuming l/d ratio of the bed = 3

Then d = 5.3 in. or 6 in.

l = 6 x 3 = 18 in.

Leaving 6 in. at the top and 6 in. at the bottom, total length = 18 + 6 + 6 = 30 in.

So l/d of the reactor = $\frac{30}{6}$ = 5.

Hence actual volume of the catalyst = 0.294 cu.ft.

If Bulk density = 0.88 gm/cc

Then weight of catalyst = 0.88 x 62.3 x 0.294 = 16.0 lb.(say)

Cost of the catalyst at 10s/0d. per lb. = £8. 0.0d.

(2) Design of Luxmasse reactor.

Space velocity = 500 v/v/hr.

Volume of the bed = $\frac{1000}{500}$ = 2.0 cu.ft.

If l/d = 3 in the bed, then

d = 11.48 in. or say 12 in.

l = 36 in.

Leaving 6 in. at the top and 6 in. at the bottom, total length = 48 in.

Hence final l/d of the reactor = $\frac{48}{12}$ = 4

Colume of the Lux bed = 2.36 cu.ft.

Weight of Lux. required = 2.36 x 1.2 x 62.3 = 176 lb.

Cost of Lux required at 1s/0d. per lb. = £8.16.0d. say £9. 0. 0d.

Amount of gas that can be treated with this Lux.

Assuming that Lux absorbs sulphur to the extent of 20 w/w of the Lux, and the gas being treated contains 25 gr.S/100 cu.ft. (Average)

Total gas that can be treated

$$= \frac{176 \times 0.2 \times 7000 \times 100}{25}$$

$$= 985{,}600 \text{ cu.ft.}$$

Average life of the Lux bed

= 985 hrs.

or = 1.5 months approximately at 8,000 hrs/annum.

Design of the Heat Exchanger.

Assume Gas/Gas heat transfer coefficient = 5 BTU/hr. $ft.^2$ ^oF

Temperature difference = 75 ^oC or 135 ^oF

$$\text{Surface area required} = \frac{11,000}{135 \times 5} = 16.3 \ ft.^2$$

or say 20 $ft.^2$

If 1/2 in. O.D. 20 B.W.G. tubes are used, then

Surface area/linear ft. = 0.1217 $ft.^2$ (average)

$$\text{Hence length required} = \frac{20}{.1217} = 164 - 165 \text{ ft.}$$

On Table 9 - (Process Heat Transfer by Kern, p.841) data for tube heat layout is given for 1 in. o.d. tube on 1.1/4 in. square pitch. Adopting this data to our design, a 6 in. i.d. shell will house 48 tubes of 1/2" o.d. in single pass.

Hence the length of the heat-exchanger

$$= \frac{164}{48} = 3.42 \text{ ft. say} = 3.5 \text{ ft.}$$

Hence surface area of the shell = 3.14 x 1/2 x 3.5

= 5.5 $ft.^2$

Design of 4 KW Preheater.

It is not desired to design this pre-heater here, but a suitable tubular type preheater, which can be placed in a 4 KW tubular furnace can be designed. Alternatively a gas burner can be used and then the preheater becomes a bank of tubes. The design is left to the choice of the individual.

Approximate heat losses due to surface radiation.

Surface area of the heat exchanger = 5.5 $ft.^2$
Surface area of 3 converters = 12.0 $ft.^2$
Surface area 3 absorbers = 38.0
Total 55.5 $ft.^2$

From McAdams (Heat Transmission by McAdams - p.179. 1954)

h_c + hr. for 100 °F (maximum) temperature difference between surface to room temperature = 2.0

Hence total heat lost due to radiation, assuming actual temperature difference = 50 °F = 55.5 x 2 x 50
= 5550 BTU/hr.
= 2 KW

Hence provision has to be made to use auxiliary heaters to make up for the surface heat losses.

Approximate working costs.

If it is assumed a basis of 8,000 hrs./annum, then gas treated in a year $= 8 \times 10^{6}$ cu.ft.

(1) Cost of Nimox/1,000 cu.ft. :

Assuming the working life of the catalyst = 1 year, the cost of Nimox/1,000 cu.ft. gas treated $= \frac{8 \times 240 \times 1,000}{8,000,000}$

$= 0.24$d.

(2) Cost of Lux/1,000 cu.ft. $= \frac{9 \times 240 \times 1,000}{985,600}$

$= 2.20$d.

(3) Cost of internal heating due to consumption of 1% H_2

$= \frac{2700 \times 18}{100,000}$

= 0.50d./1,000 cu.ft. at 18d./therm of gas.

(4) Cost due to heat losses = 2d./1,000 cu.ft. at 1d./KWH app.

Hence approximate working cost

= 0.24 + 2.20 + 0.5 + 2.0 = 5d./1,000 cu.ft.

If the gas has a calorific value of 500 BTU/cu.ft. then cost per therm = 1d.

If the radiation losses are eliminated, the cost will be = 0.6d./therm.

