THE PYROLYSIS OF THIOPHENE ON CARBON SURFACES IN THE PRESENCE OF CERTAIN INDUSTRIAL GASES

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INTRODUCTION

From the beginning of the manufacture of commercial and domestic fuel gases, the gas industries serving the public have been confronted with the removal of sulfur compounds from various gas mixtures before distribution. For domestic use high sulfur fuel gas is undesirable as this causes undue corrosion of gas mains and deterioration of meter diaphragms and gives the pungent and irritating odors accompanying the combustion of sulfur compounds. Commercially it is often necessary to keep the sulfur content of a gas at a minimum to prevent contamination of a product or to prolong the life of certain catalysts.

Sulfur exists in fuel gases in two major forms, namely inorganic and organic. Inorganic sulfur consists of hydrogen sulfide, while organic sulfur consists chiefly of carbon bisulfide, mercaptans, thiophene and carbon oxysulfide. Removal of hydrogen sulfide can be accomplished by any one of a number of processes, i.e. the iron oxide or liquid processes. The removal of organic sulfur, on the other hand, has not been as extensively investigated as the removal of inorganic sulfur. There are several patented processes available for organic sulfur removal, however, very few of these processes have found commercial application. A few processes such as oil scrubbing or adsorption of the sulfur compounds from the gas on a solid, are used to lower the organic sulfur content of a fuel gas, however, the high costs and operating difficulties make complete removal by these methods impractical.

It is understandable why the amount of work done on methods of inorganic sulfur removal from fuel gas far exceeds that of organic sulfur, for the largest quantity of sulfur in sulfur bearing gases occurs as hydrogen sulfide. Of the organic sulfur compounds, carbon bisulfide usually occurs in much larger quantities than mercaptans, thiophene, or carbon oxysulfide. In most states the organic sulfur content of fuel gases is limited to a maximum, usually not over 30 grains of sulfur per 100 cubic feet of gas at 60°F and 1 atmosphere pressure.

At the present time an extended program is being carried out on the production of synthetic liquid fuels from gases, chiefly hydrogen and carbon monoxide. The catalysts used for the conversion of hydrogen and carbon monoxide to a synthetic liquid fuel are sensitive to the action of sulfur. It is therefore necessary to have a gas mixture practically free from sulfur compounds. A search of the literature showed that the removal of thiophene from gas is quite difficult. It was therefore believed that a study of the transformation of thiophene, under the application of heat, to more easily removed types of sulfur compounds might prove beneficial.

PART I HISTORY

CHAPTER I

THE OCCURRENCE OF THIOPHENE IN FUEL GAS

The formation of organic sulfur compounds accompanies the production of practically all commercial and domestic fuel gases manufactured by high temperature processes from sulfur containing fuels. According to Gollmar (1) the concentrations and types of organic forms of sulfur constituents found in gases are dependent on such factors as (a) the amount and type of sulfur compounds found in the coal, coke or oil being used as fuel; (b) the type of gas being made; (c) the temperatures involved; (d) the time of contact between the gas and the incandescent carbon, coal or coke; (e) and possibly the types and quantities of mineral constituents found in the fuel.

In general, carbon bisulfide is the major constituent of the organic sulfur compounds found in most fuel gases, while thiophene frequently ranks second. Hutchinson (2) made a study of the distribution of organic sulfur compounds in gas, using English coals as fuel. Some of the results of his work are presented below.

Type of Gas Manufacturing Equipment	Total Organic Sulfur (gr./100ft.^{3})	Distribution of Organic Sulfur (Percent)			
		Mercaptans	C_4H_4S	CS_2	COS
Vertical retorts-continuous	31.7	4.4	12.0	66.3	17.3
	23.6	4.2	15.7	61.5	18.6
Horizontal retorts	34.5	4.1	18.3	67.2	10.4
Carburetted water gas	11.7	3.4	30.8	17.1	48.7

Kemper and Guernsey (3) report the following distribution of organic sulfur compounds. These values represent the average of several gases tested.

	Percent of Organic Sulfur Present As:		
	Thiophene	Carbon bisulfide	Carbon oxysulfide
Water gas	30	35	36
Coke oven gas	6	61	33
City gas	21	39	40

Thus it can be seen that the thiophene fraction of the organic sulfur content of a gas may be appreciably high, whereas the actual thiophene concentration is generally quite low. For most commercial and domestic uses the quantity of thiophene present in a gas is considered harmless, however, with the development of pilot-controlled continuous burner operation, more advanced metallurgical processes, and the manufacture of gas by catalysed reactions, it is often mandatory that the sulfur content of a gas be very small. In such cases the thiophene present may prove to be quite troublesome.

Methods of Thiophene Removal from Gas

Organic sulfur removal from gas can be accomplished by any one of five means:

(1) Absorption by chemicals and disposal of spent absorbent.

(2) Absorption by oil which is reclaimed by desorption, or fed to the gas making process.

(3) Adsorption by solids.

(4) Conversion to hydrogen sulfide or sulfur dioxide with subsequent treatment of the gas to remove the compound thus formed.

(5) Refrigeration and condensation.

At the present time the removal, or partial removal, of thiophene from gas is realized by methods (2), (3), or (4) of the above. There are no methods adaptable to commercial scale which are effective in removing thiophene alone. The partial removal of thiophene is accomplished concurrently with the removal of at least one other constituent from the gas.

The most widely used method for decreasing the thiophene content of a gas is oil scrubbing. This consists in scrubbing the gas with wash oil by bringing the oil and gas into intimate contact in a suitable absorption tower. Ordinarily this stage of gas purification is installed to remove the so-called "light oil" which is composed of benzene, toluene, xylene, and small quantities of other compounds, chiefly hydrocarbons. The wash oil is freed of light oil by steam distillation. On separation of the light oil into its component parts by distillation, the thiophene removed concurrently with the light oil appears in the benzene fraction (4). To remove the thiophene from the benzene, some means other than distillation is required (5). Carbon bisulfide is also partially removed in the oil scrubbing process, however, its separation from the light oil presents no serious problem.

Guernsey (6) reports that the removal of the light oil by means of oil scrubbing lowers the heating value of a gas. If the objective in oil scrubbing is to lower the thiophene content of a gas without essentially changing its heating value, this method of purification is not applicable. Another disadvantage of this process is the large amount of scrubbing oil required. Because of this, pumping costs etc. are high as well as is the consumption of steam used for wash oil recovery. It has been shown (7) that to remove 70% of all the organic sulfur by oil washing, such large amounts of oil would be required that steam consumption would be excessive.

A second process for the simultaneous removal of benzene, carbon bisulfide, and thiophene from gas is the adsorption of these constituents on activated carbon (8). The method of operation consists in having two or more chambers packed with activated carbon and so constructed as to allow temperature control by means of water cooling. One set of these chambers is connected on the gas stream while the other is reactivated by blowing steam through the bed of carbon. At the proper time the gas is diverted into the reactivated chamber and the fouled chamber blown with steam. Water cooling is necessary to maintain a low temperature during the adsorption period. This process has not been used to any extent in manufactured gas practice in this country, but has been tried in a few gas plants in England.

Hollings and Hay (9) report that active carbon is effective in removing most all of the carbon bisulfide and thiophene at the start, but the efficiency of removal of these compounds decreases with time. They also report that the process is more effective if the gas is first freed of hydrogen sulfide before being treated by active carbon. The economy of complete organic sulfur removal from gas by the active carbon process is governed by the steam consumption required for reactivating the carbon. It has been stated (7) that in general the active carbon process is more efficient than the oil scrubbing process for removing both carbon bisulfide and thiophene from gas, but that the economy of removing more than 80% of the organic sulfur by adsorption on carbon is doubtful. It will be remembered that their remarks apply to manufactured gas practice. Other considerations enter in synthesis gas practice where activated carbon may be used for the removal of final traces.

A very serious disadvantage of the adsorption method of organic sulfur removal is the fouling of the carbon bed by tarry materials. If the gas is not relatively free of tar or gum forming substance the effective life of the active carbon is quite short.

Hollings, Hutchinson and Griffith (2) report that with the active carbon process approximately 75% of all the organic sulfur in gas is removed, while with normal oil washing process about 38% of the organic sulfur is removed.

Huff and Lusby (10)(11) report that copper-uranium and cerium-uranium catalysts, in the presence of hydrogen containing gases, are effective in transforming all organic sulfur compounds into hydrogen sulfide. Copper-vanadium and copper-chromium compounds are effective in absorbing simultaneously both hydrogen sulfide and organic sulfur from gases. These catalytic absorbents can be revivified by burning off the sulfur with air. With the use of the first mentioned catalysts the gas must be free of hydrogen sulfide. The second process can be applied to raw hydrogen sulfide containing gases.

Another process is described (12) whereby the organic sulfur content of a gas is lowered with the aid of a reduced iron catalyst. The optimum temperature range for operation of the catalyst bed is from 200 to 300°C (392 to 572°F). It is necessary to remove hydrogen sulfide before passing the gas over the catalyst.

A removal of from 10% to 30% of thiophene from town gas has been reported (13) by the use of a catalyst consisting of bauxite impregnated with a solution of copper thiomolybdate. The gas was preheated to 300°C (572°F) before contact with the catalyst. This catalyst causes the formation of hydrogen sulfide which is then removed by any of the standard methods.

Work done at the Meadow-Lane Gas Works (14) has led to a conclusion that a molybdenum sulfide catalyst can be used effectively in decomposing thiophene almost completely at 300°C (572°F).

Up to the present time commercial application of catalytic processes for the removal of organic sulfur from gas has been very limited. In most cases the high cost and short life of the few effective catalysts available render their use impractical.

CHAPTER II

SYNTHESIS GAS, ITS COMPOSITION AND METHODS OF MANUFACTURE

At the present time extensive work is being conducted on the manufacture of synthetic liquid fuels from various coals, cokes, and hydrocarbon gases. In general, the processes employed involve the production of a synthesis gas consisting chiefly of hydrogen and carbon monoxide, in ratios of 1:1 to 2:1 (15), which is converted over a suitable catalyst and under the proper conditions to a mixture of olefins and aliphatic hydrocarbons.

Chief attention in the application of solid fuels has been directed to the utilization of low grade coals for the manufacture of synthesis gas. This, of course, results in a lower priced synthetic fuel. The primary reactions required for synthesis gas production from solid fuels are:

$$C + \overset{\text{Steam}}{H_2O} = CO + H_2 \text{ and } C + \overset{\text{Steam}}{2H_2O} = CO_2 + 2H_2$$

When using low grade coals, the best conditions for gasification are realized in continuously operated generators (15). In order to accomplish this, the fuel is pulverized and oxygen is admitted with the steam to burn partially some of the fuel, and thus supply the heat necessary to maintain a fixed temperature within the fuel bed. Newman (15) gives a description of the various types of generators and processes used with solid fuels which employ fixed fuel beds, fluidized beds, dust gasification processes, etc.

The gasification of subbituminous coal and lignite in externally heated retorts has also been studied (16). The heat supplied to these retorts is obtained from the burning of some combustible gas in annular spaces surrounding the fuel bed. After the coal or lignite has reached the proper temperature steam is introduced into the gasifying chamber, and by proper control, the desired hydrogen-carbon monoxide ratio is obtained. This process is made continuous by regular additions of fuel and continuous ash removal.

The conversion of methane, or natural gas, to a synthesis gas by reactions with steam requires the presence of a catalyst. A review of some of the processes and catalysts adaptable for the reactions $CH_4 + H_2O = CO + 3H_2$ and $CH_4 + 2H_2O = CO_2 + 4H_2$ are given by Storch (17). For the first reaction nickel-thoria-magnesia and nickel-iron supported on kieselguhr have been recommended, while for the second reaction nickel-alumina-magnesia on active carbon has been suggested. In the manufacture of synthesis gas by this method, an excess amount of hydrogen is formed. To keep the hydrogen-carbon monoxide ratio between 0.5 and 3, carbon dioxide may be added to the inlet gases (18). The synthesis gas ultimately can be freed of the excess carbon dioxide by scrubbing. The CO_2 thus removed is recycled to the inlet stream.

The catalysts generally used for the production of synthetic liquid fuels from the reduction of carbon monoxide are mixtures of nickel and cobalt with activating materials such as alumina, thoria, or other stable metalic oxides (17). Iron catalysts have also been used by Fischer and Tropsch (19). They report that by using iron or cobalt on various carriers, hydrocarbons ranging from ethane to solid products were obtained at atmospheric pressure and temperatures of 250 to 300°C (482 to 572°F).

Allowable Sulfur in Synthesis Gas

The occurrence of sulfur in synthesis gas greatly shortens the life of the catalysts used in synthetic liquid fuel production. The allowable total sulfur in the synthesis gas produced by German plants was not greater than 0.10 grain per hundred cubic feet (20). It is reported that a reduction of total sulfur from 0.05 to 0.01 grain per 100 cubic feet resulted in an increase of 50 percent in the life of the cobalt catalyst being employed. Since this results in a savings of 0.1 cent per 1000 cubic feet, a gas of lower sulfur content is desirable.

CHAPTER III

THE PYROLYSIS OF THIOPHENE

It has been pointed out that the presence of sulfur compounds in the synthesis gas used for the manufacture of synthetic liquid fuels is very undesirable. The extremely small quantities of sulfur compounds permissible in synthesis gas make purification of this a difficult problem. Processes are available for efficient removal of the major sulfur compounds found in gas, i.e. hydrogen sulfide and carbon bisulfide, however, very little plant scale development has been done on the removal of minor organic sulfur compounds such as thiophene, mercaptans, carbon oxysulfide, etc. Evidently, of these minor organic sulfur compounds, thiophene is the most stable. Guernsey (21) suggests that the removal of thiophene from gas by other than physical means possibly may not be practical. A review of the literature has shown that, in general, catalytic processes have little, if any, effect on thiophene, while the oil scrubbing and active carbon processes, although effective for decreasing the thiophene content of a gas, are quite expensive and rather impractical for synthesis gas purification. Therefore, it seemed desirable to look for another means of removing thiophene from synthesis gas.

The use of heat to affect a conversion of the major part of the organic sulfur to hydrogen sulfide in a gas containing hydrogen was realized as early as 1911 by Pabst (22), who proposed stoves filled with checkerbrick and heated to high temperatures for this purpose. The decomposition of carbon bisulfide at various temperatures was also studied (23), and it was found that a temperature of 1300°F (704°C) resulted in approximately 75 percent decomposition of the carbon bisulfide present. Evans (24) reports that the presence of hydrogen is favorable to the pyrolysis of carbon bisulfide. Lusby (25) has applied a heated platinum spiral to transform all the organic sulfur present in a gas to hydrogen sulfide. This, of course, requires the presence of hydrogen. Some question has been raised about the completeness of decomposition of thiophene by the spiral. Sands et al. report that complete decomposition can be effected (20).

Faragher, Morrell and Comay (110) dissolved thiophene in a purified naptha and passed this mixture through a heated tube at the rate of 0.5 cc. per minute. They obtained no decomposition of the thiophene at either 925 or 1600°F (496 or 871°C). The possibility of dithienyl formation was not investigated.

Work done by Clapham (26) at the University of West Virginia shows that at higher temperatures thiophene in the presence of hydrogen is decomposed to a large extent to hydrogen sulfide. It is reported that with a temperature of 1750°F (954°C) and a contact time of 0.019 hours, approximately 95 percent of the ingoing thiophene is converted to hydrogen sulfide when hydrogen is used as the carrier gas.

When nitrogen was used as a carrier gas the conversion of thiophene to carbon bisulfide and hydrogen sulfide was almost complete at temperatures of 2350°F (1288°C) and 2660°F (1460°C). At a temperature of 2350°F and contact times of 0.004 to 0.011 hours approximately 25 to 42% of the thiophene was converted to hydrogen sulfide. At a temperature of 2660°F and contact times of 0.0055 to 0.0085 hours approximately 2 to 16% of the thiophene was converted to hydrogen sulfide when nitrogen was used as a carrier gas. Clapham also obtained a conversion of 80 percent of the thiophene with a contact time of 0.0057 hours, temperature of approximately 1900°F (1038°C), using a synthesis gas as the thiophene carrier. In Clapham's experiments no packing was used in the pyrolysis tubes.

In part, the mechanisms for the pyrolysis of carbon bisulfide and of thiophene may be similar because hydrogen is favorable to the thermal decomposition of both compounds. This is to be expected.

It was deemed desirable to make a study of the pyrolysis of thiophene in the presence of specific gases, namely nitrogen, hydrogen, carbon monoxide, and synthesis gas, using tube packings to determine the feasibility of decomposing thermally the thiophene present in synthesis gas to compounds more easily removed. Hydrogen sulfide and carbon bisulfide are compounds possessing these properties. A furnace packing of carbon might be effective in transforming the thiophene into carbon bisulfide.

The thermal stability of thiophene requires rather high temperatures to effect appreciable pyrolysis (26). This feature limits the application of thermal decomposition as a means of removing thiophene from other than synthesis gas, as simultaneous decomposition of illuminants and other compounds responsible for the higher heating values of gas would result. Carbon might decrease the temperature required.

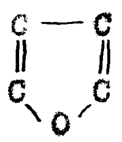
CHAPTER IV

THE CHEMISTRY OF THIOPHENE

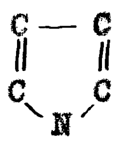
The discovery of thiophene is credited to Victor Meyer (27) who, in 1883, found that benzene obtained from the distillation of coal gave a blue color when mixed with concentrated sulfuric acid containing a small amount of isatin (28). He found that the thiophene content of the benzene obtained by this method was approximately 0.5%.

Thiophene is a heterocyclic compound belonging in the group containing also furan, and pyrrole. The structural formulae of these compounds are generally written as:

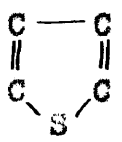
Furan



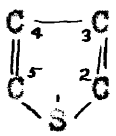
Pyrrole



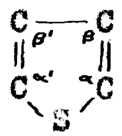
Thiophene



In these rings the atoms are designated by the following means:



or



Schomaker and Pauling (29) have shown that there is resonance in the heterocyclic rings and on a comparative basis the resonance energy of thiophene > pyrrole > furan. Thiophene is quite stable both chemically and thermally. It is this fact that makes its removal from gas a difficult problem.

A great many of the physical constants of thiophene have been determined in the laboratories of the Socony-Vacuum Co. (30), some of which are presented below.

Table I

Some Physical Constants of Thiophene

Boiling points	°C	at mm. Hg. Pressure
	71.0	500
	76.6	600
	81.45	700
	84.12	760
	85.8	800
	89.7	900

dt/dP at 760 mm. Hg,	°C/mm.	0.043
Freezing point in air,	°C	-38.30
Density gm/ml at	20°C	1.0644
	25°	1.0583
	30°	1.0524
Refractive index N_D^t at	20°C	1.5287
	25°	1.5256
	30°	1.5223
Absolute viscosity, centipoises at	20°C	0.662
	20°	0.621
	30°	0.584

There are many similarities between thiophene and benzene (27). Thiophene has a weak benzene like odor and a boiling point of 84°C at 760 mm. pressure as compared to 80°C for benzene.

There are many processes described in the literature covering the synthesis of thiophene. In general, the methods employed are the reaction of either acetylene, a diolefin, or n-butane with an elementary sulfur compound. In some cases the reaction is carried out without a catalyst, while in others a catalyst is employed.

Peel and Robinson (31) report a yield of 12 percent thiophene when acetylene is introduced into a flask of boiling sulfur. Tomkinson (32) obtained a product containing 30 to 40 percent thiophene by conducting a mixture of hydrogen sulfide and acetylene over a metallic sulfide catalyst. Briscoe, Peel, and Robinson (33) found that a temperature of 700°C (1292°F) was optimum for the production of thiophene by the interaction of acetylene and carbon bisulfide, without the aid of a catalyst. Shepard, Henne, and Midgley (34) passed butadiene through sulfur. At a temperature of approximately 420°C (788°F) they obtained a small amount of thiophene. According to Barger and Easson (35) thiophene is formed when acetylene is conducted through a tube containing pyrites heated to 300°C (572°F). This process, modified by the use of a metallic sulfide catalyst, has been patented (36). The production of thiophene on pilot plant scale has been carried out by the Socony-Vacuum Co. (37). A yield of as high as 50 percent thiophene was obtained by the vapor reaction of sulfur and n-butane when temperatures of approximately 600-650°C (1112-1202°F) were employed. It was found necessary to quench the product to prevent decomposition of the thiophene thus formed.

CHAPTER V

POSSIBLE MEANS OF THIOPHENE FORMATION IN GAS MANUFACTURING

Due to the complexity and large number of reactions possible in the manufacture of fuel gas from coal or coke, it is impossible to state definitely the exact origin of any one minor component in a gas. The original sulfur in the coal is considered to exist as (a) pyritic or marcasite sulfur, (b) organic sulfur, and (c) sulfate sulfur. When subjected to the high temperatures present in gas making operations these sulfur compounds in the fuel undergo decomposition and new sulfur compounds are formed. These compounds are distributed between the gas being made and the resulting ash or coke, depending on the particular operation being performed. Many studies have been made in an attempt to determine the origin and types of the sulfur compounds in gas manufacture.

Powell (38) found that a portion of the sulfide sulfur in coal is transformed into a sulfur-carbon combination during the manufacture of coal gas and coke. He found that this transformation took place mainly at temperatures of about 500°C (932°F).

