INVESTIGATION LEADING TO A PROCESS FOR THE SYNTHESIS OF HYDROGEN SULPHIDE FROM SULPHUR AND CERTAIN LUBRICATING OILS DERIVED FROM PETROLEUM

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C O N T E N T S

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INTRODUCTION

The primary object of the present study was to provide a process, adaptable to prevailing South African conditions, for the manufacture of hydrogen sulphide. Such a process would also be suitable for use in other countries where the gas is not obtainable naturally or from refinery operations, or as a by-product from other industries. Early in the study it was found that the literature embodying prior work was very scattered in character, and had to be sought in many different fields of research. It was therefore decided to make the record of prior work as comprehensive as possible, so as to provide, at the same time, a starting point for future workers on related subjects. For this purpose photostatic facilities were used extensively in the study of otherwise inaccessible material.

This study indicated that in some respects the results of prior work were contradictory in character. It was therefore decided that the present problem should best be approached by a reconsideration of the phenomena encountered in the light of modern interpretations of some of the physical and chemical properties of sulphur.

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CHAPTER I

PRIOR WORK AND EXISTING KNOWLEDGE.

The fact that hydrogen sulphide is evolved when sulphur is heated with certain organic compounds is mentioned in several textbooks. For example Bloxam[1] states that the gas "may be obtained in large quantity by heating a mixture of equal weights of sulphur and tallow or paraffin wax, the latter furnishing the hydrogen". Similarly Ephraim[2] mentions that "large quantities of sulphuretted hydrogen or selenuretted hydrogen are rapidly produced when organic compounds rich in hydrogen, such as paraffins, naphthalene and resins, are heated with sulphur (or selenium)." However no detailed information is forthcoming from these and other similar sources.

It is probable that the reaction may have been encountered early in chemical history, in the course of the many heating and distilling manipulations in which sulphur played a part and in which oils or other organic material may have been present either by intention or as an impurity.

According to Mellor, Scheele[3] published in 1777 the observation that he had obtained a gas, which we now know as

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[1] Bloxam: "Inorganic Chemistry", 10th Ed., p.151, J. & A. Churchill, London.

[2] Ephraim: "Inorganic Chemistry", Edited by Thorne and Roberts, 4th English Ed. p.521.

[3] Scheele: "Chemische Abhandling von der Luft und dem Feuer", Berlin Ed. p.237, published 1793; originally published Upsala 1777; through Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol.X, p.122, Longmans Green & Co. London.

hydrogen sulphide, by heating sulphur with olive oil.

The earliest published paper which can be traced in literature is that of Reimsch[1] who produced H_2S by heating a mixture of 1 part sulphur with 3 parts tallow. Reimsch also investigated the reaction between sulphur and linseed oil, and mentions that previously many medical preparations had been customarily prepared by the action of sulphur on turpentine and other oils. Referring to the preparation of H_2S from tallow by his method Reimsch says: "I therefore consider that one may thus prepare hydrogen sulphide most simply and purely, for one can stop the operation at any moment without harm to the mixture; and whenever one so requires it is only necessary to heat the flask somewhat, and the gas is again evolved at once."

In 1871 Galletly[2] published improvements on this method. He substituted "solid paraffin" (presumably paraffin wax) for the tallow with encouraging results. He also gave directions for applying the reaction to supply the gas for laboratory purposes. In further experiments he found that "heavy paraffin oil" could be used as an alternative to the wax. If, however, stearic acid was used a

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[1] Reimsch: Journal für praktische Chemie, 4, 136 (1838). In no subsequent publication is this reference correctly given. In the interests of historical accuracy the original paper was traced, and the author's name and other particulars as given here are correct.

[2] Galletly: Chemical News, 23-24, 162 (1871).

"milky fluid" was observed in the outlet tube. This fluid, he stated, consisted of water mixed with finely divided sulphur.

In 1879 Fletcher[1] published a description of the method used by him to generate H_2S for analytical purposes by heating sulphur and paraffin wax. He stated that a wash-bottle was not required, and that smooth evolution of the gas could be promoted by the presence of "a few pieces of broken tobacco - pipe shank". Shortly afterwards Johnstone[2] wrote to the same Journal, commenting adversely on the method. He stated that he and others had used a similar method "as far back as 1872", and that he had given it up after twelve months' trial on account of repeated explosions.[3]

Lidoff[4] obtained H_2S by adding "petroleum naphtha" to sulphur heated to a temperature of 350°C - 400°C. Charitchkoff[5] examined certain Caucasian oils containing sulphur, and expressed the opinion that the reaction between paraffin and sulphur, with dehydrogenation, could proceed completely till the stage of carbon formation.

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[1] Fletcher: Chemical News, 40, 154 (1879).
[2] Johnstone: Chemical News, 40, 167 (1879).
[3] These two papers have been wrongly quoted by later workers. One error has been to group them as "Johnstone and Fletcher", as if the two papers were of joint authorship. In addition the year of publication has been wrongly stated. The references here given are correct, as checked from the published papers after prolonged searching.
[4] Lidoff: Chem. Zentr., 52, 22 (1882).
[5] Charitchkoff: Chem. Zeitung, 26, 731 (1903).

In 1887 Markownikoff and Spady[1] reported investigations on the dehydrogenation of naphthenes by means of sulphur with evolution of H_2S. They heated 70 g. octonaphthene (C_8H_{16}), rigorously purified, with 12 g. sulphur in a closed tube at 210° - 220°C until no sulphur apparently remained. The reaction product was fractionated and the main portion distilled between 118° - 123°C. The remainder consisted of a "viscous, stinking oil". By the formation of derivatives they confirmed that the sulphur had effected dehydrogenation of the octonaphthene with the formation of Xylol.

Prothière[2] called attention to the neglect of the reaction between sulphur and organic materials as a means of H_2S production in chemical practice. In place of tallow or paraffin wax Prothière used vaseline (i.e. petroleum jelly). He recommended as the best proportions 30 parts vaseline with 70 parts sulphur. If less vaseline was taken the output of H_2S fell considerably. He found that the gas was free from undesirably contamination apart from ordinary air, and described suitable apparatus for applying the reaction for laboratory purposes. Prothière's method is distinguished from all prior and later work by the proportions of materials chosen by him, representing a larger ratio of sulphur to hydrocarbon material than that recommended by any other worker.

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[1] Markowmikoff and Spady: Ber. 20, 1850 (1887).
[2] Prothiere: Pharmaceutische Zeitung, 48, 78 (1903)

In 1908 Erdmann[1] published his well-known paper on "thiozonide" in which he set out the basis for his theory that there exists an active form of sulphur, which he termed "thiozon" (S_3) on the analogy of ozone. He considered that this active form of sulphur was present mainly in sulphur heated to about 160°C. Among many experimental results he reported that linalöol could react with sulphur to form a "dithiozonide". At 150°C there was no reaction, but at 160°C a reaction started, with rapid evolution of H_2S. Erdmann's theory has not been received with favour in later years, and his concept of the existence of an S_3 molecule at about 160°C is out of keeping with modern views on the molecular behaviour of sulphur. However a valuable aspect of his work that remains is the fact that he called attention to the necessity of considering and explaining sulphurisation reactions in the light of an understanding of the molecular structure of sulphur itself.

In 1909 Kruyt[2] reported work carried out at the van't Hoff Laboratory on the mixing of sulphur with several organic liquids, and found, inter alia, that in the system paraffin wax/sulphur separate molten layers formed. Between 150° and 160°C H_2S was evolved, and in consequence further work on this mixture, and on sulphur mixtures with other high-boiling aliphatic hydrocarbons, was not pursued. In heating sulphur with other organic liquids difficulties due to H_2S

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[1] Erdmann: Annalen 362, 133 (1908).
[2] Kruyt: Z.physikal. Chem. 64, 486 (1909).

evolution were also repeatedly encountered.

Spanier and von Engler[1] found that no noticeable reaction occurred after heating n-hexane with sulphur in a sealed tube at 210°C for 24 hours. n-Butane and n-heptane heated similarly at 300° - 350°C yielded thiophene and thiophene derivatives. With olefines there was a vigorous reaction, with H_2S evolution. Hexylene was heated with sulphur in a sealed tube at 210°C for 24 hours. When the tube was opened a large volume of H_2S escaped and the remaining material in the tube was dark brown in colour. On being subjected to distillation this residue gave off more and more H_2S, while the greater portion distilled over with increasing temperature, yielding a brownish-yellow tarry distillate. The final residue was a coke-like mass. When hexylene was heated to boiling point (68°C) at atmospheric pressure with sulphur no reaction was noticeable.

In 1912 Eggleston[2] disclosed a process for utilising crude petroleum containing a high proportion of sulphur, such as was obtained from the oilfields of Beaumont (Texas) and other localities. Such "sour crudes" were regarded as very undesirable in the petroleum industry at the time, and

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[1] Spanier and von Engler: "Zur Kenntnis der Wirkung des Schwefels auf Kohlenwasserstoffe und des Schwefelgehaltes der Erdole": Dissertation, Karlsruhe, 1910; through Friedmann: Petroleum Zeitschrift, 11, 694 (1916).

[2] Eggleston: U.S. Patent No. 1,018,040 of 1912.

difficulties arising out of the presence of sulphur and sulphur compounds in processing operations, or in petroleum distillates and preparations, remain an important problem in petroleum technology to the present day.

Eggleston considered that in the particular types of crudes with which he was concerned the sulphur appeared to be present mainly in the form of a solution. He found that by distilling at a temperature of 300° - 500°F much of this sulphur was converted to H_2S which, he suggested, could be applied in H_2SO_4 manufacture. He worked out a system of operating three stills systematically as a group, so as to obtain the gas at optimum concentration, and he treated the final oil with open steam in order to expel dissolved H_2S. The main object of his process, as disclosed in his claims, was the improvement of the crude by lowering its sulphur content, and the H_2S was regarded a useful by-product.

In 1915 Bacon[1] patented in the United States a metallurgical process for copper recovery from solutions obtained by the lixiviation of copper ores and furnace residues with acid. The process required the precipitation of the copper by H_2S, and the patent directed that this gas be generated cyclically from sulphur (recovered later in the process) by heating with a hydrocarbon material such as "hydrocarbon residue". Bacon recommended in this instance a temperature range of about 300° - 360°C owing to the dissociation at higher temperatures of the H_2S formed. He

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[1]Bacon: U.S. Patent No. 1,151,236 of 1915.

preferred to use as low a proportion of hydrocarbon material as possible so as to obtain finally a dense type of coke, which might be useful for metallurgical work.

In 1917 Drakeley[1], in the course of an investigation on certain types of fires occurring in coal mines, demonstrated experimentally that H_2S could readily be formed from coal and pyrites in several ways. In addition he carried out a series of experiments in which he heated sulphur with bituminous coal in the presence and absence of moisture respectively. He proved that H_2S was evolved in all these cases and that the greatest yield was obtained when moisture was present. Under these conditions the heating of 6 g. sulphur with 100 g. coal gave 4.783 g. sulphur in the form of H_2S, and 1.373 g. sulphur remained in the residual coke. The experiments were carried out at atmospheric pressure and at a temperature of 500°C.

Brooks and Humphrey[2] reported in 1917 on the effect of sulphur on the oxidation of hydrocarbons with particular reference to asphalt. They considered that at elevated temperatures sulphur accelerated the oxidising action of air on these compounds. "It is possible", they state "that when petroleum oils are heated with sulphur, complex sulphur

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[1] Drakeley: J. Chem. Soc. 111, 853 (1917).
[2] Brooks and Humphrey: Ind. Eng. Chem. 9, 746 (1917).

compounds are first formed and that these compounds are more or less completely decomposed on continued heating, since in the case of the artificial asphalts described in this paper the final products contained from 2 - 9% sulphur". This paper contains the following significant statement in a footnote: "We find that in order to employ this reaction as a cheap source of H_2S a large excess of oil is required. Although much coke is deposited, nothing like the results expressed by the equation

$$C_{25}H_{50} + 25S \longrightarrow 25H_2S + 25C$$

can be attained. Two or more parts of oil to one of sulphur give excellent results and an oil should be selected boiling above 200°C".

Bacon and Davis[1] disclosed methods of purifying sulphur on a large scale by holding a molten body of sulphur at a temperature of 340° - 400°C for sufficient time to decompose any oil or other organic matter present by reaction with the sulphur. This process is of special interest in view of the later development of a perfected method in some respects analogous to this, for producing sulphur of a very high purity.

In Europe at this period the interest of workers in the reaction between sulphur and hydrocarbons was stimulated largely by the hope that analogies of theoretical value might

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[1]Bacon and Davis: U.S. Patents Nos. 1,374,897 and 1,374,898 of 1921.

be drawn which could assist in the explanation of the effects of the treatment of hydrocarbons by oxygen. At Dresden Graefe[1] reported the results of an investigation in which he treated petroleum oil with oxygen, sulphur and selenium respectively. The oil used had a S.G. of 0.921 at 15°C, and gave no distillate below 350°C. It contained 0.28% sulphur before use.

Graefe heated 50 g. of oil with 5 g. sulphur to 300°C for 25 hours, and obtained a final product which had a melting-point of 450°C. In the course of the reaction he examined two samples of the gas evolved and obtained the following figures :

	Sample I.	Sample II (15 minutes later)
H_2S	68.3%	59.4%
Volatile Hydrocarbons	3.7%	4.4%
Heavy Hydrocarbons	2.8%	3.4%

By extracting the residue with ether-alcohol he obtained 44.6% of asphaltic compounds, with an "average molecular weight" of 580. Unfortunately, Graefe does not report on the sulphur content of the residue, so that no conclusions can be drawn as to the extent of conversion.

The work of Siebeneck[2] was more complete in character. In his paper - "Der Einfluss der Elemente der Sauerstoffgruppe

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[1]Graefe: Z. für angewandte Chemie, 34, 509 (1921).
[2]Siebeneck: Petroleum Zeitschrift, 18, 281 (1922).

auf Paraffine" he reports investigations concerning the reaction with paraffin wax of oxygen, sulphur, selenium and tellurium respectively. His paraffin wax was a commercial grade, of melting point 51°C, derived from a Borysław crude oil. The ultimate composition of the wax used was as follows :

C	83.93%
H	14.13%
Other constituents, expressed by Siebeneck as oxygen	1.94%
	100.00%

His initial experiments dealt with the action of atmospheric air and oxygen on paraffin wax, with production of saponifiable fatty acids and other compounds - work of profound interest with which we cannot deal here.

Siebeneck commenced his investigations on the sulphur reaction by heating 5 g. wax with 1 g. powdered sulphur and obtained evidence of the evolution of H_2S at 150°C. However he found it necessary to heat up to 220°C to obtain fairly constant production of gas. Thereafter he transferred the material to a flask and heated for a further five hours at the same temperature, finally obtaining a carbonaceous deposit insoluble in organic solvents.

Working on a larger scale Siebeneck heated 200 g. paraffin wax for 72 hours at a temperature of approximately

230°C, adding successive portions of sulphur totalling 65 gr. This periodical addition of sulphur was observed to maintain the evolution of the H_2S. Siebeneck considered that by-products such as CS_2 were also present in the gas, though this point was not, apparently, definitely confirmed. The residue was a brownish-black oily carbonaceous mass ("fettkohlig") with a "characteristic, not unpleasant, aromatic smell".

After thorough extraction with CS_2 and ether-alcohol the extracted residue was a black amorphous mass which could not be melted or sublimed. If heated above 500°C it decomposed giving off fumes smelling of sulphurous acid, and finally a shining black mass of pure carbon was obtained. Siebeneck also conducted a series of investigations on the "solubility" of the residue in strong acids and alkali. The extracted residue was submitted to combustion analysis, and found to be of the following composition:

C	64.06%
H	0.05%
S	34.18%

On the basis of these figures Siebeneck arrived at a so-called molecular formula of $(C_5S)x$ for the residue, and noted the almost complete dehydrogenation of the paraffin wax in the course of the experiment. He also observed that if the extracted residue was again heated to approximately 300°C with a further excess of paraffin wax, a further evolution of H_2S was obtained.

In the same year Rakusin[1] reported experiments in which paraffin wax (M.P. 56°C) was heated with sulphur in a glass bulb immersed in an oilbath at 190° - 205°C. The H_2S evolved was absorbed in a U-tube filled with pumice moistened with NH_4OH, and followed by a guard tube containing $CaCl_2$. Rakusin found that less than 50% of the sulphur taken, and only 3.12% of the paraffin wax taken, entered into the reaction. These low yields were, presumably, due to the relatively low temperature of the oil-bath.

We also find that suggestions were made at this period in the U.S.A. that the reaction between sulphur and hydrocarbons should be utilised for the production of H_2S required in certain industrial and metallurgical processes. In 1921 Hanley[2] published the results of experiments in relation to the removal of arsenic from zinc electrolytes in the wet process for the production of zinc. In this process it was necessary to remove almost completely, before electrolysis, any metals more electro-negative than zinc. The process used for the removal of arsenic was treatment with SO_2 to reduce the compounds present to the trivalent condition followed by precipitation with H_2S.

As an alternative to generating this gas by the customary acid - ferrous sulphide method Hanley experimented

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[1]Rakusin: Petroleum Zeitchrift, 18, 581 (1922).
[2]Hanley: Chem. Met. Eng. 24, 693 (1921).

with heavy oil and sulphur mixtures under various conditions. He found that under no circumstances could a yield in excess of about 80% (based on the weight of sulphur) be obtained. He also found that the optimum ratio of sulphur to oil depended mainly on the type of end-product desired. He stated that if it was intended to use the by-product as an asphalt substitute, then not more than 10% of sulphur on the weight of the oil should be used. If, however, the recovery of this by-product was not required then the proportion of sulphur could be raised to about 50% on the weight of the oil, the final product being then coke-like in character.

Hanley obtained his best yield of H_2S (namely 82% based on the weight of the sulphur used) in an experiment in which he used a specially prepared oil. This oil was a fuel oil from Coalinga District, California, prepared by distilling with both outside heat and live steam till 57% of the volume had been removed by distillation, i.e. till the low-boiling fractions had been removed. In the H_2S process his working temperature was between 150° - 205°C and the time of heating in this successful experiment was 11 hours, the by-product being 84% of asphalt based on the weight of oil used. Other methods tried by Hanley involved the use of other fuel oils (with or without prior "topping"), cylinder oil, as well as road oil and distillation residues, with times of heating varying from 3½ hours to 24 hours. His final conclusion was

that the conventional method of H_2S preparation was preferable, as there would be difficulty in obtaining commercial fuel oil pre-treated in the above manner.

The action of sulphur on a "yellow oil" obtained from the Riebeck Montan Works was investigated by Bielenberg[1]. He found that on heating to 130°C H_2S was obtained. With increase in temperature to 190°C more and more sulphur was found to react, and the iodine value of the oil was found to increase. The product had a sulphur content of 6.4%, and when distilled gave off more H_2S. No clear description of the nature of the original oil is given in the paper, but as the boiling range is stated to be 205° - 260°C the oil appears to have been an unrefined product. The original oil had an iodine value of 57, indicating the probable presence of unsaturated compounds.

An industrial application was aimed at by Bindschedler and Rugeley[2] who in 1925 patented a process "for the economic production of hydrogen sulphide gas in a state of great purity so that it will be suitable for the manufacture of sulphydrates used in denitrating nitrocellulose silk". In their application they refer to the already known reaction in which H_2S was obtained by reacting sulphur with "tar oil or petroleum products like Mexican crude oil, heavy petroleum

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[1] Bielenberg: Braunkohlenarchiv 4, 40 (1923).
[2] Bindschedler and Rugeley: U.S. Patent No. 1,565,894 of 1925.

oil, paraffin oil, and asphalt". They claimed improvements consisting in refluxing the volatile hydrocarbons formed, and purifying the H_2S by passage through charcoal, or similar materials such as silica gel. They also considered it desirable to raise the temperature of the process in its final stages to nearly 400°C in order to complete the reaction. They considered that at such temperatures undesirable compounds such as mercaptans, might be formed, but considered that these would be adequately removed by the charcoal or silica gel.

In examples of the process the following particulars were given :-

(a) 1000 lbs. sulphur were mixed with 1500 lbs. Mexican fuel oil in an iron kettle provided with a stirrer and gradually heated till 400°C. In this instance approximately 500 lbs. petrol and other light products were distilled off and recovered separately by condensation. The H_2S was washed with "cracked oil" till free of sulphur and then purified by passage through charcoal. The coke obtained from the reaction vessel was recommended for briquette manufacture or other purposes, such as use in producer gas plants.