If a reduction in operating cost is required of this unit, then major cuts can be obtained on

(1) Cost of Luxmasse

(2) Cost due to heat losses.

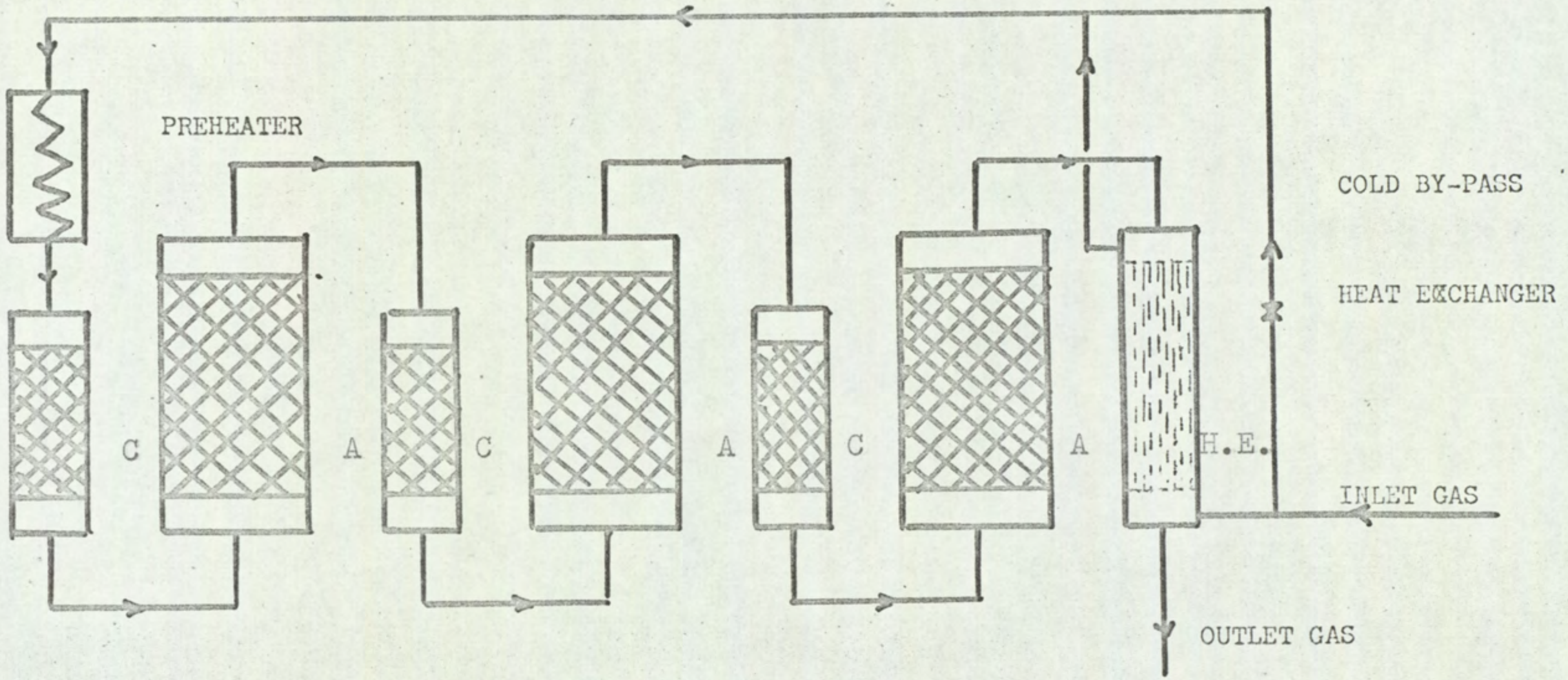


FIGURE 13 PROCESS FLOW DIAGRAM FOR THE PROPOSED 1000 ft^3/Hr DESULPHURIZATION UNIT

C = CONVERTERS

A = ABSORBERS

The cost of Luxmasse at this price is reasonable, but a search can be made for a cheaper variety of iron-oxides, which can be worked at a temperature of 300 - 400 °C.

Heat losses should be avoided as far as is practicable, by proper lagging, and proper housing of the unit.

Figure Nos. 13 are given to illustrate the design.

APPENDIX 3.

Specification of conversion catalysts and Hydrogen-sulphide Absorbents.

(A) Manufactured by Peter Spence and Sons Ltd., Widnes, Lancashire.

A.1. Nimox: Provisional Specification for 1/8 in. Tablets and 1/8 in. Extrudates.

These materials are chemically identical and are made to the following chemical specifications :-

Loss on calcination at 550 °C = 5% by wt. max.
NiO = 3.5% by wt. min.
MoO_3 = 10% by wt. min.
$Na_2 + K_2O$ as Na_2O = 0.09% by wt. max.
SiO_2 = 0.8% by wt. max.

	Tablets	Extrudates.
Bulk Density	0.88 gm/cc	0.75 gm/cc
Surface area	265 m^2/gm	286 m^3/gm
Active base	Alumina	
Price	10/0d. per lb.	