Wibaut (39) made a study of the reactions of sugar char and sulfur vapor at temperatures of 700 to 900°C (1292 to 1652°F). It was found that some of the sulfur is fixed by the carbon, and sulfurous carbon containing 1 to 2 percent sulfur is obtained.

By passing hydrogen sulfide over sugar char at temperatures of from 1500 to 1700°F (816 to 927°C) with subsequent analyses of the char for the presence of sulfur, Huff and Holtz (40) showed the formation of a carbon-sulfur complex on the char.

Griffiths (41) reported that higher sulfur coals give higher sulfur containing gases. He maintains that the sulfur content of a gas is increased with prolonged carbonizing times and excessive heats.

Eaton, Hyde, and Hood(42) used tracer techniques to follow the sulfur distribution during the carbonization of coals. They made pyrites from active sulfur and mixed this with coal which was then carbonized in a coke oven. Samples of the coal, coke, and gas were counted with a Geiger Counter. The following distribution of the sulfur during coking was found:

	Pyritic Sulfur % Coal Sulfur	Organic & Sulfate Sulfur % Coal Sulfur	Total Sulfur % Coal Sulfur
Coal	100	100	100
Coke	66	73	70
Gas	23	26	25

(Note: Organic and Sulfate Sulfur obtained by difference). The tar formed during coking operations was not examined.

Brewer and Ghosh (43) made a study of the effects of various atmospheres on the distribution of sulfur during the carbonization of coal. They report that ammonia, hydrogen, and nitrogen are effective in the order named in removing sulfur from the coal.

It is thus seen that when coal is subjected to the high temperatures involved in gas making operations, the decomposition of the original sulfur compounds present in the coal results in new types of sulfur compounds, which are distributed between the gas and the remaining carbon or ash. Coincident with this, there occurs the formation of sulfurous carbon compounds. These compounds might possibly react with any hydrogen present to form thiophene, however, it is more likely that any reaction with hydrogen would favor the formation of hydrogen sulfide. It is quite possible that the appearance of a carbon-sulfur complex during the heating of coal is a source for carbon bisulfide formation.

Morgan (44) discusses the possible means for the formation of $CH_2=$ type radicals during the carbonization of coal. It is possible that these radicals combine to form acetylene or ethylene which react with hydrogen sulfide, carbon bisulfide, pyrites, or some other sulfur compound to form thiophene (see page 19).

To demonstrate the possibility that this mechanism is that occurring in gas manufacture, Steinkopf (45) passed illuminating gas through boiling sulfur and obtained only traces of thiophene. He next performed a similar experiment using acetylene with sulfur and obtained good yields of thiophene. Appreciable amounts of thiophene were found by

Steinkopf (46) when illuminating gas was passed over pyrites; or acetylene or ethylene were passed over sulfur. The formation of thiophene in gas may be catalysed by the presence of mineral compounds in the primary fuel.

CHAPTER VI

PROBABLE COMPOUNDS FORMED FROM THE THERMAL DECOMPOSITION OF THIOPHENE

It has been shown that at higher temperatures thiophene can be thermally decomposed to more simple types of sulfur compounds (see Chapter III). The combination of carbon, hydrogen, and sulfur in the thiophene molecule may permit the formation of a relatively large number of pyrolysis products from thiophene. The following sections are included, therefore, to indicate some of the compounds which might occur when thiophene is decomposed and to briefly outline means of preparation of these compounds. Since the chief aim of this project is the removal from synthesis gas of the sulfur introduced in the form of thiophene, the discussion here will be limited only to sulfur compounds.

Hydrogen Sulfide. The physical properties and methods of formation of hydrogen sulfide can be found in almost any elementary inorganic text. It will suffice here to mention this compound as one likely to occur when thiophene is thermally decomposed. The large fraction of hydrogen in synthesis gas, (see page 10) should favor the formation of hydrogen sulfide as one of the products of pyrolysis in the presence of this gas.

Carbon Bisulfide. The method most generally used for the manufacture of carbon bisulfide is the interaction of sulfur and carbon by the application of heat (47)(48). Commercially, this is realized by continuously feeding charcoal and sulfur into a furnace heated by graphite electrodes. The carbon bisulfide thus formed is condensed and purified. For most efficient operation temperatures around 1000°C (1832°F) are employed. Stull (49) gives a discussion of the thermodynamics of carbon bisulfide formation from carbon and sulfur.

Huff (50) states that the reaction of hydrogen sulfide with hot carbon is responsible for the formation of carbon bisulfide in gas. This reaction is the basis of a patent (51) for carbon bisulfide manufacture.

The decomposition of carbon oxysulfide to carbon bisulfide and carbon dioxide has also been studied (52). It is reported that lower temperatures favor the formation of carbon bisulfide by this process. At 600°C (1112°F) the decomposition of carbon oxysulfide occurs to the extent of 49 percent. Of this, 43 percent is carbon bisulfide and carbon dioxide while the remaining 6 percent consists of carbon monoxide and free sulfur.

Carbon Oxysulfide. The occurrence of carbon oxysulfide in various gases has been reported by Hutchinson (2). He shows that in carburetted water gas the carbon oxysulfide may constitute as much as 38 percent of the organic sulfur present.

Ferguson (53) studied the reaction:

$$4CO + 2SO_2 = 4CO_2 + S_2$$

at temperatures ranging from 1000 to 1200°C (1832 to 2192°F). Concurrently with the formation of carbon dioxide there appears small amounts of carbon oxysulfide. The presence of a large excess of carbon monoxide favors the formation of the oxysulfide. It is possible that the formation of carbon oxysulfide may result from the interaction of carbon monoxide and various sulfur compounds other than sulfur dioxide.

Mercaptans. The quantities of mercaptans occurring in manufactured gases are quite small (2). Generally, the mercaptans present in gas exist as methyl and ethyl mercaptans. Powell (54) states, however, that mercaptan compounds usually are not present in detectable quantities in coke oven gas produced at higher temperatures.

Minor Organic Sulfur Compounds. Arctowski (55) obtained small quantities of carbon subsulfide, C_2S_3, by conducting carbon disulfide through a heated quartz tube. Stock and Praetorius (56) found that temperatures in the range of 1000 to 1100°C (1832 to 2012°F) gave the best yields of the subsulfide by this method.

A monosulfide of carbon has been reported by Dewar and Jones (57)(58). Carbon bisulfide, cooled in liquid air, was subjected to a silent discharge. On heating to room temperature a flash occurred yielding a brown compound which was believed to be a polymer of carbon monosulfide.

Nahsen (59) and Anwers and Bredt (60) obtained small amounts of isomeric dithienyls by conducting thiophene through a tube maintained at a dull red heat.

Other minor sulfur compounds such as thio-ethers and disulfides have been reported in gas, but usually these occur in such low concentrations as to be of practically no significance (1).

Undoubtedly there is apt to be the formation of small amounts of elementary sulfur accompanying the pyrolysis of thiophene. With the application of carbon compounds as packing in the pyrolysis tubes a loss of sulfur to such packing is quite likely. Holtz (40) reports the formation of a carbon-sulfur complex when hydrogen sulfide is passed over hot carbon.

Practice in the Removal of Specific Sulfur Compounds from Gas

It is pertinent for the removal of thiophene from synthesis gas by thermal decomposition into more elementary types of sulfur compounds, that methods be available for the removal from the gas of the sulfur products thus formed. From the discussions of the previous section, it is clear that among the sulfur-containing products resulting from the pyrolysis of thiophene, hydrogen sulfide and carbon bisulfide will be the most abundant. The need for the removal of these compounds will be greater than for minor sulfur compounds, therefore, the methods employed in hydrogen sulfide and carbon bisulfide removal from gas will be discussed in greater detail. A comprehensive survey here is not intended, but rather a brief review of the more important methods employed by gas industries to lower the sulfur content of various gases.

Hydrogen Sulfide. For the removal of hydrogen sulfide from gas, one of the methods employed most widely is the iron oxide process. A description of this process can be found in almost any text book on gas technology. Essentially, hydrogen sulfide is absorbed on a bed of iron oxide supported on some type of inert material such as wood shavings. The reactions occurring during sulfur removal are:

$$(1) \quad Fe_2O_3 \cdot xH_2O + 3H_2S = Fe_2S_3 + (x + 3)H_2O$$

$$(2) \quad Fe_2O_3 \cdot xH_2O + 3H_2S = 2FeS + S + (x + 3)H_2O$$

The desirable reaction (1) occurs under alkaline conditions. The sulfide is revivified in place by admitting air in low concentrations simultaneously with the gas, or by cutting the box off the gas stream and adding air slowly. Sometimes the oxide is removed from the box. On revivification outside the box the fouled material is wetted down and spread out to allow maximum contact with the air. For efficient hydrogen sulfide removal the humidity and oxygen content of the gas must be controlled. Schobel (61) maintains that water should be sprayed on the boxes to effect humidity control and an air admission of 1.2% air is optimum. Operating under these conditions, with a temperature below 120°F

(49°C), an average hydrogen sulfide removal from refinery oil gas of 86.5% over an eight month period was obtained.

The Seaboard process for hydrogen sulfide removal from gas has been discussed by Sperr (62)(63) and Herbst (64). In this process a solution of approximately 3.0 to 3.5 percent sodium carbonate is used to scrub the gas. This process also removes some of the carbon dioxide and hydrocyanic acid. The primary reactions are:

$$H_2S + Na_2CO_3 = NaHS + NaHCO_3$$

$$CO_2 + H_2O + Na_2CO_3 = 2NaHCO_3$$

$$HCN + Na_2CO_3 = NaCN + NaHCO_3$$

Regeneration of the carbonate is obtained by blowing air through the fouled solution. Sperr reports that 80 to 90 percent of the hydrogen sulfide can be economically removed by this process, and that other sulfur compounds are not affected.

A number of installations for gas manufacture employ the Ferrox Sulfur Recovery and the Nickel Sulfur Recovery Processes for the purification of gases. The two processes are the same except for the solutions used and are effective in removing hydrogen sulfide and hydrocyanic acid. Sperr (65) and Mann (66) have described the Ferrox process which consists in scrubbing the gas with a suspension of iron in an alkaline solution. The reactions occurring on absorption are:

(1) $Na_2CO_3 + H_2S = NaHS + NaHCO_3$

(2) $Fe_2O_3(H_2O)_x + 3H_2S = Fe_2S_3(H_2O)_x + 3H_2O$

Reaction (2) occurs to only a minor extent. On aeration the hydrosulfide is oxidized mainly to sulfur.

The Thylox process utilizes a solution of essentially neutral thioarsenate salt for the absorption of hydrogen sulfide from gas. During absorption, a higher arsenate salt is formed, i.e. some of the oxygen is replaced by sulfur. The reaction occurring on hydrogen sulfide removal is expressed as:

$$Na_2As_2S_5O_2 + H_2S = Na_4As_2S_6O + H_2O$$

By reactivation with air the thioarsenate solution is restored and free sulfur is formed. Jacobson (67) maintains that a removal of about 98 percent of the hydrogen sulfide can be obtained by this process. He also reports that the presence of hydrocyanic acid results in an increase in the soda consumption. The process was patented by Gollmar (68)(69).

The Girdler Corporation has developed a process whereby hydrogen sulfide is removed from gases with the aid of an amine, in particular, triethanolamine or diethanol amine (70)(71). These compounds are mixed with water and the solution thus formed passed countercurrent to the gas. By this method hydrogen sulfide and any other acid component of the gas may be effectively decreased. Regeneration is accomplished by heating the fouled liquid to drive off the gaseous impurities.

Organic Sulfur. The use of oil scrubbing for lowering of the organic sulfur content of a gas has been discussed (see page 5). Oil scrubbing not only removes a large fraction of the thiophene present, but also lowers the carbon bisulfide and mercaptan content of a gas. Although it is possible to remove essentially all of the carbon bisulfide and mercaptans from a gas by means of oil scrubbing, it is not economically feasible as the volume of oil thus required is excessive (7), and would lead to an undesirable reduction in the light oil vapors and illuminants.

The Athion Process for carbon bisulfide removal has been described by Rudkuk (72). By this method carbon bisulfide is absorbed on an alkaline cellulose material, which is converted by the carbon bisulfide to viscose. For efficient operation the gas must be freed of tar, ammonia, hydrogen sulfide, and carbonic acid.

Some studies have been made to determine the effect of a heated surface on carbon bisulfide. Pabst (22) found that in the presence of hydrogen and at a temperature of 1200°F (649°C), carbon bisulfide decomposed to hydrogen sulfide. He proposed the theory that a reaction similar to the reversal of the formation of carbon dioxide water gas takes place, i.e.

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

After the removal of hydrogen sulfide the gas could be reheated and a further decrease in the carbon bisulfide content thus obtained. This method would probably also lower the mercaptan fraction of a gas. Evans (24) reports that

that the presence of nickel or iron catalyses the decomposition of carbon bisulfide by the application of heat.

At the present time a study is being made of the effectiveness of secondary amines on the simultaneous removal of carbon bisulfide and carbon oxysulfide from gas (73). Although the work is still on a laboratory scale, it is reported that good removal of these compounds is realized when a gas is scrubbed with either piperidine or morpholine. This process has little or no effect on the thiophene present.

A catalytic process has been described (74) in which finely divided nickel at a temperature of 300°C (572°F) is used in the presence of hydrogen, to lower the hydrogen sulfide and carbon bisulfide content of a gas. Another process (75) employs a catalyst of a metallic oxide on a porous gel to oxidize the hydrogen sulfide or carbon bisulfide to either sulfur or sulfur dioxide.

Organic Sulfur Removal from Synthesis Gas

An examination of the German synthesis gas plants (20) revealed processes for organic sulfur removal from the gases produced. The soda-iron process consists in contacting the synthesis gas with a soda-iron oxide catalyst maintained at 390 to 500°F (199 to 260°C) to oxidize effectively the organic sulfur compounds present which then remain on the catalyst as sodium sulfate. This process has little affect on the thiophene present. A conversion of the organic sulfur present to hydrogen sulfide, which was ultimately removed, with the aid of an iron oxide catalyst containing 6 to 7 percent chromic oxide was employed. In some German plants, the synthesis gas, freed of hydrogen sulfide, was heated to approximately 2200°F (1204°C) and rapidly quenched to affect a conversion of the organic sulfur present to hydrogen sulfide.

CHAPTER VII

ANALYTICAL METHODS

Hydrogen Sulfide and Mercaptans

The method most employed for the quantitative determination of hydrogen sulfide and mercaptans is that one devised by Tutweiler (76)(77). Although a separate determination of hydrogen sulfide and mercaptans is impossible, the method is quite accurate and very rapid. Essentially the procedure is to collect a known volume of gas, subject this to a slight vacuum, and slowly add iodine solution, with vigorous shaking, until an end point is obtained using starch as the indicator. Knowing the normality of the iodine solution, the volume of iodine added, and the original volume of gas, the sulfur present as hydrogen sulfide plus mercaptans can be determined.

The Gas Chemists Handbook (78) recommends a method for hydrogen sulfide determination whereby the gas is scrubbed by a sodium hydroxide solution. This is acidified and titrated with iodine solution, using starch as an indicator.

Shaw (79) has devised a method for the separate determinations of hydrogen sulfide and mercaptans. The procedure for these determinations consists of two parts. Step (1): A known volume of gas is passed through a scrubbing train containing a 10 percent solution of cadmium chloride buffered with sodium carbonate. After sampling, the solution is acidified with concentrated hydrochloric acid, chilled to 10°C, and an excess of iodine added - the excess being titrated with standard thiosulfate. From this the sulfur present as hydrogen sulfide and mercaptans is obtained. Step (2): After passing a known volume of gas through a scrubbing train identical to the one used in step (1) the scrubber solution is neutralized with acid to a methyl orange end point and sufficient water and hydrochloric acid are added to dilute the solution and yet give a concentration of 3 gm/liter of free HCl. Under these conditions cadmium sulfide is in suspension and cadmium mercaptides in solution. After filtration, the cadmium sulfide precipitate is redissolved in acid and an excess of iodine added, this being back titrated with standard thiosulfate. Step (2) gives the sulfur present as hydrogen sulfide while by difference of step (1) and step (2) the sulfur present as mercaptans is obtained. Shaw has devised a special flask which acts as a scrubbing bottle and also an analysis bottle. This special flask is required for step (1) and step (2) as the major part of the analytical procedure must be carried out under a slight vacuum to minimize contact of the solutions with air.

Determinations of hydrogen sulfide by colorimetric methods have been employed. These methods give more satisfactory results when the hydrogen sulfide present is small. A process has been employed using lead acetate (80) for the colorimetric determination of hydrogen sulfide. A standard moist lead acetate paper is subjected to a known quantity of gas. The amount of black lead sulfide thus formed on the paper is determined by comparison to a blackened wedge, which having been calibrated gives a measure of the hydrogen sulfide present. The application of methylene blue (81) or silver cyanide (82) for hydrogen sulfide determinations also has proved successful.

Carbon Bisulfide and Carbon Oxysulfide

For the determination of carbon bisulfide in gas, the Gas Chemists Handbook (83) recommends a process whereby a known volume of dried gas is passed through an absorption train containing sodium hydroxide solution covered with an etheral solution of triethylphosphine. A volume of gas sufficient to give a coloring of the etheral layer of three caustic scrubbers is required. When this condition is satisfied, the caustic solutions are mixed, filtered, and the precipitate dried. The weight of $(C_2H_2)_3PCS_2$ thus obtained multiplied by 0.392 gives the carbon bisulfide present.

Several investigators have studied the reaction of carbon bisulfide with an alcoholic potash solution, thus forming a xanthate, as a method for carbon bisulfide determination. Harding and Doran (84) developed a procedure in which a known volume of gas is scrubbed with alcoholic potash. This is acidified and a measured amount of copper acetate is added. The amount of acetate added must be in excess of that required to precipitate cupric xanthate. The precipitate is then filtered and potassium iodide added to the filtrate. The iodine thus formed is titrated with standard thiosulfate.

An examination of this method by Huff (85) indicated that cupric xanthate was not completely precipitated in solutions of low concentration. A procedure is recommended whereby smaller volumes of scrubbing solutions are employed, and after acidification with a measured excess of acetic acid, copper acetate added as above. This is allowed to stand overnight to insure complete precipitation. After filtration, the filtrate is evaporated to dryness, redissolved in 5 cc. of 1:15 hydrochloric acid solution, a measured amount of potassium iodide added, and the iodine thus formed titrated with standard thiosulfate. Huff maintains that 0.02 mg. of carbon bisulfide can be qualitatively determined by this method. The method is not of high precision quantitatively.

Desy (86) has developed a colorimetric analysis for carbon bisulfide based on the xanthate reaction. In this process the color produced from a known volume of gas containing carbon bisulfide is compared against the colors obtained from xanthate solutions of various concentrations.

The Institute of Gas Technology (87) has devised a method for the separate determination of carbon bisulfide and carbon oxysulfide in gas. The method consists of two parts. Part (1): a known volume of gas is passed through a series of scrubbers containing alcoholic potash, thus removing carbon bisulfide and carbon oxysulfide. For quantitative absorption it is necessary to keep the scrubbing solutions cooled to 0°C. A determination of the total sulfur (see page 41) before and after the scrubbers gives the sulfur present as the sum of these constituents. Part (2): a repetition of part (1) is performed with the exception of the total sulfur determinations, instead, the scrubber solutions are diluted with water recooled to 0°C, acidified, thus forming xanthic acids, and titrated with iodine solution using starch as the indicator. The equations representing the reactions occurring in step (2) are:

$$CS_2 + KOEt \longrightarrow KS\text{-}CS\text{-}OEt$$

$$COS + KOEt \longrightarrow KS\text{-}CO\text{-}OEt$$

and:

$$2HS\text{-}CS\text{-}OEt + I_2 \longrightarrow EtO\text{-}CS\text{-}S\text{-}S\text{-}CS\text{-}OEt + 2HI$$

$$2HS\text{-}CO\text{-}OEt + I_2 \longrightarrow EtO\text{-}CO\text{-}S\text{-}S\text{-}CO\text{-}OEt + 2HI$$

Letting the sulfur present as carbon bisulfide be represented by S_B and that as carbonyl sulfide by S_c two equations can be established.

$$S_B + S_c = \text{Decrease in total sulfur (Step 1).}$$

$$\tfrac{1}{2}S_B + S_c = \text{Sulfur obtained by } I_2 \text{ titration (Step 2).}$$

By a simultaneous solution of these equations the carbon bisulfide and carbon oxysulfide can be obtained.

Thiophenes

For the direct determination of thiophene two types of analyses are available, i.e. colorimetric determinations and the transformation of thiophene into a thiophene derivative having some specific property facilitating its isolation. Of the colorimetric methods the indophenine reaction (88)(89)(90)(91)(92)(93) is by far the most popular. Essentially, this determination is used for the estimation of the thiophene content of benzene. Approximately 0.4 grams of isatin are dissolved in 1000 ml. of concentrated sulfuric acid to which a little nitric acid has been added. A quantity of this is shaken with a known amount of the benzene being analysed. The blue color thus produced is compared with that obtained when benzene of a known thiophene content is shaken with the same volume of isatin-sulfuric acid mixture as used with the unknown. Unfortunately the presence of unsaturated hydrocarbons also give the blue coloring, while toluol, phenol, or tertiary bases give a brown to blue color (90). The reaction taking place, with thiophene, i.e. the indophenine reaction, is:

$$C_8H_5NO_2 + C_4H_4S = C_{12}H_7NOS + H_2O$$

An excellent review of the colorimetric methods available for thiophene determinations is given by Steinkopf (93).