(b) 875 lbs. crude oil was first heated to 200°C and then mixed in an iron kettle with 1000 lbs. molten sulphur. The kettle was provided with a stirrer

as before. In this instance, however, the light distillates were refluxed by means of an air-cooled reflux condenser with baffle-plates. Heating was carried on till 400°C and the H_2S purified as before.

Apart from the other claims in this patent a specific claim was made for a ratio of sulphur/oil of approximately 0.8/1.2 parts by weight, and for carrying the reaction as high as 350° - 400°C. No mention is made of the duration of heating and no figures are given for the percentage yield of gas obtained or of the approximate yields that might be expected.

Attention was again called to the laboratory aspects of H_2S production in a paper by Henwood, Garey, Goldberg and Field[1]. They used paraffin wax and sulphur, with finely divided, previously ignited, asbestos as a base in which the reaction mixture was incorporated. They reported that a large yield of the gas was obtained which was pure and did not require washing.

Sedlaczek[2] listed a large number of products resembling artificial asphalts, or substitutes for asphalt, which might be made by the action of sulphur on coal tar, pitch, and

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[1] Henwood, Garey, Goldberg and Field: J. Franklin Inst. 199, 685 (1925) through Chem. and Ind. 44, (New Series), 584 (1925).

[2] Sedlaczek: Teer 24, 436 (1926).

various oils. Numerous older patents are mentioned in the paper, most of which claimed special mixtures with fillers and the like. The paper makes no reference whatever to the chemical reactions involved, nor is it indicated that H_2S is a by-product of many of the operations which are specified.

Reference has already been made to the importance in petroleum technology of difficulties arising out of the presence of sulphur or sulphur compounds. An immense amount of work has been done on these problems both from the viewpoint of refining practice and the viewpoint of the ultimate application of the petroleum products concerned. Most of this work has aimed at reducing the sulphur content of petroleum products marketed to what is regarded as a safe limit in each respective instance. The recovery of the sulphur as H_2S or in some other form has in most instances been regarded as being of less importance. Consequently, this type of work is not of direct value in the present investigation, but certain papers cover important ground of common interest. For example the paper presented by Borgstrom and Emmet Reid to the Petroleum Division of the American Chemical Society in 1927 gives the results of a search of the literature on "Sulphur Compounds in Mineral Oils" made under the auspices of the American Petroleum Institute. In this paper[1] was listed a large number of sulphur compounds that have been

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[1] Borgstrom and Emmet Reid: Oil and Gas Journal, 26, 352 (1927).

identified in petroleum, with the original references. Borgstrom and Emmet Reid point out that "all books on petroleum devote more or less space to sulphur and its removal. The information they give is usually indefinite when they come down to details". Their paper was thus intended to be a means of referring back to prior work on sulphur or specific sulphur compounds in petroleum. The paper deals only superficially with H_2S, being more concerned with free sulphur and organic sulphur compounds.

Dunlap's[1] paper on the "Effect of Sulphur in Liquid Fuels" deals with the effect of sulphur in fuel or lubricating oils when used in internal combustion engines. Dunlap approaches the subject, however, from the viewpoint of the chemical reactions that can be specifically reproduced in the laboratory under conditions approximating to those in an engine, and his discussion is therefore of considerable interest in relation to the present work. He states that when sulphur is heated to 210°C with the heavier petroleum fractions it begins to take hydrogen from the hydrocarbon and form an olefine, with evolution of H_2S. He makes the specific statement that "almost quantitative yields of H_2S can be obtained by heating to 300°C a solution of 1% free sulphur in kerosene" and that a similar reaction occurs with the heavier oils or paraffin wax.

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[1] Dunlap: Chem. Met. Eng. 34, 298 (1927).

Dunlap also carried out experiments to determine whether similar reactions occurred with ferrous sulphide instead of sulphur. Ferrous sulphide was carefully purified from free sulphur and was heated with engine oil and paraffin wax respectively to 340°C for about 2 hours. Small quantities of H_2S were obtained in both instances, and Dunlap considered that free iron was formed, thus simulating what might occur under engine conditions, along with other reactions, which would ultimately tend to the formation of carbon deposits and engine sludge.

The thermal decomposition of organic sulphur compounds was the subject of an investigation by Faragher, Morrell and Comay[1] who reported in 1928 the results of studies on certain sulphur compounds which were selected as representative of the types considered to be present in petroleum. The materials selected were mercaptans, alkyl sulphides, thiophene, and in addition elementary sulphur. In the case of elementary sulphur the experimental procedure was to dissolve 0.2 g. sulphur in 100 g. purified petroleum naphtha and vapourise the solution at an average temperature of 496°C at an approximate rate of 0.5 ml. per minute. It was found that H_2S was the only final product of the reaction. A similar experiment carried out at 316°C also gave H_2S as the final product but the yield was lower.

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[1] Faragher, Morrell and Comay: Ind. Eng. Chem., 20, 527 (1928).

In the course of their work on other sulphur compounds heated in naphtha solution Faragher, Morrell and Comay noted that when isoamyl disulphide was distilled at atmospheric pressure H_2S was evolved in large quantity. In general they found that naphtha solutions of almost all the organic sulphur compounds with which they worked, when vapourised and highly heated, gave off H_2S as the major product of decomposition. The exception was thiophene, which gave off no H_2S even when heated up to 871°C in the vapour phase.

The possibility of utilising the sulphur/hydrocarbon reaction for the production of H_2S for laboratory use, already referred to earlier in the literature, was again noted by Gfeller and Schaefer in 1929[1]. The mixture recommended by them consisted of 25 parts paraffin wax, 15 parts sulphur and 5 parts asbestos fibres. The wax was ground up and intimately mixed with the sulphur. The asbestos was then worked in thoroughly. This mixture, they stated, could be stored for long periods, and could readily be used by heating. No information as to yields was given, nor was it stated why the asbestos was introduced.

Glass and Emmet Reid[2] reported in 1929 observations on the course of the reaction between benzene and sulphur.

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[1] Gfeller and Schaefer: Schweizerische Apotheker Zeit, 10, 110 (1929).
[2] Glass and Emmet Reid: J. Am. Chem. Soc., 51, 3428 (1929).

From a mixture of 50 g. sulphur and 39 g. benzene, which was heated at 350°C for 24 hours, they obtained 6.3 g. H_2S, 8.6 g. unchanged benzene, 1.8 g. thiophenol and 27.8 g. of a mixture of diphenyl sulphide, diphenyl disulphide, and diphenylene disulphide, as well as 22.1 g. of a "hard glass-like tar". The "loss" of S in the experiment was calculated as 22.4 g.

In 1931 Scudder and Lyons[1] reported the results of an investigation undertaken to ascertain whether the use of certain catalysts might affect the reaction between sulphur and various hydrocarbon materials, and to establish the optimum conditions for H_2S evolution. Their initial experiments were carried out in a 12" Pyrex test-tube, fitted with stopper and delivery tube and suspended in an electrically heated air-bath, the H_2S being collected in graduated vessels over water saturated with H_2S. It was found that the results were "low and erratic" and sulphur volatilised from the mixture and collected in the delivery tube.

Further experiments were carried out in 250 cc. Pyrex distilling flasks, and lump pumice was added to the reaction mixture. The pumice was found to be "advantageous" in the case of paraffin wax, but did not affect other hydrocarbons used. An attempt was then made to find more effective catalysts and the following other materials were tried :

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[1] Scudder and Lyons: Proceedings Indiana Academy of Science, 40, 185 (1931).

Cadmium sulphide, finely divided iron, aluminium, zinc, cobalt, nickel, lead, antimony, bismuth, silver, bone charcoal, silica, gilsonite, calcium oxide, arsenious oxide, lampblack, tar, "Norit" (a proprietary brand of bleaching carbon), and anhydrous aluminium chloride.

The method used was to allow the gas to pass through a solution of cadmium chloride, and to record the temperature of the reaction mixture at the moment when precipitation of cadmium sulphide first became noticeable. These observed "temperatures at initial evolution of H_2S" were reported as lying between 240° - 259°C when 3 g. sulphur were heated with 10 g. paraffin wax (M.P. 65°C) in the presence of the "addition agents", as compared with an initial temperature of 265° - 270°C when the same mixture was heated without "addition agents".

In a further series of experiments the effects of the catalysts on the yield of H_2S were determined. The following summary of the results was given: "It was found that when paraffin or ozokerite was used carbon was the most effective, anhydrous aluminium chloride gave almost as good results, iron (80 mesh or less) was about 75% as effective and in all other cases the effect was negligible. When flux oil or road oil was used none of the above had any appreciable effect. With black oil the gas yield was not affected by carbon but the purity was greater and with asphalt the yield was lowered slightly".

Among the results of numerous experiments the following were the most significant yields of H_2S reported (expressed as percentage of sulphur evolved as H_2S) :

Reaction Mixture.	Yield of H_2S %
20 g. ozokerite, 6 g. sulphur 15 g. pumice,	26.2
20 g. ozokerite, 6 g. sulphur 6 g. lampblack,	51.0
40 g. paraffin wax 12 g. sulphur, 20 g. pumice 6 g. lampblack,	59.5
20 g. paraffin wax, 7.5 g. sulphur, 15 g. pumice,	39.3
20 g. asphalt 6 g. sulphur, 15 g. pumice,	33.3
30 g. flux oil, 20 g. sulphur, 20 g. pumice, 6 g. lampblack,	46.1
40 g. black oil, 20 g. sulphur, 20 g. pumice, 6 g. lampblack,	68.3
40 g. black oil, 20 g. sulphur, no pumice, no lampblack,	68.0
45 g. road oil 15 g. sulphur, no pumice, no catalyst,	70.0
40 g. road oil, 10 g. sulphur, no pumice, no catalyst,	69.7

Scudder and Lyons summarised their conclusions as follows: "Finely divided carbon is a decidedly positive catalyst for the preparation of hydrogen sulphide by the action of sulphur on hydrocarbons. When lampblack is added to paraffin and ozokerite sulphur mixtures the yields are

practically doubled. In the case of road oil and flux oil the addition of finely divided carbon has no effect. With asphalt the carbon seems to slightly lower the yield while with black oil the yield is unaffected but the purity of the gas was higher. Evidently the reason that the addition of carbon does not cause an increase in yields with the oils and asphalt is that they contain sufficient free carbon to catalyse the reaction". They considered the effect of anhydrous aluminium chloride was "about equal" to that of carbon, but was not additive to the effect of the carbon. The purity of the H_2S evolved was estimated by absorption in dilute caustic soda solution, and was found to range from 96 - 100% as long as the temperature of the reaction mixture was kept below 300°C. Above this temperature the purity deteriorated rapidly, and at 500° it was found in the various experiments to be between 25% and 64%. In the case of paraffin wax it was found that on heating from 300°C to 500°C "the increase in yield up to that temperature was about 10%".

Several important difficulties are encountered in assessing the results of this work. For example the temperature of initial H_2S evolution in the case of the sulphur/paraffin wax reaction without catalysts, is given as 265° - 270°C, whereas all other workers have observed H_2S production from similar mixtures at considerably lower temperatures. This fact makes it difficult to estimate the significance of the observation that the "addition agents" caused a lowering

of the initial reaction temperature to about 240° - 259°C. Other difficulties arise out of the nature of the catalysts or "addition agents" used. Some of them, such as lampblack gilsonite, are substances containing hydrocarbon compounds which would probably themselves yield H_2S by reaction with sulphur. Quite apart, therefore, from possible catalytic effects, their addition to the reaction mixture actually increases the proportion, and changes the characteristics of, the hydrocarbon material in an indefinite manner. Conversely such materials as finely divided lead, silver, or iron can combine directly with the sulphur present, thereby reducing the effective sulphur/hydrocarbon ratio in the experiments.

Nellensteyn and Thoenes[1], working in Holland, investigated further the effects of sulphur on hydrocarbons in order to throw light on the question whether, and to what extent, sulphur may have played a part in the formation of bituminous asphalt. They pointed out that asphalts extracted from various sources contained notable percentages of sulphur. This sulphur was not an essential constituent, yet it was found to be almost constantly associated with asphalt compounds.

In a series of carefully planned experiments Nellensteyn and Thoenes reacted sulphur with paraffin wax, paraffin oil, Venezuelan lubricating oil, and "Edeleanu extract" from lubricating oil stock, respectively. The experimental method used was as follows :- In a flask of 150 cc. capacity the

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[1]Nellensteyn and Thoenes: Chem. Weekblad, 29, 582 (1932).

respective quantities of sulphur and hydrocarbon material were heated, the temperature being noted from a thermometer submerged in the mixture. For mixing purposes and to assist in removing the gas formed, a stream of dry oxygen-free nitrogen was slowly led through the mixture. The gas evolved was cooled by a Liebig's condenser and any condensed liquid was collected. Thereafter the gas was passed through an absorption column packed with iron oxide ("ijzeraarde") and $CaCl_2$ which served to remove H_2S. The increase in weight of the column gave the H_2S formed. As control on the efficiency of absorption by the column the gas passed finally through a wash-flask filled with an "alkaline lead solution" (presumably alkaline lead acetate solution). In addition the following determinations and observations were made :

(1) Sulphur content of the residue and distillate.

(2) Insoluble matter in the residue. (This carbonaceous material is referred to as "cokes" in the paper).

(3) Asphaltene content of the residue (ether soluble).

(4) Combustion analysis of the residue and determination of "mean molecular weight".

(5) Ultramicroscopic examination of the residue.

The results which are specially relevant to the present work may be summarised as follows :-

(a) Experiments with paraffin wax: 50 g. paraffin wax, free of oil, were heated with 10% sulphur (5 g.) At 152°C the formation of H_2S was first noted. The mixture was held at 260°C for 350 minutes. The total weight of sulphur found evolved as H_2S was 4.84 g. At the same time 4.82 g. "cokes" were formed, with no asphaltenes.

(b) Experiments with paraffin oil: 50 g. paraffin oil (sulphur content 0.26%) were heated with 5 g. sulphur. At 146°C the reaction commenced. The temperature was rapidly raised to 260°C and held at that temperature. After 4½ hours heating scarcely any more H_2S was formed, and the experiment was stopped at this point. 4.98 g. H_2S were found by absorption, corresponding to 4.69 g. sulphur. This represented a yield of 94% on the sulphur used. In addition 0.7% sulphur was found remaining in the oil. 2.04 g. "cokes" and 1.47 g. asphaltenes were found in the residue.

In similar experiments determinations were made at intervals during the heating and it was found that after 50 minutes heating the reaction was about 80% completed, the remaining portion of the reaction requiring continued heating for a total time of 4½ hours. The use of a larger proportion of sulphur caused a sharp fall in the percentage yield of H_2S. Thus an increase of the weight of sulphur to 10 g./50 g. oil resulted in a yield of 68% H_2S based on the weight of sulphur taken.

In a further experiment with paraffin oil the temperature was raised to 300°C. This noticeably increased the speed of reaction, but only 69% of the sulphur was recovered as H_2S when 5 g. sulphur/50 g. paraffin oil were used. Reduction of the proportion of sulphur increased the percentage yield of H_2S. Thus 2.5 g. sulphur/50 g. oil at 300°C gave a yield of 94% H_2S on the sulphur used. A similar experiment carried out at 210°C proceeded so slowly that it was not carried to completion.

(c) Experiments with Venezuelan lubricating oil stock:

This oil was an unrefined heavy fraction obtained by steam distillation of a Venezuelan crude. It had, prior to use, a sulphur content of 1.22%. The reaction commenced at 135°C. After four hours heating at 260°C 5.01 g. H_2S were evolved, corresponding to 4.72 g. sulphur, while 1.40% sulphur remained in the oil. (It is not specifically stated what weights of materials were used in this experiment, but the results indicate that the quantities were probably 5 g. sulphur/50 g. oil, as in the other series of experiments).

(d) Experiments with Edeleanu-extract from Venezuelan lubricating oil: This extract had a S.G. of 1.018 and consisted mainly of hydrocarbons of low hydrogen content ("Waterstofarme koolwaterstoffen"). The reaction was noticeable at 124°C, and at 160°C was as vigorous as previously observed with paraffin oil at 260°C. At the end of 4 hours

heating at 220° - 260°C the yield of H_2S was 4.91 g., corresponding to 4.62 g. sulphur. The yield of asphaltenes was high - 6.21 g., and "cokes" 2.67 g. (In this instance the proportion of materials used was again presumably 5 g. sulphur/50 g. oil). This experiment is of special interest because of the particular hydrocarbon material used, as the Edeleanu process extracts the olefines and aromatic compounds from petroleum oils by the use of liquid SO_2 as a solvent.

Nellensteyn and Thoenes determined the elementary composition of the various hydrocarbon materials before and after reaction with sulphur, and found that while the carbon content remained almost constant the percentage of hydrogen decreased, as would be expected. When the weight of H_2S formed in each instance was plotted against the asphaltenes plus "cokes" virtually straight lines were obtained.

The conclusion reached was that at least the main reaction consisted of a pure ("suivere") dehydrogenation, and that no polymerisation was involved.

The remainder of the paper by Nellensteyn and Thoenes deals more particularly with the bearing of the observations on asphalt formation and its possible theoretical basis. These aspects lie outside the field of the present work.

Jaza and Blanke[1] found that with graphite or gas

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[1]Jaza and Blanke: Z.anorg. Chem. 210, 81 (1933).

carbon sulphur is retained on heating, due mainly to capillary condensation. In the case of active carbon these processes were supplemented by chemisorption and dissolution.

Wibaut[1] found that when sulphur was heated with carbon a portion remained so strongly bound that it could not be removed by the usual solvents and could only be removed by heating to 1000°C, when it was evolved as H_2S. He suggested that the cause was a chemisorption of the sulphur in the carbon, on the analogy of the behaviour of oxygen with carbon.

The effect of catalysts on the reaction between H_2S and olefines in the vapour phase was investigated by Duffey, Snow, and Keyes[2]. The best catalysts found were nickel on kieselguhr, phosphoric acid on activated charcoal, and certain clays. At temperatures between 200° - 300°C it was found that mercaptans were formed, and that the formation of alkyl disulphides was negligible.[3]

Little is known with certainty as to the chemical structure of lubricating oils. Nikewska[4] reviewed the work done hitherto in this field and stated: "With regard to the higher boiling fractions falling in the lubricating oil range practically nothing is known beyond the fact that they

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[1] Wibaut: Z.anorg. Chem. 211, 398 (1933).
[2] Duffey, Snow, and Keyes: Ind. Eng. Chem. 26, 91 (1934).
[3] Presumably it was found possible to avoid the catalyst poisoning that has been encountered with nickel on kieselguhr in hydrogenations in the presence of H_2S or mercaptans.
[4] Nikewska: Ind. Eng. Chem. 28, 970 (1936).

consist of a mixture of aliphatic, naphthenic, and aromatic hydrocarbons in various proportions, contaminated perhaps with small amounts of sulphur and nitrogen derivatives and products of hydrocarbon oxidation". He also reported the results of a long programme of research in the course of which hydrocarbons that might be of significance in the lubricating oil range were prepared synthetically, with the object of correlating, where possible, physical properties with chemical structure.

Taylor[1] heated sulphur with hydrocarbons at 440°C and obtained an insoluble carbonaceous residue. After free S had been removed the residue could not be identified with any known compound. The composition ratio of the residue was approximately 1 atom S : 2 atoms C. Taylor considered that the composition and nature of the residue obtained was evidence of its being a definite compound, rather than a mixture.

In 1935 Thiessen[2] reported work on the behaviour of sulphur during coal carbonisation. He found that about 45% of the original sulphur present in the coal substance, and about 60% of the sulphur originally present as pyrites remain in the coke, the rest forming H_2S and other volatile compounds.

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[1] Taylor: Mem. Manchester Phil. Soc. 79, 99 (1935).
[2] Thiessen: Ind. Eng. Chem. 27, 473 (1935).

Warren and Burwell's[1] classical paper was published in 1935. This work provided much of the experimental basis for a new understanding of the molecular constitution and behaviour of sulphur, and from it has grown the modern conception of the nature of sulphur and the significance of its changes on heating. Warren and Burwell showed that rhombic sulphur, S_8, had a molecular structure consisting of a puckered 8 - atom ring, with an S - S distance of 2.12Å, and a bond angle of 105°. The closest distance of approach found for atoms in neighbouring molecules was about 3.3Å. They pointed out that although rhombic sulphur changes over to the monoclinic form above 96°C there is much chemical evidence to support the view that the molecule continues to have the S_8 structure at temperatures somewhat higher than the melting point. They suggested that the change to the viscous form of sulphur might be interpreted in terms of the opening of the S_8 rings, with the formation of irregular chains which tangle together and cause the great increase in viscosity.