Recommended use: Hydro-desulphurization and Selective hydrogenation of gas streams.

A. 2. Comox: Specification for Comox Desulphurization Catalyst. 1/8 in. and 1/16 in.

Extrudates :

(On the basis of material heated to 1200 °F)

(a) Max. % wt. loss at 1200 °F = 4.00
(b) Min. % wt. Cobalt Content as CoO = 3.50
(c) Min. % wt. Molybdenum content as MoO_3 = 12.50
(d) Max. % wt. $Na_2O + K_2O$ = 0.09
(e) Max. % wt. SiO_2 = 0.80
(f) Max. % wt. Fe = 0.10
(g) Primary base alumina
(h) Bulk density = 0.75 ± 0.05 and 0.8 ± 0.05
(i) Surface Area = 235 m^2/gms. min.

Price : 10s/- per lb.

A.3. Peter Spence Luxmasse.

1/8 in. Extrudates

Bulk density = 1.20 ± .06 gm./cc.

Loss on drying = 3% by weight maximum

Iron oxide content = 46.0% by weight minimum

Above information supplied by Peter Spence and Sons Ltd., Widnes, Lancashire.

B. Conversion Catalyst Manufactured by I.C.I.

B.1. 41 - 3 and 41 - 4 Cobalt oxide/molybdenum-oxide/alumina Catalysts in Pellets/Extrusion forms respectively.

Analytical Composition : not given.

Bulk density - 69 lb./ft^3. and 50 - 57 lb./ft^3. respectively.

Chief use - Vapour-phase hydrodesulphurization of gases and petroleum fractions.

Process temperatures - Recommended 300 - 450 °C

Process pressures - 1 - 70 atmospheres

Liquid space-velocities - 0.2 - 5.0 per hour

The Catalysts do not retain the hydrogen sulphide when the sulphur content reaches 3.0%

B.2. I.C.I. Catalyst 32 - 4, Zinc Oxide/binder

Granules 3.0 m.m. to 4.7 m.m. diameter

Bulk density - 69 lb./ft^3.

It is a Zinc Oxide Catalyst in spherical pills form and is used for the removal of small concentrations of hydrogen-sulphide and organic sulphur compounds from gases before they come into contact with nickel catalysts. The catalyst is normally used in the temperature range of 350 - 450 °C at a space velocity of 400 hrs. It may be used at pressures ranging from atmospheric to over 50 atmospheres. The catalyst absorbs hydrogen sulphide at room temperature but has a longer lifetime when operating in the recommended temperature range. At break-through of H_2S, the catalyst will contain an average of more than 18% w/wt Sulphur. If the flow can be reversed, then the catalyst can be further used, and then at discharge will contain 25% w/wt. sulphur.

When used at 20 °C. then at S.V. of 400 v/v/h, it will absorb 6% w/wt. of sulphur. See Figure

(The above information supplied by I.C.I.)

C. B.A.S.F. Catalysts:

C.1. Cobalt/molybdenum Catalyst 0852.

(1) Base = Activated alumina
(2) MoO_3 = 10%
(3) CoO = 4%
(4) Surface area = 200 m^2/g.
(5) Average pore volume = 0.45 cm^3/gm
(6) Bulk density = 66 - 0.75 j/cc.

The above catalyst is used for the pressure catalytic hydrogen refining of all home stocks. It effects the reduction of sulphur, nitrogen, and oxygen compounds, the hydrogenation of unsaturated compounds, and the removal of metallic impurities.

Its total life is claimed to be several years, and requires regeneration after a year. It can be repeatedly regenerated.

Regeneration can be carried out in air at about 500 °C. Preferably to be done in the presence of an inert gas or steam.

2. Ni/Mo Catalyst No. 7846

NiO = 4%
MoO_3 = 10%
Base = Active earth
Surface area = 200 m^2/g.
Bulk density = 0.59 - 0.72
Stable up to 500 °C, - life 5 years.

Applications:

Refining of all kinds of middle oils with H_2 under pressure. Reduces S, N, and O compounds. Hydrogenates unsaturated bonds. Removes metallic impurities.

D. The Harshaw Chemical Co., Cleveland, Ohio, U.S.A.

Catalyst H T - 100

Recommended for nitrogen and sulphur removal but information not supplied.

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Table No. 99. Decomposition or organic sulphur in coal gas with added carbonyl sulphide at atmospheric pressure.

1	2	3	4	5	6	7	8
S.V.	T_1	T_2	T_3	Org. S out	H_2S out	Total S out	Decomposition
v/v/hr.	°C	°C	°C	p.p.m.	p.p.m.	p.p.m.	%
1592	397	370	325	7.5	-	-	-
4280	398	370	328	9.2	-	-	-
7280	400	370	330	9.2	-	-	-
10400	412	382	340	9.5	-	-	-
15560	410	380	340	8.7	-	-	-
35500	350	406	402	8.5	600	608.5	98.5
38000	362	410	405	7.5	-	-	-
41000	340	398	398	9.4	-	-	-
41000	345	400	420	12.2	-	-	-