Another method for the determination of thiophene in aromatic fractions containing no unsaturated compounds utilizes Deniges reagent (94), which consists of 5 grams of mercuric oxide dissolved in a solution of 20ml. of concentrated sulfuric acid in 100 ml. of distilled water. The procedure requires vigorous shaking of 20 ml. of Deniges reagent with 2 ml. of the sample for a period of about three hours. The resulting mixture is filtered, the precipitate washed, dried, and then weighed. The percent thiophene by weight is given by: $\frac{3.79x}{S}$ where x is the grams of precipitate $(HgO,HgSO_4)_2C_4H_4S$ and S is the specific gravity of the sample.

The method most applicable to the determination of thiophene in gas is a total sulfur determination (see below) before and after a scrubber containing some solution suitable for complete thiophene removal from the gas. Hutchinson (2) has found that concentrated sulfuric acid is effective in removing thiophene from gas, however, it is necessary to remove hydrogen sulfide before scrubbing the gas with sulfuric acid.

Total Sulfur Determinations

In general, the processes wherein total sulfur determinations are made, consist in converting all the various types of sulfur compounds present into one specific type which can be quantitatively identified. The method most frequently employed is the transformation of the sulfur-containing compounds into sulfur dioxide and sulfur trioxide by combustion, the SO_2 and SO_3 thus formed usually being separated from the products of combustion by a suitable scrubbing solution which is subsequently analysed.

The Referee's method (95) involves the burning of a known volume of gas while simultaneously volatilizing ammonium carbonate placed adjacent to the test burner. The products of combustion pass through a tube containing glass beads and into a condenser. After burning sufficient gas the system is thoroughly washed and the washings added to the condensate obtained during the experiment. This solution is made acidic and the sulfur compounds oxidized to sulfates with bromine. An excess of barium chloride is added, the solution is filtered, and the filtrate is dried and weighed. From this the sulfur present can be determined.

Another combustion method for total sulfur is recommended by Altieri (77)(96). In this the gas is also burned, thus converting the sulfur compounds to sulfur dioxide and sulfur trioxide. The products of combustion are scrubbed with a dilute sodium carbonate solution which is back titrated with standard acid using methyl orange indicator. The Na_2CO_3 thus consumed gives a measure of the sulfur compounds present. This method is not effective for the determination of elemental sulfur in gas.

Wilson and Kemper (97) have employed tetrahydroxy quinone as the indicator for a barium chloride titration when sodium carbonate solution is employed as the scrubbing medium for total sulfur determinations by combustion. The object in this is to minimize the errors introduced by oxides of nitrogen formed on combustion which are affective in partially neutralizing the sodium carbonate.

Lusby (25) has devised a method for total sulfur whereby the gas being analysed, in the presence of sufficient hydrogen, is passed over a platinum spiral heated to a bright orange color. The sulfur compounds present are thus converted to hydrogen sulfide which is readily determined with the aid of a Tutweiler analysis.

The Determination of Specific Sulfur Compounds in Gas

Work done at the Institute of Gas Technology by Hakewill and Rueck (87) has resulted in a tentative procedure for determining individual sulfur compounds in gas. The process recommended by them consists in passing the gas through a train of absorbers containing solutions for the specific removal of various sulfur bearing constituents of the gas with a total sulfur determination before and after the removal of each type of sulfur compound. The solutions found most effective and the order in which they should appear in the scrubbing train are listed below.

(1) 10% cadmium chloride buffered with sodium carbonate for the simultaneous removal of hydrogen sulfide and mercaptans.

(2) Concentrated sulfuric acid for the removal of thiophenes.

(3) 10% potassium hydroxide-ethyl alcohol solution for the removal of carbon bisulfide and carbon oxysulfide.

The separate determination of hydrogen sulfide and mercaptans by the use of a cadmium chloride-sodium carbonate solution has been previously described (see page 35) as well as the determination of carbon bisulfide in the presence of carbon oxysulfide (see page 38).

PART II EXPERIMENTAL

CHAPTER VIII

A DESCRIPTION OF THE FLOW PROCESS EMPLOYED

Essentially the procedure employed for studies of the thermal decomposition of thiophene was (a) to meter from high pressure cylinders the thiophene carrier gas (b) divide this gas into two parts, one part being partially saturated with thiophene vapor (c) mix the resulting gas streams and pass this mixture through a high temperature zone containing various packings, and (d) analyse the resulting gas for various sulfur compounds. The apparatus used in the experiments presented herein was very similar to that employed by the Institute of Gas Technology (87) to determine methods of analysis of gases for various sulfur compounds.

The gas being employed as a thiophene carrier from a high pressure cylinder was reduced in pressure by a standard reducing valve. To realize better control, a needle valve was installed after the reducing valve. The gas was next subjected to the purification process chosen, after which it was passed through a set test meter (A) (see Figures IA, IB, and IC), and subsequently dried over activated alumina (B). At this point the carrier gas was divided into two streams. Each stream passed through a needle valve (C) and a flow meter (D)(E). One stream went directly to the furnace while

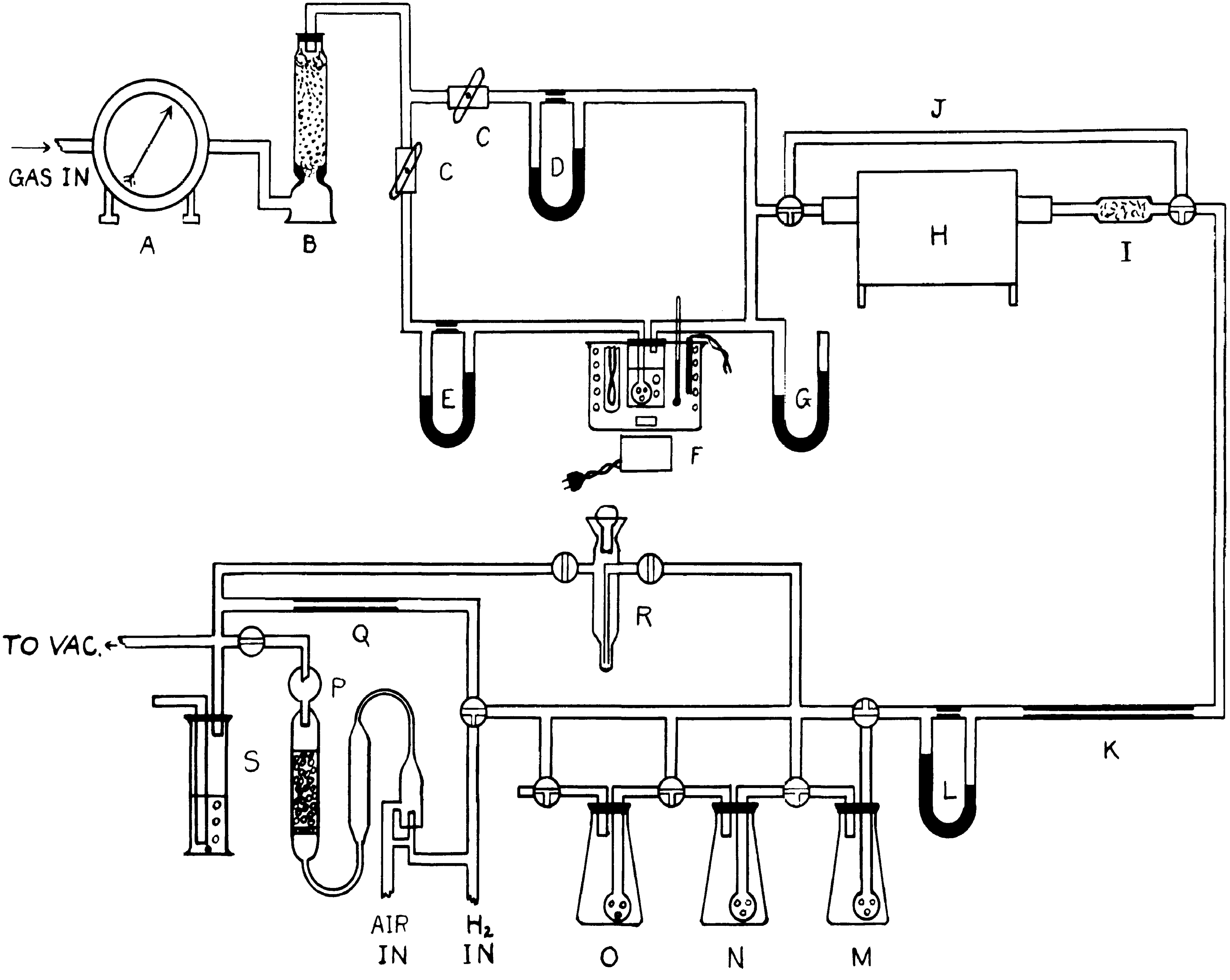


Figure I-A
Equipment Used in Studies of the Thermal Decomposition of Thiophene

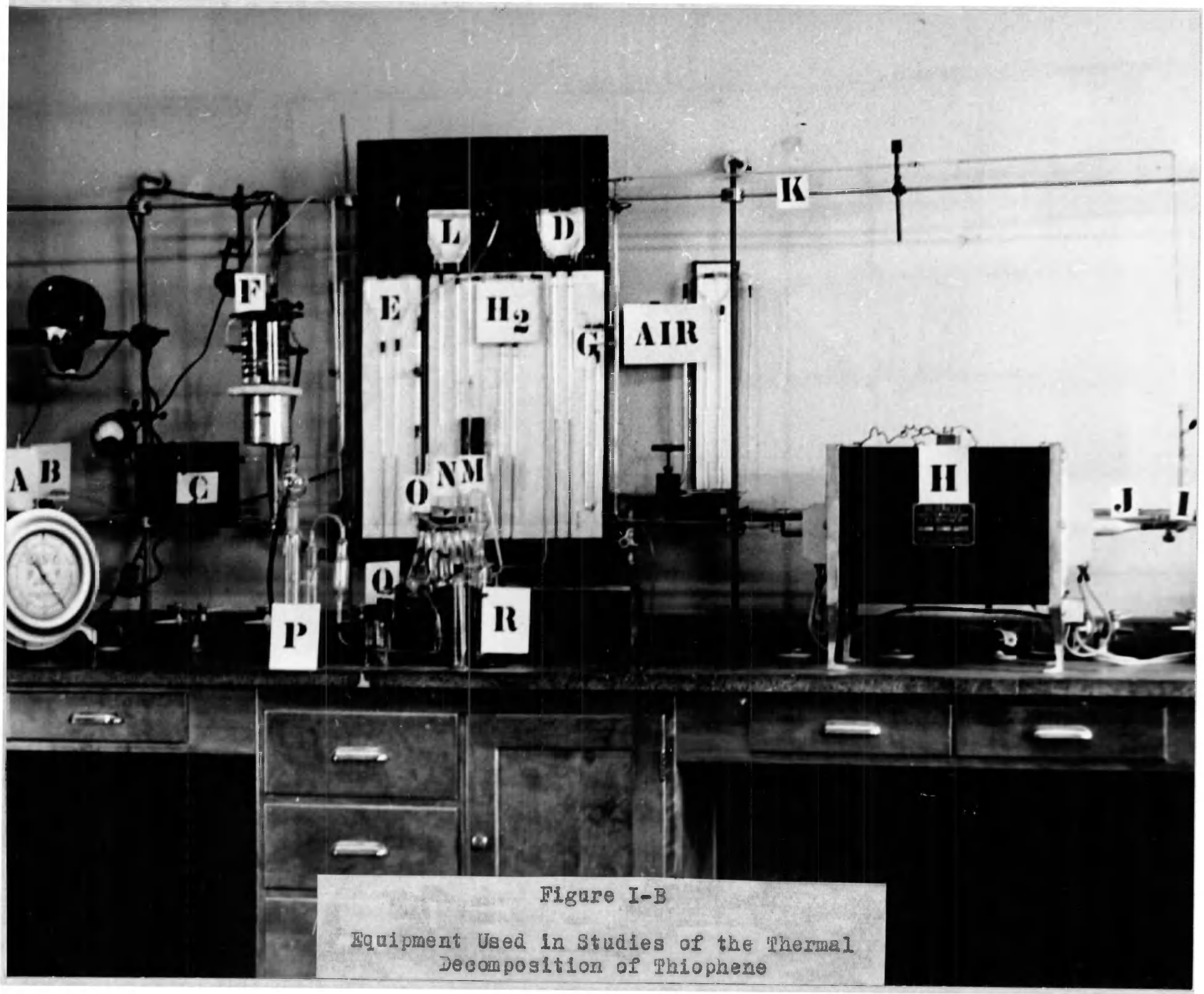


Figure I-B

Equipment Used in Studies of the Thermal Decomposition of Thiophene

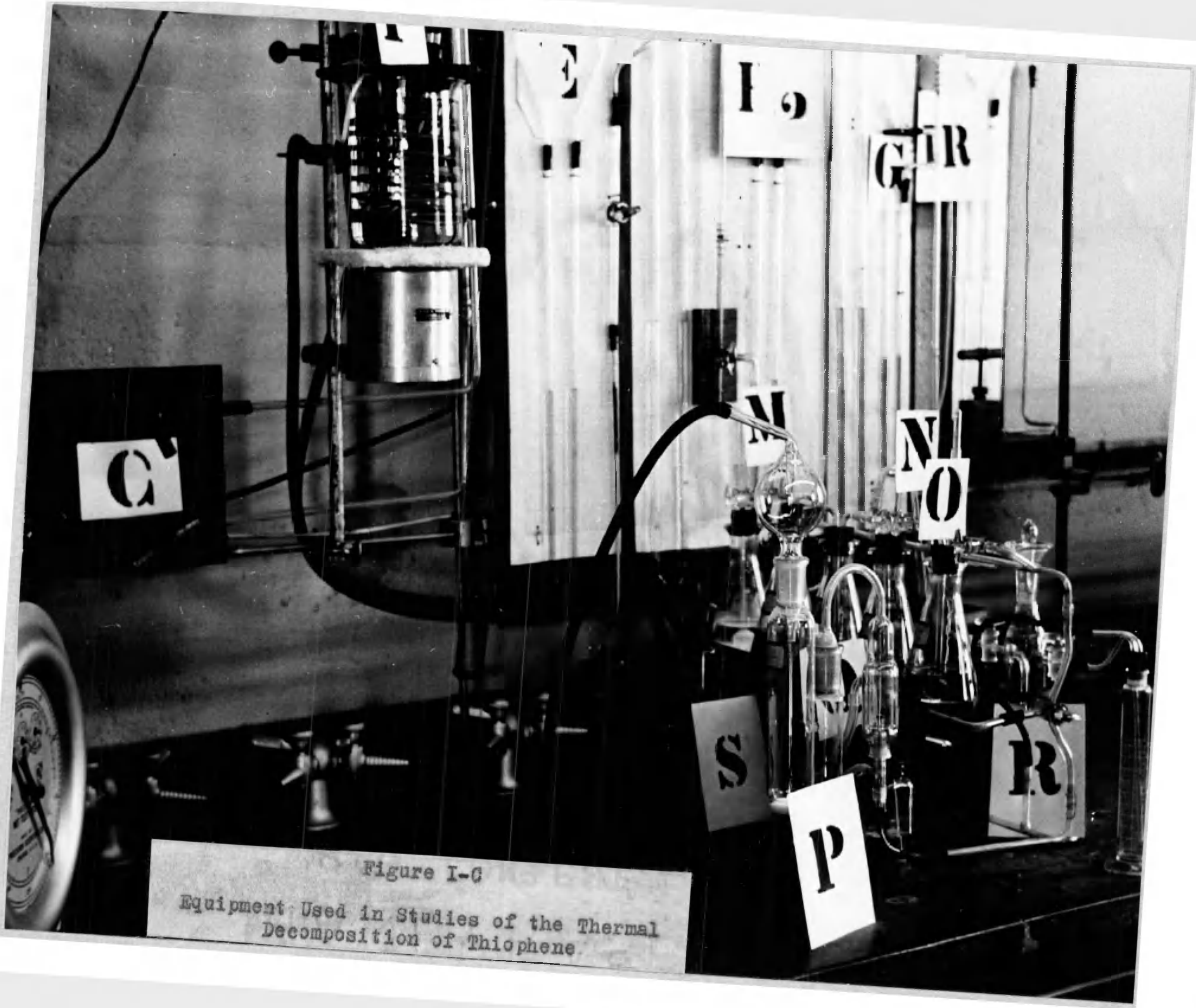


Figure I-C

Equipment Used in Studies of the Thermal Decomposition of Thiophene

the other was first bubbled through thiophene maintained at a constant temperature.

To direct the carrier gas-thiophene mixture through the furnace, various size combustion tubes of sillimanite or quartz were used. From the furnace the resulting gas was passed through a cotton filter (I) to remove any solid material present. A by-pass (J) was installed around the furnace to facilitate analysis of the gas mixture entering the pyrolysis tube. The gas from the high temperature zone, after passing through the cotton filter, was sent through a section of capillary tubing (K), to maintain approximately atmospheric pressure at the inlet of the furnace. This was necessary as suction was applied to the exit of the gas from the system. The gas next passed through a flow meter (L) and into a manifold which was employed to direct the gas in one of several directions. For total sulfur analysis of the exit gas from the furnace the stream was directed to the burner (P). This could be by-passed through the capillary (Q) directly to the vacuum line. This capillary was installed to effect a pressure drop approximately equal to that developed by the burner, thus when the gas was diverted from the vacuum line to the burner the variation of gas flow and pressures throughout the system was minimized.

Before going to the burner the gas stream could be directed through various combinations of absorbers (M) to remove hydrogen sulfide and mercaptans, (N) to remove thiophenes, and (O) to remove carbon bisulfide and carbon oxysulfide (see page 43). Upon determination of the total sulfur by combustion before and after any one of these, the sulfur present as the various compounds thus removed could be determined. Thus (M)(N) and (O) represent all the absorbers required for complete removal of the compounds mentioned above.

For a determination of hydrogen sulfide alone, the gas mixture could be directed to a Shaw flask (R)(79), which was followed by a trap.

To maintain a constant, yet adjustable vacuum on the system a mercury relief valve (S) was placed in the vacuum line. By continued bubbling of air through the mercury a vacuum equal to the head of mercury in the trap was thus obtained.

Specific Equipment Used and Method of Operation

Gas Meter and Drier. The wet meter used for measuring gas volumes in these experiments was of a standard make, having an accuracy of 0.001 cubic foot. This was equipped with a thermometer and manometer to permit correcting the gas volume readings to some chosen standard condition.

Since the exit gas from the above test meter was saturated with water vapor it was necessary to install a drying tube on the meter outlet. This consisted of a tube containing approximately 250 ml. of activated alumina. To obtain an indication of the moisture content of the alumina, this was soaked in a solution of approximately 5 percent cobalt chloride and subsequently dried at 450°F (232°C). After this treatment the alumina was blue when dry and light pink when wet. At such a time that the color interface between the wet and dry alumina approached the gas outlet of the drying bottle, the alumina was removed and dried again at 450°F.

Flow Meters (D),(E) and (L),(Figure I). These consisted of capillary tubing of short lengths and of a diameter sufficient to give appreciable readings on the manometers. The division of the carrier gas before the furnace was maintained in such a manner that the larger volume of gas bypassed the thiophene bubbler. At the beginning of a run the gas streams entering the furnace were proportionated to the desired value by adjusting needle valves (C). The needle valve settings were not changed at any time during an experimental run.

Thiophene Saturator (F). The thiophene saturator was composed of a suitable bubbling tube inserted in a flask of thiophene, which in turn was immersed in a constant temperature bath. The bubbling tube was made by first blowing a bulb on the end of a glass tube, then several small holes were made in the bubble. To maintain a constant temperature in the bath, a 25 watt candle-shaped light was used as a heating element. An immersion type thermoregulator, with a sensitivity of ±0.25°F, was used to control the heating cycle of the light bulb. To effect better control of the bath temperature, cold water was passed through a set of coils immersed in the bath. A magnetic stirrer was used to obtain agitation of the bath water. With this arrangement it was possible to maintain the bath within ±0.5°F of the desired temperature.

The thiophene used in these experiments was obtained from the laboratories of the Socony-Vacuum Oil Company, whose analysis of this material showed 99 mole percent thiophene.

Furnace (H). The furnace used to heat the reaction tubes was of the glo-bar type, with a heating zone of approximately 15 inches in length. To maintain the temperature at a constant value a standard type indicator-controller was used which was operated with the aid of a base metal thermocouple installed in the furnace. Temperature control was realized by the automatic switching of the glo-bar leads to a high or low voltage tap on an autotransformer connected in the furnace circuit. The desired operating temperature range governed the transformer taps thus used. With this arrangement it was possible to maintain the furnace temperature within -5°F. Because of the time required to raise the temperature of the furnace from room to operating temperatures a timing device was installed to turn the furnace on several hours before an actual experiment.

The filter (I) following the furnace consisted of a tapered ground glass joint which was drawn down at the ends and sealed to 6 mm. tubing. This was packed with cotton for a length of approximately 2 inches.