The continued interest of the petroleum industry in the possibility of turning H_2S from an undesirable constituent of refinery gases into a useful chemical material is widely indicated both in the scientific and in the patent literature. For example Murray[2] disclosed in his patent a process for recovering H_2S from the gases obtained in the course of distilling

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[1] Warren and Burwell: J. Chem. Physics, 3, 6 (1935).
[2] Murray: U.S. Patent No. 2,052,892 of 1936.

crude oil containing over 1% S. Murray also suggested that sulphur might then be recovered from the H_2S.

Bacon and Fanelli's paper[1] on the purification of sulphur appeared in 1942. After citing numerous examples of contradictory data in the prior work on various properties of sulphur they pointed out that these could largely be explained in terms of traces of impurities which might cause unexpectedly serious variations. The previously accepted methods for sulphur purification, including repeated crystallization from CS_2, repeated distillation, with or without vacuum, and other techniques were examined and found to be ineffective for rigorous purification. Finally a new method of purification was worked out and its effectiveness confirmed by exhaustive tests. The method was based on long-continued boiling of sulphur in the presence of a suitable oxide which should be sufficiently basic to react with inorganic or organic acids present and decompose persulphides. The preferred reagent for this purpose was magnesium oxide. Details of the method will be found later in this work, where the technique of purification is applied experimentally. Bacon and Fanelli's paper also provided a valuable test for the presence of minute traces of organic impurities in sulphur.

In 1943 Bacon and Fanelli[2] published their paper on the viscosity of sulphur. The profound importance of this

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[1] Bacon and Fanelli: Ind. Eng. Chem. 34, 1043 (1942).
[2] Bacon and Fanelli: J. Am. Chem. Soc. 65, 639 (1943).

work arises firstly from the fact that, for the first time, the viscosity values of molten sulphur were established over a wide range of temperatures with high accuracy and by methods that gave consistent and reproducible results. However, the paper goes beyond this achievement. It relates the experimental findings to the theoretical conception of the molecular structure of sulphur and its changes on heating, and the work of Warren and Burwell and their predecessors is shown to be supported by the results obtained. In addition the effect on viscosity of the presence of various impurities and reagents is given, and a chemical theory is provided which accounts for what were previously inexplicable variations in the viscosity of sulphur under certain conditions.

Bacon and Fanelli's research was undertaken because the two investigations of the subject by earlier workers had yielded irregular results. In particular the results previously obtained had varied when made with rising and falling temperatures respectively. Preheating the sulphur had also yielded different viscosity values. Bacon and Fanelli formed the opinion that these inconsistencies arose out of the continued presence of traces of some impurity in the sulphur used by the previous workers, despite their utmost efforts at purification. They found that the presence of even very slight traces of organic matter could result in irregular results. Accordingly the preparation of rigorously pure sulphur was an essential precedent to any further progress.

This pure sulphur was prepared by their special method referred to above which is fully described later.

With this purified sulphur, and with an improved capillary-tube apparatus, viscosity values were obtained which were reproducible, and were not affected by the prior heating or cooling of the sulphur. The values found differed from hitherto accepted figures. At 120°C the viscosity was found to be 12 centipoises, and on heating this fell to a minimum of approximately 7 centipoises at 157°C. Above about 160°C the viscosity rose steeply to a maximum of 932 poises at 186° - 188°C, and thereafter declined with further rise in temperature.

Bacon and Fanelli repeated their determinations using sulphur containing slight traces of organic matter, and proved that the viscosity of the sulphur was lowered if the sample was preheated, due to the formation of some reaction product of pronounced activity. This product could be gradually eliminated by repeated heating, with a corresponding shift of viscosity values towards the normal range.

The effect of adding SO_2, H_2SO_4, H_2S, NH_3 and amines, and the halogens, was investigated in further experiments. Hydrogen sulphide was found to have a profound effect on the viscosity. When it was passed into pure sulphur for 1½ hours while the temperature was being raised from 125° - 190°C the sulphur at no time reached the highly viscous stage, and it attained a maximum viscosity of only 0.90 poise

as contrasted with about 930 poises for untreated sulphur. Additional experiments with varied conditions and heating lent support to the view that the effectiveness of H_2S was due to the formation of some reaction product with the sulphur, rather than being directly due to the presence of dissolved H_2S. This led to the hypothesis that the active reaction products formed were the hydrogen persulphides. The same hypothesis could explain the effectiveness of the presence of traces of organic matter when sulphur is heated.

To test the validity of the hypothesis hydrogen persulphide was separately prepared and added to pure sulphur, and the viscosity over the same temperature range as before was determined with rising temperature. Despite much loss of persulphide by decomposition on heating the traces remaining were effective in greatly reducing the viscosity, and the sulphur did not pass through the usual viscous stage.

Of the other reagents tested sulphur dioxide and sulphuric acid were found to be ineffective as viscosity reducers. Ammonia was slightly effective, due (it was presumed) to the formation of minute quantities of hydrogen sulphide and hydrogen persulphide by reaction with the sulphur. Of the halogens bromine, iodine and chlorine were increasingly effective in that order.

After discussing and rejecting several prior explanations which had been advanced to account for the peculiar viscosity/temperature relationship of sulphur, Bacon and

Fanelli put forward a new theory based on the modern view of the molecular structure of sulphur. They accepted Warren and Burwell's work, which had shown the sulphur molecule to be an eight-numbered puckered ring, while the S_8 molecule persisted at temperatures "not too far above the melting point". They advanced the theory that the increase in viscosity of sulphur is due to the rupturing of the rings, forming chains which lengthen and which tangle with one another. Thus in liquid sulphur, between its melting point and approximately 160°C, the equilibrium S_8 (rings) $\rightleftharpoons$ S_n (chains) prevails. Near the melting point the S_8 rings greatly predominate. As the temperature reaches 160°C, however, with the rupturing of the rings the chains predominate and the viscosity rises rapidly, reaching a maximum at about 187°C as the chains increase in length. Thereafter the observed fall in viscosity to boiling point was explained as being due to shortening of the chains with rising temperature.

Since the high viscosity involved the polymerisation of sulphur in long chains, the effectiveness of hydrogen sulphide, of hydrogen persulphides, and of the halogens could be explained as a shortening of the chains, with the hydrogen or halogen atoms taking up terminal positions in the shortened chains, thus:

H-S-S-S ..... S-S-S-H

or I-S-S-S ..... S-S-S-I

The fact that these added materials persist so

strongly in the sulphur, despite heating, was adduced as additional evidence in favour of this view.

The work of Bacon and Fanelli in establishing so firmly the experimental data relating to the viscosity/temperature relationship of pure sulphur was immediately followed by the mathematical formulation of a quantitative theory by Powell and Eyring[1] for the equilibria, and also for the viscosity of molten sulphur, in the light of currently accepted views of the behaviour of long-chain polymers. This theoretical study was directly based upon Bacon and Fanelli's experimental results.

A further contribution to fundamental knowledge of the molecular structure of sulphur was made by Chia-Si Lu and Donohue[2] who in 1944 published the results of their studies of sulphur and various sulphur compounds by the method of electron diffraction. They confirmed that the S_8 molecule is a puckered ring, with an S-S distance of $2.07\text{Å} \pm 0.02\text{Å}$ and with the angle S-S-S equalling $105^\circ\ 2^\circ$. They discussed various possible molecular models that might satisfy these requirements, including a regular puckered ring, a "tub" form, a "cradle" form, and a "butterfly" form. The significance of these descriptions is apparent from the diagrams published in the paper.

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[1] Powell and Eyring: J. Am. Chem. Soc. 65, 648 (1943).
[2] Chia-Si Lu and Donohue: J. Am. Chem. Soc. 66, 818 (1944).

Armstrong, Little and Doak[1] sulphurized various higher olefines with the object of throwing light, by analogy, on the chemistry of rubber vulcanisation. When the reactions were carried out at moderate temperatures (approx. 120° - 140°) they found that the sulphur appeared to combine with the olefines without degradation or elimination of hydrogen sulphide. They suggested that cross links, apparently consisting of polysulphides, had been formed between olefine molecules.

The fact that liquid sulphur can be supercooled in bulk to about 50°C, was established by Fanelli[2]. In the form of droplets the liquid sulphur could, he found, be supercooled to room temperature. Fanelli determined the viscosity values of the supercooled liquid down to 50°C, and found that the nature of this was essentially similar to that of sulphur in the temperature range approximately 115° - 160°C.

McKinney, Mayberry & Westlake[3] investigated the action of sulphur on the residual extracts obtained in the refining of lubricating oils by modern solvent processes. These processes remove from the crude lubricating oil stock the unsaturated, sludging or gum-forming constituents, which

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[1] Armstrong, Little and Doak: Ind. Eng. Chem. 36, 628 (1944).
[2] Fanelli: J. Am. Chem. Soc. 67, 1832 (1945).
[3] McKinney, Mayberry & Westlake: Ind. Eng. Chem., 37, 177 (1945). (Portions of the work were disclosed in U.S. Patent No. 2,354,868 of 1/8/44 issued to McKinney and Mayberry).

can be recovered from the solvent as viscous naphthenic liquids. It was found that sulphur is only slightly soluble in these extracts; but on heating above 140°C a reaction takes place with evolution of H_2S. Experiments carried out with eight types of refining extracts from various sources showed that, by varying the proportions of sulphur and duration of heating, black asphalt-like products could be obtained with useful physical properties. In samples heated moderately there remained about 10% free sulphur, soluble in sodium sulphide, but reheating the products to 170° - 180°C caused the reaction to go further, with further hardening of the artificial asphalt formed.

In 1945 Bacon and Boe[1] published the results of their work on the production of H_2S by the reaction between sulphur and certain heavy hydrocarbons and methane respectively. They used a petroleum oil containing no fractions boiling below 290°C, and having the following characteristics :-

Gravity (°API)		20.5
Flash point (°F)		175
Saybolt Furol Viscosity (seconds at 100°F)		193
Bottom Settlings, plus water		0.3%
Pour point (°F)	Above	50

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[1] Bacon and Boe: Ind. Eng. Chem. 37, 469 (1945).

In preliminary experiments they found that 250°C was a suitable working temperature. At 200°C the reaction was slow and incomplete. At 300°C the reaction was faster than at 250°C but the yield of H_2S was not increased.

Bacon and Boe found that the minimum ratio of oil/sulphur which gave satisfactory results was 1 : 1. In their most successful experiments approximately 80% of the sulphur was evolved as H_2S. Working on a larger scale they heated 15 lbs. oil with 15 lbs. sulphur in a stainless steel vessel 12 inches in diameter and 19 inches deep, fitted with a vertical water-cooled reflux condenser. The vessel was fitted with a thermocouple and was heated in a brick oven by indirect heat from a gas burner.

The purity of the gas evolved as checked in some experiments by absorption in iodine solution. It was found that 99.9 - 100% was absorbed, and the H_2S was "of high purity and free of carbon disulphide, thiophene, and hydrolysable organic sulphides". The loss of weight of the vessel in the course of each experiment was taken as the weight of H_2S evolved, and this assumption was confirmed in some instances by analysis of the residue. Thus in respect of one run the following data were given:

Weight of oil	15 lbs.
Weight of Sulphur	15 lbs.
Time of heating	3 hours
Temperature	240° - 250°C

Loss of weight (Weight of H_2S evolved)	11.31 lbs.

These figures were checked by analysis of residue and it was found that the residue contained :-

	%
Free sulphur (CCl_4 Soluble)	1.99
Combined sulphur (CCl_4 Insoluble)	21.04
Oil and other substances soluble in CCl_4	20.43
Carbon and other substances insoluble in CCl_4	56.54

Thus the total weight of sulphur found in the residue was 4.29 lbs., indicating the evolution of 10.71 lbs., representing 11.38 lbs. H_2S.

The following table gives the results of three other runs:

(Weight of sulphur used in each of these runs was 15 lbs.)

Wt. of Oil, lbs.	Heating Time, Hours	Temp. °C	Loss of Wt. lbs.	% Loss of weight based on weight of S
10	7	220 - 251	8.31	55.4
15	1	240 - 244	6.19	42.2
15	5	240 - 255	12.06	80.4

Bacon and Boe used methane successfully in another series of experiments and stated that in the form of natural gas "it offers an excellent source of cheap hydrogen for producing H_2S by direct reaction". The reaction was preferably carried out in two stages, as follows :-

$$CH_4 + 4S \longrightarrow 2H_2S + CS_2 \quad (1)$$

$$CS_2 + 2H_2O \longrightarrow 2H_2S + CO_2 \quad (2)$$

The activity of a large range of catalysts was tested and much valuable information recorded. The best reaction temperatures were found to be 600° - 650°C for reaction (1) and 200° - 300°C for reaction (2), and the H_2S finally obtained was free from sulphur dioxide, carbon monoxide, oxygen or mercaptans. The carbon dioxide present could be removed by known methods.

Additional particulars in relation to the work done on the reaction between petroleum oil and sulphur, and suggested data for plant design, were embodied in a memorandum prepared by Boe[1]. The means of heating in small-scale experiments was an oil bath. The flask, fitted with a reflux condenser, was weighed before and after heating, and the loss of weight was taken as the weight of H_2S evolved. This procedure was repeated with various proportions of materials, times of heating, and temperatures. Experimental results varied from low yields, obtained at about 200°C or with an insufficient period of heating, to a yield of 83% of H_2S

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[1] Private communication from Texas Gulf Sulphur Company.

calculated on the sulphur taken. This yield was obtained when 80.1 g. of light fuel oil was heated with 30 g. sulphur for 5 hours at 250°C. In the larger-scale experiments, with a stainless steel reaction vessel, heavy fuel oil was used under varied conditions with analogous results. A maximum yield of 84.5% of H_2S, based on the sulphur was heated with 15 lbs. heavy fuel oil for seven hours at 220° - 249°C. Boe considered that 5 hours heating, with equal weights of sulphur and oil, and an operating temperature of 240° - 250°C, would give satisfactory results on a large scale, and that a yield of approximately 80% could be expected. With three hours heating the yield would be about 75%, all based on the weight of sulphur.

The residue was found to consist of a porous coke which inflamed spontaneously if exposed to the air when hot.

Boe made suggestions for the design of a possible large-scale plant based on these experimental results. The suggested plant consisted of large stainless steel kettles, analogous to the laboratory unit, heated over a brickwork furnace using oil or gas fuel. Three such vessels would give fairly continuous working, and a heating period of three hours was suggested. Each kettle would require a reflux condenser to return any hydrocarbons volatilised and to minimise sulphur losses. The provision of a manhole on the side of the kettle near the bottom was proposed for emptying out the residue at the end of each cycle. As an alternative it was proposed

that the vessel be lifted up bodily by a crane and the contents tipped out.

As an alternative to heating by burners it was suggested that the Dowtherm system might be used, utilising the vapour of a high-boiling substance as the heating medium in a suitable jacket. For purification of the gas (if required) a scrubber filled with activated charcoal or silica gel was suggested. Other proposals related to plant for liquefying the H_2S in cylinders by cooling and compression, and provision of the necessary buildings, services and equipment.

While Bacon and Boe's work was in progress Thacker and Miller[1] published their paper on carbon disulphide production. This dealt with the conditions required for optimum yield of CS_2 using methane and sulphur at approximately 700°C in the presence of catalysts. It was found that catalysts of the activated clay type were most effective. With activated alumina containing a small proportion of chromium oxide a yield of CS_2, representing over 90% of the methane charged, was obtained. Under the recommended conditions of working the process proceeded without appreciable side-reactions, according to the equation:

$$CH_4 + 4S \longrightarrow CS_2 + 2H_2S$$

The reactions of aliphatic hydrocarbons with sulphur were investigated by Rasmussen, Hansford and Sachanen[2] from

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[1] Thacker and Miller: Ind. Eng. Chem. 36, 182 (1944).
[2] Rasmussen, Hansford and Sachanen: Ind. Eng. Chem. 38, 376 (1946).

the special viewpoint of the production of olefines, diolefines, and thiophene. Using n-butane they obtained, by varying the working conditions, good yields of thiophene, butadiene, and n-butylene in various proportions. In this paper an interesting distinction was drawn between the differing course of the reaction at (a) 300° - 400°C, and (b) 600° - 650°C (the reaction temperature preferred for the purpose in view). It was pointed out that "if a hydrocarbon such as n-butane is bubbled through molten sulphur at a temperature in the range 300° - 400°C the exit gas stream will contain considerable amounts of H_2S but no olefines. Dehydrogenation has evidently taken place, but the unsaturated products have undergone secondary reaction with sulphur (or perhaps partially with H_2S) and largely remain in the molten sulphur. If the butane is passed into a zone of sulphur vapour at 444°C, and the mixed gases are heated together to about 600° - 650°C the product gases may contain appreciable amounts of butylene, butadiene, and thiophene, provided the reaction time is not too long". The following equations were suggested as possible stages in an "ideal case" where thiophene was the end product, together with H_2S :

$$C_4H_{10} + \tfrac{1}{2}S_2 \longrightarrow C_4H_8 + H_2S \quad (1)$$

$$C_4H_8 + \tfrac{1}{2}S_2 \longrightarrow C_4H_6 + H_2S \quad (2)$$

$$C_4H_6 + S_2 \longrightarrow C_4H_4S + H_2S \quad (3)$$

The work covered by this paper was carried out under exceptionally difficult corrosive conditions, and observations

of value in the choice of materials of construction were recorded.

In 1946 Fanelli[1] reported comprehensive work on the possibility of modifying the viscosity of sulphur. It will be recalled that in the course of prior work Fanelli and his colleagues had established the importance of small proportions of certain impurities in affecting the viscosity changes of sulphur on heating, and had worked out a method of preparing sulphur free from such traces. Fanelli was able to apply this knowledge to the converse problem of deliberately modifying the viscosity behaviour of sulphur, so as to render it more amenable handling and utilization in the liquid state.

Starting with H_2S as modifying reagent Fanelli found that this gas, when bubbled through molten sulphur in an open system, reduced the viscosity, but the reduction was limited by the fact that most of the H_2S remained in the gaseous state and "only a fraction dissolves in the liquid sulphur". Thus the effectiveness of H_2S increased with pressure. The addition of the hydrogen persulphides in liquid form to liquid sulphur in a closed system was also very effective. Heating sulphur in the presence of various hydrocarbons and their derivatives was shown by Fanelli to be effective through the mechanism of hydrogen sulphide and persulphide formation. For example when sulphur mined by the

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[1] Fanelli: Ind. Eng. Chem., 38, 39 (1946).

Frasch process, normally containing minute proportions of oil, was heated above 180°C sufficient H_2S and hydrogen persulphides were quickly produced to reduce greatly the viscosity of the sulphur. In this type of treatment repeated heating in an open system resulted in loss of these compounds with consequent recovery of higher viscosity values.

Fanelli repeated the work using chlorine, iodine, and bromine, which had been known to alter the viscosity of liquid sulphur. He found that of these three halogens chlorine was most effective, and sulphur containing 2% chlorine showed viscosity values mainly below 15 centipoises throughout the liquid temperature range. Iodine and bromine were also effective, and increasing concentrations of any of the three reagents gave lower values, tending towards a low limiting value. In open systems the effectiveness of the reagents was diminished due to their volatility, so that bromine and iodine under such conditions were more effective than chlorine. Fanelli also investigated the corrosion resistance of aluminium and of 18-8 and other stainless steels to mixtures of liquid sulphur with the halogens mentioned above, with a view to applying the results on an industrial scale.

Discussing the work Fanelli showed that it supported his interpretation of the viscosity changes of sulphur in terms of the opening of the puckered S_8 rings to give

polymerisable chains, which could be kept short by the presence of hydrogen or the halogens in terminal positions of the segments. In the case of iodine this theory appeared to be in conflict with the accepted view that sulphur and iodine cannot combine directly. Fanelli considered, however, that the great and rapid reduction in the viscosity of sulphur above 160°C, in the presence of traces of iodine, indicated that under these conditions some form of chemical combination does take place, and that it persists through a wide temperature range.

A valuable review article on the sulphurization of unsaturated compounds was published in 1946 by Westlake[1]. Although many of the reactions considered fall outside the scope of the present work the critical comment and discussion is of great interest.