As noted above, to maintain a pressure on the furnace inlet approximately equal to atmospheric, a capillary tube (K) was installed. This was either 1 or 2 mm. bore and about 18 inches long. These dimensions depended on the gas being used as a thiophene carrier.

Absorbers (M), (N) and (O). The absorbers used to remove specific sulfur compounds from the furnace exit gas were made of a design similar to the thiophene saturator, but of 500 ml. capacity.

Absorber for Hydrogen Sulfide Determination (R). This flask was made according to Shaw's specifications (79). The absorber was followed by a trap which consisted of a tube submerged in a solution which was of the same composition as that contained in the Shaw flask.

Burner for Total Sulfur Determination (P). The total sulfur determination apparatus used in these experiments was a modification of the one recommended by the American Society for Testing Materials (96) for the determination of sulfur in liquid petroleum fractions. A modification of the burner was necessary to adapt this for gases. The liquid sample bottle was removed and a small length of aluminum tubing having a 2 mm. bore was inserted in the burner inlet and sealed with sealing wax. This modification was necessary to give the gas sufficient velocity to prevent flash back of the flame.

When an inert carrier gas was employed it was necessary to introduce hydrogen into the gas stream to maintain a flame on the burner. This hydrogen, being mixed with the sulfur bearing carrier gas just prior to entrance into the burner, was metered by means of a flow indicator similar to those described above. Control of the hydrogen flow was obtained by means of a pressure reducing valve and a needle valve on the high pressure cylinder supplying the hydrogen thus used.

The air required for combustion likewise was metered by means of a capillary tube and manometer. Control was made possible by means of a needle valve on the inlet side of the flow meter. The slight vacuum applied to the burner was sufficient to maintain the air flow required. Purification of the air was effected just prior to entrance into the burner by first passing this through a scrubbing bottle containing concentrated sulfuric acid and then through a bottle containing normal sodium carbonate.

As previously mentioned, the burner by-pass line contained a section of capillary tube to minimize flow and pressure variations, when the gas stream was diverted directly to the vacuum system. This capillary consisted of a tube 1 mm. in bore and approximately 10 inches in length.

Analytical Procedures and Solutions

Total Sulfur Determinations. There are many variations of the combustion method for determining the total sulfur content of a gas. A few of these methods were described in Chapter VII. For the experiments here a rapid, but accurate determination was desired, therefore the method suggested by Altieri (77) for sulfur determination in combustible liquids was modified to allow similar analyses on gases. Essentially, the sulfur compounds were converted to sulfur dioxide and sulfur trioxide by combustion, with the simultaneous absorption of these compounds in a solution of sodium carbonate. The carbonate thus consumed was determined by titration with sulfuric acid of known concentration, using methyl orange as an indicator.

The concentration of the sodium carbonate solution used, as well as the sulfuric acid, was approximately 0.0639 normal. This concentration is also recommended by Altieri. For standardization of these solutions a commercially standardized 0.1 N hydrochloric acid was employed, by titrating a 10:1 solution of this acid against the sodium carbonate solution, which in turn was titrated against the sulfuric acid, methyl orange being employed as the indicator in both cases. Both the sodium carbonate and the sulfuric acid used were of C.P. grade.

With a thiophene content of approximately 630 grains per hundred cubic feet of gas it was found that 25 ml. of the sodium carbonate solution was sufficient for complete sulfur removal from the burner exit gas when the volume of gas burned was 0.1 cubic foot. To increase the volume of solution in the scrubber, approximately 25 ml. of distilled water were added to the carbonate solution.

The Institute of Gas Technology (37) recommends the use of a 10 percent solution of sodium bicarbonate as the scrubbing medium for total sulfur determinations by combustion.

analysis of this solution is carried out by neutralization to the methyl orange end point with one N hydrochloric acid, followed by the addition of an excess of one ml. of the acid. Fifteen ml. of saturated bromine water is added and the solution boiled until the color of bromine disappears. The solution is then treated with 10 ml. of 10 percent barium chloride, boiled for an hour, and filtered. The weight of the dried precipitate gives the sulfur present as barium sulfate. This method was compared to the one suggested by Altieri (77), and the results by both methods differed by less than 1 percent. The chief difficulty with all gravimetric methods is the time involved in carrying out each analysis.

Hydrogen Sulfide - Mercaptan Absorbing Solution. As previously mentioned, the determination of hydrogen sulfide plus mercaptans was made by a total sulfur analysis of the gas before and after these two components had been removed from the gas. The solution used for the simultaneous absorption of hydrogen sulfide and mercaptans consisted of 100 ml. of a 10 percent cadmium chloride solution to which 15 ml. of approximately one normal sodium carbonate had been added. This solution has been recommended by the Institute of Gas Technology (87). To effect complete removal of the sulfur present as hydrogen sulfide and mercaptans, one, and sometimes two, scrubbing bottles were required. The reason for using two such scrubbers is discussed in a later section.

Thiophene Absorbing Solution. Hutchinson (2) has recommended the use of concentrated sulfuric acid for the removal of thiophenes from gas. Experiments by the Institute of Gas Technology (87) have verified the use of sulfuric acid for this purpose. It is necessary, however, to remove the hydrogen sulfide and mercaptans (98) prior to the removal of thiophene by this method, consequently the sulfuric acid scrubbing bottles were placed after the cadmium chloride scrubber. To insure complete removal of the thiophenes, two acid scrubbers were installed, followed by a normal sodium carbonate solution to remove any resulting acid mist. In all three of the above scrubbing bottles 100 ml. of solution were used. To determine the sulfur present as thiophenes in the gas leaving, or entering, the furnace, a total sulfur analysis was made before and after the thiophene scrubbing train and the thiophene content determined by difference. It has been recommended (99) that before an analysis is made on the gas leaving the sulfuric acid bottles, at least 0.3 cubic foot of gas should be passed through the acid to remove any oxides of sulfur arising from the acid itself. In the experiments here at least 0.5 cubic foot of gas was allowed to pass through the bottles before analysis.

Carbon Bisulfide and Carbon Oxysulfide Absorbing Solutions. For the simultaneous removal of carbon bisulfide and carbon oxysulfide from gas a 10 percent solution of alcoholic potash has been recommended (37). This solution was made by rapidly grinding 10 grams of potassium hydroxide pellets into a powder and dissolving this in 110 ml. of 95 percent ethyl alcohol. The solution was made up fresh prior to each analysis, cooled to 0°C, and maintained below 5°C during absorption. Before exposing the gas being tested to this solution it is necessary to remove the hydrogen sulfide, mercaptans, and thiophenes; this scrubber therefore followed the sulfuric acid previously mentioned. In most cases a single absorbing bottle was sufficient for removing all the carbon bisulfide and carbon oxysulfide present. To determine the quantity of sulfur present in the gas as both bisulfide and oxysulfide of carbon a total sulfur determination was made before and after the removal of these compounds by the alcoholic potash.

By a rather unique method (87) it is possible to determine the sulfur present as carbon bisulfide or carbon oxysulfide alone. The method, described herewith, was used in these experiments when it was believed that carbon oxysulfide, as well as carbon bisulfide, might be present in the gas. The reactions representing the absorption of carbon bisulfide and carbon oxysulfide in an alcoholic potash are given below (see page 39):

$$(a) \quad CS_2 + KOEt \longrightarrow KS{-}CS{-}OEt$$

$$(b) \quad COS + KOEt \longrightarrow KS{-}CO{-}OEt$$

If this mixture is kept chilled at approximately 0°C and acetic acid is added the reactive xanthic acids are formed. These are readily oxidized by iodine to give the corresponding disulfides:

$$\text{(c)}\quad 2HS\text{-}CS\text{-}OEt + I_2 \longrightarrow EtO\text{-}CS\text{-}S\text{-}S\text{-}CS\text{-}EtO + 2HI$$

$$\text{(d)}\quad 2HS\text{-}CO\text{-}OEt + I_2 \longrightarrow EtO\text{-}CO\text{-}S\text{-}S\text{-}CO\text{-}EtO + 2HI$$

From equations (a) and (c) it is seen that one mole of carbon bisulfide requires one atom of iodine for neutralization while from equations (b) and (d) it is seen that one mole of carbon oxysulfide requires one atom of iodine for neutralization also. Letting S_D be the sulfur present as the disulfide and S_O be the sulfur present as the oxysulfide, there results:

$$\tfrac{1}{2}S_D + S_O = \text{Titratable sulfur.}$$

From the total sulfur analysis before and after the potash scrubbing bottle, there results:

$$S_D + S_O = \text{Total sulfur loss.}$$

A solution of these equations simultaneously gives the sulfur present as carbon bisulfide as well as carbon oxysulfide.

Two such analyses, when necessary, were employed to determine the carbon bisulfide and carbon oxysulfide in the sulfur bearing gas leaving the furnace, after the hydrogen sulfide, mercaptans, and thiophenes had been removed. To determine the sulfur loss by scrubbing the gas with alcoholic potash, a total sulfur determination was made before and after the potash scrubber by means of combustion. Subsequent to this, a second portion of the gas was scrubbed free of carbon bisulfide and carbon oxysulfide by replacing the above scrubbing solution with freshly prepared alcoholic potash. After passing a known volume of gas, the bottle of solution was removed and diluted approximately 1:1 with distilled water. The mixture was again chilled to 0°C and acidified with glacial acetic acid to the phenolphthalien end point, the acid being added dropwise with an excess of three drops. Keeping the solution chilled, 5 ml. of starch solution (200 gm. soluble starch in 1000 ml. of water) were added and this was titrated with 0.01 normal iodine solution. Although the starch end point is fairly difficult to determine, reasonable accuracy can be obtained with practice. It is of course necessary to correct these titrations by means of a blank. The iodine solution used for these determinations was prepared by dissolving 12.7 grams of iodine and 20 to 25 grams of C.P. potassium iodide in as little water as possible, and then diluting this to a liter. This 0.1 normal stock solution was diluted 10:1 for use in experimental analysis. Standardization of these iodine solutions was obtained with the aid of a commercial standard of sodium thiosulfate.

Hydrogen Sulfide Determination. The procedure employed for the determination of hydrogen sulfide will be discussed in detail here. It is a modification of the method detailed by Shaw (79) which modification was necessary because of the presence of large quantities of hydrogen sulfide. The procedure recommended by Shaw has been previously discussed in Chapter VII. Essentially, this method consists in absorbing the hydrogen sulfide and mercaptans in an alkaline cadmium chloride solution. This solution is then neutralized to the methyl orange end point with normal hydrochloric acid after which an excess of acid is added to give a solution containing 3 grams of free HCl per liter. At this concentration the cadmium sulfide is in suspension and the cadmium mercaptide in solution. This is filtered and the sulfide dissolved with concentrated hydrochloric acid, and treated with iodine which is back titrated with thiosulfate.

Due to the large quantities of hydrogen sulfide present in the experiments here reported, the cadmium sulfide formed on absorption masked the methyl orange indicator, and it was impossible to determine the end point occuring with the addition of acid. Because of this, the correct pH for cadmium mercaptide dissolution could not be obtained. Brewer and Ghosh (100) modified Shaw's method by adjusting the pH of the absorbing solution (0.3 percent free acid) before scrubbing the gas. The object in this was to retain the cadmium mercaptide in solution. This method was tried under the conditions of the experiments here and it was found that after two scrubbing bottles hydrogen sulfide or mercaptans, were still present in the gas.

It was believed that perhaps another indicator, i.e. one that is not masked by the yellow cadmium sulfide, might prove successful, however, there are very few satisfactory indicators in the pH range below methyl orange. It is necessary to have an indicator with a pH range no greater than that for methyl orange due to the presence of carbon dioxide and hydrogen sulfide.

The following procedure was finally devised for the determination of hydrogen sulfide in gas. Following Shaw's recommendation a scrubber was used followed by a trap, each containing 15 ml. of 10 percent cadmium chloride solution with 2 ml. of normal sodium carbonate as a buffer. Before exposure to the gas, 2 ml. of normal hydrochloric acid were required to neutralize each of these solutions to a methyl orange end point. Since these two solutions were combined before analysing for sulfur by Shaw's method, a total of 4 ml. of normal acid were required to neutralize the mixture to a methyl orange end point. After passing the gas through the two scrubbers the color of cadmium sulfide was apparent in the first bottle only, therefore a quantity of normal acid between 2 and 4 ml. was required for neutralization of the combined solutions.

In order to obtain a concentration of 3 grams of free acid per liter it is necessary to have 8.3 ml. of normal acid in 100 ml. above that required for neutralization of the cadmium chloride-sodium carbonate solution. Since 2 to 4 ml. of acid are needed for neutralization, 11.3 ml. of acid were added to a quantity of water sufficient to bring the volume of the combined scrubber solutions to 100 ml. The maximum pH variation of such a procedure is ±0.05 pH units. After dilution, the mixture was filtered through a Gooch crucible, and the cadmium sulfide redissolved with 10 ml. of concentrated hydrochloric acid. This was diluted to 50 ml., an excess of iodine solution added, and back titrated with sodium thiosulfate using starch as an indicator.

A few hydrogen sulfide determinations were made using 11.8 and 10.8 ml. of normal acid, instead of the 11.3 mentioned above, in a volume of water sufficient to dilute the scrubber solution to 100 ml. In all cases the deviation was within 2 percent.

In order to find the sulfur present as mercaptans only, the quantity of sulfur determined as hydrogen sulfide was subtracted from that value of sulfur obtained as hydrogen sulfide plus mercaptans by combustion methods (see page 50).

It should be emphasized that the results obtained by this modification of Shaw's procedure are not considered to be of a high order of accuracy. This method of hydrogen sulfide determination was employed as a last resort. However, it was believed that the results thus obtained would show reasonably well the approximate quantity of hydrogen sulfide and mercaptans present in the gases in question.

CHAPTER IX

QUALITATIVE EXPERIMENTS

Choice and Preparation of Pyrolysis Tube Packings

The chief objective in the thermal decomposition of thiophene was the transformation of this compound into types of sulfur products capable of easy removal from gas. It was believed, therefore, that pyrolysis tube packings of some form of carbon might be beneficial not only by increasing the surface present, but also by aiding in the formation of carbon bisulfide. On this basis it was decided that coke be used as a tube packing. A commercial grade coke was chosen. This was crushed and screened to a size range of $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. The ash content of the coke thus employed was 15.0 percent on a dry basis while the sulfur content was found to be 0.55 percent, also on a dry basis.

To study the effect of the mineral compounds present in the coke a form of carbon low in ash content was chosen as a pyrolysis tube packing under conditions comparable to those during which coke was used. For this purpose a sugar char was prepared. Domestic sugar cubes were first charred in an open refractory dish until the major part of the volatiles had been distilled off. This char was next broken into small pieces and further charred in a combustion tube at approximately 2000°F (1093°C) for six hours. By placing a water seal at one end of the combustion tube it was possible to tell when charring was complete. After cooling, the sugar char was removed and broken into small pieces which were screened to a size of $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. The ash content of this char was found to be 0.64 percent on a dry basis.

A third packing of porcelain was chosen for a study of surface effects alone as compared to coke and sugar char. Porcelain balls approximately $\frac{1}{2}$ inch in diameter were obtained and these were soaked in aqua regia overnight and then thoroughly washed and dried.

Preliminary Experiments

Before any qualitative studies of the thermal decomposition of thiophene were undertaken over a carbon surface, a few preliminary tests of the method of operation of the equipment employed were made. With the use of nitrogen as a carrier gas it was necessary to introduce hydrogen into the gas stream just prior to the burner used in total sulfur determinations. The object of this was to maintain the flame necessary to effect a conversion of the sulfur compounds present in the gas to sulfur dioxide and sulfur trioxide. To determine the hydrogen rate necessary to give an optimum size flame, the burner was ignited and inserted into the chimney of the absorption apparatus. Sufficient air was also introduced into the burner by applying a vacuum to the outlet of the sulfur determination apparatus. The flow rate of the hydrogen was then adjusted by means of the reducing valve on the hydrogen cylinder and the reading on the hydrogen flow indicator noted. Keeping the same rate, the hydrogen flow was measured by observing the time required to fill a gas burette with the hydrogen. This rate was found to be 900 ml. per minute.

For the preliminary experiments a carrier gas of nitrogen was used to introduce thiophene into a high temperature zone. To obtain the maximum nitrogen flow rate for efficient operation of the sulfur determination apparatus a process similar to that described above was used. After igniting the hydrogen and inserting the burner in the chimney the nitrogen flow rate was varied to obtain a flame that did not blow out or extend too far up into the chimney. This rate was noted on the wet test meter and was found to be approximately 0.1 cubic foot in 5.25 minutes.

In order to obtain better accuracy, it was decided that a fairly high concentration of thiophene in the gas entering the pyrolysis tube should be used, therefore a value of approximately 250 grains of sulfur as thiophene per hundred cubic feet of gas was chosen. By adjusting the temperature of the bath surrounding the thiophene saturator to 70°F (21.1°C) it was possible to obtain the high thiophene percentages required in the gas as well as obtain assurance against thiophene condensation in the uncooled gas lines. The thiophene content of the inlet gas to the furnace was brought to the desired value by increasing the rate of gas flow through the thiophene saturator and analysing the gas mixture after each change in the flow rates. With a gas containing 250 grains of sulfur as thiophene per hundred cubic feet, approximately 15 ml. of the 0.0639 normal sodium carbonate solution were consumed in scrubbing the sulfur dioxide and trioxide from the products of combustion of the sulfur lamp.

System Calibrations

Although the use of rubber tubing throughout the system was kept at a minimum and all glass tubing joints were as close as possible, it was deemed necessary to determine any errors introduced by the rubber tubing and few rubber stoppers present. To achieve this, a total sulfur determination was made on a gas sample taken just after the point of mixing of the carrier gas stream and the gas stream saturated with thiophene. This was compared to a total sulfur analysis of the mixed gases after these had passed through the entire system, including the train of empty scrubbing bottles used in selective absorption. It was found that these two analyses agreed within 2 percent. This agreement is at least as good as that expected due to variations in the constant temperature bath surrounding the thiophene saturator.

Russel (101) states that the presence of oxides of nitrogen in gases give erroneous results when analysis of the scrubbing solutions used for total sulfur determinations by the lamp method is made by back titrations. To make certain such errors would not be present under the conditions of the experiments here, a total sulfur determination, employing a back titration of the sodium carbonate scrubbing solution with hydrochloric acid, was made on the exit gas from a pyrolysis tube packed with coke, while using nitrogen as a carrier gas. This was compared to an analysis of the same gas by the use of a gravimetric method as given by Parr (102). The deviation between these two methods of analysis was within one percent, which is within the accuracy of the apparatus. It was therefore concluded that the errors introduced by any oxides of nitrogen were negligible.

The methods of control of the gas flow in this apparatus were quite satisfactory. Having adjusted the ratio of gas flow into two streams, which could be done rapidly, and having adjusted the total flow to the desired value, it was not necessary to readjust the total flow rate any more frequently than every half hour. Usually it was not necessary to readjust the ratio of gas flow in the two streams at any time during an experimental run.

The Formation of a Carbon Sulfur Complex

Holtz (40) made a study of the formation of a carbon sulfur complex on sugar char when nitrogen, containing hydrogen sulfide was passed over char heated to temperatures of 1500 to 1700°F (816 to 927°C). It was found that approximately 2 to 3 hours were required to bring such a complex to equilibrium with the gas, when the gas, containing approximately 450 grains of hydrogen sulfide per hundred cubic feet, was passed over char at a rate of 0.58 cubic foot per hour.

A few trial experiments indicated that thiophene gave similar results when passed over coke heated to high temperatures. Nitrogen containing 221 grains of sulfur as thiophene was introduced over coke, at 1900°F (1038°C) and at the rate of 1.41 cubic feet per hour, and total sulfur determinations were made periodically on the exit gas from the furnace. It was found that approximately three hours were required to set up an equilibrium between the carbon-sulfur complex on the coke and the sulfur bearing constituents in the gas. The results of this experiment are presented below.

Table II

Disappearance of Thiophene Sulfur over Coke

	Sulfur Calculated as Thiophene (Grains per 100 Cubic Feet)	
Time (Hrs.)	Furnace Inlet	Furnace Outlet
0	222	175
0.75	222	201
1.75	222	216
2.25	222	220
2.75	222	221

It is possible the partial pyrolysis of the thiophene resulted in the formation of hydrogen sulfide and carbon bisulfide, as well as other sulfur compounds, which in turn reacted with the carbon present to form a complex on the coke. In all experiments sufficient time was allowed to saturate the pyrolysis tube packings with this carbon-sulfur complex.

Qualitative Studies of the Pyrolysis of Thiophene

Before any quantitative work was begun it was necessary to make a few trial experiments to determine such factors as the temperatures required to give appreciable thermal decomposition of thiophene as well as the contact times necessary at each of these temperatures. For a trial, a one inch (I.D.) Sillimanite combustion tube was chosen and packed with coke screened to a size of ¼ to ½ inch in diameter. Using nitrogen as a carrier gas, containing approximately 240 grains of sulfur as thiophene per hundred cubic feet, passed through the furnace at a rate of 1.41 cubic feet per hour, four different furnace temperatures were employed, i.e. 1400, 1600, 1800 and 2000°F (760, 871, 982, and 1093°C). A determination of the thiophene present in the furnace exit gas under each of the above conditions gave the following results:

Table III

Decomposition of Thiophene over Coke in an Atmosphere of Nitrogen

Furnace Temp. (°F)

Furnace Temp. (°F)	Gas Rate (Cu.Ft./Hr.)	Sulfur as Thiophene (Grains/100 Cu.Ft.) Inlet Gas	Exit Gas
1400	1.41	242	138
1600	1.41	234	102
1800	1.41	236	61
2000	1.41	236	0

From these determinations it was decided to use furnace temperatures of 1625, 1775, and 1900°F (885, 968, and 1038°C). This temperature range insured the thermal decomposition of thiophene to the extent of 50 to 100 percent when nitrogen was employed as the carrier gas.