Bryce and Hinshelwood[2] investigated the reactions between paraffin hydrocarbons and sulphur vapour. They considered the reactions to be approximately of the first order with respect to the hydrocarbon, and nearly independent of the vapour pressure of the sulphur. They also found that H_2S was the only gaseous product "formed in considerable amount". Ethane, propane, n-butane, and n-octane respectively were used in a series of experiments, and it was found that

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[1] Westlake: Chem. Reviews, 39, 219 (1946).
[2] Bryce and Hinshelwood: J. Chem. Soc. 136, 3379 (1949).

there was a great increase in the rate of reaction when the higher compounds were used. Analysis of the end-products indicated very little CS_2 or mercaptans and no thiophenes. Traces of acetylenes were found. Accompanying the gaseous products was a "dark-coloured involatile tar" which proved too intractable to be analysed. The general conclusion reached was that "the primary reaction for all the hydrocarbons is assumed to be the removal of a hydrogen atom, with the formation of alkyl and HS radicals".

In 1949 Panelli[1] published data on the solubility of hydrogen sulphide in sulphur in the temperature range 120° - 445°C. He used a special absorption bulb in which sulphur could be melted and held at the required temperature while H_2S was passed through. The H_2S dissolved was determined directly by increase in weight, due precautions being taken in relation to possible sources of error, such as variations of pressure and the replacement of the air in the bulb by H_2S. Panelli noted that sulphur which had been saturated at elevated temperatures evolved up to 90% of the absorbed H_2S when the bulb was kept closed during cooling to the point of solidification. If, however, the cooling took place more quickly to solidification, under atmospheric pressure, most of the absorbed gas remained in the solidified sulphur and on standing was slowly evolved over a period of

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[1] Panelli: Ind. Eng. Chem. 41, 2031 (1949).

days. Fanelli related this observation to his previous work on the subject (already discussed above) and considered that the long-chain hydrogen persulphides formed during the solution of H_2S in molten sulphur persist in the solid, and only slowly revert to H_2S and sulphur rings.

The results obtained by Fanelli showed that the solubility of H_2S in liquid sulphur increases with rising temperature, and is at an almost constant maximum between about 245° - 370°C. Thereafter the solubility declines, and above 390°C it falls away rapidly to its minimum value at the boiling point of sulphur. In the range of maximum solubility the weight of H_2S dissolved is 0.188 g./100 g. sulphur.

Finally Fanelli discusses the "conflicting and surprising results" obtained by a number of prior investigations of this and related subjects, and explains them as being due to the unwarranted assumption that the solubility of H_2S in liquid sulphur under the experimental conditions involved is so small that it can be ignored[1].

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[1] Certain additional references to prior work will be found in succeeding chapters where the context requires their mention.

CHAPTER TWO

E X P E R I M E N T A L

(a) MATERIALS AND REAGENTS

Lubricating Oil: The oil used was a highly refined lubricating oil prepared from a paraffin-base crude. It was free from additives and was purchased to the following specification:

Gravity (A.P.I.)		27.5 - 29.5
Flash-point (Cleveland Open Cup).		460°F Minimum
Viscosity (Saybolt) at	100°F	530
"	130°F	244
"	210°F	66
Carbon Residue		0.43% Maximum.

In the reports which follow this material is referred to whenever the term "oil" is used without special description or qualification.

Sulphur: Except where otherwise mentioned the sulphur used was the chemically pure grade, in the form of rhombic crystals, manufactured by British Drug Houses Ltd. Numerous samples of so-called pure flowers of sulphur were tested and found to contain organic impurities that were likely to cause erratic observations in some parts of the work. Accordingly this material was not used.

For certain parts of the investigation it became necessary to use sulphur rigorously free from traces of organic impurities. As no such material was available it was prepared as part of the present study, as described later. The starting material used for this purpose was high-purity medicinal grade sulphur (African Explosives and Chemical Industries Ltd.), sold on the following typical analysis:

Moisture at 105°C	0.10%
Total Residue on burning (assisted by external heat)	0.09%
Organic Residue	0.01%
Chlorides as Cl	18 parts per million
Arsenic as As_2O_3	0.3 part per million
Selenium as Se	0.1 part per million
Sulphur (by difference)	99.8%
Matter insoluble in CS_2	Negligible.

Paraffin Wax: This was a highly-refined grade of M.P. 52°C prepared for use in the food industries. It was free from sulphur and oil.

Oxygen, Chlorine and Ammonia: These were cylinder grade gases.

Nitrogen: This gas was required to be free from traces of oxygen, which might react with the sulphur or oil under experimental conditions. Nitrogen available commercially

did not fully meet this specification. A special supply of pure nitrogen was obtained from the purifying plant used for filling electric lamps.

Spent Oxide: This was the crude product obtained from the purifier section of the Port Elizabeth and Johannesburg gas-works after repeated re-vivication and re-use.

Spent Oil: This was lubricating oil, of the same original specification as given above, drained from an engine after use during 1,000 miles travel.

Lead Acetate Solution: (Qualitative reagent for testing for presence of H_2S): This was prepared by pouring a saturated solution of lead acetate into 100 ml. of normal sodium hydroxide solution until the precipitate just failed to dissolve on vigorous stirring. Test paper was prepared by dipping a strip of filter paper in this solution. It was used while still damp.

Potassium Iodate Solution: This was used as primary standard in the standardisation of the thiosulphate solution used in iodometric estimations. It was prepared by drying potassium iodate crystals at 120°C, cooling in the desiccator, and weighing directly. A $^{N}/10$ standard solution was made up with 3.567 g./litre, 15.0 g. potassium iodide being added before final dilution to this volume.

Cadmium Chloride (Alkaline): This solution was made up to

contain 32.0 g. anhydrous cadmium chloride/litre. To each litre of this solution were added 600 ml. of ammonium hydroxide solution (S.G. 0.880).

Cadmium Chloride (Acid, for selective precipitation of H_2S in presence of mercapatans): This was made up by dissolving 100 g. anhydrous cadmium chloride in 1 litre water and then adding 10 ml. concentrated hydrochloric acid. The proportion of acid is critical for accurate results. If it is too low the mercaptans are precipitated with the sulphides. If it is too high H_2S is evolved and lost.

All other reagents were made up in accordance with customary analytical practice, except where otherwise indicated in specific experiments.

(b) ANALYTICAL METHODS.

In view of the special nature of some of the analytical problems involved it was necessary to make a study of analytical methods and procedures that appeared to be adaptable to the conditions.

The main analytical problems encountered may be grouped as follows:

(A) Checks on the purity of the sulphur used.

(B) Estimation of sulphur in presence of certain petroleum products.

(C) Estimation of H_2S evolved, as an indication of the yield from various mixtures and procedures.

(D) Estimation of the purity of the H_2S evolved under optimum conditions.

These problems were studied firstly in the light of conventional practice. Where such methods were not suitable, or could not be satisfactorily adapted, a study was made of original papers in the particular field.

The findings may be summarised as follows:

(A) It became apparent that the purity of the sulphur used could be of great importance in some of the experimental investigations, and that samples of sulphur which could validly be classified as pure by usually accepted standards might yet

contain traces of impurities which could affect the results. For example Bacon and Fanelli[1], in their paper on the viscosity of sulphur showed that the sulphur used by prior workers, though repeatedly purified by accepted methods, nevertheless retained traces of organic impurities which caused erratic and unreliable behaviour in the viscosity determinations. In another paper, Bacon and Fanelli[2] gave details of a new method of sulphur purification, by which such impurities could be eliminated. They also gave particulars of a new test by which the presence and concentration of organic impurities could be detected and estimated.

By means of this test it was possible to maintain a check on the purity of the sulphur used in the present work. The test procedure is described later in this work.

(B) The estimation of sulphur and sulphur compounds in the presence of petroleum products has been the subject of numerous studies during the past two generations, and it remains a matter of great importance in petroleum technology. The generally accepted methods fall broadly into two classes, namely:

(1) Methods used to establish arbitrary standards of purity in specific products. These include, for example, such

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[1] Bacon and Fanelli: J. Am. Chem. S. 65, 639 (1943).
[2] Bacon and Fanelli: Ind. Eng. Chem. 34, 1043 (1942).

tests as the "Doctor" test which is primarily intended for the detection of mercaptans in motor fuel, paraffin oil and similar products. The specification of the test (I.P.-30/44) lays down directions for the preparation of the "Doctor" solution (sodium plumbite) and its use in conjunction with flowers of sulphur, and directs how precipitation or discolouration in samples tested under certain specific conditions may be reported in such terms as "passes", "positive", "very slight", and the like. Another example is the "corrosive sulphur" test (I.P. - 64/45) in which the corrosion of copper strips under specific conditions is interpreted in a specified manner in relation to the sulphur content of certain petroleum products, with a view to their suitability in ultimate use. Many similar tests are to be found in the literature, and in the testing procedures of such bodies as the A.S.T.M.

These methods were unsuitable for the present purpose.

(ii) Methods of analysis yielding quantitative results of general application. These are the methods with which the present work is concerned. The main alternative methods may be summarised as follows:

(I) Eschа method: This involves fusion of the sample with Eschа mixture (magnesium oxide and sodium carbonate). It is unsuitable for use with the materials encountered in the present investigation, due to possible volatilisation.

(II) Carius method: This well-established method for estimating sulphur in the presence of organic compounds is based on the oxidation of the sample by nitric acid when heated

in a miniature pressure vessel formed by sealing a strong glass tube. When thus treated the sulphur and sulphur compounds present are oxidised to sulphates and are estimated by means of barium chloride.

In spite of its wide applicability in other work this method of sulphur estimation cannot be reliably used where aliphatic sulphides are present, as sulphones are formed by the action of the nitric acid and may remain undecomposed at the end of the experiment.

(III) Lamp Method: This method is widely used for the determination of sulphur in petroleum compounds that are suitable for burning by means of a wick in a suitably designed lamp system in which the SO_2 in the combustion gases is absorbed in a suitable alkaline solution and precipitated, after oxidation, as barium sulphate. The standard apparatus and procedure are specified by the A.S.T.M. (Specification D 90 - 41T) and by other authorities. Improved lamps and procedures have also been described in the literature, for example by Edgar and Calingaert.[1]

The lamp method, though primarily used with products that are easily fed through the wick (e.g. paraffin oil and other light products) can be used with somewhat heavier materials by first diluting them with a diluent solvent free from sulphur, or of known sulphur content.

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[1] Edgar and Calingaert: Ind. Eng. Chem. Analytical Ed., 2, 104 (1930).

The difficulty in applying this method in the present work arose from the fact that the samples might contain free carbon and sulphur in suspension which would upset the working of the lamp.

(IV) Methods based on combustion to SO_2 at atmospheric pressure: These methods depend for their accuracy on the promotion of complete combustion by a large heated surface, such as quartz packing.[1] The SO_2 may be absorbed in acidified hydrogen peroxide solution and the increase in acidity titrated, as in the well-known Monier-Williams method. This method would have been used if a bomb had not been available.

(V) Bomb method: In this method the sulphur-containing sample is oxidised in a bomb by means of sodium peroxide at atmospheric pressure or oxygen under high pressure. The products of oxidation are collected in water or sodium carbonate solution, oxidised completely to sulphates by means of bromine water, and precipitated as barium sulphate. The oxygen bomb's construction is closely similar to that of the bomb used for calorimetric work. For a bomb of 300-350 ml. capacity the oxygen pressure recommended by the A.S.T.M. is not less than 25 atmospheres.

The oxygen bomb method is accurate and of general application to organic materials. A study of all the alternatives led to the adoption of this method as the standard

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[1] An improved method has been described by Hagerman: Ind. Eng. Chem. 19, 381 (1947).

procedure in the present work. Specific details in regard to the procedure are given later.

(C) A study of the analytical work in this field revealed an unusual variety of methods relating to the quantitative estimation of H_2S evolved from various experimental mixtures and procedures. As far as could be ascertained no two workers reported using the same methods of H_2S estimation. For example Scudder and Lyons[1] absorbed the gas directly in a solution of cadmium chloride. Nellensteyn and Thoenes[2] used an absorption system containing iron oxide and $CaCl_2$, and estimated the H_2S by direct increase in weight of the absorption vessel. Bacon and Boe[3] estimated the H_2S evolved by noting the loss of weight of the reaction vessel in the course of the experiment.

Examination of these and other methods indicated certain difficulties. Direct precipitation of the H_2S as cadmium sulphide was too cumbersome when applied to the estimation of moderately large quantities of gas, due to the large volumes of cadmium chloride solution required, and the chances of error in dealing with the bulky precipitates from the absorption vessels. These problems could, however, be overcome by the use of a separate absorption solution followed

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[1] Scudder and Lyons: Proc. Indiana Acad. Sci. 40, 185 (1931).
[2] Nellensteyn and Thoenes: Chem. Weekblad. 29, 582 (1932).
[3] Bacon and Boe: Ind. Eng. Chem. 37, 469 (1945).

by precipitation of an aliquot portion by means of cadmium chloride solution. This is the best of the gravimetric methods and was used in some of the present work.

The method of absorption by active forms of iron oxide (which is based in principle on the gasworks method of purifying coal-gas containing H_2S) is satisfactory when it is followed by a sensitive guard vessel as a precaution against losses. The difficulty, however, arises in ensuring the free passage of the gas through the oxide mass, which tends to pack and resist the gas flow. Attempts were made to minimise this difficulty by mixing the oxide with carriers of various types, but the resistance to gas flow was still too great.

It is possible that Nellensteyn and Thoenes used iron oxide absorbent in the form of granules, which would lessen this difficulty. However the best oxide absorbents which were obtainable in the course of the present work suffered from this drawback, and it was felt that their use would introduce unnecessary risks of inaccuracy into the procedure.

Of the long-established methods of H_2S estimation the most well-known is estimation by means of iodine. This is accepted by all authorities consulted as an accurate method, subject to the limitation that the H_2S content of the solution must not exceed 0.04%, thus avoiding the reversal of the reaction:

$$I_2 + H_2S \rightleftharpoons 2HI + S$$

This limitation of concentration rendered the direct absorption

and estimation of H_2S in fairly large preparations too inconvenient for regular use. However it was felt that the facility and accuracy of estimations using the iodine method could be retained if the method were used in conjunction with a suitable intermediate absorption solution.

A procedure of this type is that given by Snell and Biffen[1] which was used satisfactorily with modifications to suit the working conditions. The original method is intended for the estimation of sulphides or hydrosulphides in solution. Iodine solution is added in excess to the sample, and the solution is rendered acid in reaction. The excess iodine is titrated with sodium thiosulphate. To adapt this method to the requirements of the present work, the H_2S evolved experimentally was absorbed in a solution of NaOH, with suitable precautions against loss. In addition to the results obtained by the iodometric method certain sulphide solutions were estimated by the zinc sulphate precipitation method. This method has been largely used in the leather and other industries for the estimation of sulphide in the presence of other contaminants. It depends on the titration of the solution with standard zinc sulphate in the presence of a specific concentration of ammoniacal ammonium chloride solution which prevents the precipitation of zinc hydroxide.

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[1] Snell and Biffen: "Commercial Methods of Analysis", First Ed., p.171, McGraw-Hill, New York.

The absorption solutions were titrated in this manner with the use of lead acetate as an outside indicator. Details of both procedures will be found later in this work.

(D) Portions of the experimental work were directed primarily to finding suitable proportions of sulphur/oil, and suitable operating conditions, to obtain reasonable yields of H_2S. At the same time it was considered desirable to estimate the purity of the H_2S produced.

The method used for such estimations in prior work was mainly direct absorption in iodine solutions. However it was considered desirable to study what additional methods were available for a more definite differentiation of such possible impurities as mercaptans.

A study of the literature yielded several papers bearing on this and allied problems. The work of Faragher, Morrell and Monroe[1], and of Bell and Agruss[2] provided analytical schemes for various mixtures of organic sulphur compounds. The relevant portions of these methods were used as a guide in analysis, with necessary modifications. Details are given in conjunction with the respective experiments concerned.

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[1] Faragher, Morrell and Monroe: Ind. Eng. Chem. 19, 1281 (1927).
[2] Bell and Agruss: Ind. Eng. Chem., Analytical Ed., 13, 297 (1941).

(c) BEHAVIOUR AND PROPERTIES OF SULPHUR/OIL MIXTURES.

A supply of oil sufficient for the entire work was bulked and thoroughly mixed. Initial experiments were undertaken to confirm that the oil was free from low-boiling fractions which would render it unsuitable for use at a later stage.

50 ml. oil were heated in a distilling flask of 250 ml. capacity, fitted with thermometer. The flask was carefully heated in an air-bath, the side-tube being connected to a watercooled condenser. Observations were made at 50°C and at each additional 50°C thereafter till 350°C. At no point was any liquid distilled in this distillation range. Above about 270°C slight fumes were noted, which were inflammable. It was concluded that no volatile fractions were present that would hinder later work.

The oil was then tested for the presence of sulphur and sulphur compounds. 25 ml. oil were diluted with 25 ml. pure benzene, free from sulphur, and the mixture was thoroughly shaken with approximately 50 g. mercury. The surface of the mercury was not noticeably darkened, and no separation of sulphide occurred.

To test for the presence of H_2S and mercaptans in the oil 10 ml. thereof were shaken with an equal volume of alkaline cadmium chloride solution. The oil was allowed to rise to the top of the solution. There was no precipitate.

Finally 25 ml. of oil were heated in a beaker to 250°C and held at this temperature for fifteen minutes, while lead acetate test paper was held close to the surface. There was no darkening of the paper.

Preliminary observations of the behaviour of a mixture of oil and sulphur on heating were then made. Approximately equal weights of oil and sulphur were mixed by shaking in a large test-tube. It was noted that at room temperature portions of the sulphur remained suspended for several minutes before settling.

The test-tube was carefully heated over a burner, with mixing, the temperature being noted frequently. As the temperature rose a portion of the sulphur appeared to go into solution. At approximately 115°C the sulphur melted. At approximately 155°C evolution of H_2S could be detected by lead acetate paper and also by smell. With further heating the mixture darkened and evolution of H_2S increased. The experiment was discontinued at 300°C, when the contents of the tube consisted of a carbonaceous mass, similar in appearance to asphalt.

The observation that a portion of the sulphur appeared to dissolve in the oil was checked in a confirmatory experiment. The previous experiment was repeated, up to the point where the sulphur had all melted. The mixture was thoroughly shaken and allowed to stand, when the remaining sulphur formed a well-defined pool below the clear oil. The whole was then allowed to cool slowly to room temperature,

when it was found that crystalline sulphur was deposited from the oil layer. The crystals were elongated and extended mainly vertically from the solid layer that had previously formed the pool of surplus sulphur below the saturated oil. This observation was noted for further study at a later date when the crystal form could be determined by optical or other physical measurements.

As a guide in the planning of further work, it appeared desirable to repeat this experiment on a quantitative basis and determine the solubility of sulphur in the oil at a suitable temperature. In choosing the temperature for the determination, the main requirements were that it should be higher than the melting-point of the sulphur while yet below the figure at which reaction between the materials appears to occur. The temperature finally chosen was 125°C.

The solubility of sulphur in the oil at this temperature could not be determined by customary methods, and it was necessary to devise a method using the oxygen bomb. 50 g. oil were heated to 130°C in a Pyrex beaker. In a separate beaker 20 g. sulphur (constituting a large excess) were carefully melted, heated to the same temperature, and mixed with the oil with thorough stirring. The mixture was placed in a thermostatically controlled electric oven and allowed to cool to 125°C, and to reach equilibrium. The excess sulphur settled in a pool at the bottom of the beaker, leaving a clear, saturated solution above.

A sample of approximately 2 g. of the clear saturated

solution was rapidly decanted (while still in the oven) into a previously tared silica crucible which had been left in the oven to await this operation. The sample was allowed to cool and was weighed. Its sulphur content was then determined by the oxygen bomb method.

The apparatus used was a Mahler-Cook bomb, of 650 ml. capacity. The weighed sample of saturated oil, contained in a silica crucible as mentioned above, was placed in the bomb, and arranged for firing by means of pure iron wire approximately 7 cm. in length, coiled in a spiral and dipping into the sample. 5 ml. distilled water, containing 0.5 g. pure sulphur-free sodium carbonate, were also placed in the bomb, which was closed and sealed by means of lead wire. Oxygen from a cylinder was slowly admitted into the bomb (which was at the same time checked for leaks) until the pressure reached 25 atmospheres. The valve of the bomb was closed, and it was disconnected from the cylinder and placed vertically in a container of cold water. The firing electrodes were connected to a 12 volt battery, and the sample was fired. Thereafter the apparatus was allowed to stand for 20 minutes, and was removed from the water after which the pressure was slowly released through the valve. The bomb was opened carefully, and the inner surface and cover were carefully and repeatedly washed. The washings and the solution from the bomb, totalling about 250 ml., were filtered with the usual precautions, acidified with 2 ml. concentrated HCl, and any

sulphites present were oxidised by the addition of 10 ml. saturated bromine water. The solution was brought to the boil, and 10% barium chloride solution was added with stirring till present in slight excess. The precipitated barium sulphate was filtered off and ignited in a Gooch crucible in the usual manner and finally weighed.