Having found that the decomposition of thiophene, in a nitrogen atmosphere over coke, was complete at a gas rate of 1.41 cubic feet per hour and a furnace temperature of 2000°F (1093°C), it was believed that a study of the pyrolysis of thiophene at the same temperatures mentioned above but at shorter contact times might yield useful information. To achieve this purpose smaller diameter quartz tubes were obtained. A $\frac{3}{4}$ inch I.D. tube would give a contact time of approximately $\frac{1}{2}$ that obtained with a 1 inch tube and a $\frac{1}{2}$ inch I.D. tube would give a contact time of $\frac{1}{4}$ of that obtained with a 1 inch tube, therefore it was decided that such tubes packed with coke should be tried. The reason for changing the pyrolysis tube diameter rather than the gas flow rate was to maintain the same conditions at the burner used for total sulfur determinations.

For a comparison of coke, sugar char, and porcelain as pyrolysis tube packings, it was believed that the use of the larger tube only, i.e. the 1 inch I.D. Sillimanite tube, would be sufficient if the three furnace temperatures previously mentioned be employed with each type of packing.

The Comparison of Furnace Temperatures and Pyrolysis Tube Temperatures

Having chosen the furnace temperatures and size of pyrolysis tubes, as well as the packing to be used in each, it was necessary to secure some idea of the temperature gradient within the tubes under each of the chosen conditions. To achieve this a "Vycor" tube was placed through the center of the pyrolysis tube and the annular space packed with the material in question. A base metal thermocouple was then inserted within the Vycor tube, and the furnace was brought to the desired temperature. After allowing sufficient time to obtain thermal equilibrium the thermocouple within the Vycor tube was moved an inch at a time from one end of the pyrolysis tube to the other, and the temperature was noted at each point. The results of these determinations are presented in Tables IV, V, VI, VII and Figures II, III, IV, and V. Average tube temperatures were obtained by graphical integration of the curves above 600°F.

The Determination of Contact Times Within the Furnace

In order to determine gas contact times within the furnace it was necessary to determine the volume of packing used in each pyrolysis tube. As a first step, the quantity of packing material required to fill each tube for the length of the furnace was obtained. A graduated cylinder was then filled with an amount of water sufficient to cover the packing, which was then also placed in the cylinder. The resulting change in the volume of water was used as a measure of the volume of packing required to fill that length of the pyrolysis tube exposed to the high temperatures within the furnace. This volume was subtracted from the volume of the pyrolysis tube effective for the thermal decomposition of thiophene. From the corrected volumes and gas flow rates, the following contact times were obtained:

Tube Diameter (Inches)	Packing	Approx. Contact Time (Seconds)
1	Coke	11.9
1	Porcelain	11.9
¾	Coke	7.3
½	Coke	3.0

Table IV

Calibration of Pyrolysis Tube Temperature Versus Furnace Temperature
1 Inch I.D. Sillimanite Tube
Coke Packing

Inches From End of Tube	Tube Temperatures (°F) Corresponding to Furnace Temperatures (°F) of			
	1625	1700	1775	1900
0	600	600	630	640
1	870	900	930	980
2	1150	1200	1240	1330
3	1390	1460	1500	1660
4	1490	1580	1630	1800
5	1540	1650	1710	1850
6	1580	1690	1750	1880
7	1610	1710	1770	1910
8	1620	1720	1780	1920
9	1620	1730	1790	1930
10	1620	1740	1790	1930
11	1620	1740	1790	1930
12	1610	1730	1790	1920
13	1590	1720	1780	1910
14	1570	1690	1750	1880
15	1530	1610	1710	1860
16	1460	1560	1640	1800
17	1340	1450	1500	1650
18	1080	1200	1240	1330
19	810	880	920	960
20	580	590	620	600
Average Temp.	1390°F	1460°F	1521°F	1643°F

Table V

Calibration of Pyrolysis Tube Temperature Versus Furnace Temperature
1 Inch I.D. Sillimanite Tube
Porcelain Packing

Inches From End of Tube	Tube Temperatures (°F) Corresponding to Furnace Temperatures (°F) of			
	1625	1700	1775	1900
0	560	560	560	600
1	750	860	860	940
2	1100	1170	1200	1300
3	1320	1400	1480	1610
4	1480	1560	1640	1770
5	1550	1620	1720	1860
6	1580	1660	1760	1900
7	1600	1690	1780	1920
8	1620	1700	1800	1930
9	1630	1710	1810	1930
10	1630	1710	1810	1930
11	1630	1700	1810	1930
12	1620	1700	1800	1930
13	1600	1680	1790	1920
14	1590	1660	1760	1910
15	1560	1620	1720	1840
16	1480	1560	1650	1780
17	1340	1410	1510	1650
18	1100	1170	1230	1340
19	750	870	880	980
20	560	560	570	600
Average Temp.	1400°F	1467°F	1535°F	1660°F

Table VI

Calibration of Pyrolysis Tube Temperature Versus Furnace Temperature
¼ Inch I.D. Quartz Tube
Coke Packing

Inches From End of Tube	Tube Temperatures (°F) Corresponding to Furnace Temperatures (°F) of			
	1625	1700	1775	1900
0	570	600	600	620
1	930	980	980	980
2	1280	1340	1380	1420
3	1470	1550	1610	1730
4	1560	1640	1710	1840
5	1600	1680	1750	1890
6	1630	1710	1780	1920
7	1640	1720	1800	1940
8	1650	1730	1810	1950
9	1660	1740	1820	1950
10	1660	1740	1820	1950
11	1660	1740	1820	1950
12	1660	1740	1820	1950
13	1650	1730	1810	1940
14	1630	1720	1800	1930
15	1600	1680	1780	1900
16	1550	1640	1740	1850
17	1460	1570	1690	1720
18	1270	1360	1380	1480
19	950	980	980	980
20	560	600	600	650
Average Temp.	1460°F	1535°F	1610°F	1740°F

Table VII

Calibration of Pyrolysis Tube Temperature Versus Furnace Temperature
½ Inch I.D. Quartz Tube
Coke Packing

Inches From End of Tube	Tube Temperatures (°F) Corresponding to Furnace Temperatures (°F) of			
	1625	1700	1775	1900
0	560	580	600	600
1	880	1010	1050	1090
2	1240	1350	1380	1470
3	1480	1560	1560	1750
4	1560	1640	1700	1840
5	1600	1680	1750	1890
6	1630	1710	1770	1910
7	1640	1720	1790	1920
8	1650	1730	1810	1940
9	1660	1740	1820	1950
10	1650	1740	1820	1950
11	1650	1740	1820	1950
12	1650	1730	1810	1930
13	1630	1720	1790	1910
14	1610	1710	1770	1890
15	1590	1670	1750	1880
16	1560	1630	1700	1830
17	1480	1550	1550	1730
18	1250	1370	1380	1460
19	880	990	1040	1040
20	560	570	600	600
Average Temp.	1460°F	1540°F	1615°F	1745°F

Figure II

Temperature Gradient Across 1 inch Tube

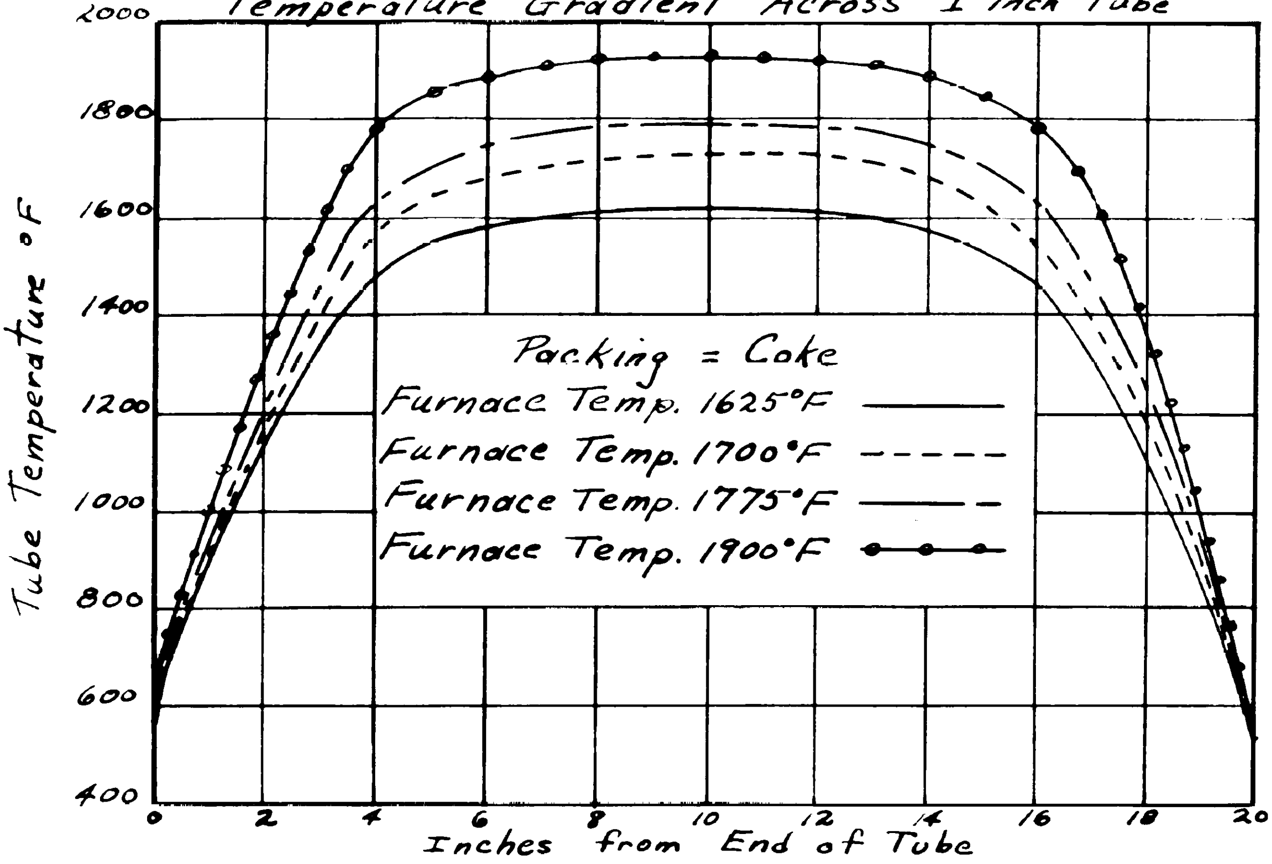


Figure III

Temperature Gradient Across 1 inch Tube

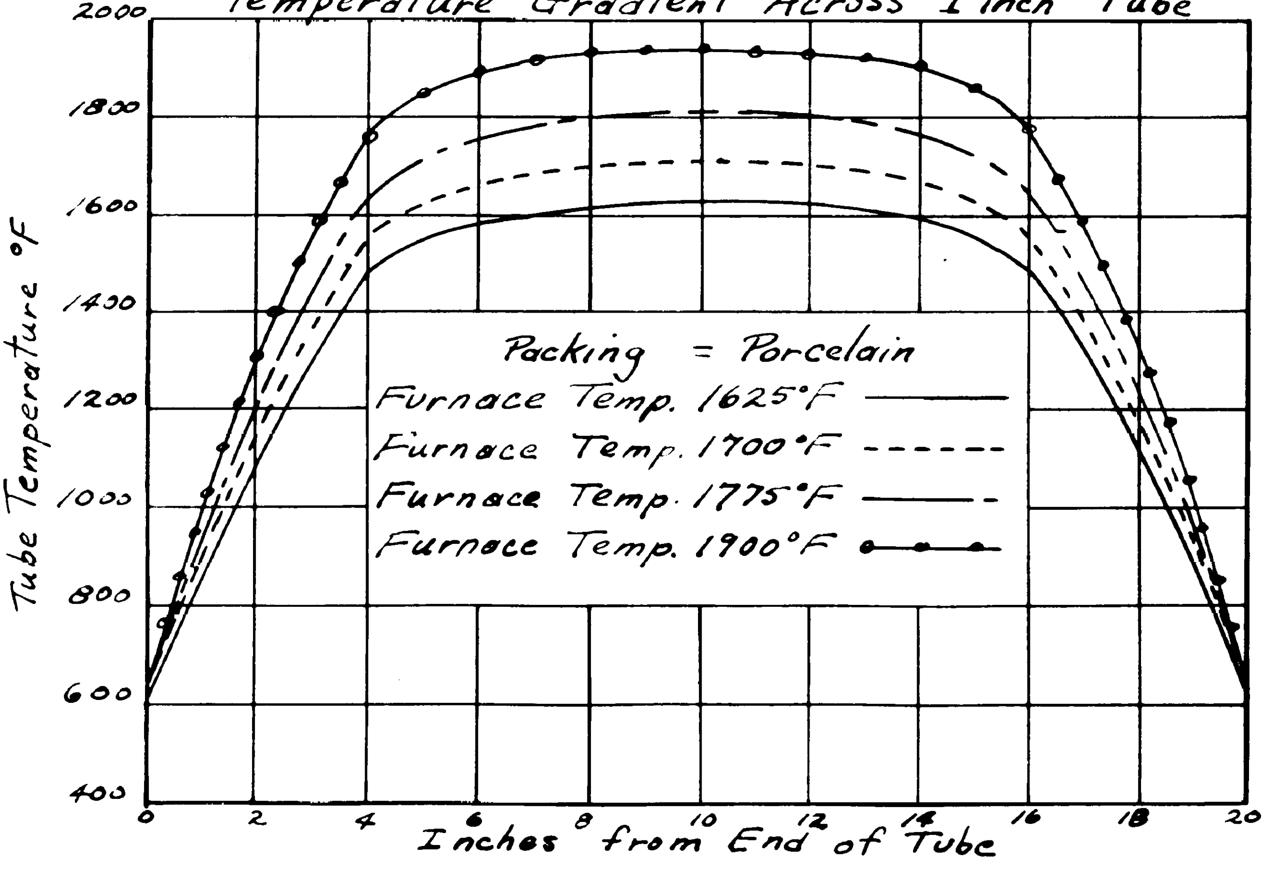


Figure IV

Temperature Gradient Across 3/4 inch Tube

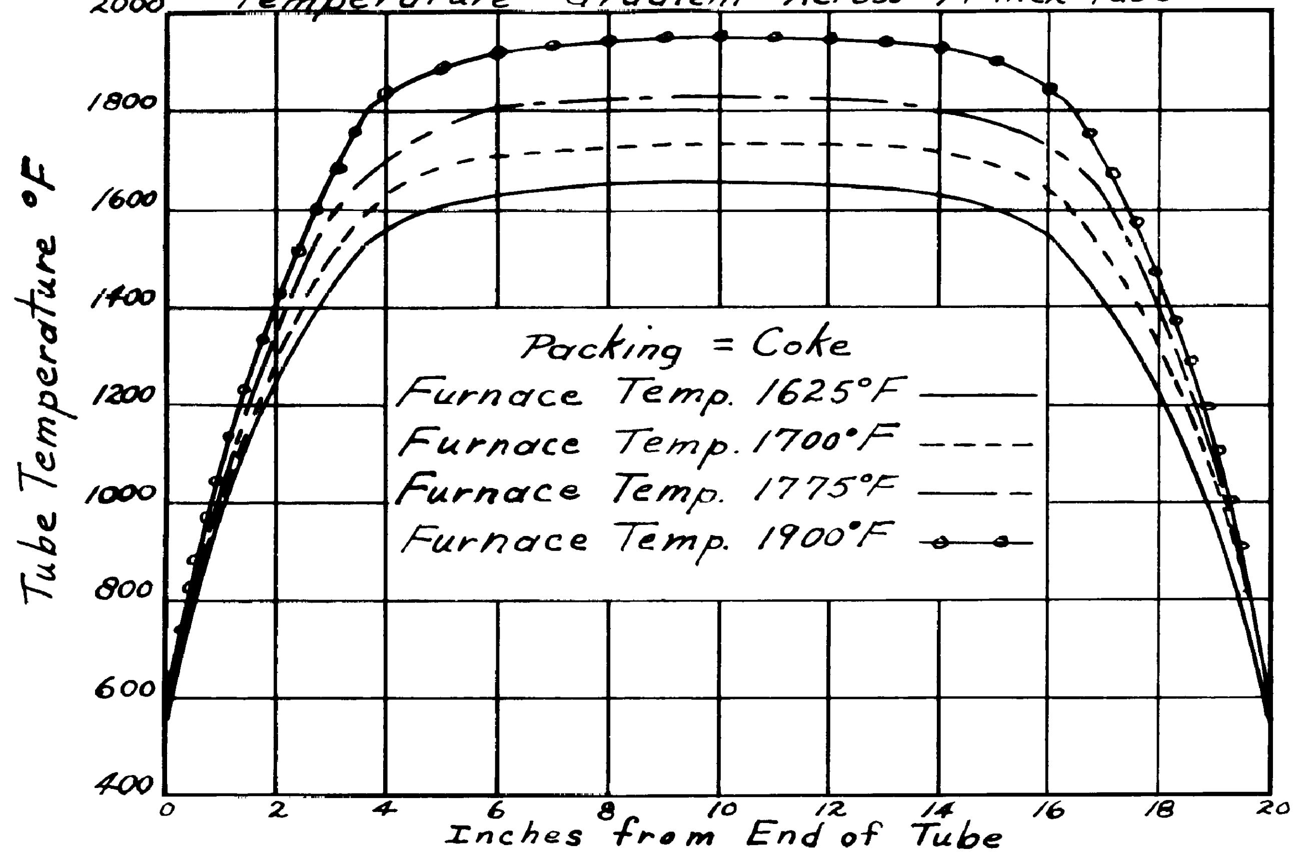
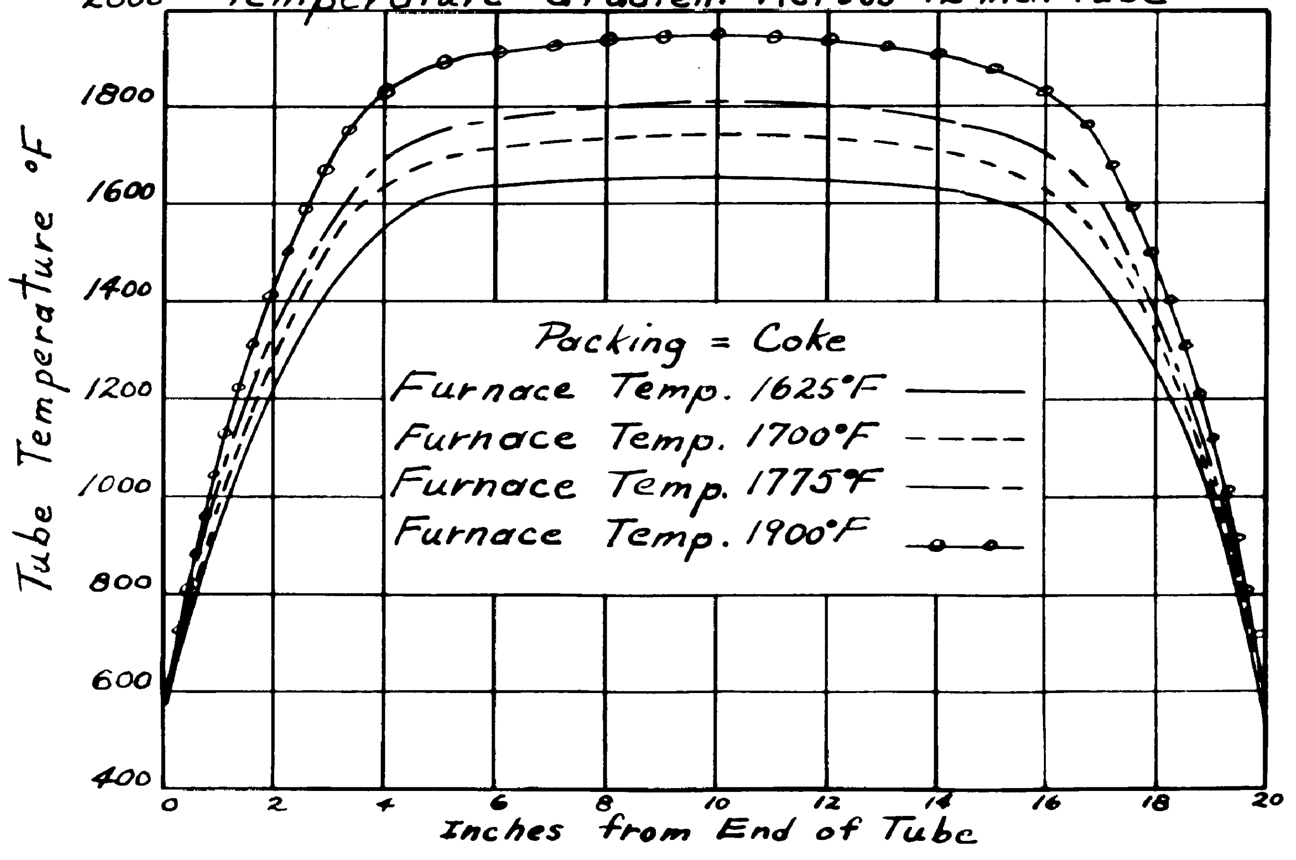


Figure V

Temperature Gradient Across 1/2 inch Tube



CHAPTER X

THE THERMAL DECOMPOSITION OF THIOPHENE IN THE PRESENCE OF NITROGEN

Nitrogen was chosen as a thiophene carrier gas in order to study the thermal decomposition of thiophene in the presence of an inert gas. The nitrogen used in these experiments had been compressed over water and an analysis by the company supplying this gas was given as:

Nitrogen = 99.5 + %
Oxygen = less than 0.45%
Inerts = trace

Two samples of this gas were analysed by means of a Haldane gas analysis apparatus and the nitrogen was found to contain 0.15 percent oxygen. To determine the error introduced by the presence of this oxygen, a few trial experiments were made. It was found that of the total sulfur in the exit gas from the pyrolysis tubes, a maximum of 4 percent was in the form of carbon oxysulfide. The nitrogen was therefore used as received and the carbon oxysulfide formed during the pyrolysis of thiophene was reported simultaneously with the carbon bisulfide. The small amount of water vapor originating in the nitrogen compressor was of course removed by the activated alumina.