Found: Solubility of sulphur in oil at 125°C (by oxygen bomb method):

7.01 g./100 g. saturated oil.

The determination was repeated, using a different procedure which may be termed the "substratum method". 37.10 g. oil were heated to 130°C in a Pyrex beaker and 13.93 g. sulphur (constituting a large excess) were added carefully. After shaking to facilitate solution of the sulphur the mixture was allowed to cool to 125° and attain equilibrium at this temperature overnight in a thermostatically controlled oven. The next morning 25 ml. substratum solution (the preparation and nature of which are described in the following Section) were preheated to 125°C and poured into the beaker, which was left in the oven for a further two hours to allow stratification to be clear and complete. The heating element was then switched off, and the beaker was allowed to cool to room temperature before being removed. The surplus sulphur now formed a solid layer below the substratum liquid while the oil floated on top. The oil and substratum were poured off, together with any suspended crystals that had been formed in the oil while cooling. The

solid lower layer of surplus sulphur was washed free of oil by means of petroleum ether which had previously been saturated with sulphur at room temperature. The "disc" of sulphur was removed from the beaker by very gentle warming and inverting, washed with water to remove traces of substratum solution, dried, washed again with saturated petroleum ether, dried again and weighed. By difference this gave directly the weight of sulphur which had been dissolved in the oil at the temperature of saturation. It should be noted that in carrying out this estimation any globules of sulphur which may fortuitously become separated from the lower pool should be weighed with the "disc" when solidified. They are readily distinguishable both by their shape and by the fact that they are deposited well below the oil layer. In contrast, any dissolved sulphur deposited as the oil layer cools has a fine crystalline structure. It is never deposited below the oil layer, and is readily poured off with the oil.

An alternative technique may also be used. After stratification into the three layers has taken place the saturated oil layer (still at 125°C) is removed by means of a large-bore pipette. In doing this portions of the substratum layer just below the oil should also be taken with the latter to ensure complete removal of the oil. Before use the pipette is warmed to 125° to avoid chilling of the oil when it is introduced. By this technique crystallisation of the sulphur in the oil layer is completely avoided. The remaining steps are as already described, except that for

added convenience any globules of separated sulphur may be re-fused with the "disc", if so desired, before final washing drying and weighing.

Found: Solubility of sulphur in oil at 125°C (by substratum method): 7.13 g./100 g. saturated oil.

Observation of the behaviour of the oil and sulphur on heating was now repeated with known quantities of the materials. 50 g. oil were weighed in an evaporating dish. 10 g. sulphur were added and stirred with a glass road. The mixture was heated over a burner and asbestos gauze, with frequent stirring. At approximately 120°C the sulphur appeared to have melted, and the mixture was vigorously stirred in order to dissolve as much sulphur as possible. It was observed that the remainder of the sulphur formed a molten pool below the oil. At this temperature the sulphur pool was yellow and mobile.

Heating was continued, with stirring, and at approximately 150°C a faint smell of H_2S could be noticed. At approximately 160°C lead acetate test-paper was darkened.

During the heating it was observed that the pool of sulphur underwent its characteristic increase in viscosity[1],

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[1] To avoid repetitive descriptions the terms "viscous form" or "viscous state" will henceforth be used, and where so used should be taken to refer to that characteristic, and rapid, increase in viscosity which takes place normally when sulphur is heated between 163°C and 188°C. This temperature range will accordingly be termed the "viscous range" or "viscous stage".

with the result that mixing became difficult. The oil was also becoming darker.

Heating was continued, and at approximately 230°C H_2S was being evolved at a sufficient rate to cause slight effervescence. Stirring was not effective in dispersing the sulphur uniformly through the mixture, and it remained largely at the bottom. The portions dispersed took the form mainly of fairly large elongated globules which could be observed, after stirring, on the sides of the dish and on the rod, surrounded by oil.

The temperature was allowed to rise to 280°C and the evolution of gas continued, while the mixture became thicker and uneven in texture due to the formation of agglomerations, apparently of a carbonaceous character. The layer nearest to the bottom of the dish became too hard to stir and heat conduction became inefficient. Finally the temperature was raised to 300°C for five minutes. At this stage H_2S evolution had become very slow, and the experiment was concluded by an examination of the residue after cooling to room temperature. The bottom layer was found to be of a dense carbonaceous character, and could be loosened only by breaking. The remainder of the residue consisted of a crumbly mass of asphaltic-looking matter, dispersed in agglomerated form in the less viscous portions of the residue.

It was observed that as heating continued and the temperature of the mixture rose above 270°C light-coloured fumes were evolved, which were considered to be hydrocarbon

break-down compounds. The fumes were inflammable. The time taken from the moment of first evolution of H_2S to the point where heating was stopped was 2½ hours.

The experiment indicated the importance of correlating the physical and chemical characteristics of sulphur with the phenomena observed. It was also noted that the conditions for heat transfer in the latter part of the experiment were very unsatisfactory, due to the formation of a dense layer of semi-solid material on the bottom of the vessel. The impression was formed that the presence of the viscous pool of sulphur at the bottom of the dish appeared to contribute to these unsatisfactory conditions.

To form a more reliable opinion on the behaviour of the sulphur pool and the oil respectively during heating a series of experiments was undertaken. Approximately 10 ml. oil and 5 g. sulphur were carefully heated to 125°C in a test-tube, with frequent stirring by means of a thermometer immersed in the sulphur. It was found very difficult to avoid local overheating of the test-tube, and when this occurred a darker layer of sulphur, consisting presumably of the viscous form, could be seen.

Whenever the mixture was agitated the sulphur dispersed in the form of droplets in the oil. When agitation stopped the droplets fell to the bottom and the sulphur pool was re-formed below the oil.

As the mixture was heated further there was slight

darkening, but no increase in viscosity till approximately 160°C, above which temperature the viscosity of the sulphur layer increased rapidly, with darkening. Agitation was ineffective at this stage in dispersing the sulphur even temporarily in the oil. At the same time the smell of H_2S became noticeable, and lead acetate paper was darkened.

Heating was stopped at 180°C. The mixture was allowed to settle and the oil layer was poured off as quickly as possible. Much of the viscous sulphur was found at the bottom of the tube, while a portion was carried out, in the form of large globules, by the oil.

It was thus apparent that adequate intermixture of the oil and sulphur layers, even of a temporary character, could be expected only while the sulphur is a mobile liquid. Furthermore it was clear that any method of reacting the materials would be unsatisfactory if it involved heating the oil and sulphur simultaneously from cold without special precautions.

As an initial improvement on this method the experiment was repeated, but the oil and sulphur were pre-heated separately to 125°C before being mixed. The surplus sulphur, after saturation of the oil, fell to the bottom to form a clear pool of yellow liquid. Thereafter heating above 160°C caused the same changes as before.

It was considered desirable to ascertain whether the abovementioned difficulties, encountered in heating, were

characteristic only of the particular mixture used, or whether the behaviour of sulphur when heated with other hydrocarbon materials was similar. The lastmentioned experiment was therefore repeated with the exception that refined paraffin wax (M.P. 52°C) was substituted for the oil. Both the paraffin wax and the sulphur were preheated to 125°C before mixing. As before the sulphur formed a yellow pool below the wax, and on further heating behaved as in the previous experiment.

As a result of these observations an improved technique was introduced.

In an evaporating dish 50 g. oil were weighed and heated on an asbestos-gauze mat to 130°C. 10 g. sulphur were weighed separately. Of this quantity 1 g. sulphur was added to the oil with stirring. The mixture was heated and H_2S evolution was noted at approximately 170°C. No sulphur fell to the bottom of the dish, nor was a viscous layer formed. The temperature was allowed to rise to 235°C, and a further 1 g. sulphur was added, with stirring. The mixture was heated further to 250°C and a further 1 g. sulphur was added. These additions resulted in such a vigorous evolution of gas that stirring for sulphur dispersion proved unnecessary. For the remainder of the experiment the temperature was taken up to 280°C, and the rest of the sulphur was added in 1 g. lots at intervals of ten minutes. Thereafter the temperature was held at this level

until evolution of H_2S became very slow. The total time from the adding of the first portion of sulphur till the end of the experiment was 2¾ hours.

At no point was the formation of a viscous layer of sulphur noted. Scraping with a glass rod served to keep the bottom of the dish sufficiently clear to maintain heat transfer.

When the dish was cooled to room-temperature the residue was found to be nearly free from hard particles of carbon and consisted almost entirely of asphaltic material in agglomerated lumps, suspended in oily liquid. When rubbed the lumps readily dispersed in the oil, with the formation of a material similar in appearance to a thin asphalt.

(d) A SUBSTRATUM METHOD FOR THE SEPARATION OF SULPHUR/OIL LAYERS.

In order to form a more complete opinion as to the initial mixing problems likely to be encountered in a process in which sulphur is heated with oil, with the primary object of H_2S evolution, it was considered desirable to observe the stratification of the liquids at a temperature below the point of initial evolution of H_2S. As a result Kruyt's observation[1] that liquid sulphur did not mix with paraffin wax at any point below the reaction temperature was found to be correct both in respect of paraffin wax and of the petroleum oil used in the present work, with the reservation, however, that the hydrocarbon phase of the mixture must be saturated with sulphur at the temperature of observation.

As the literature yielded no suitable method for the convenient separation of the upper layer (paraffin wax, oil, or the like) from the lower pool of molten sulphur a new method was worked out experimentally. It is reported for the benefit of future workers both in this field and in other fields where a similar technique may be useful.

The principle underlying the method was as follows: If, under the conditions of the molten sulphur/oil system there is added an additional liquid component (henceforward

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[1] Kruyt: Z. physik. Chem. 64, 486 (1909).

referred to as the substratum) of greater density than the oil, but lower density than the liquid sulphur, then the oil should form an upper layer, and the sulphur a lower layer, with the substratum separating them. Under ideal conditions this separation would be sharp and complete. Such a substratum liquid would need to have the following characteristics:

(i) Its boiling point must be above the working temperature.

(ii) It must not react with either the sulphur or the oil at working temperature.

(iii) Its viscosity under experimental conditions must be low enough to allow ready settlement of the liquid sulphur.

(iv) It must be stable at the working temperature and must not mix with, or dissolve appreciable quantities of either the oil or the sulphur.

(v) It must be readily separated from the other components at the final stages of the experiment.

Based on many exploratory experiments the following standard method was established for testing the suitability of likely substratum materials of suitable boiling point :-

(i) In a large test-tube equal quantities of oil and of the proposed substratum were heated to-

gether to 125°C, mixed thoroughly and allowed to stand. Any substratum which mixed with, or formed an emulsion with, the oil, was rejected.

(ii) If clear separation occurred the contents of the test-tube was reheated to 125°C and held at that point. In a separate test-tube a quantity of sulphur, in excess of that required to saturate the oil, was melted, heated to 125°C, and poured into the oil and substratum with mixing. The test-tube with the three components was allowed to stand in an oven previously heated to 125°C, and it was noted whether clear separation occurred, and whether the surplus sulphur settled satisfactorily as a clear liquid pool. Any substratum not satisfying these requirements was rejected.

(iii) Where the above observations were satisfactory the test-tube (containing a clear upper layer of oil floating on a middle layer of clear substratum which was underlain by a clear pool of molten sulphur) was allowed to cool to room temperature, and the behaviour of the substratum was observed.

(iv) Thereafter, if necessary, special methods were devised to improve the behaviour of the substratum as much as possible, as indicated in the reports of the respective experiments.

As it appeared likely that concentrated aqueous solutions of suitable inorganic salts would have some of the required properties, saturated solutions of sodium chloride, calcium chloride, and magnesium chloride respectively were prepared at 25°C, and tested by the standard procedure described above. Observations were as follows :-

SODIUM CHLORIDE - There was no clear separation of the oil from the substratum, due apparently to crystallisation at the interface.

CALCIUM CHLORIDE - The substratum clouded slightly. The viscosity was too high for the liquid sulphur to settle completely.

MAGNESIUM CHLORIDE - The substratum remained clear but the viscosity was too high for the sulphur to settle satisfactorily.

Of the three the magnesium chloride substratum approached nearest to the requirements, but did not fully satisfy them.

Glycerol (S.G. 1.260) was next tested by the standard procedure. Although glycerol reacts with sulphur at elevated temperatures[1] it was stable under the experimental conditions.

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[1] Lawrie: "Glycerol and the Glycols" p. 215 states that glycerol and sulphur react at 290-300°C to give allyl mercaptan and diallyl hexasulphide.

It also complied with the remaining requirements, until cooled. On cooling the glycerol substratum clouded, with the formation of a white dispersion presumably of colloidal sulphur, due to slight solubility of sulphur in glycerol at the working temperature.

Lactic acid (80%) was tested by the standard procedure and complied with all requirements till cooled. On cooling a white dispersion formed, presumably colloidal sulphur.

The experiments with glycerol and lactic acid substrata respectively were repeated, but instead of cooling gradually, an excess of cold water was added to the substratum by pipette. The colloidal dispersions formed as before. The experiments were again repeated, with the addition of an excess of cold, concentrated, hydrochloric acid as cooling medium. The colloidal dispersions formed as before.

The experiment with glycerol as substratum was repeated, but while the contents of the test-tube was at 125°C the upper layer of oil was pipetted off. Ethyl alcohol (96%) was then added cautiously to the substratum until it cooled to room temperature. Much of the alcohol evaporated in the first stages of this addition, but by constant replacement there remained, in the cooled mixture, alcohol approximately equal to the volume of the glycerol substratum. No cloud of colloidal sulphur formed.

The experiment with lactic acid as substratum was now repeated, and ethyl alcohol was used in the same manner as

coolant and diluent. It was equally effective in preventing the formation of the dispersion.

The effectiveness of ethyl alcohol was considered to be due to solution of the traces of sulphur which would otherwise be precipitated on cooling[1]. However this procedure could not be regarded as satisfying the requirements originally postulated, since it did not avoid the initial error due to the solution of traces of sulphur in the substratum.

In finding the answer to this problem many expedients were tried unsuccessfully. Finally it was decided to investigate whether the addition of magnesium chloride solution (which had remained free from sulphur in the earlier experiments) might prevent the solution and subsequent dispersion of sulphur in the glycerol or lactic acid.

The experiment in the glycerol as substratum was therefore repeated, but instead of dilution with ethyl alcohol the substratum was diluted by the addition of approximately half its volume of an aqueous solution of magnesium chloride, saturated at 25°C. No cloud of colloidal sulphur formed, and the substratum remained clear on standing. The same result was obtained when lactic acid was used under similar conditions.

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[1] Although not commonly regarded as a sulphur solvent, ethyl alcohol dissolves, at 25.3°C, 0.052 g. rhombic sulphur per 100 ml. solution (Yost & Russell: "Systematic Inorganic Chemistry of the Fifth and Sixth Group non-Metallic Elements", p. 279, Prentice-Hall, New York).

Although both glycerol and lactic acid thus gave satisfactory results with this procedure, it was decided to choose glycerol for the remaining work on account of its ready availability in a state of high purity and its neutral character.

A mixed substratum was prepared by adding one part by volume of a solution of magnesium chloride saturated at room temperature to two parts by volume of glycerol. This mixture was tested by the standard procedure originally outlined, and was found to satisfy all requirements excepting that its boiling point was too low. In a further series of tests it was confirmed that, to provide a margin of safety, not less than 30% by weight of magnesium chloride solution must be present in the mixture. It was found that by saturating the magnesium chloride solution at 100°C its initial boiling point could be raised to 133°C at 760 mm. This solution contained 42.2% $MgCl_2$. When cooled to room temperature crystals were deposited, but if the hot saturated solution was mixed with the glycerol and then cooled no crystals were deposited. These observations provided the data for making up the final substratum. The magnesium chloride solution was made up at the above concentration and temperature, and 43 g. were mixed with 86 g. glycerol and allowed to cool naturally. The substratum was clear and remained stable under the experimental conditions. It gave sharp separations, with the oil layer above, and the sulphur layer below the substratum.

The new method was found to be adaptable to several purposes. It was used initially (as mentioned above) to study the problem of mixing in order to confirm whether Kruyt's observations in relation to paraffin wax also applied to the petroleum oil used in this investigation. It was also used as an additional means of estimating sulphur solubility at temperatures above the melting point. For this purpose the technique described in Section (c) above was used.

An unexpected additional use of the method was in distinguishing pure sulphur from sulphur in which impurities were present or in which a reaction with oil had previously been initiated. In both cases separations were imperfect as compared with the clear separations obtained with pure sulphur.

(c) OBSERVATION OF AN INDUCTION PERIOD IN RELATION TO THE EVOLUTION OF FREE HYDROGEN SULPHIDE.

In the course of the experiments performed and described the impression was gained that the temperatures at which evolution of free H_2S was first observed, as indicated by lead acetate paper, appeared to vary in an unaccountable manner, even when the experimental conditions were considered to be similar. At first this variation was considered to be a reflection of reasonable experimental error, within the limitations of the method of working. As the work proceeded, however, this provisional explanation seemed increasingly inadequate and the decision was taken to investigate the phenomenon.

Several of the previous experiments were repeated and variations in the temperature of initial free evolution of H_2S were again found. 50 g. sulphur were then cautiously melted and heated to 125°C in a Pyrex beaker, and 5 ml. oil, previously heated to the same temperature were added with stirring. The beaker was suspended in an air-bath and the mixture was heated very carefully and slowly, the temperature being raised at the rate of approximately 1°C per minute, with constant stirring. The presence of H_2S was tested for by means of moistened lead acetate paper held close to the surface of the liquid.

In the temperature range 125° - 163°C there was no indication of H2S evolution nor was there any increase in the

viscosity of the sulphur. Above 163°C the viscosity of the sulphur increased in the characteristic manner but no H_2S evolution was indicated. Heating was continued to 185°C without any indication of H_2S evolution being obtained.

These observations were such as to be regarded at first with caution, since they differed apparently from the results of prior work and also from the previous experiments already described in the present work. The experiment was accordingly repeated, and the observations were carefully confirmed.

The experiment was again repeated, and the temperature raised to 200°C, still without indication of evolution of free H_2S. The mixture was then allowed to cool naturally. At 100°, when the sulphur layer had solidified at the bottom of the beaker, the excess oil was decanted off and the sulphur was allowed to cool to room temperature. The remaining oil was swabbed off the surface by means of filter paper, and the appearance of the sulphur was noted. During the course of the experiment the colour of the sulphur had changed only to a light brownish-yellow. The oil, at the conclusion of the experiment, was quite clear and only slightly more amber-coloured than at the start.

After natural cooling the materials were further examined as follows :-

(i) Lead acetate paper was held close to the unbroken (fused) surface of the sulphur. No H_2S was indicated.

(ii) The sulphur was coarsely crushed by means of a glass rod. Immediately the smell of H_2S was noticed, and lead acetate paper darkened when held close to the broken lumps.

(iii) The crushed lumps of sulphur were rapidly transferred to a beaker and covered with a watch-glass. After a few minutes lead acetate paper was inserted under the watch-glass and was darkened by the gas present in the beaker.

(iv) The oil previously decanted from the surface of the sulphur was transferred to a small test-tube and corked, a strip of lead acetate paper being suspended internally from the cork, near the surface of the oil. There was no darkening of the test paper within 24 hours.

The observations made in the whole series of experiments lent strong support to a hypothesis that under certain circumstances there exists an induction period during which free H_2S is not evolved, despite heating of the reaction mixture much above the temperatures at which H_2S evolution had been observed by several previous investigators and also in the present work.

It was reasonable to suppose that the apparent conflict between these and prior observations must be due to some variable or variables not hitherto noticed. The previous

work was again studied in this light, and ultimately a further series of experiments was devised to find the explanation.

The first possible explanation was that the variation was due to using a low proportion of oil/sulphur. To eliminate this variable the main experiment was repeated with a larger proportion of oil. 50 g. sulphur were heated with 25 g. oil in a Pyrex beaker suspended in an air-bath, with the same precautions and method of working as before. The mixture was heated slowly (approximately 1°C rise per minute) through the range 125° - 200°C, with constant testing by means of lead acetate paper. The observations were the same as before, and no free H_2S was indicated by the test paper.

The second variable which required consideration was the rate of heating. In the earlier experiments the rate of heating had been as rapid as was consistent with maintaining a controllable rate of gas evolution, whereas in the present series heating had been slow (approximately 1°C rise per minute). Accordingly the last-mentioned experiment was repeated, with all conditions identical, excepting that the heating was carried out more rapidly, though still carefully. In the course of the experiment the temperature was raised from 125°C to 200°C in 10 minutes. The observations were the same as before and again no free H_2S was indicated by the test paper.

There remained the possibility that the variable was associated with some circumstance due to the different methods of heating. In the earlier experiments the method of heating

had been by burner protected by an asbestos-gauze mat. In the present series the means of heating had been an air-bath. A logical comparison of the two methods of heating, taking into consideration the even character of the air-bath method, and the uneven and vigorous nature of the other, led to the conclusion that the variable must arise from some change consequential on local overheating of portions of the reaction mixture.

An experiment was therefore devised to test this hypothesis. The previous experiment was repeated with all conditions identical, excepting that when a temperature of 140°C had been reached approximately 1 ml. of the mixture was deliberately overheated to a dark-brown colour by applying a bunsen flame at the side of the beaker for a moment. The temperature of the remainder of the mixture was not noticeably changed. The flame was immediately removed and the mixture thoroughly stirred, so that the small overheated portion became well dispersed. Careful heating was then re-commenced by means of the air-bath as previously, and testing was continued as before with lead acetate paper. At 160°C the test paper showed first indications of H_2S evolution. At 180°C the indications were strong. At 200°C the first bubbles of gas were seen rising in the mixture, and at 250°C the evolution was general and vigorous.

The experiment was repeated, with all conditions identical, except that from 125°C onwards the mixture was

heated over a burner protected by an asbestos-gauze mat and local overheating occurred naturally. The observations were the same as in the previous experiment.

Finally 50 g. sulphur, previously melted and heated to 125°C were mixed with 25 g. oil at the same temperature. To the mixture was added 2 g. of the darkened residue from the previous experiment. Thereafter the mixture was thoroughly stirred and heated carefully on the air-bath with precautions against local overheating. The observations were the same as those obtained in the experiment, already described above, in which a small portion of the mixture had been deliberately overheated. The test paper first indicated the evolution of free H_2S at 160°C, and further heating increased the rate of gas evolution as before.

It was now decided to test whether the phenomena thus observed and confirmed were characteristic only of the particular oil used, or whether they could also be observed in the case of other heavy paraffin hydrocarbons. For this test refined paraffin wax of M.P. 52°C was taken as alternative material in place of the oil.

50 g. sulphur were melted in a Pyrex beaker and heated to 125°C, and 25 g. paraffin wax, separately melted and heated to the same temperature, were added with stirring. The mixture was heated carefully by means of an air-bath from 125°C - 200°C with frequent agitation and testing by lead acetate paper. The observations were in all respects similar to those made when oil was used under similar conditions.

Above 163°C the viscosity of the sulphur increased as before and no free H_2S evolution was indicated in the entire heating range of the experiment.

The experiment with paraffin wax was repeated with all conditions identical excepting that the previously described technique of deliberately overheating approximately 1 ml. of the mixture was again used. Once again, as in the case of the experiments with oil, this resulted in free evolution of H_2S being indicated by lead acetate paper at approximately 160°C, and increasing gas evolution thereafter as the temperature was raised.

It was concluded that there appears to be an induction period in the reaction between sulphur and certain heavy aliphatic hydrocarbons during which the evolution of gaseous hydrogen sulphide is so far retarded as to be unobservable by means of lead acetate test-paper. Due to the existence of this induction period the temperature at which free H_2S is first indicated by test-paper is raised by approximately 40°C above the usually observed figures for the same materials. It appeared likely that during this period some unstable product is formed within the sulphur and persists when the molten sulphur is allowed to solidify and remain unbroken; but on breaking up the solidified mass gaseous H_2S is evolved. The existence of the induction period is demonstrable only if local overheating is avoided. If local overheating occurs initial evolution of free H_2S takes place

at the usual temperature and no induction period is observed. As long as local overheating is avoided the phenomenon appears to be independent of the rate of heating.

(f) THE EFFECT OF VISCOSITY - REDUCING AGENTS ON THE TEMPERATURE OF INITIAL FREE EVOLUTION OF HYDROGEN SULPHIDE.

The work of Bacon and Fanelli, as already described, had proved that the presence of hydrogen sulphide or persulphides in liquid sulphur causes a fall in its viscosity. Apart from other findings the observations made in the present study, and particularly those reported under section (e) above, carried the implication that the converse of Bacon and Fanelli's theory might also be true, and that there might be a relationship between the fall in viscosity and the temperature of initial evolution of free H_2S in the reactions being studied. To investigate this aspect of the matter a series of experiments was planned in which the viscosity of the liquid sulphur was deliberately reduced by means of ammonia and the halogens (other than fluorine) which had been shown by previous workers to be viscosity-reducing agents for sulphur.

50. g. sulphur were mixed with 25 g. oil, preheated to 125°C as in previous experiments, and the mixture was cautiously heated in an air-bath to 180°C, with avoidance of local overheating. No H_2S was indicated by test-paper. The mixture was allowed to cool to 130°C and ammonia gas was bubbled through for two hours, the temperature being held at 125° - 130°C during this period. The mixture was then cautiously re-heated in the air-bath to the viscous range, and there was no noticeable fall in viscosity, the sulphur behaving normally. At neither 160° C nor at 180°C was H_2S indicated

by lead acetate test-paper. The NH_3 did not prove an effective viscosity reducing agent for sulphur under the present experimental conditions, and no conclusions, either positive or negative, could therefore be drawn from the observations.

The experiment was repeated, but in place of ammonia gas chlorine was passed in a slow stream for five minutes through the mixture while it was held at 125 - 130°C. The mixture was then cautiously heated in an air-bath. The sulphur never attained the viscous state. At 160°C test-paper first indicated evolution of H_2S. At 190°C first bubbles of gas could be noticed. At 200°C evolution of H_2S was continuing, but slowly, and it remained slow till approximately 240°C, when there was general evolution of H_2S from the reaction.

To examine the effect of bromine under similar conditions the experiment was again repeated but in place of chlorine 1 g. bromine (equal to 2% on the weight of sulphur taken) was added at 125°C. The mixture was cautiously heated in the air-bath. No viscous state was encountered. At 150°C the test-paper indicated first evolution of H_2S. At 170°C the first bubbles of gas were noticeable. Between 180°C and 230°C gas evolution was sluggish, as observed with chlorine. Above 230° general and brisk evolution of H_2S was observed.

The experiment was now again repeated but iodine was substituted as the viscosity-reducing agent. To the sulphur/oil mixture at 125°C was added 0.75 g. iodine corresponding to 1.5% on the weight of sulphur taken. The iodine appeared to

dissolve. On heating cautiously in the air-bath the viscous stage was never encountered. At 160° the test-paper showed first indications of H_2S. At 180°C the first bubbles of gas were noticeable, at 200°C the rate of evolution was increasing, and at 220°C there was general evolution of gas. It was observed that in this experiment, with iodine as viscosity-reducer, there was no period of sluggish gas evolution, as had been noted in the experiments with chlorine and bromine described above, and the evolution of gas became progressively faster as the temperature was raised within the experimental range. An explanation for this phenomenon will be suggested in a later chapter.

The series of experiments indicated that after treatment by reagents which reduce the viscosity of liquid sulphur in the temperature range when it would normally become exceedingly viscous no induction period occurs in the evolution of free H_2S. Under these conditions, despite absence of local overheating, and the maintenance of the same precautions as observed in the previous series of experiments, the temperature of initial evolution of free H_2S was in the "normal" range 150° - 160°C. The halogens chlorine bromine and iodine all gave the same observation in this regard, while iodine was the most satisfactory from the viewpoint of uninterrupted evolution of gas and ease of manipulation.

The work with iodine was finally repeated, with the substitution of refined paraffin wax (M.P. 52°C) for the oil,

so as to test whether the observation was also valid in respect of this material. 50 g. sulphur were melted and heated to 125°C. 25 g. paraffin wax were melted, pre-heated to the same temperature and mixed with the sulphur. The mixture was cautiously heated in an air-bath to 180°C without any indication of H_2S evolution. It was then allowed to cool to 140°C and 0.25 g. iodine, representing 0.5% on the sulphur taken, was added with stirring. The mixture was heated cautiously in the air-bath.

No viscous stage was encountered. At 160°C evolution of H_2S was indicated by test-paper. At 205°C bubbles of gas could be seen rising in the liquid, and at 280°C evolution of H_2S was brisk and general.

(g) BEHAVIOUR OF SPENT OXIDE/OIL MIXTURES.

In further investigations of the phenomena associated with H_2S evolution it appeared desirable to find some form of sulphur in the processing of which the phenomena associated with large viscosity changes would probably not be encountered. Since it was now clear that these problems were greater with the pure forms of sulphur than in the presence of viscosity-reducing agents a search was made for some form of sulphur in which such agents might be present naturally as contaminants. Finally a material meeting these requirements was found in the form known as "spent oxide". This is the purifying mass finally rejected by coal-gas manufacturing plants after repeated use in the absorption of H_2S from the gas stream. The material, as originally charged into the purifying boxes, consists substantially of a mixture of ferrous and ferric hydroxides prepared to allow gradual passage of the gas. The main absorption process may be represented by the following reactions:

$$Fe(OH)_2 + H_2S \longrightarrow FeS + 2H_2O$$

$$2Fe(OH)_3 + 3H_2S \longrightarrow Fe_2S + 6H_2O$$

When the sulphides accumulate the mass is exposed to the air, and the hydroxides are re-formed with the liberation of sulphur. This cycle of absorption and revivification is repeated until the mass contains too high a proportion of sulphur to work efficiently, and it is then replaced.

It is clear that the spent oxide contains numerous

impurities, which cannot here be discussed in detail. From the present viewpoint it may be regarded as an impure form of sulphur in the presence of iron hydroxides, ferrocyanides and other compounds, and contaminated by contact with the vapours of tar, naphthalene and other organic by-products of gas manufacture. The sulphur content of spent oxide may reach about 50% in rich samples.

In the present work spent oxide was obtained from the municipal coal-gas plants at Port Elizabeth and Johannesburg, and extractions of ferrocyanides and thiocyanates were carried out by well-known methods as an exercise in handling the material. It was found to be too lumpy in its natural state for efficient processing, and grinding was necessary.

For the main experiments a representative sample was taken from a bag of spent oxide by repeated mixing, coning, and quartering. The material was not purified in any way. The sample was then ground finely by pestle and mortar, a brownish powder being obtained, which was used in the further experiments.

The free sulphur content of the material was determined by extraction with carbon disulphide. After drying at 100°C, 20 g. were weighed into a stoppered flask of 250 ml. capacity, and repeated extractions were made by lengthy shaking and decantation with three successive portions of carbon disulphide totalling 300 ml. The solutions were mixed and filtered rapidly. The residue was washed out on to the filter by means

of 50 ml. carbon disulphide, and the filter was finally washed with a further 50 ml. of the solvent in case sulphur had been deposited by evaporation.

The combined filtrates were evaporated over a water-bath, and when reduced to approximately 75 ml. the evaporation was completed in a tared beaker, and the weight of sulphur deposited was thus obtained.

Found: Free sulphur in sample of spent oxide 31.5%
Repeat 31.6%

The behaviour of spent oxide/oil mixtures was then investigated. A small quantity of the powder was added to the oil in a test-tube and shaken. A suspension formed which settled slowly. On heating over a burner the mixture frothed and darkened, and lead acetate test-paper indicated the evolution of H_2S.

The experiment was repeated under controlled conditions. In a Pyrex beaker 50 g. oil were taken, and 20 g. finely ground but undried spent oxide were added while stirring with a thermometer. The mixture was heated in an air-bath. At 90° - 120°C frothing occurred, which was ascribed to the disengagement of water vapour. Heating was continued while stirring with the thermometer. At 145°C the evolution of H_2S was indicated by lead acetate paper. At approximately 180°C gas was being evolved with effervescence. The temperature was

further raised and held between 250° - 260°, while the gas was vigorously evolved.

During the heating there was no noticeable increase in viscosity. At the temperature at which an abrupt increase in viscosity occurs in pure sulphur (approximately 163°C) special note was taken of the behaviour of the mixture but there was no similar change in viscosity. As is apparent from the low temperature at which lead acetate test-paper was first darkened, no induction period occurred in the evolution of free H_2S.

This experiment was now repeated with the same conditions, except that above 125°C the mixture was not stirred. It was expected that, with the high proportion of impurities present in the spent oxide, there would be a tendency for very much settlement and packing to take place on the bottom of the vessel. However, this did not occur to an inconvenient extent, and the material remained mainly in suspension in the oil, being agitated by the evolution of gas. The experiment ran the same course as the previous one, and the partial settlement did not interfere with the heating.

The residue from both the experiments consisted of a dark asphaltic liquid, with portions more highly carbonised in lumps, similar to the residues obtained in the experiments with sulphur. In this liquid were suspended the remaining solid and insoluble constituents of the spent oxide.

The residue was placed in an oven and held at 125°C

for seven hours, to allow settlement to occur. The solids settled well and the asphaltic supernatant liquid could be decanted.

At no point in the experiments was difficulty encountered due to viscosity increases or retardation of gaseous H_2S evolution. It thus appeared that the spent oxide contained sulphur the viscosity behaviour of which was profoundly modified by the presence of other constituents. The presence of the remaining iron compounds and other impurities gave less difficulty than had been expected. This was ascribed to the fine grinding which had first been carried out, and to the fact that the reaction of the sulphur caused the particles to disintegrate still further as the sulphur was removed in the form of hydrogen sulphide.

(h) PREPARATION OF SULPHUR RIGOROUSLY FREE FROM ORGANIC IMPURITIES.

In the work reported up to this point the observation of viscosity changes in liquid sulphur under the various reaction conditions was made subjectively by noting the increased or decreased resistance to stirring. It was now decided to attempt to follow certain of the changes objectively by means of a suitable instrument. Since no available instrument was adaptable to the unusual conditions of the experiments the decision was taken to design and construct a special viscometer, details of which are given later. As an essential preliminary to this work it was necessary to provide a supply of sulphur, rigorously free from organic impurities, for use as a comparison and calibration standard. Since such material could not be obtained commercially it was prepared by Bacon and Fanelli's method, slightly modified in practical details.

700 g. high-purity ground sulphur, originally supplied by African Explosives and Chemical Industries Ltd., (specification given in Section (a) above) were carefully melted in a Pyrex beaker and held at 120° - 125°C until all moisture had been driven off, as indicated by the disappearance of the tendency to froth. 5 g. pure dry finely powdered magnesium oxide were added and well stirred in the sulphur, and heating was continued further, on a ring-burner, until the sulphur boiled. Boiling was continued for four hours, and meanwhile a thermostatically controlled oven was pre-heated to 125°C.

The boiled sulphur was allowed to stand until the temperature fell to 130°C and the beaker was placed in the oven and allowed to settle overnight at 125°C. The next morning the preparation was found to have settled very satisfactorily, with clear light-coloured liquid sulphur overlying a small layer of somewhat darker material mixed with the excess magnesium oxide.

A special filter was prepared by blowing a hole of about 12.5 mm. diameter in the bottom of a round-bottomed flask. The bottom of the flask was then covered to a depth of about 15 mm. with glass wool, packed down by pressing with a glass rod until no free channels remained. The neck of the flask was lagged with asbestos rope. The filter, completely prepared, was pre-heated to 125°C by being left overnight in the oven along with the beaker of liquid sulphur.

The next morning the heated filter was rapidly removed from the oven to a previously prepared stand, and the liquid sulphur was decanted through it. The dark portion that had settled out in the beaker was rejected together with a small portion of the clear sulphur close to it.

The filtrate, consisting of clear light-coloured liquid sulphur, was received in a Pyrex beaker, and was held at 125°C while a further 4 g. pure dry magnesium oxide were added. Heating was then continued and the sulphur was brought to boiling point (as on the previous day) and kept boiling all day (7 hours). In the evening the boiled sulphur was again transferred to the pre-heated oven and allowed to settle over-

night at 125°C.

On the following three days the preparation was again filtered each morning and after the addition of 3 g. magnesium oxide was reboiled the whole day as before (7 hours per day). It was then noted that no further darkening at the bottom of the vessel was occurring on boiling, and it was therefore considered safe to stop the boiling process at this point. After settlement overnight the sulphur was finally filtered next morning and allowed to solidify in an evaporating dish, previously freed from possible organic contamination by boiling with acidified sodium dichromate, washing, and drying under dustless conditions.

The final preparation was a sparkling, clear, light-amber liquid, which when shaken did not adhere to the side of the vessel. When solidified at room temperature it was of a light yellow colour and consisted of a dense mass of interlocked crystals. The yield was approximately 400 g.

The following additional observations are placed on record for the benefit of future workers :-

(i) The initial boiling period is the most difficult one, due partly to the presence of traces of moisture in the sulphur. For the first boiling it was necessary (as mentioned above) to use a ring burner for heating. Thereafter, however, boiling was much easier, and from the second day

onward an ordinary burner was sufficient.

(ii) Precautions must be taken against flashing of sulphur vapour. This risk occurs above about 250°C, and the flashing takes place when air enters the vessel and mixes with the sulphur vapour to form an explosive mixture. A simple and reliable method of preventing this is to keep the opening just adequate to act safely as a vent, but sufficiently closed to ensure that the atmosphere in the vessel consists at all times predominantly of sulphur vapour.

(iii) The losses by volatilisation, despite the very prolonged boiling, are unexpectedly slight. Air-cooling of the upper portions of the vessel condenses most of the volatilised or sublimed material and it flows back to the preparation.

(iv) Overnight settlement at 125°C results in such efficient separation of the clear liquid sulphur from the impurities and excess oxide that it is possible, by careful decanting, to avoid filtration. This simplification of the method involves the rejection of larger proportions of the material at each stage, to avoid risk of contamination.

The absence of organic impurities from the final preparation of purified sulphur was confirmed by Bacon and Fanelli's test. A new Pyrex test-tube was rigorously cleaned by boiling with sulphuric acid-sodium dichromate mixture. Shortly before the test the tube was emptied and immediately washed with twice-distilled water, and was dried upside down in a position protected from dust. About 3 g. purified sulphur were heated in the test-tube and held at boiling point for three minutes, and allowed to cool and solidify in the tube. The sulphur remained the same colour as before the test, and the inner surface of the bottom of the test-tube was not blackened.

(i) CONSTRUCTION OF A SPECIAL VISCOMETER AND OBSERVATION OF VISCOSITY CHANGES.

In the design and construction of the special viscometer required the difficulties encountered fell broadly into two classes:

(i) Those associated normally and characteristically with viscosity determinations on pure sulphur, and

(ii) Special difficulties arising out of the present experimental conditions.

Considerations of space preclude a detailed account of all the problems involved, but a summary thereof is essential in considering the design and technique required. Prior to 1943 the accepted data on the viscosity of sulphur were based mainly on the determinations of Rotinjanz[1], Kellas[2], and Farr and McLeod[3]. These results were not, in many respects, mutually consistent. In particular the viscosity values found differed according to the previous thermal history of the sample. For example prior heating gave lower values for the maximum viscosity found. The work of Bacon and Fanelli[4] provided the explanation for these inconsistencies. Reliable and consistent data were obtained on the

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[1] Rotinjanz: Physik. Chem. 62, 609 (1908).
[2] Kellas: J. Chem. Soc. 113, 903 (1918).
[3] Farr and McLeod: Proc. Roy. Soc. 97, 80 (1920).
[4] Bacon and Fanelli: J. Am. Chem. Soc. 65, 639 (1943).

viscosity of sulphur and these values were shown to be independent of the previous thermal history of the sulphur used. Bacon and Fanelli showed that (apart from differences in experimental technique) the presence of minute traces of organic impurities in sulphur profoundly affected the viscosity changes, and that the strenuous efforts of prior workers to purify their sulphur by numerous sublimations, crystallisations and other manipulations had in fact, not yielded pure sulphur.

The apparatus used by Bacon and Fanelli in their viscosity determinations was based on a special capillary tube method, and other capillary methods have been applied in many other investigations. Poiseville's equation may readily be used in relation to such apparatus, and calibration is relatively easy.

The simplicity and reliability of a capillary tube method were so apparent as to make this the method of choice in the present experiments, had the conditions been suitable. The following circumstances, however, made the use of this type of apparatus undesirable:

(1) Although rigorously purified sulphur was now available and would be used for calibration and standardisation the main experiments involved the use of sulphur which had been heated with oil. It was possible that traces of oil or carbonaceous matter might be drawn into the capillary tube and grossly affect the result.