Method of Operation

Before beginning an actual experiment several steps were necessary to insure proper operating conditions. As a first step the furnace was brought to the desired temperature and the constant temperature bath containing the thiophene saturator adjusted to 70°F (21.1°C). The nitrogen was then admitted to the system and the gas flow rates so adjusted as to obtain the previously chosen thiophene concentration in the gas and the correct contact time over the pyrolysis tube packing. Until such a time as all settings were made, the gas was directed around the furnace, however, as soon as these adjustments were completed the flow was diverted through the pyrolysis tube within the furnace. Shortly thereafter a total sulfur determination was made on the exit gases. This analysis was repeated at intervals of about 30 minutes until the total sulfur concentration of the exit gas remained constant. At such a time it was assumed that the system was sufficiently purged of air and that the carbon-sulfur complex, previously discussed, was in equilibrium with the sulfur bearing gases. The gas containing the products of pyrolysis of thiophene was then passed through a single cadmium chloride-sodium carbonate scrubber to remove the hydrogen sulfide and mercaptans present. Again at intervals of 30 minutes total sulfur determinations were made until the sulfur content of the exit gas from this scrubber was constant. This process was repeated using two sulfuric acid scrubbers and then one or two alcoholic potash scrubbers, depending on the quantity of carbon bisulfide present.

The thiophene in the gas entering the pyrolysis tube was determined by means of a total sulfur analysis of the gas when by-passed around the furnace.

Discussion of Some of the Equilibria Involved

Due to the complex nature and uncertain mechanisms of the reactions involved in the thermal decomposition of thiophene, it was considered undesirable to make a study of the kinetics of these reactions. For a similar reason, comprehensive thermodynamic predictions were also considered not feasible, however, a few proposed reactions were examined.

Employing an inert gas as a carrier for thiophene it was believed that the following reactions would be the predominant ones:

$$\text{(A)} \quad C_4H_4S = \tfrac{1}{2}CS_2 + 2H_2 + 7/2C$$

$$\text{(B)} \quad C_4H_4S = H_2S + H_2 + 4C$$

A calculation of the equilibrium constants of these two reactions at 1625°F (885°C) and 1900°F (1038°C) (see Appendix) gave the following results.

Reaction	Equilibrium Constant at: 1625°F	1900°F
(A)	1.5×10^8	6.1×10^7
(B)	2.5×10^9	4.0×10^8

From this it is seen that equilibrium considerations favor the formation of hydrogen sulfide over the formation of carbon bisulfide when an inert gas is used as the thiophene carrier. Since the systems are not necessarily in true equilibrium, kinetic as well as equilibrium effects are important, consequently sound predictions based on equilibria alone are not possible. Other reactions also must be considered. Thus, simultaneously with these reactions the formation of carbon bisulfide is probably taking place due to the reaction of hydrogen sulfide with any carbon present. Huff states (50) that the interaction of hydrogen sulfide and carbon is probably partly responsible for the carbon bisulfide formed during gas making operations.

Experimental Results

Using nitrogen as a carrier gas, thiophene was passed over (a) coke, (b) sugar char, and (c) porcelain surfaces at furnace temperatures of 1625, 1775, and 1900°F (885, 968, and 1038°C), and at gas contact times of 11.9, 7.3 and 3.0 seconds over the coke, and 11.9 seconds over both the sugar char and porcelain. The results of these experiments are presented in Table VIII and Figure VI. It is seen that, in general, at temperatures above 1700°F (927°C), and contact times greater than 3 seconds, thiophene was decomposed into carbon bisulfide to a greater degree than into hydrogen sulfide, irrespective of the type of packing present. The percentage of carbon bisulfide in the exit gas from the pyrolysis tube was greatest when sugar char was used as a tube packing, whereas, the percentage of hydrogen sulfide was lowest under these conditions. This fact is believed to have resulted from one or both of the following causes, (a) the greater porosity of the char presented a larger surface area of carbonaceous packing per unit volume as compared to the other packing materials, or (b) the presence of mineral compounds in the coke were beneficial to the formation of hydrogen sulfide.

It is seen from Figure VI that for the three types of packing employed, the relative effectiveness as a surface for the thermal decomposition of thiophene was (a) coke, (b) sugar char, and (c) porcelain. It is also pointed out that an increase in contact time resulted in a greater conversion of thiophene into carbon bisulfide, but had relatively little effect on the amount of hydrogen sulfide formed.

At temperatures of 1625 and 1900°F (885 and 1038°C) the degree of pyrolysis of thiophene varied less with conditions, other than temperature, than at 1775°F (968°C). At 1625°F the pyrolysis of thiophene had just begun, whereas at 1900°F the decomposition of thiophene was almost complete, therefore under these conditions the effects of contact time and type of packing were not as pronounced as at 1775°F.

From Figure VI it is also seen that an increase in temperature resulted in a slight decrease in the percentage of hydrogen sulfide plus mercaptans in the exit gas from the pyrolysis tube. This decrease in hydrogen sulfide plus mercaptans with an increase in temperature may have been caused by a greater degree of decomposition of these compounds at the higher temperatures as well as the reaction of hydrogen sulfide with the carbon present.

Table VIII. The Thermal Decomposition

Furnace Temp. (°F)	Type of Pyrolysis Tube Packing*	Contact Time (Sec.)	Total Sulfur as Thiophene in Gas Entering Pyrolysis Tube (Gr./100 cu.ft.)
1625	A	11.9	249
1775	A	11.9	253
1900	A	11.9	253
1625	A	7.3	260
1775	A	7.3	258
1900	A	7.3	262
1625	A	3.0	260
1775	A	3.0	262
1900	A	3.0	262
1625	B	11.9	238
1775	B	11.9	246
1900	B	11.9	246
1625	C	11.9	259
1775	C	11.9	259
1900	C	11.9	266

* Tube Packing
A - $\frac{1}{4}$ to $\frac{1}{2}$ inch coke
B - $\frac{1}{4}$ to $\frac{1}{2}$ inch sugar char
C - $\frac{1}{2}$ inch porcelain balls

Note: All gas volumes corrected to 60°F, 30 inches of mercury, and saturated with water vapor.

of Thiophene in the Presence of Nitrogen

Total Sulfur in Gas Leaving Pyrolysis Tube (Gr./100 cu.ft.)	Percent of Total Sulfur in Gas Leaving Pyrolysis Tube as:		
	C_4H_4S	H_2S + Mer.	CS_2
237	74.0	16.9	9.3
244	38.5	12.3	49.2
244	7.8	11.9	80.3
254	77.0	16.2	6.9
257	50.2	15.9	34.7
258	13.6	12.4	74.0
258	77.0	14.4	8.4
256	59.2	10.2	30.2
255	18.4	10.6	71.0
232	79.0	9.5	11.8
242	43.8	5.4	50.9
244	7.8	9.4	82.8
252	83.0	11.1	5.9
251	62.5	10.7	26.7
260	12.7	8.5	78.8

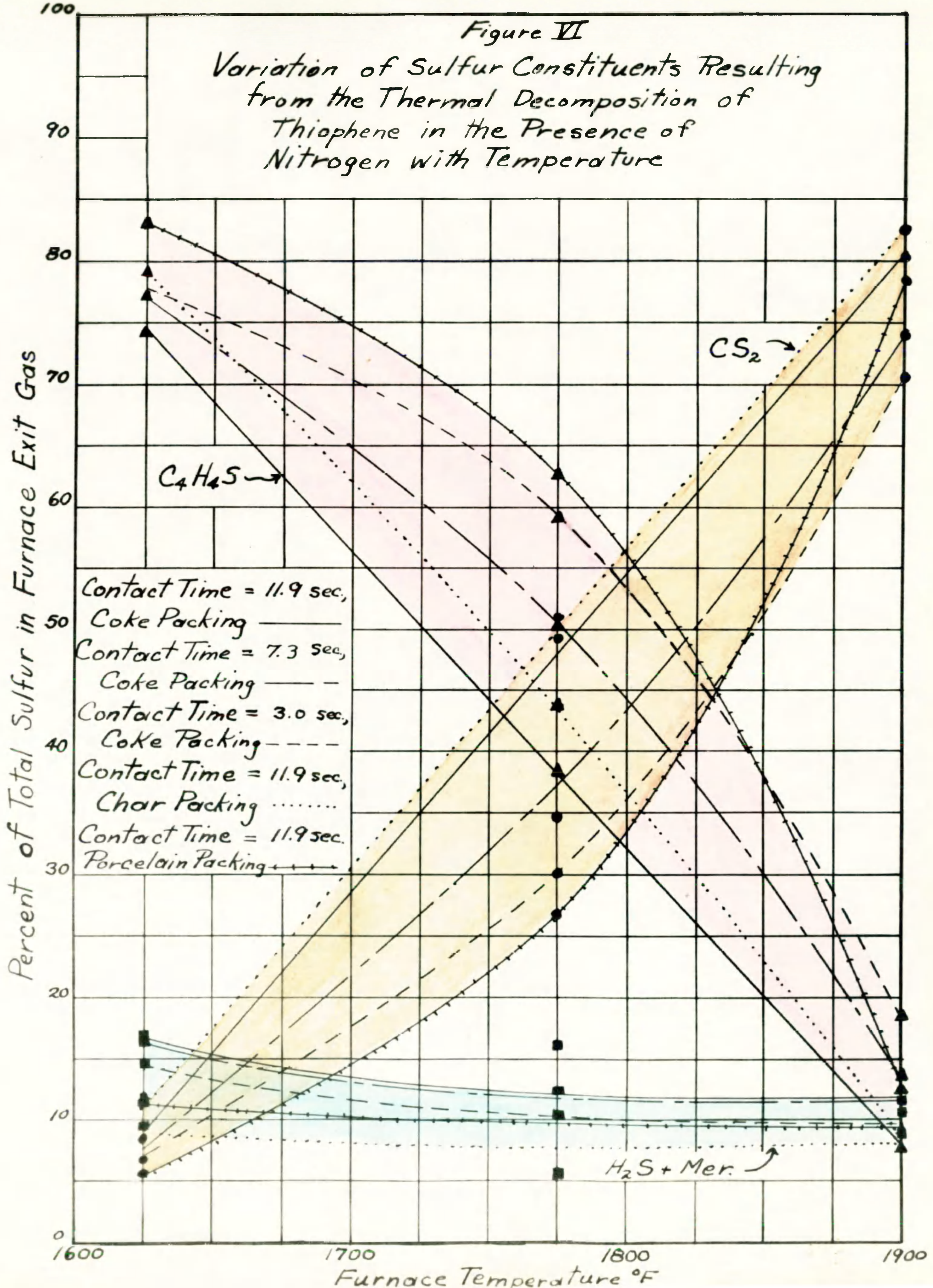


Figure VI

Variation of Sulfur Constituents Resulting from the Thermal Decomposition of Thiophene in the Presence of Nitrogen with Temperature

CHAPTER XI

THE THERMAL DECOMPOSITION OF THIOPHENE IN THE PRESENCE OF HYDROGEN

Before making a study of the pyrolysis of thiophene in the presence of synthesis gas, it was believed that a series of experiments employing hydrogen as a thiophene carrier would be beneficial, since hydrogen is one of the major constituents of synthesis gas (see Chapter II).

An analysis of the hydrogen used in this series of experiments was given by the company supplying this gas as follows:

Hydrogen = greater than 99.5%
Nitrogen = trace
May contain a trace of hydrocarbons
and water vapor.

An analysis of the hydrogen was also made with the aid of a Haldane gas analysis apparatus and the oxygen content was found to be less than 0.1 percent. It was believed that if any of the above mentioned hydrocarbons excaped the activated alumina drying bottle they would soon be decomposed at the high temperatures employed during the studies here.

Method of Operation

The use of hydrogen as a thiophene carrier necessitated changing of the orifices on the flow indicators throughout the system in order to retain the accuracy previously realized when nitrogen was the carrier gas. The new orifices were made by drawing several one mm. tubes down to a very small capillary at one end. Experimental determinations were made to obtain the correct gas rates after these new orifices had been installed.

Qualitative runs showed a large percentage of hydrogen sulfide and no carbon bisulfide in the effluent gas from the pyrolysis tubes when hydrogen was employed as a thiophene carrier. It therefore seemed advisable to make a change in the absorption train used to remove these constituents from the gas. Instead of the single cadmium chloride-sodium carbonate scrubber previously used in the nitrogen experiments, two were installed. For the removal of thiophene, two sulfuric acid scrubbers, followed by a sodium carbonate scrubber, were employed. Spot tests were made for the presence of carbon bisulfide with the use of an alcoholic potash scrubber following the scrubbing train of cadmium chloride and sulfuric acid.

A few trial experiments showed that at 1900°F (1038°C) thiophene was completely decomposed, while at 1775°F (968°C) it was approximately 35% decomposed. It was therefore believed desirable to choose a fourth temperature of operation between 1625 and 1775°F (885 and 968°C) to obtain a more complete picture of temperature effects on the pyrolysis of thiophene in the presence of hydrogen. For this purpose a temperature of 1700°F (927°C) was chosen.

Discussion of Some of the Equilibria Involved

The reactions believed to be of primary importance in the thermal decomposition of thiophene in the presence of an inert carrier gas have been discussed on page 82. It is quite possible that as a first step both of these reactions took place in the presence of hydrogen, but it was also necessary to consider the conversion of any carbon bisulfide formed to hydrogen sulfide by the interaction of the carbon bisulfide and hydrogen, i.e.

$$\text{(C)} \quad CS_2 + 2H_2 = 2H_2S + C$$

The equilibrium constants for this reaction were calculated at temperatures of 1625 and 1900°F (885 and 1038°C). The results thus obtained are presented below.

Temperature (°F)	Equilibrium Constant
1625	150
1900	19

Insofar as equilibrium considerations are concerned, it is probable that the major part of the carbon bisulfide would be converted to hydrogen sulfide.

Experimental Results

Hydrogen gas was used as a carrier to introduce thiophene over surfaces of coke, sugar char, and porcelain at furnace temperatures of 1625, 1700, 1775 and 1900°F (885, 927, 968 and 1038°C). At each of these temperatures studies were made of the decomposition of thiophene at contact times of 11.9, 7.3 and 3.0 seconds when coke was used as a pyrolysis tube packing and at a contact time of 11.9 seconds when sugar char and porcelain were used as tube packings. The results of these experiments are presented in Table IX and Figure VII.

In all cases it was found that much less time was required for the attainment of equilibrium conditions in the pyrolysis tube when using hydrogen as a thiophene carrier than when using nitrogen as a carrier gas. This may perhaps be due, in part at least to the greater diffusibility of hydrogen as compared to nitrogen across the surface film barrier.

Upon examination of Figure VII it is seen that in the presence of hydrogen, thiophene was completely decomposed at 1825°F (996°C), regardless of the contact times or type of surface present. It is also to be noted that the resulting sulfur compounds arising from the decomposition of thiophene consisted only of hydrogen sulfide plus mercaptans. Spot tests were made for carbon bisulfide under various conditions, but in no case was it possible to detect this compound.

Apparently there was present in the coke some material which acted catalytically toward the formation of hydrogen sulfide at the lower temperatures, for the degree of decom-

Table IX. The Thermal Decomposition

Furnace Temp. (°F)	Type of Pyrolysis Tube Packing*	Contact Time (Sec.)	Total Sulfur as Thiophene in Gas Entering Pyrolysis Tube (Gr./100 cu.ft.)
1625	A	11.9	240
1700	A	11.9	240
1775	A	11.9	232
1900	A	11.9	232
1625	A	7.3	237
1700	A	7.3	237
1775	A	7.3	236
1900	A	7.3	246
1625	A	3.0	235
1700	A	3.0	234
1775	A	3.0	234
1900	A	3.0	234
1625	B	11.9	234
1700	B	11.9	231
1775	B	11.9	228
1900	B	11.9	236
1625	C	11.9	233
1700	C	11.9	232
1775	C	11.9	232
1900	C	11.9	234

* Tube Packing
A - 1/4 to 1/2 inch coke
B - 1/4 to 1/2 inch sugar char
C - 1/2 inch porcelain balls

Note: All gas volumes corrected to 60°F, 30 inches of mercury, and saturated with water vapor.

of Thiophene in the Presence of Hydrogen

Total Sulfur in Gas Leaving Pyrolysis Tube (Gr./100 cu.ft.)	Percent of Total Sulfur in Gas Leaving Pyrolysis Tube as:		
	C_4H_4S	H_2S + Mer.	CS_2
240	59.0	41.0	Negl.
239	46.0	54.0	"
229	21.9	78.5	"
228	0.0	100.0	"
237	64.5	35.5	"
237	51.0	49.0	"
232	26.4	73.8	"
242	0.0	100.0	"
235	66.8	33.2	"
233	54.0	45.5	"
233	25.3	74.7	"
234	0.0	100.0	"
232	80.0	20.0	"
231	64.0	35.9	"
227	28.6	71.1	"
236	0.0	100.0	"
233	85.8	14.2	"
231	70.2	29.8	"
232	30.2	69.8	"
232	0.0	100.0	"

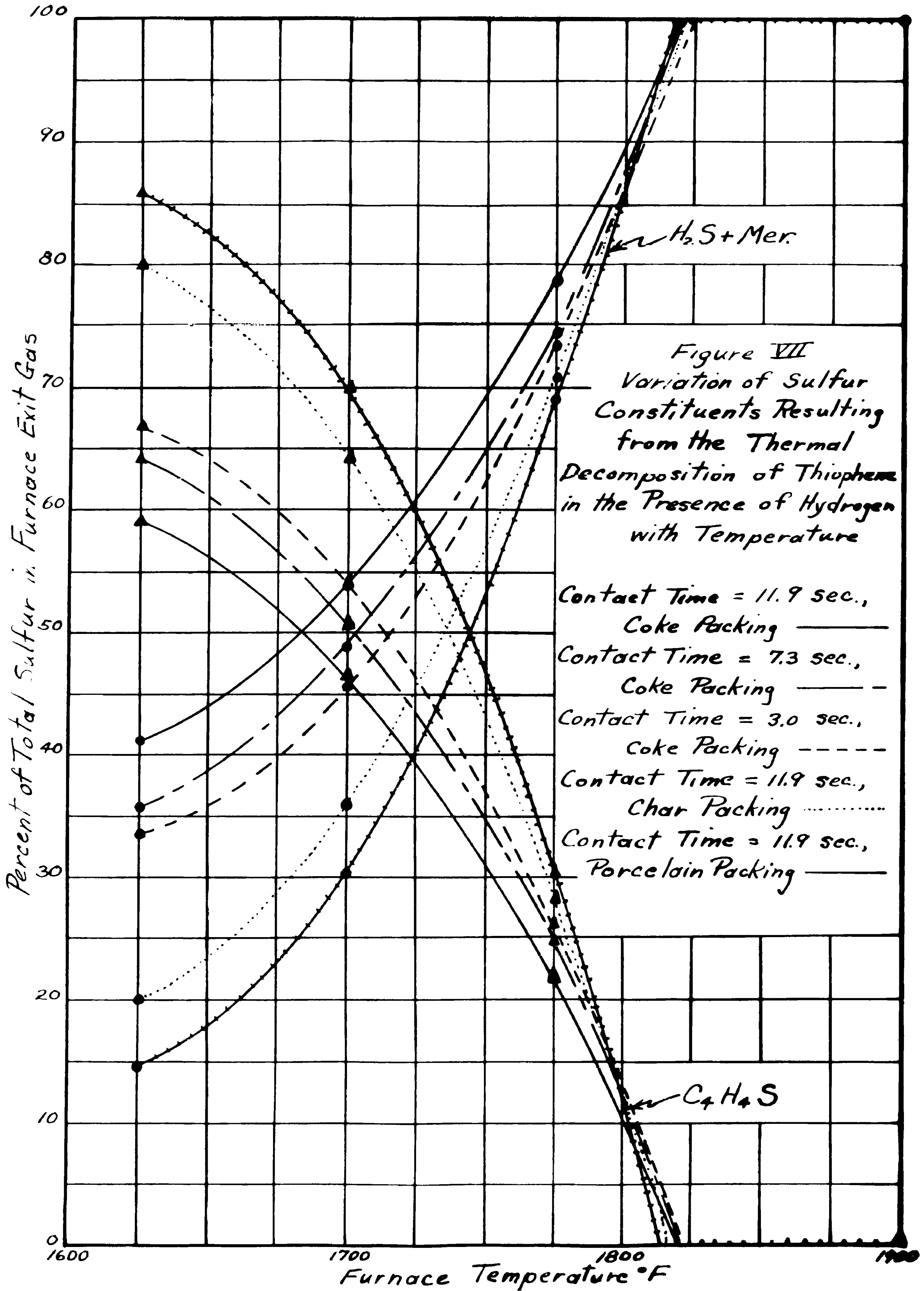


Figure VII
Variation of Sulfur Constituents Resulting from the Thermal Decomposition of Thiophene in the Presence of Hydrogen with Temperature

position of thiophene was greater at the lower temperatures when using coke at a contact time of 3.0 seconds than when using char or porcelain at a contact time of 11.9 seconds. At the higher temperatures the catalytic material in the coke showed little advantage. This was probably again due to the fact that the reaction was so nearly complete that the difference could not be great in any event. It is also seen that when using coke as a tube packing the effects of contact time were not so pronounced when hydrogen was used as a carrier gas as compared to nitrogen.