(ii) Pure sulphur flows cleanly from a glass capillary tube, leaving no residues on the walls. Such clean separation could not be expected under the present experimental conditions.

For these reasons designs based on capillary tubes in any form were rejected.

On first consideration it appeared that a suitable instrument might be designed on the well-known "falling sphere" principle, provided that some means could be provided to observe the start and finish of the steel ball's traverse through sulphur which might become too dark for direct visual observation. Much thought and effort were expended on devising a suitable electrical apparatus for this purpose. In the proposed apparatus the vertical tube was to have been provided externally with energised coils at suitable levels. The steel ball, in its fall past these respective coils, was to have altered the conditions of magnetic flux and so made observation possible. To avoid the corrosive action of the sulphur the ball was intended to be chromium-plated.

This design was not proceeded with, mainly because of the difficulty in arranging accurate control of the release of the ball and because of the large volume of test sample required for each determination. The decision was confirmed by a study of the apparatus and experiments

described by Broome and Thomas[1]. These workers used search coils and an oscillatory valve circuit for a similar purpose in investigating the viscosity of bitumen and other opaque materials, and found numerous precautions and special provisions to be necessary.

Investigation of various further alternative principles on which the viscometer might be constructed finally led to consideration of designs based on mechanical rotation. These fall into two main classes, namely the MacMichael type and the Stormer[2] type. In the former type of instrument a cylindrical outer cup containing the liquid under test is rotated at constant speed, and the torsion on a centrally positioned smaller cylinder is observed under standard conditions. The Stormer type of instrument, in its best form, has a fixed cylindrical outer cup, containing the sample under test. Within this cup a cylindrical rotor of smaller diameter rotates concentrically, being driven through a system of gears and pinion actuated by a cable-suspended falling weight[3].

The viscometer ultimately constructed for the present work used the principle of the Stormer, with rotation of a solid cylindrical rotor centrally in a fixed cylindrical

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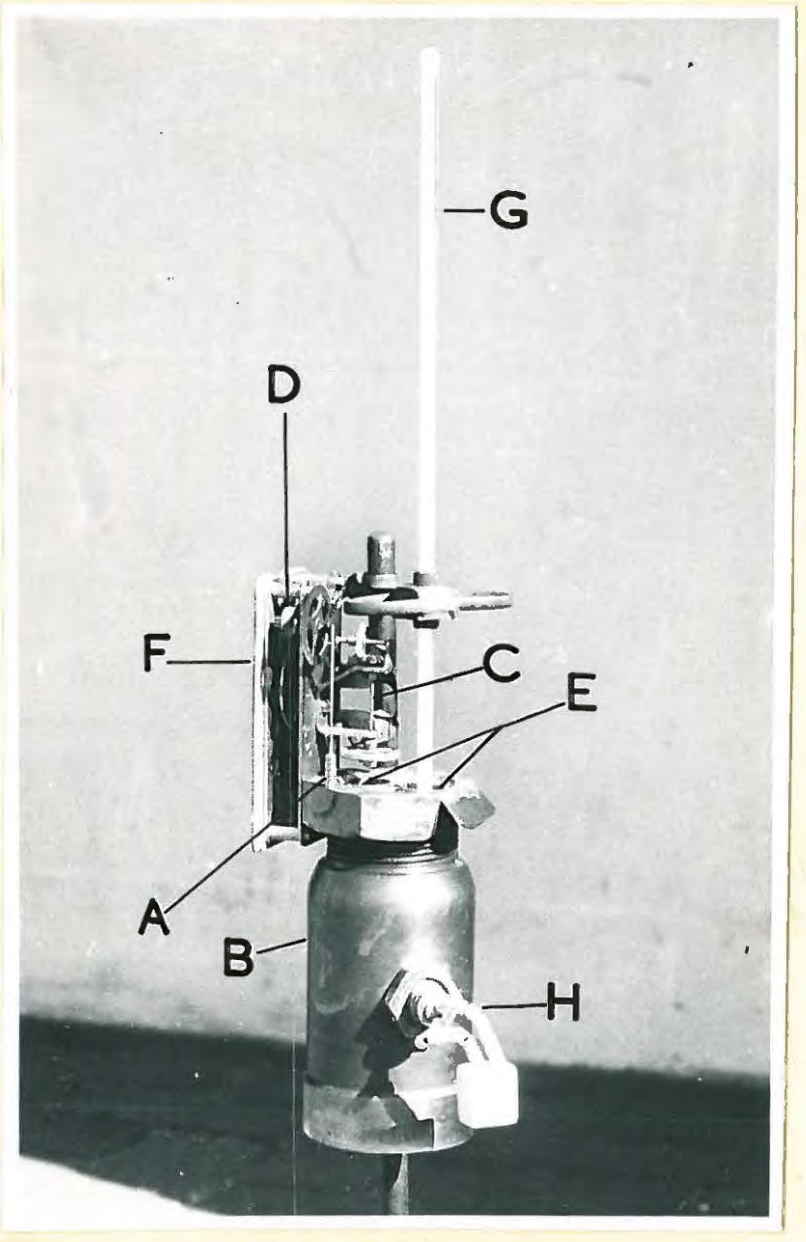
[1] Broome and Thomas: J. Soc. Chem. Ind. 50, 424 (1931). Previous workers along similar lines were Moore & Cuthbertson: Ind. Eng. Chem. Anal. Ed. 2, 419 (1930), and Symmes and Lantz: Ind. Eng. Chem. 1, 35 (1929).

[2] Stormer: Trans. Am. Ceramic Soc. 11, 597 (1909). See also Ind. Eng. Chem. 12, 587 (1920).

[3] An illustration and description will be found in Merrington: "Viscometry", p.68, Edward Arnold & Co., London.



PHOTOGRAPH OF SULPHUR VISCOMETER

The asbestos lagging has been removed. The rotor is shown detached from its spindle. In the working position it would be out of sight in the left-hand cup.

Dimensions: Rotor cylinder 4.3 mm. diameter x 12.5 mm. high
Rotor shaft diameter 1.1 mm.
Cups 20.0 mm. diameter x 51.0 mm. high (inside measurements).

A - Rotor B - Oil-bath C - Spindle shaft with coupling D - Drum with driving wire suspended E - Cups F - Dials (facing left) G - Thermometer H - Electrical Connections

cup, but differed in all details due to special and unusual conditions of the experiments, for which the Stormer instrument would be unsuitable. The viscometer constructed is shown in the attached photograph. The following particulars will indicate its features and the method of operation:

The mechanism consists of a train of gears driven by the uncoiling of a fine Monel wire from a horizontal gunmetal drum. From the wire is suspended a weight, the size of which may be chosen as required. By means of bevel gears the motion is transmitted at right angles to a vertical shaft and coupling to which is attached a stainless steel rotor. By means of an integrating mechanism (adapted from an electrical watt-hour meter) the number of revolutions of the rotor may be read on a dial. A suitable locking arrangement allows the fall of the weight to be started at will.

Below the rotating and integrating mechanism is the assembly whereby the sample is held in the correct position and at the required temperature. The rotor, which projects from the vertical shaft and coupling mentioned above, is immersed centrally in a cylindrical glass cup containing the sample. The cup projects below the cover into an oil-bath contained in a large outer vessel lagged with asbestos. A second cup, identical in every way with the one in which the rotor revolves, is situated alongside it and heated identically. Its function will be referred to below.

The oil-bath is thus entirely enclosed by the

cover. As a safety measure against the development of pressure in the vessel a vent is provided at the side, and is covered by a deflector plate to prevent any possible contamination of the sample by oil vapour. The oil-bath is heated electrically by an immersed element controlled through an external resistance.

A problem which gave much difficulty was making reliable provision for temperature observation. It was impossible to place the thermometer bulb near the rotor as this would have caused turbulence. Placing it adjacent to the inner wall of the test vessel would have detracted from the truly cylindrical shape required in an instrument working on the Stormer principle. On the other hand the simple expedient of taking the temperature of the oil-bath as being the temperature of the sample would have involved errors analogous to those encountered by Rotinjanz when he observed air-bath temperatures.

The problem was finally solved by providing a second cup alongside the test cup, as described above. The dimensions of the two cups were in every way identical and they were so placed as to be identically heated by the oil-bath. In use both cups were filled with the same amount of sample material, the rotor being immersed in the one cup and the thermometer bulb in the other.

The entire oil-bath assembly was arranged so as to be readily lowered from or raised to the rotor, and two registering marks ensured that the assembly was fixed finally

at the same position each time an observation was made.

In use the instrument could be operated in two alternative ways:

(i) A fixed number of revolutions of the rotor could be chosen and the time taken to complete this number could be observed at each respective temperature.

(ii) A known time could be chosen for each observation, and the number of revolutions of the rotor during that time could be determined at each respective temperature.

Method (i) was used for operation of the viscometer and proved adaptable to the special conditions.

Under ideal conditions the preferred material of construction for the rotor would have been glass, or glass-coated metal. As this construction could not be provided a study was made of alternative materials, resulting finally in the use of stainless steel. The type used was 18-8, and the choice was made on the basis of the corrosion data published by Fanelli[1], who found that at 210°C this material was corroded by sulphur to the extent of only 0.000002 inches per month. This is well below the limit of 0.00035 inches per month established by the U.S. Steel Research Laboratory as the standard for a "fully resistant" metal.

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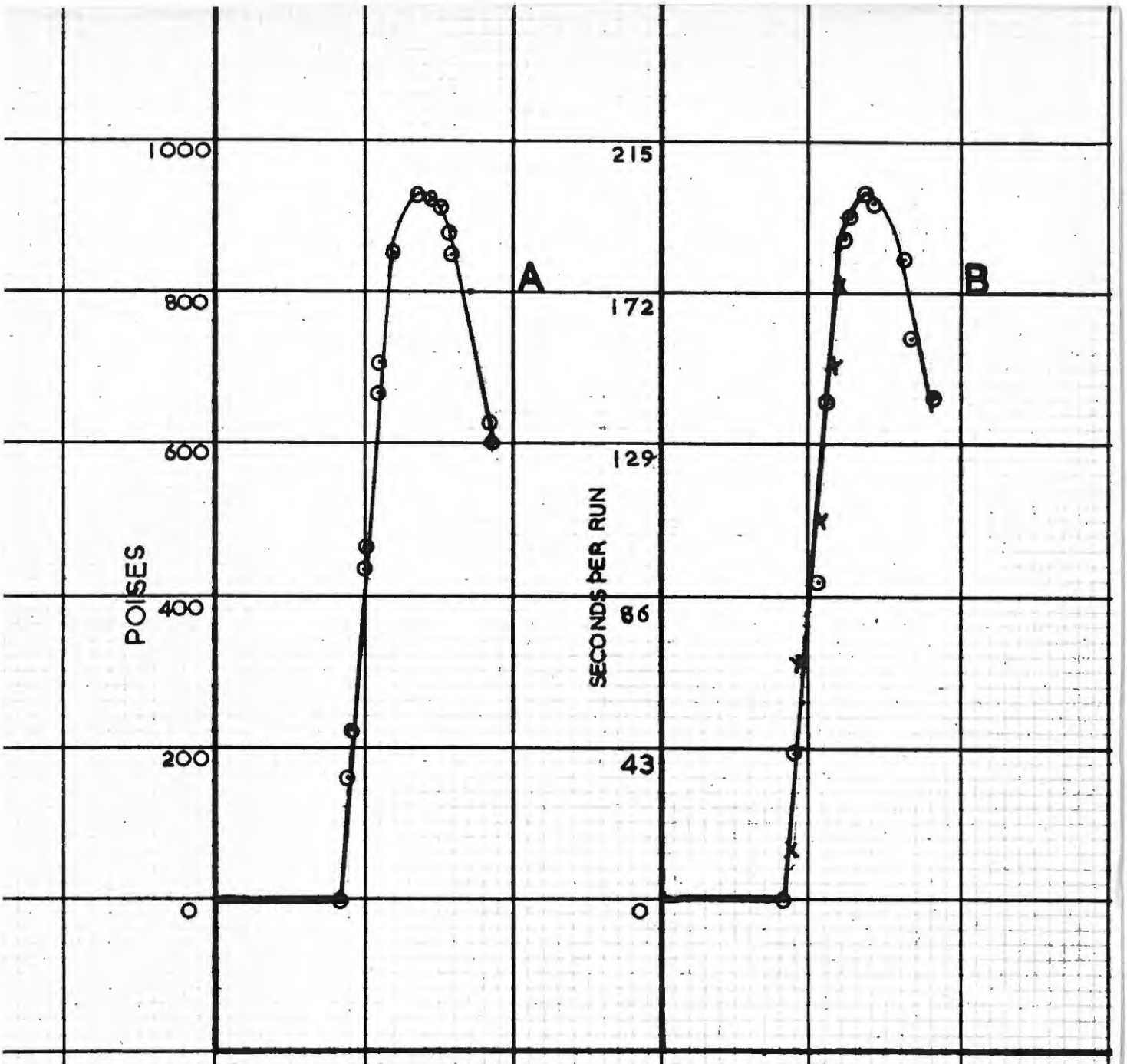
[1] Fanelli: Ind. Eng. Chem. 38, 42 (1946).

The viscometer as thus described could have been used without special calibration for directly comparative observations. However, it was desired to make observations in terms of absolute units. It was clear from the literature that no satisfactory method could be applied to derive these figures by theoretical calculations from the dimensional data and operating conditions. In particular the "end effects" of the rotor were an unpredictable disturbing factor, apart from other sources of error.

It was therefore decided to calibrate the instrument directly by the use of a material of known viscosity, and in place of the customary standards (glycerol, castor oil and others) it was decided to use the ideal material for the purpose - pure sulphur. The material used was specially purified sulphur the preparation of which has been described above.

The instrument was set up in a position protected as far as possible from vibration. The glass cups which had already been rigorously cleaned, were fitted in the cover of the oil-bath, which was screwed into position. The oil-bath assembly was turned and lifted close to working level. Each cup was charged with 20 g. specially purified sulphur, which was melted by switching on the immersion element of the oil-bath. The assembly was then lifted further to the registering mark. This brought the rotor centrally into the main cup. Into the second cup was lowered the thermometer



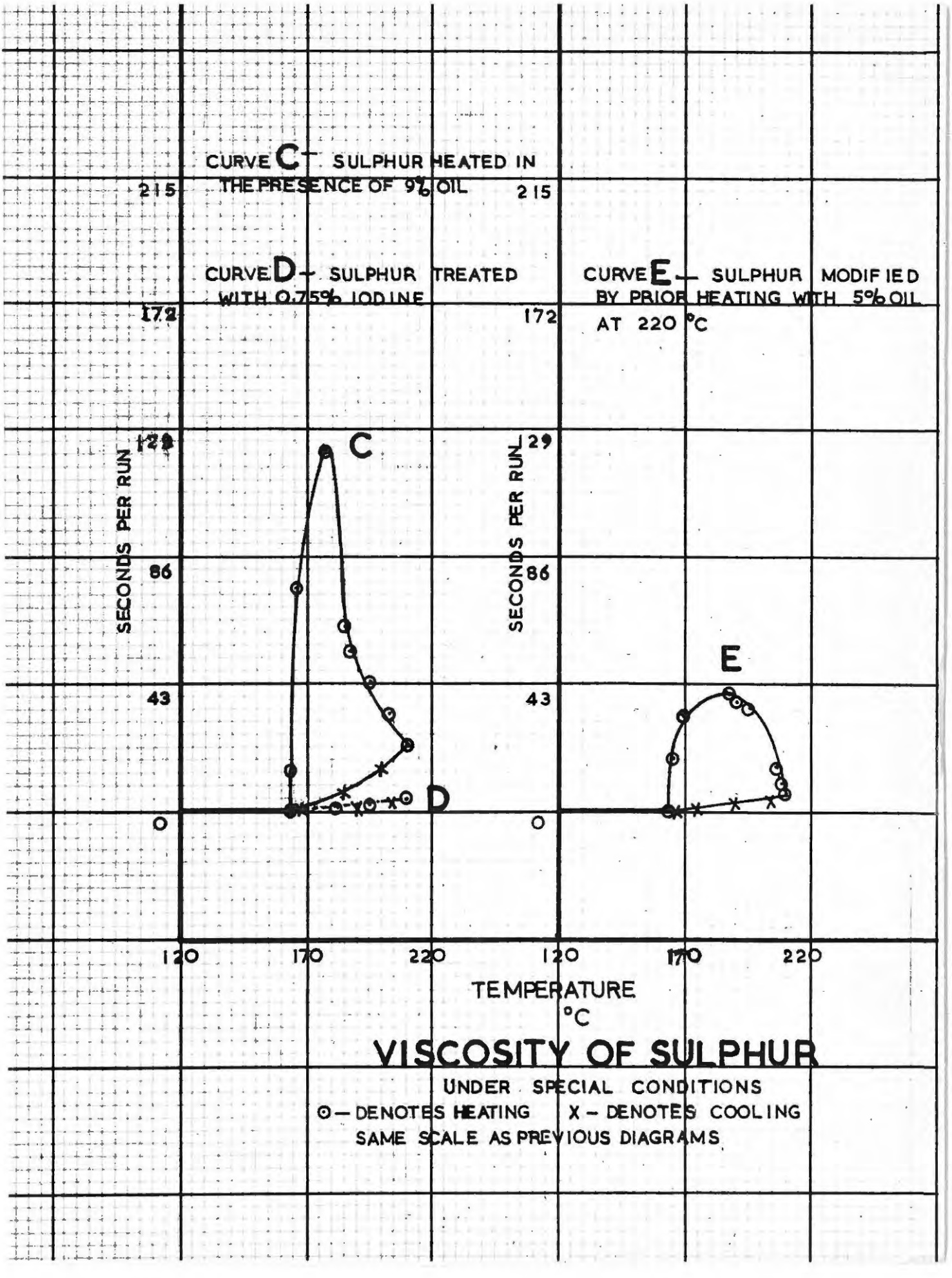
VISCOSITY OF PURE SULPHUR

CURVE A : PLOTTED FROM BACON & FANELLI'S DATA

CURVE B : EXPERIMENTAL RESULTS – SULPHUR VISCOMETER

⊙ – DENOTES HEATING X – DENOTES COOLING

NOTE : ON ALL THE CURVES THE HEAVY LINE IN THE TEMPERATURE RANGE BELOW 162° REPRESENTS MINOR VISCOSITY CHANGES TOO SMALL TO BE PLOTTED ON THE SAME SCALE



VISCOSITY OF SULPHUR

UNDER SPECIAL CONDITIONS

⊙ — DENOTES HEATING X — DENOTES COOLING

SAME SCALE AS PREVIOUS DIAGRAMS

supported from its own bracket above. The temperature was allowed to rise to 120°C, at which the first reading was taken.

The requisite weight was attached to the fine wire driving the mechanism. Two weights, namely 20 g. and 60 g., covered the entire range of the experiments. The smaller weight covered the relatively less viscous stages, while the larger weight gave runs of reasonable duration even at the highest viscosities. The drum was revolved to coil on the wire, and was stopped when the pointer on the dial registered zero. A run consisted of 75 revolutions of the rotor. With an overall gear ratio of 15 : 1 this corresponded to five revolutions of the pointer, i.e. 50 divisions on the dial. The fall of the weight in each run was timed by means of a stop-watch.

The calibration and other runs of the viscometer are shown in the diagrams attached. The shape of the viscosity curve obtained for pure sulphur is closely similar to that obtained by Bacon and Fanelli by an entirely different method. By plotting the curve on the same scale as that used by these workers it became possible to read off the corresponding viscosity values in terms of poises or centipoises. The temperature range covered in all the experiments was 120° - 210°C.

With pure sulphur the curve is almost flat from 120°C to just below 163°C. Above this there is a steep rise to the maximum at approximately 188°C, after which there is a

decline. The values obtained during the heating cycle are plotted as circled dots. Thereafter the instrument was allowed to cool gradually, and further runs were made during the cooling period. These are shown as crosses. The fact that they fall on, or near, the heating curve confirms the previous readings, and gives proof of the purity of the sulphur which had been prepared. It will be recalled that traces of organic impurities would have prevented such similarity in the heating and cooling curves.

Further runs were planned and made so as to yield information as to the viscosity changes during the induction period and after modification of the sulphur.