Indications of Catalytic Effects in the Thermal Decomposition of Thiophene in Hydrogen Containing Gases

Since, as indicated above, the pyrolysis of thiophene in the presence of hydrogen was found to be more complete at a furnace temperature of 1625°F (885°C) when coke was used as the tube packing compared with sugar char, the suggestion arose that the presence of some material in the coke catalyzed the formation of hydrogen sulfide. An important difference between the coke and sugar char used as tube packings is the higher ash content of the coke. The coke had an ash content of 15 percent whereas the sugar char contained 0.64 percent ash, both on a dry basis. Since iron oxide has been used as a catalyst with soda to remove organic sulfur from synthesis gas (20), it appeared that there might be a material such as iron present in the coke that was effective in catalyzing at the lower temperatures, the decomposition of thiophene in the presence of hydrogen. It seemed desirable, therefore, to obtain information upon the pyrolysis of thiophene in the presence of iron supported on an inert material while using a carrier gas of hydrogen, and also to further substantiate the catalytic effect of the coke ash by using this ash as a pyrolysis tube packing while employing hydrogen as a thiophene carrier gas.

The Preparation of Iron and Coke Ash Catalysts

In order to study the pyrolysis of thiophene in the presence of small quantities of iron, it was necessary to choose some inert material as a supporter. For this purpose porcelain balls, approximately $\frac{1}{2}$ inch in diameter, were used. These were soaked in aqua regia overnight and then thoroughly washed. The balls were heated slightly and quickly immersed in a solution of approximately 10 percent iron chloride. This was repeated except that a 10 percent solution of ammonium oxalate was used. The balls were then placed in a combustion tube and heated to 2000°F (1093°C), during which time dry hydrogen was passed through the tube. This resulted in a tightly adherent iron coating on the porcelain.

In order to prepare coke ash for a pyrolysis tube packing the following procedure was employed. Sufficient coke was burned in a muffle furnace to obtain a quantity of ash which would fill the pyrolysis tube. No clinkering occurred; the ash was light and fluffy. The ash was mixed with a sugar solution and the mixture filtered to remove the excess solution. From this ash paste, small pellets were made and dried at approximately 120°C. These were then placed in a combustion tube and heated to 2000°F (1093°C), during which time the sugar was burned off by passing air through the tube. Under these conditions the ash sintered sufficiently to allow subsequent handling.

Experimental Results of the Thermal Decomposition of Thiophene in the Presence of Catalytic Materials

At furnace temperatures of 1625, 1700, 1775 and 1900°F (885, 927, 968 and 1038°C) thiophene, carried by hydrogen, was passed over iron supported on porcelain at a contact time of 11.9 seconds. The results of these experiments are presented in Table X. It is seen that iron is effective in catalyzing the decomposition of thiophene into hydrogen sulfide at the lower temperatures. This effect becomes less pronounced at the higher temperatures. It is quite possible, therefore, that iron in the coke is at least partially responsible for the greater degree of pyrolysis at the lower temperatures when coke is used as a tube packing as compared with sugar char.

Employing a furnace temperature of 1625°F (885°C) and a carrier gas of hydrogen, thiophene was passed over coke ash at a contact time of 11.9 seconds. The results of this experiment are presented in Table XI. The coke ash was not only effective in the complete conversion of the thiophene into hydrogen sulfide, but also absorbed a large portion of the sulfur for an appreciable length of time. After 7 hours the ash had not yet become completely saturated with sulfur. It was noted that although absorption was not complete, the rate of sulfur removal decreased after approximately 3 hours of operation.

Table X

The Pyrolysis of Thiophene in the Presence of Iron Supported on Porcelain

Conditions:

Carrier Gas = Hydrogen

Contact Time = 11.9 Seconds

Furnace Temp. (°F)	Type of Pyrolysis Tube Packing*		Total Sulfur as Thiophene in Gas Entering Pyrolysis Tube (Gr./100cu.ft.)	Total Sulfur in Gas Leaving Pyrolysis Tube (Gr./100cu.ft.)	Percent of Total Sulfur in Exit Gas as:	
					C_4H_4S	H_2S
1625	C	No Iron	233	233	85.8	14.2
1700	C		232	231	70.2	29.8
1775	C		232	232	30.2	69.8
1900	C		234	232	0.0	100.0
1625	D	Iron	224	224	67.9	32.1
1700	D		226	222	51.8	48.2
1775	D		229	229	24.4	75.6
1900	D		234	234	0.0	100.0

* Tube Packing

C - ½ inch porcelain balls

D - Iron supported on ½ inch porcelain balls

Table XI

The Pyrolysis of Thiophene in the Presence of Coke Ash

Conditions:

Carrier Gas = Hydrogen

Contact Time = 11.9 Seconds

Total Sulfur as Thiophene in Gas Entering

Pyrolysis Tube = 214 gr./100 cu.ft.

Hours of Operation	Sulfur Lost From Gas to Packing (Gr./100 cu.ft.)	Percent of Entering Sulfur in Exit Gas
0.75	209	2.2
1.25	204	4.5
2.00	201	6.0
3.00	192	10.5
4.00	159	25.5
5.00	78	62.5
6.00	46	75.6
7.00	44	78.8

Note: Spot tests showed that all of the sulfur in the exit gas from the pyrolysis tube was in the form of H_2S during the entire experiment.

Ratio of the weight of sulfur removed from the gas to the total weight of ash present:

(a) After 3 hours of operation = 0.0064
(b) After 7 hours of operation = 0.0105

CHAPTER XII

THE THERMAL DECOMPOSITION OF THIOPHENE IN THE PRESENCE OF CARBON MONOXIDE

The composition of synthesis gas has already been shown to consist of hydrogen and carbon monoxide (Chapter II). As in the case of a hydrogen carrier gas it was believed desirable to study the thermal decomposition of thiophene in the presence of carbon monoxide in the hope that this would aid in the explanation of the results obtained when thiophene is present in synthesis gas.

The carbon monoxide, used in the experiments here, was analysed by the company supplying this gas, who gave the following results:

Carbon Monoxide	96.8%
Carbon Dioxide	0.36%
Hydrogen	0.97%
Nitrogen	1.0%
Sat. Hydrocarbons	0.8%

Approximately 1.19 mg./liter of iron
and 0.3202 mg./liter of sulfur.

The small percentage of nitrogen in the gas was considered harmless. The carbon dioxide in the presence of the carbonaceous packings used in the pyrolysis tubes, was converted at least partially to the monoxide. This fact was probably true also in the case of porcelain packings for a carbon deposit was formed quite rapidly on the porcelain as a result of the decomposition of thiophene. It was believed that part of the saturated hydrocarbons would be removed from the gas by the activated alumina bottle and those hydrocarbons still remaining would be decomposed at the high temperatures employed within the pyrolysis tubes. The presence of small amounts of hydrogen in the carbon monoxide was considered permissible since the ultimate objective of the studies here was to determine the feasibility of pyrolysis as a possible means of removing thiophene from synthesis gas.

The presence of iron, probably as carbonyl, in the carbon monoxide was very undesirable. It has been pointed out that the coke used in experiments in which nitrogen and hydrogen were used as a thiophene carrier contained some material which acted catalytically toward the formation of hydrogen sulfide. It was quite possible that any iron in the carbon monoxide might also act as a catalytic material, therefore special treatment for the removal of this impurity was deemed necessary. This is further discussed below. The presence of sulfur in the carbon monoxide was also considered undesirable, however this compound was partially removed simultaneously with the iron.

Method of Operation

The removal of iron and sulfur from carbon monoxide was accomplished by passing the impure gas over a heated copper surface prior to the meter used for the measurement of gas volumes. A pyrex tube, approximately ¼ inch I.D. and 15 inches long, was alternately packed with copper gauze and copper shot. This was contained in an electrically heated tube furnace which was maintained at a temperature of 350°C (662°F) or better. The purifier was reactivated after approximately 8 hours of operation by treatment with concentrated hydrochloric acid, after which the copper was washed with distilled water. Blank determinations on the carbon monoxide showed that some sulfur still existed after the gas had been passed over the heated copper. The sulfur introduced with the carbon monoxide was less than 2 percent of the total sulfur entering the pyrolysis tubes, therefore it was not believed necessary to purify the gas further.

The same orifices in the flow indicators were used with carbon monoxide as had been used with nitrogen, since these gases have the same molecular weight. Having made a few qualitative experiments it was decided that a scrubbing train consisting of (a) one cadmium chloride-sodium carbonate scrubber, (b) two concentrated sulfuric acid scrubbers, and (c) one or two alcoholic potash scrubbers, be used to remove the various sulfur constituents from the gaseous mixture arising from the thermal decomposition of thiophene. The use of carbon monoxide as a thiophene carrier necessitated the separate determinations of carbon bisulfide and carbon oxysulfide.

Discussion of Some of the Equilibria Involved

The reactions possibly occurring with the decomposition of thiophene in the presence of nitrogen and hydrogen have been discussed previously. It was believed that, with the application of carbon monoxide as a thiophene carrier gas, a new set of reactions would predominate. These reactions were expressed as:

(D) $C_4H_4S + CO = COS + 4C + 2H_2$

(E) $2COS = CO_2 + CS_2$

(F) $H_2 + \frac{1}{2}S_2 = H_2S$

The equilibrium constants for these reactions at 1625 and 1900°F (885 and 1038°C) were found to be:

Reaction	Equilibrium Constant at 1625°F	1900°F
(D)	3.3×10^8	6.6×10^7
(E)	0.0370	0.0403
(F)	30.9	14.5

From this it was concluded that thiophene, in the presence of carbon monoxide, would decompose to carbon bisulfide, carbon oxysulfide, carbon and hydrogen. The carbon oxysulfide, however, would also tend to decompose partially to the bisulfide.

Experimental Results

Using carbon monoxide as a carrier gas, thiophene was introduced over a coke surface at furnace temperatures of 1625, 1775 and 1900°F (885, 968 and 1038°C), and at contact times of 11.9, 7.3 and 3.0 seconds. Thiophene carried by carbon monoxide was also passed over sugar char and porcelain surfaces, maintained at the same temperatures as above, at a contact time of 11.9 seconds. The results of these experiments are presented in Table XII and Figure VIII.

From Figure VIII it is seen that the thiophene decomposition - furnace temperature curves are very similar to those obtained using nitrogen as a carrier gas. A more complete decomposition of thiophene, however, appears to have been obtained by using nitrogen as a thiophene carrier than by using carbon monoxide. A rather strange phenomenon occurred with the use of carbon monoxide which might help to explain this difference in thiophene decomposition when using nitrogen and carbon monoxide gases as carriers. The carbonaceous materials, both coke and sugar char, used as pyrolysis tube packings became heavily coated with a gray-black mossy material when carbon monoxide was used as a thiophene carrier. Apparently this was some form of carbon, or carbon-oxygen-sulfur compound, for treatment with concentrated hydrochloric acid or aqua regia had no apparent effect. Due to insufficient time this coating was not analysed further. This coating over the packing probably reduced the effectiveness of the surfaces. With the use of porcelain as a tube packing only a tight adherent coating occurred.

It was found that approximately 2 hours were required to attain equilibrium between the tube packings and the sulfur bearing gases. This was comparable to conditions present when using nitrogen as a thiophene carrier and tended to indicate that the mossy compound formed on the carbonaceous packings contained sulfur.

Concurrently with the formation of carbon bisulfide and carbon oxysulfide there resulted small quantities of hydrogen sulfide and mercaptans. It is to be noted that the quantities of hydrogen sulfide and mercaptans increased with an increase in temperature. This was probably due to the presence of small amounts of hydrogen in the carbon monoxide used as a thiophene carrier as well as hydrogen resulting from the decomposition of thiophene.

Table XII. The Thermal Decomposition of

Furnace Temp. (°F)	Type of Pyrolysis Tube Packing*	Contact Time (Sec.)	Total Sulfur as Thiophene in Gas Entering Pyrolysis Tube (Gr./100 cu.ft.)
1625	A	11.9	248
1775	A	11.9	248
1900	A	11.9	238
1625	A	7.3	241
1775	A	7.3	257
1900	A	7.3	257
1625	A	3.0	181
1775	A	3.0	249
1900	A	3.0	247
1625	B	11.9	257
1775	B	11.9	248
1900	B	11.9	256
1625	C	11.9	258
1775	C	11.9	263
1900	C	11.9	260

* Tube Packings
A - $\frac{1}{4}$ to $\frac{1}{2}$ inch coke
B - $\frac{1}{4}$ to $\frac{1}{2}$ inch sugar char
C - $\frac{1}{2}$ inch porcelain balls

Note: All gas volumes corrected to 60°F, 30 inches of mercury, and saturated with water vapor.

Thiophene in the Presence of Carbon Monoxide

Total Sulfur in Gas Leaving Pyrolysis Tube (Gr./100 cu.ft.)	Percent of Total Sulfur in Gas Leaving Pyrolysis Tube as:				
	C_4H_4S	H_2S + Mer.	H_2S	CS_2	COS
237	84.9	3.4	---	8.4	3.4**
235	49.4	8.9	2.5	17.8	23.8
229	5.7	21.4	7.9	37.6	35.4
229	85.5	1.3	---	3.3	5.3**
242	54.5	7.0	4.1	22.4	16.1
242	8.7	19.0	9.1	41.3	31.0
179	95.6	0.0	---	2.2	2.2**
243	72.7	5.0	1.2	13.9	8.4
237	27.1	10.0	6.7	41.3	21.5
252	89.1	4.3	---	5.5	1.2**
246	59.9	6.9	6.5	23.6	9.8
256	14.1	12.5	9.8	63.3	10.2
256	88.4	8.6	---	-3.1-	
258	62.0	8.1	3.1	21.7	8.1
258	12.8	16.7	8.5	62.8	7.7

** These values are questionable due to the small quantities of sulfur involved.

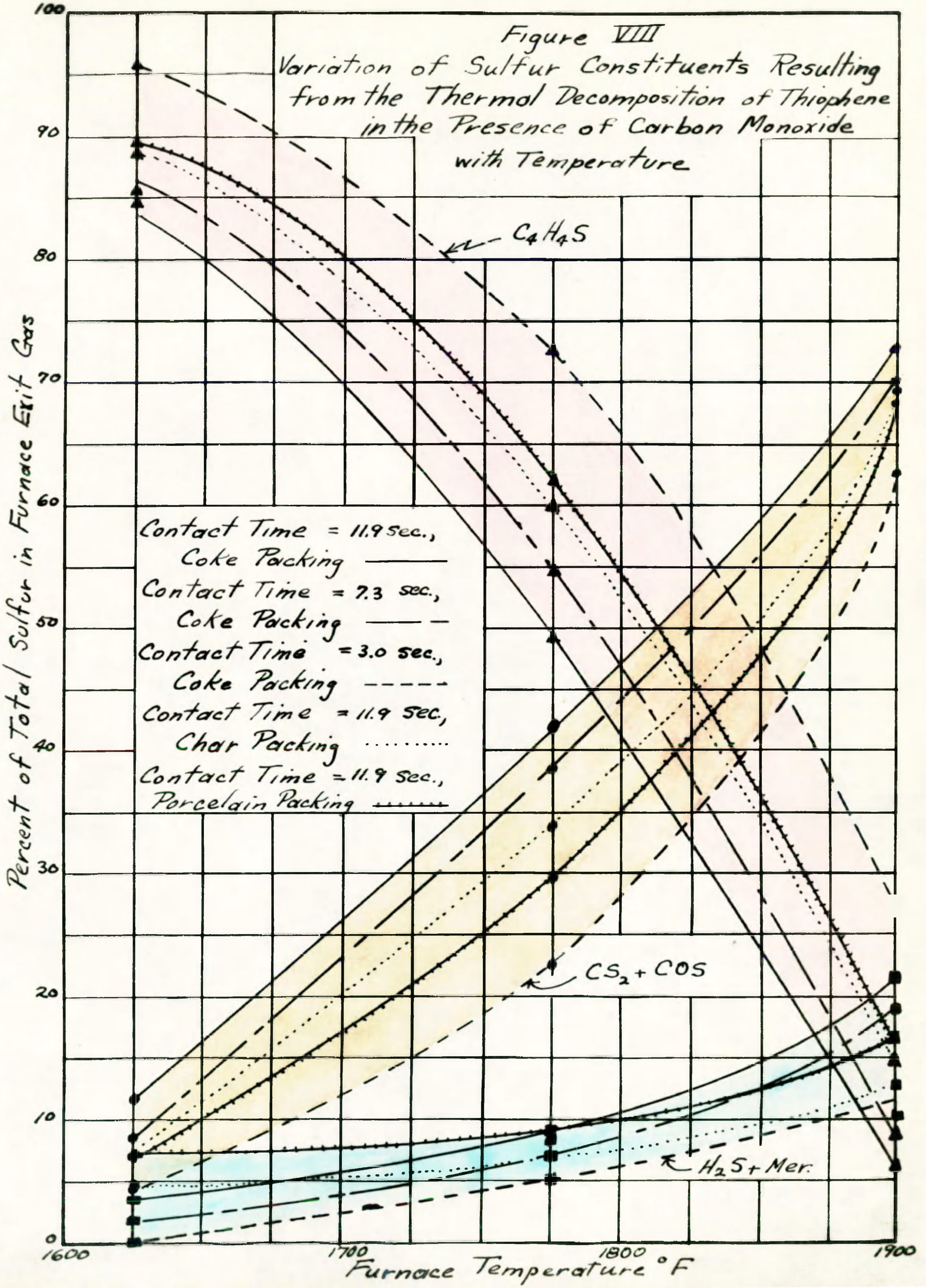


Figure VIII
Variation of Sulfur Constituents Resulting from the Thermal Decomposition of Thiophene in the Presence of Carbon Monoxide with Temperature

CHAPTER XIII

THE THERMAL DECOMPOSITION OF THIOPHENE IN THE PRESENCE OF SYNTHESIS GAS

The results obtained from experiments using hydrogen and carbon monoxide as thiophene carrier gases indicated that at a furnace temperature of approximately 1900°F (1038°C), the pyrolysis of thiophene would offer a means of removing this compound from synthesis gas. Studies were made, therefore, using a synthesis gas as a thiophene carrier, of the pyrolysis of thiophene under the same conditions as were employed when hydrogen and carbon monoxide were used as thiophene carriers.

The hydrogen-carbon monoxide ratio of manufactured synthesis gas may vary from 1:1 to 2:1 (15). From previous experiments the thermal decomposition of thiophene was shown to be more complete in the presence of hydrogen than in the presence of carbon monoxide. From this it appeared that the pyrolysis of thiophene would be less complete if a 1:1 mixture of hydrogen-carbon monoxide, as compared to a 2:1 mixture, were employed as a thiophene carrier. It was decided, therefore, that studies of the thermal decomposition of thiophene in the presence of synthesis gas with a 1:1 hydrogen to carbon monoxide ratio would yield worth-while information. This synthesis gas was made from the same gases used in experiments in which hydrogen and carbon monoxide were employed individually as thiophene carriers.

Method of Operation

Rather than trying to control the flow of two individual gases, i.e. hydrogen and carbon monoxide, and still keep a constant mixture of synthesis gas, it was decided to mix hydrogen and carbon monoxide in a single cylinder. An old carbon dioxide cylinder was filled to approximately 550 p.s.i. pressure with carbon monoxide. Before adding hydrogen the gas was tested for oxygen and found to contain less than 0.7 percent. Hydrogen was next added to the cylinder until the total pressure was approximately 1100 p.s.i. It was assumed that approximately a 1:1 hydrogen-carbon monoxide mixture was present. Upon analysis of this prepared synthesis gas the following results were obtained:

Hydrogen	53.7%
Carbon Monoxide	44.5%
Carbon Dioxide	1.4%
Oxygen	0.3%

This mixture was considered satisfactory and was employed as a carrier gas.

It was possible then to use the same system of gas flow control as had been previously employed. New orifices on the flow indicators, however, were necessary.

The removal of iron carbonyl, sulfur and oxygen from the synthesis gas was effected by the use of copper maintained at 350°C (662°F) or higher, as discussed in Chapter XII.

A few qualitative experiments indicated the presence of large quantities of hydrogen sulfide in the gas leaving the pyrolysis tube. This necessitated the rearrangement of the scrubbing train for removing specific sulfur compounds from the gases leaving the pyrolysis tube. A scrubbing train consisting of (a) two cadmium chloride-sodium carbonate bottles, (b) two concentrated sulfuric acid bottles, followed by a scrubber of normal sodium carbonate, and (c) one alcoholic potash bottle was employed. The determination of hydrogen sulfide alone was made by means of a modified Shaw analysis (see page 58).

On the basis of a few trial experiments it seemed advisable to study the pyrolysis of thiophene at a furnace temperature of 1700°F (927°C) in addition to temperatures of 1625, 1775 and 1900°F (885, 968 and 1038°C). Under each set of conditions, therefore, the four temperatures above were employed.

Discussion of Some of the Equilibria Involved

In addition to the reactions previously mentioned as possibly occurring with the thermal decomposition of thiophene in the presence of specific gases, it was believed that with the application of synthesis gas as a thiophene carrier, one other reaction should be considered, namely:

$$\text{(G)} \quad COS + H_2 = H_2S + CO$$

The calculated equilibrium constants were found to be:

Temp. (°F)	Equilibrium Constant
1625	11.2
1900	30.2

It is seen that at the high temperatures employed here, hydrogen sulfide would probably be formed as a result of this reaction.

Simultaneously with this reaction the formation of hydrogen sulfide should have resulted from reactions (E) and (C) (see pages 105 and 91):

$$\text{(E)} \quad 2COS = CO_2 + CS_2$$

$$\text{(C)} \quad CS_2 + 2H_2 = 2H_2S + C$$

The greater predominance of reaction (C) should favor largely the formation of hydrogen sulfide instead of carbon bisulfide or carbon oxysulfide.

Experimental Results

A synthesis gas composed of 53.7 percent hydrogen and 44.5 percent carbon monoxide was used to carry thiophene over (a) coke, (b) sugar char, and (c) porcelain while employing furnace temperatures of 1625, 1700, 1775 and 1900°F (885, 927, 968 and 1038°C). At each of these temperatures thiophene-coke contact times of 11.9, 7.3, and 3.0 seconds were employed, while with the use of sugar char or porcelain as pyrolysis tube packings the contact time was 11.9 seconds.

The results of these experiments are presented in Table XIII and Figure IX.

Very little time was required to establish equilibrium conditions within the pyrolysis tube when synthesis gas was employed as a thiophene carrier. It was noted that the mossy coating obtained on the coke and sugar char when carbon monoxide was used as a carrier gas (see page 106) did not form when synthesis gas was used as a thiophene carrier.

Analysis of the gas leaving the pyrolysis tubes showed negligible quantities of carbon bisulfide or oxysulfide. This undoubtedly was due to the greater affinity under the experimental conditions of hydrogen for the sulfur present.

From Figures VII and IX it is seen that at the lower temperatures the thermal decomposition of thiophene in the presence of synthesis gas is comparable to results obtained using a hydrogen carrier gas. At the higher temperatures the use of hydrogen as a thiophene carrier gave better results than did synthesis gas.

Using synthesis gas as a carrier and coke as a pyrolysis tube packing it was found that contact time was an important factor, particularly at the lower temperatures. As the temperature was increased the pyrolysis of thiophene became more complete and contact time had less effect.

As was the case with a hydrogen carrier, the presence of some mineral compound in the coke seemed effective for the conversion of thiophene to hydrogen sulfide. From Figure IX it is seen that the decomposition of thiophene, in the presence of synthesis gas, is much less when sugar char is used as a pyrolysis tube packing as compared to coke packing at the corresponding contact time.

Table XIII. The Thermal Decomposition of

Furnace Temp. (°F)	Type of Pyrolysis Tube Packing*	Contact Time (Sec.)	Total Sulfur as Thiophene in Gas Entering Pyrolysis Tube (Gr./100 cu.ft.)
1625	A	11.9	262
1700	A	11.9	247
1775	A	11.9	238
1900	A	11.9	230
1625	A	7.3	260
1700	A	7.3	260
1775	A	7.3	246
1900	A	7.3	243
1625	A	3.0	260
1700	A	3.0	261
1775	A	3.0	261
1900	A	3.0	261
1625	B	11.9	250
1700	B	11.9	255
1775	B	11.9	255
1900	B	11.9	255
1625	C	11.9	255
1700	C	11.9	257
1775	C	11.9	256
1900	C	11.9	255

* Tube Packing
A - $\frac{1}{4}$ to $\frac{1}{2}$ inch coke
B - $\frac{1}{4}$ to $\frac{1}{2}$ inch char
C - $\frac{1}{2}$ inch porcelain balls

Note: All gas volumes corrected to 60°F, 30 inches of mercury, and saturated with water vapor.

Thiophene in the Presence of Synthesis Gas

Total Sulfur in Gas Leaving Pyrolysis Tube (Gr./100 cu.ft.)	Percent of Total Sulfur in Gas Leaving Pyrolysis Tube as:			
	C_4H_4S	H_2S + Mer.	H_2S	CS_2
260	55.6	44.3	---	Negl.
248	41.5	58.5	37.5	"
233	25.2	74.8	---	"
226	3.5	96.5	79.2	"
260	64.3	35.4	29.6	"
260	50.0	50.0	35.0	"
245	30.0	69.8	63.7	"
246	4.9	95.1	80.5	"
255	81.2	18.8	10.5	"
259	73.0	27.8	13.9	"
257	57.6	42.4	27.6	"
257	9.8	90.2	73.0	"
247	78.9	21.1	8.1	"
253	71.3	28.8	14.9	"
254	46.5	53.5	46.8	"
253	5.1	94.9	85.0	"
254	77.1	22.8	9.8	"
255	72.5	27.4	11.4	"
256	48.8	51.2	46.1	"
256	5.5	95.3	83.1	"

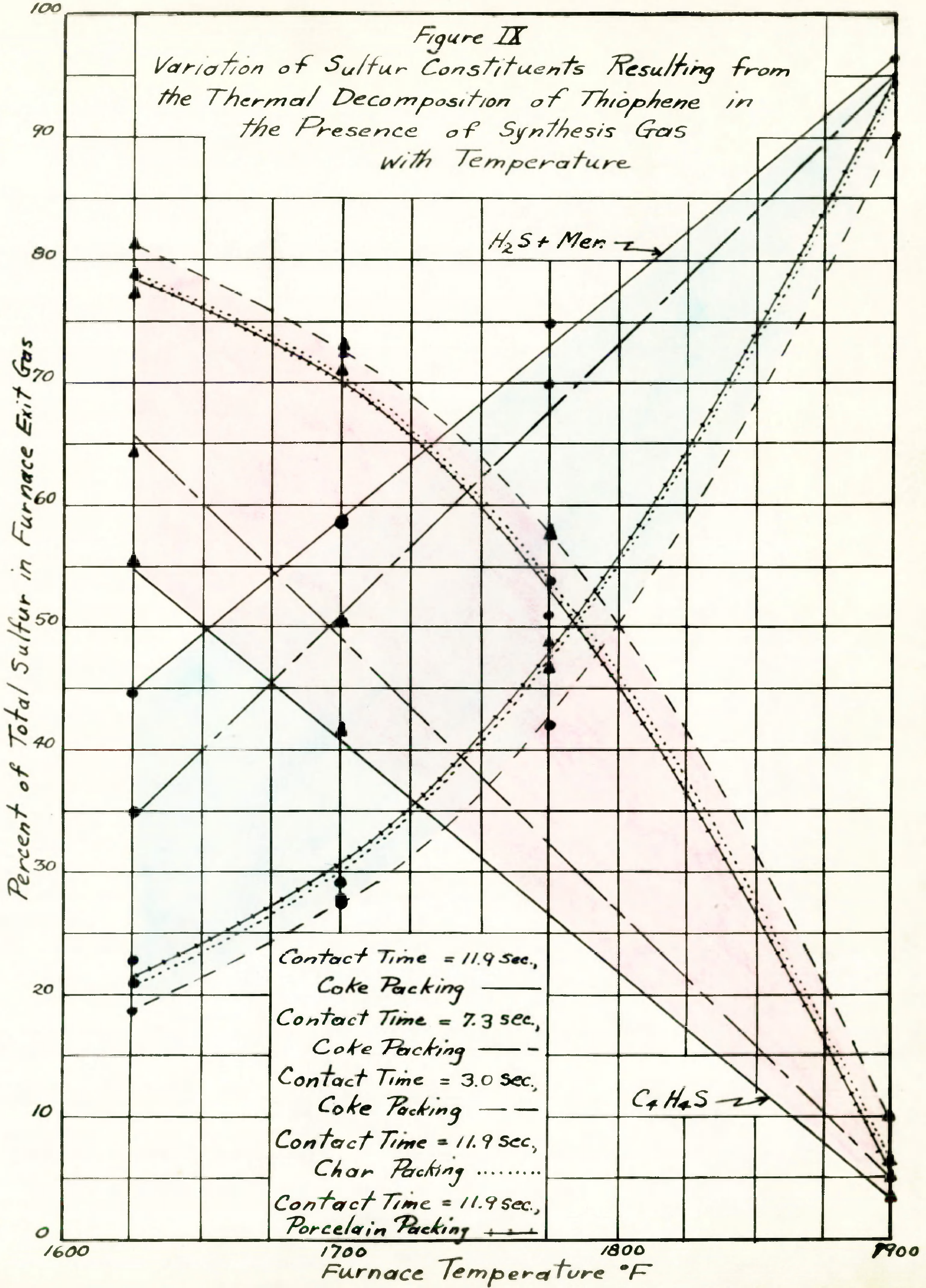


Figure IX
Variation of Sulfur Constituents Resulting from the Thermal Decomposition of Thiophene in the Presence of Synthesis Gas with Temperature

SUMMARY AND CONCLUSIONS

It has been shown that thiophene is decomposed approximately 90 to 95 percent at a furnace temperature of 1900°F (1038°C), with a contact time of 11.9 seconds over coke, sugar char, and porcelain when using nitrogen, or carbon monoxide, or synthesis gas as thiophene carriers. With the use of nitrogen as a carrier gas, the thiophene sulfur was transformed chiefly into carbon bisulfide and small quantities of hydrogen sulfide and mercaptans. With carbon monoxide as the carrier gas, thiophene yielded carbon bisulfide and carbon oxysulfide with small quantities of hydrogen sulfide and mercaptans. In the presence of a synthesis type gas containing 53.7 percent hydrogen and 44.5 percent carbon monoxide, the thiophene sulfur was transformed into hydrogen sulfide and mercaptans with negligible quantities of carbon bisulfide and oxysulfide. At a furnace temperature of 1900°F (1038°C), and with a contact time of 11.9 seconds, thiophene sulfur was completely transformed into hydrogen sulfide over coke, sugar char, and porcelain when hydrogen was used as a carrier gas.

It was found that in all cases at the lower temperatures thiophene decomposition was most complete over a coke packing. It appeared, therefore, that some mineral constituent in the coke was beneficial in the formation of hydrogen sulfide, particularly when hydrogen and synthesis gas were used as thiophene carriers. This suggests the possibilities of the catalytic conversion of thiophene sulfur to compounds capable of easy removal from gases. It should be pointed out that the thermal decomposition of thiophene in gases low in hydrogen may give carbon which rapidly covers any surfaces present. This would probably limit catalyst life; however, since the thiophene content of most gases is quite low it is possible that carbon from the pyrolysis of thiophene alone would not be a serious problem.

On the basis of these experiments it is believed that the thermal decomposition of thiophene offers a means of lowering the sulfur present as thiophene in synthesis gas. Unless this decomposition can be catalyzed to permit the use of lower temperatures, the use of high temperatures may limit this method of thiophene removal to gases which are not thermally decomposed at 1900°F (1038°C) or less, and to gas processes that can economically subject the thiophene containing gas to such elevated temperatures.

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APPENDIX

Thermodynamic Constants

ΔH° in calories per gram mole

ΔF° in calories per gram mole

Cp in calories per gram mole per degree Kelvin

I Thiophene

$\Delta H^{\circ}_{291} = 24,500$ (104)

$\Delta F^{\circ}_{298} = 27,600$ (104)

$Cp = -7.02 + 0.10045T - 6.325 \times 10^{-5}T^{2}$ (105)

II Carbon bisulfide

$\Delta H^{\circ}_{291} = 28,670$ (106)

$\Delta F^{\circ}_{298} = 17,600$ (107)

$Cp = 9.76 + 0.006102T - 18.94 \times 10^{-7}T^{2}$ (108)

III Hydrogen

$Cp = 6.88 + 0.000066T + 2.79 \times 10^{-7}T^{2}$ (108)

IV Carbon

$Cp = 1.8$ (108)

V Hydrogen sulfide

$\Delta H^{\circ}_{291} = 5,260$ (107)

$\Delta F^{\circ}_{298} = 7,840$ (107)

$Cp = 6.48 + 0.00556T - 12.04 \times 10^{-7}T^{2}$ (108)

VI Carbon monoxide

$\Delta H^{o}_{291} = -26,780$ (106)

$\Delta F^{o}_{298} = -32,810$ (107)

$Cp = 6.25 + 0.002091T - 4.59 \times 10^{-7}T^{2}$ (108)

VII Carbon oxysulfide

$\Delta H^{o}_{291} = -33,300$ (107)

$\Delta F^{o}_{298} = -39,600$ (107)

$Cp = 8.32 + 0.007224T - 21.46 \times 10^{-7}T^{2}$ (108)

VIII Carbon dioxide

$\Delta H^{o}_{291} = -94,400$ (107)

$\Delta F^{o}_{298} = -94,260$ (107)

$Cp = 6.85 + 0.008533T - 24.8 \times 10^{-7}T^{2}$ (108)

Thermodynamic Calculations

The first set of calculations are presented in detail to show the methods employed in determining equilibrium constants. Subsequent to this the thermodynamic calculations are briefly outlined for each reaction.

I Equilibrium constants for the reaction

$C_4H_4S = \frac{1}{2}CS_2 + 2H_2 + 7/2C$ at 1625 and 1900°F (885 and 1038°C)

$\Delta H^{o}_{291} = 14,335 - 24,700 = -10,365$ (Reaction is exothermic)

$\Delta F^{o}_{298} = 8,800 - 27,600 = -18,800$

$\Delta F^{o} = -RT\ln K$

$18,800 = 2 \times 298 \times 2.303 \log K$

$K = 5.2 \times 10^{13}$ at $298^\circ K$

$\Delta Cp = 31.96 - 0.09727T + 6.169 \times 10^{-5}T^2$

$\Delta H^o = \quad C_p dT$

$= \Delta H_o + 31.96T - \frac{0.09727T^2}{2} + \frac{6.169}{3} \times 10^{-5}T^3$

Substituting $T = 291^\circ K$ and solving for ΔH_o:

$\Delta H_o = -16,050$

(A) To find K at $t = 1625^\circ F$ ($1158^\circ K$) by use of the Van't Hoff equation.

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$$

$$\ln K_T - \ln K_{298} = \left[\frac{-\Delta H_o}{RT} + \frac{\Delta a \ln T}{R} + \frac{\Delta b}{2R}\,T + \frac{\Delta C}{6R}\,T^2 \right]_{298}^{1158}$$

$$2.303(\log K - 27.42) = \left[\frac{16050}{2T} + \frac{31.96}{2} \times 2.303 \log T - \frac{0.09727}{4}\,T + \frac{6.169}{12} \times 10^{-5}T^2 \right]_{298}^{1158}$$

Solving: $K = 1.5 \times 10^8$ at $1625^\circ F$.

(B) By a similar solution: $K = 6.1 \times 10^7$ at $1900^\circ F$ ($1311^\circ K$)

II Equilibrium constants for the reaction

$C_4H_4S = H_2S + H_2 + 4C$ at 1625 and $1900^\circ F$ (885 and $1038^\circ C$)

$\Delta H^o_{291} = -5,260 - 24,700 = -29,960$

$\Delta F^o_{298} = -7,840 - 27,600 = -35,440$

$\log K = 25.85$ at $298^\circ K$

$\Delta Cp = 27.58 - 0.09482T + 6.233 \times 10^{-5}T^2$

$\Delta H_o = -34,470$

(A) At $t = 1625^\circ F$ ($1158^\circ K$)

$$2.303(\log K - 25.85) = \left[\frac{34,470}{2T} + \frac{27.58}{2} \times 2.303 \log T - \frac{0.09482}{4}\,T + \frac{6.233}{12} \times 10^{-5}T^2 \right]_{298}^{1158}$$

$K = 2.5 \times 10^{9}$

(B) By a similar solution: $K = 4.0 \times 10^{8}$ at 1900°F (1311°K)

III Equilibrium constants for the reaction

$2H_2 + CS_2 = 2H_2S + C$ at 1625 and 1900°F (885 and 1038°C)

$\Delta H^{o}_{291} = -10{,}520 - 28{,}670 = -39{,}190$

$\Delta F^{o}_{298} = -15{,}680 - 17{,}600 = -33{,}280$

$\log K = 24.28$ at 298°K

$\Delta Cp = -8.76 + 0.004878T - 0.1072 \times 10^{-5}T^{2}$

$\Delta H_{0} = -36{,}837$

(A) At t = 1625°F (1158°K)

$$2.303(\log K - 24.28) = \left[\frac{36{,}837}{2T} - \frac{8.76}{2} \times 2.303 \log T + \frac{0.00488}{4} T - \frac{0.1072}{12} \times 10^{-5}T^{2}\right]_{298}^{1158}$$

$K = 150$

(B) By a similar solution: $K = 19$ at 1900°F (1311°K)

IV Equilibrium constants for the reaction

$C_4H_4S + CO = COS + 4C + 2H_2$ at 1625 and 1900°F (885 and 1038°C)

$\Delta H^{o}_{291} = -33{,}300 - 24{,}700 + 26{,}730 = -31{,}220$

$\Delta F^{o}_{298} = -39{,}600 - 27{,}600 + 32{,}510 = -34{,}690$

$\log K = 25.30$ at 298°K

$\Delta Cp = 30.05 - 0.09518\,T + 6.212 \times 10^{-5}T^{2}$

$\Delta H_{0} = -36{,}450$

(A) At t = 1625°F (1158°K)

$$2.303(\log K - 25.30) = \left[\frac{36{,}450}{2T} + \frac{30.05}{2} \times 2.303 \log T - \frac{0.09518}{4} T + \frac{6.212}{12} \times 10^{-5}T^{2}\right]_{298}^{1158}$$

$K = 3.3 \times 10^8$

(B) By a similar solution: $K = 6.6 \times 10^7$ at 1900°F (1311°K)

V Equilibrium constants for the reaction

$2COS = CO_2 + CS_2$ at 1625 and 1900°F (885 and 1038°C)

$\Delta H^o_{291} = -94,400 + 28,670 + 66,600 = 870$

$\Delta F^o_{298} = -94,260 + 17,600 + 79,200 = 2,540$

$\log K = -1.850 = 8.150 - 10$

$\Delta Cp = -0.3 + 0.00015\ T - 0.008 \times 10^{-5} T^2$

$\Delta H_o = 952$

(A) At t = 1625°F (1158°K)

$$2.303(\log K + 1.850) = \left[\frac{-952}{2T} - \frac{0.3}{2} \times 2.303 \log T + \frac{0.00015}{4}\ T - \frac{0.008}{12} \times 10^{-5} T^2\right]_{298}^{1158}$$

$K = 0.0376$

(B) By a similar solution: $K = 0.0403$ at 1900°F (1311°K)

VI Equilibrium constants for the reaction

$H_2 + \frac{1}{2}S_2 = H_2S$ at 1625 and 1900°F (885 and 1038°C)

$$\Delta F^o_T = -19,200 + 0.947 \times 2.303\ T \log T + 0.00165\ T^2 - 3.7 \times 10^{-7} + 1.65\ T$$

as given by Lewis and Randall (109)

$\Delta F^o = -RT\ln K$

By a substitution of temperatures

$K = 30.9$ at 1625°F (1158°K)

$K = 14.5$ at 1900°F (1311°K)

VII Equilibrium constants for the reaction

$COS + H_2 = H_2S + CO$ at 1625 and 1900°F (885 and 1038°C)

$\Delta H^{o}_{291} = -5,260 - 26,780 + 33,300 = 1,260$

$\Delta F^{o}_{298} = -7,840 - 32,510 + 39,600 = -750$

$\log K = 0.546$ at $298^{o}K$

$\Delta Cp = -2.47 + 0.00692\ T + 2.04 \times 10^{-7} T^2$

$\Delta H_o = 1,684$

(A) At t = 1625°F (1158°K)

$$2.303(\log K - 0.546) = \left[\frac{-1,684}{2T} - \frac{2.47}{2} \times 2.303 \log T + \frac{0.00692}{4}\ T + \frac{2.04}{12} \times 10^{-7} T^2 \right]_{298}^{1158}$$

$K = 11.2$

(B) By a similar solution: K = 30.2 at 1900°F (1311°K)