The cup was charged with 20 g. sulphur as before, but 1.8 g. oil equal to 9% were added, and heating was carried out carefully as before. When the sulphur had melted agitation, to bring the two materials in contact, was provided by over-running the rotor temporarily. Observations were made as before through the temperature range 120° - 210°C. It should be noted that in this experiment the shaft of the rotor passed through a thin supernatant layer of oil. It was for this reason that the shaft had been made so thin. With such a small diameter the shaft turned freely in the oil, while the rotor turned in the sulphur. In preliminary tests no difference in readings could be noticed at 120° - 130°C when the oil layer was present or absent respectively. Furthermore, with increasing sulphur viscosity the relative

significance of this error would further diminish. At no time was it of importance in relation to the overall experimental error.

The conditions of this run corresponded generally to those of the previously described induction period experiments. The curve shows between 120°C and 160°C the same low viscosity values as pure sulphur. Thereafter there is a sustained rise to a well-defined maximum, after which there is a sharp fall. The contrast between this curve and that of pure sulphur is seen, however, in the shift of the temperature of maximum viscosity from 186° - 188°C to about 176°C. Furthermore the fall thereafter is rapid, while the curve as a whole is lower than that of pure sulphur. It is significant that the viscosity readings during the cooling period are much lower than those obtained during the heating period.

Very different from both these curves is that obtained with sulphur which had been modified by prior heating with oil. Pure sulphur was heated in a Pyrex beaker with 5% oil to 220°C, and allowed to cool. The supernatant oil was removed from the solid sulphur by means of filter paper. The viscometer cups were each charged with 20 g. of this sulphur and were heated through the same range as before. The viscosity values above 160°C were low as compared both with pure sulphur and with pure sulphur tested in the presence of the oil. The rise of the curve is very slight.

At 205°C the viscosity is almost as low as at 120°C.

To complete the series sulphur was tested in the presence of iodine, which had been previously been proved to be an effective modifying agent. 20 g. pure sulphur were taken as before, and the sample was heated in the viscometer in the presence of 0.15 g. iodine, equal to 0.75%. Mixing was effected as before by over-running the rotor for a short while. The viscosity values obtained were very low and were distinguished by their uniformity over the whole temperature range. The curve is virtually a straight line, and the observations during cooling were virtually identical with the values during heating.

These results are of much interest, and will be discussed later in relation to the general theoretical aspects of the study.

(j) PREPARATION OF MODIFIED SULPHUR.

Following on the observations made in the previous experiments it appeared likely that by pre-treating the sulphur to be used in the final gas evolution work, it should be possible to improve the working conditions and to achieve a more even production of gas with avoidance of the induction period. It was therefore decided to modify the viscosity characteristics of a sufficient quantity of sulphur to serve as starting material in the evolution experiments.

Three alternative procedures were now available for the purpose :-

(i) The sulphur could be pre-treated by the use of chlorine, bromine, or iodine, the last-named being the preferred reagent on the basis of the experimental experience.

(ii) The sulphur could be pre-treated by heating with a small proportion of oil to the required temperature.

(iii) A portion of the sulphur could be pre-treated by either of the above methods and then added to the remainder of the sulphur with thorough mixing.

Of these procedures method (ii) was chosen as being most suitable and convenient.

Small-scale preparations were first undertaken, 20 g. sulphur were melted and heated to 125°, and 1 g. oil, representing 5% on the sulphur, was preheated and mixed with the

sulphur. The mixture was heated in a beaker over a gauze mat with stirring, and the heating was continued through the viscous stage and taken up to 220°C. The mixture was allowed to cool and was found to be brownish-yellow in colour when solid, smelling very slightly of H_2S. In cooling through the range 188° - 163°C the sulphur did not become viscous. The cooled and solidified preparation had traces of [illegible] oil on its surface, and the conclusion was drawn that 5% oil was an unnecessarily high proportion to use.

The experiment was repeated, with the use of 2% oil on the weight of the sulphur. The preparation, when finally solidified, was free from excess oil, and similar in appearance and properties to that obtained in the previous experiment.

The behaviour of the modified sulphur when heated further with excess oil was now observed. 10 g. modified sulphur were melted and heated with 50 g. oil (20% w/w) in a beaker on a gauze mat. At 150°C the evolution of H_2S was indicated by lead acetate paper. In the range 163° - 188°C the viscosity of the sulphur did not noticeably increase. At about 200°C H_2S evolution increased considerably, and by 220°C the gas was being evolved with brisk and sustained effervescence. The heating was continued up to 280°C for three hours, when scarcely any further H_2S was being given off. The final residue when cold was a soft mass of asphaltic appearance, with agglomerations that could be dispersed by means of a glass rod.

The experiment was repeated with a lower proportion of oil/sulphur. 10 g. modified sulphur were heated with 10 g. oil through the same temperature range and with the same procedure as before. Once again it was found that there was no noticeable increase in viscosity, and the evolution of H_2S took place as before. There was, however, a contrast between the two residues. The residue finally obtained when the lower proportion of oil was used contained hardened, coke-like, carbonaceous masses.

The main preparation of modified sulphur was then undertaken. 686 g. sulphur were melted and preheated to 125°C in a Pyrex beaker over a gauze mat. 14 g. oil were added and the heating was continued, with stirring, through the viscous range and up to 220°C and held at this temperature for five minutes. The sulphur was then poured into four evaporating dishes (to yield easily handled shapes) and allowed to solidify. The modified sulphur, slightly brownish in colour, was finally broken up and stored for use in the later experiments.

(k) PREPARATION OF HYDROGEN SULPHIDE BY REACTION OF SULPHUR WITH OIL.

(i) Design of Evolution and Absorption System: Using the observations and data available it was now possible to design a suitable system for the controlled evolution of H_2S and its quantitative estimation. After many changes the apparatus and arrangement finally used were as follows:

The evolution vessel was a wide-mouth Pyrex round-bottomed flask of 250 ml. capacity. A 3-hole rubber stopper was fitted, carrying a gas outlet tube, a thermometer reaching into the liquid, and a nitrogen supply tube reaching almost to the bottom of the flask. Through this latter tube a supply of pure nitrogen, controlled by a reducing valve and secondary stopcock, could be used to flush out the system at any desired stage. The gas outlet tube was prolonged vertically 50 cm. above the flask, to act as an air-cooled condenser. It was then bent at a right angle and led into absorption vessel No. 1, holding 400 ml. normal sodium hydroxide solution. From here the residual gas passed to absorption vessel No. 2, holding 50 ml. of the same solution. Any unabsorbed gas passed to absorption vessel No. 3, which held 20 ml. ammoniacal solution of cadmium chloride as a guard. The outlet tube from this vessel led to a manometer flask charged with water tinted with fluorescin for easy observation. This flask was connected through a needle-valve to the laboratory vacuum line. A third tube, open at one end to the atmosphere, extended from close to

the bottom of the manometer flask vertically through the stopper, and projected 25 cm. above it. By providing a suitable height of water in the flask it was thus possible to arrange with certainty at all times that the suction applied just counterbalanced the back-pressure of the various absorption vessels.

The evolution flask was heated over an open-type electric spiral, protected by a wide sand bath sufficiently large to take all the contents of the flask in the event of cracking, with allowance for frothing. The sand reached approximately to the level of the mixture in the flask at the start of each experiment. Before the apparatus was used the rubber stopper and connector were boiled in dilute sodium hydroxide solution to ensure absence of sulphur from the surfaces.

When in use the evolution flask was first charged with the required weight of oil which was heated to approximately 125°C. The required weight of previously prepared modified sulphur was then added gradually with continued but cautious heating, so that the sulphur was melted but did not rise above this temperature, thus avoiding possible losses due to premature evolution of H_2S. The mixture of oil and sulphur was stirred by means of the thermometer. The evolution flask was then closed and all connections made tight. Gas-tightness of the apparatus as a whole, including the absorption system, was checked by admitting a little nitrogen,

so that the pressure indicated in the manometer flask tube amounted to approximately 10 cm. of water. If the level in the tube remained steady when the nitrogen inlet as well as the final outlet tube from the apparatus were closed the assembly was regarded as gas-tight.

The vacuum connection was now opened very cautiously so that the manometer tube indicated a suction of about 3 cm. water. Heating of the evolution flask was started and the temperature was allowed to rise until visible bubbles in the oil indicated continuous gas evolution. As soon as the gas started bubbling in the absorption vessels the vacuum was adjusted so as just to counterbalance the back-pressure and allow regular working of the absorbers.

The evolution of gas was regulated by heating at as even a rate as possible, so as not to cause errors by over-running the absorbers. When this occurred it was promptly indicated by a yellow precipitate of cadmium sulphide in the guard vessel. With careful working it was possible to complete a preparation without obtaining more than a negligible haze in the guard vessel.

The series of preparations was planned so as to yield, if possible, a progressive set of results which would be of greater interest than individual and isolated experiments. For this purpose the full weight of oil required for the preparations was placed in the evolution flask at the commencement of each series. The sulphur was added in stages, the yield of gas from each stage being estimated

separately. The conclusion of each stage was determined by the virtual cessation of gas bubbling, whereupon heating was stopped and a stream of pure nitrogen was admitted to flush the remaining H_2S from the evolution system through the absorbers. The evolution flask was then allowed to cool to approximately 125°C before the next increment of sulphur was added.

The total residue from the evolution experiment was weighed in the evolution flask (which had been previously tared). To minimise errors it was necessary to scrape off and return to the flask any particles adhering to the thermometer and to the nitrogen inlet tube. The adherent material still remaining was washed with carbon tetrachloride, and the solvent evaporated with gentle heat. This material was added to the main portion of the residue before it was weighed. The residue was then removed from the flask, after thorough mixing and portions were taken for the sulphur estimations and other experiments described later.

At the conclusion of the experiments there adhered to the outlet tube a small quantity of liquid considered to consist of lighter petroleum fractions arising from the decomposition of the oil, and carrying a little sulphur. This deposit was also removed as completely as possible and estimated with the remainder of the residue as previously described.

It will be recalled that some prior workers reported considerable difficulties due to sulphur sublimation. With

the present method of working sublimation was much reduced. When it occurred the sulphur condensed mainly on the neck of the flask and in the vertical condenser tube from which it was melted back to the preparation from time to time by heating cautiously for a few moments by means of a small bunsen flame.

(ii) Quantitative Preparation of the Gas under Varied Conditions: Following the procedure described above H_2S was evolved from known weights of oil under controlled conditions, with the addition of known weights of modified sulphur. In all the experiments to be described in this Section the evolution of the gas was carried out in the temperature range 160°C - 290°C. The time taken per run was approximately proportionate to the weight of sulphur added at that respective stage. Timing from the first observation of gas bubbles to the point when bubble formation appeared to cease, the time taken was approximately 1 hour for a run using 10% sulphur on the weight of the original oil.

For quantitative estimation of the H_2S evolved the absorption solutions from each respective run (contained in absorption vessels 1 and 2) were combined and were made up to 500 ml. Of the well-mixed solution 5 ml. were diluted to 100 ml. for iodometric titration. Of this solution 5 ml. were taken for each estimation, mixed with a further 25 ml. water in the titration flask. A known volume of N/10 iodine solution, representing an excess, was added, the solution being

acidified with dilute HCl and the excess iodine being titrated with N/10 sodium thiosulphate, using starch indicator at the end of the reaction. Titrations were repeated till two agreed within 0.1 ml.

This method was used for the absorption solutions from all the experiments in which 10% of sulphur (on the weight of the oil) had been used in the respective run. For those in which a lower proportion of sulphur was used the estimation was made by the zinc sulphate method[1] so as to avoid errors that might be caused by the excess sodium hydroxide present. The procedure used was that well-established in the leather industry where analogous problems are encountered in the analysis of sodium sulphide solutions. A stock solution was made up by preparing N/2 ammonium hydroxide and adding 12.5 g. ammonium chloride per litre thereof. The stock solution had a pH of 10.0. To each sample taken for titration an equal volume of this solution was added. Its function was to prevent precipitation of zinc hydroxide. The sample was then titrated with standard zinc sulphate containing 14.35 g. $ZnSO_4.7H_2O$/litre, using basic lead acetate as an external indicator. Titrations were repeated till two agreed within 0.1 ml.

The respective preparations of hydrogen sulphide

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[1] Procter: "Leather Chemists Pocket Book", 3rd Ed. p.114, E & F.N. Spon, London.

were as shown below. In all the tables the weights of sulphur are given in terms of pure sulphur, and the ratios are based on the weight of oil originally taken in each series.

Series I: This consisted of two runs to check the working of the apparatus under operating conditions. The resulting solutions from the absorbers were used partly for testing the technique of estimation and partly for the preparation of sodium sulphide as further described later. The residue was used in later timber preserving experiments.

Series II: This consisted of two runs for the preparation of H_2S from mixtures containing low proportions of sulphur/oil. The residue was also used in the timber preserving experiments. Details of the gas evolution are as follows:

SERIES II

Wt. of oil taken 78.03 g.

Run No.	Wt. of S. added. g.	Percent. S added	Wt. of H_2S evolved, g.	Wt. of S evolved as H_2S, g.	Nature of Residue
1	1.95	2½	1.62	1.52	Asphaltic
2	3.90	5	3.52	3.31	Asphaltic
Total (1 & 2)	5.85	7½	5.14	4.83	Asphaltic

These results showed that higher sulphur ratios could be used without undue coke formation.

Series III: This consisted of five runs to cover the range of sulphur/oil proportions from 5% to 45%. The successive increments of sulphur were added to the same oil, as previously described. The residue was mixed and weighed, and its sulphur content was determined by the oxygen bomb method, full particulars of which have been given in an earlier section. Details of the results are as follows:

SERIES III

Wt. of oil taken 84.18 g.

Run No.	Wt. of S added g.	Percent. S added	Wt. of H_2S evolved	Wt. of S evolved as H_2S g.	Nature of Residue
1	4.21	5%	4.08	3.84	Thin, asphaltic
2	8.42	10%	7.81	7.35	Asphaltic
3	8.42	10%	7.47	7.03	Asphaltic with slight coking
4	8.42	10%	7.31	6.88	Coke increasing
5	8.42	10%	7.36	6.93	Coke increasing

Wt. of final residue	63.78 g.
Sulphur content of residue (by oxygen bomb method.)	6.97%
Wt. of sulphur in residue	4.45 g.

Since the sulphur was added successively at each stage to the oil it is possible to combine the results so as

to cover the range cumulatively:

SERIES III - CUMULATIVE RESULTS.

% Wt. of S on original oil	Wt. of S reacted. g.	Wt. of H_2S evolved g.	Wt. of S evolved as H_2S g.	% Wt. of S evolved as H_2S
5	4.21	4.08	3.84	91.21
15	12.63	11.89	11.19	88.59
25	21.05	19.36	18.22	86.55
35	29.47	26.67	25.10	85.17
45	37.89	34.03	32.03	89.81

Sulphur balance:

(a) Total sulphur added 37.89 g.

(b) Total sulphur evolved as H_2S 32.03 g.

(c) Sulphur in residue 4.45 g.

Thus sulphur unaccounted for (unabsorbed gases, trace compounds and experimental errors)

= a - (b c)

= 1.41 g.

In the course of the experiments the nature of the residue at the conclusion of each stage of evolution was also noted. It was found that the residues from Runs Nos. 1 - 2 were mainly soft and asphaltic in character without hard coke deposits. From Run No. 3 to Run No. 5 the coke formation increased, and after the final run the coke was denser and harder.

(iii) Tests for By-Products and Estimation of Gas Purity: The H_2S evolved passed, with volatile contaminants (if any) to the cold sodium hydroxide absorption solution, as previously described. The main possible by-products (other than incondensible and unabsorbed gases) were therefore collected in the absorbers in three possible forms, namely:

(a) in solution in, or in combination with, the sodium hydroxide solution, or at a later stage with the sodium sulphide formed, or

(b) as an insoluble liquid condensate forming a separate layer; or

(c) as a precipitate.

It was observed that in the absorption solutions from each of the five runs there was a slight dark suspension or precipitate. The suspension was hazy and ill-defined. It was also observed that a condensate of amber-coloured oil formed on the surface of certain absorption solutions. It was not observed in Runs Nos. 1 and 2 but only in the succeeding evolutions.

No reference to the suspension or slight precipitate could be found in the literature. After much further study its formation was ascribed to the prior formation of traces of carbon disulphide, which will therefore be dealt with at this point.

The best methods given in the literature for the detection or estimation of carbon disulphide depend on the

formation of a xanthate in the presence of an alcohol and alkali hydroxide, followed by estimation as xanthic acid or precipitation as a metal salt such as copper xanthate. Such methods could not be applied to the present solutions because of the great excess of alkali sulphide, while the addition of a copper salt would precipitate copper hydroxide or sulphide.

The method finally devised for detecting carbon disulphide took advantage of its reaction with sodium sulphide, with the formation of sodium thiocarbonate[1] thus:

$$Na_2S \qquad CS_2 \qquad CS_3.Na_2$$

It was clear that any carbon disulphide evolved would have reacted in this manner as soon as sodium sulphide had been formed by the H_2S passing into the absorber, and that the sodium thiocarbonate would be present in the absorbers. This reasoning led to an explanation of the probable nature of the precipitate mentioned above. The formation of soluble sodium thiocarbonate depends on the presence of sodium sulphide, which, as stated above, must be formed by prior reaction between H_2S and sodium hydroxide absorption solution. It is clear that during the absorption cycle there may at times be a relatively large proportion of sodium hydroxide not yet converted to sulphide. The hypothesis is thus suggested that at such times instead of formation of the soluble sodium thiocarbonate there are formed one or more basic and less soluble

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[1] Bernthsen: "Organic Chemistry", 1941 Ed. p. 332, Blackie & Son, London.

compounds, which would constitute the slight precipitate observed. Analogous support for this explanation is found in the fact that in prior work basic and insoluble thiocarbonates have been observed in addition to the soluble normal salts of calcium and magnesium[1]. Although the precipitate was very slight a confirmatory experiment was performed by acidification. It was reasoned that if the above hypothesis is correct then careful acidification should convert the compounds to thiocarbonic acid. A further study of the literature yielded the data that thiocarbonic acid is insoluble in water but soluble in various organic solvents including ether. It was furthermore learned that, though an unstable compound, its stability was greatly increased in the presence of dilute acid. Accordingly a sample of the precipitate, suspended in the absorption solution, was taken by pipette and shaken in a test-tube with about the same volume of ether. Hydrochloric acid (2N) was added drop by drop with frequent shaking until the solution was acid to litmus. Some H_2S was evolved and a white cloud of colloidal sulphur was formed. The precipitate under test was found to have dissolved.

An endeavour was now made to ascertain the nature of the precipitate more definitely by specific tests and if possible by the formation of a derivative. From each of the absorption solutions from Runs 1 to 5 in Series III 10 ml.

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[1] Mellor: "Comp. Treatise on Inorg. and Theoretical Chemistry", Vol VI pp. 125 and 127, Longmans Green & Co., London.

were withdrawn together with the suspended precipitate, giving a representative sample. The mixed sample was filtered through acid-washed filter paper and the filter paper was washed and dried at 90°C. Since the precipitate was too slight to remove from the paper segments thereof were used for the further experiments. A segment of the paper was carefully burnt at the end of a platinum wire which had previously been rigorously cleaned and heated to bright red heat. The wire was then heated in a bunsen flame, and sodium was identified by its characteristic flame colouration.

The remainder of the filter paper, with precipitate was transferred to a beaker and boiled for ten minutes with a large excess of water. It was noted that the suspended particles appeared to become lighter in colour, which was regarded as an indication that a portion was going into solution.

The beaker was allowed to cool and dilute hydrochloric acid was added very carefully until the solution was neutral to litmus, so as to avoid errors if any hydroxide had been carried over. A saturated solution of mercuric chloride was then added and a yellow precipitate was obtained. This was considered analogous to the yellow precipitate of mercuric thiocarbonate obtained by Zeise by mixing ammonium thiocarbonate with a mercuric salt[1]. The compound under test was thus accepted provisionally as being sodium thiocarbonate,

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[1] Mellor: ibid. p. 1284

precipitated under the basic conditions of the experiments. The conclusion was therefore drawn that traces of carbon disulphide had been formed as by-products of the gas evolution[1].

Tests for the presence of mercaptans in the gas evolved were now made. If mercaptans had been formed they would have passed into the absorbers forming sodium mercaptides. Ten ml. were taken from each of the five absorption solutions from Series III, mixed, and filtered. The filtrate was made neutral to litmus by means of dilute hydrochloric acid. Free H_2S and sulphides were precipitated by addition of 10% cadmium chloride solution which had been acidified with 10 g. concentrated HCl/litre. This method avoided the precipitation of any mercaptans, which would have occurred if the cadmium chloride solution had been alkaline[2].

The solution was again filtered and an equal volume of pure benzene was added. An excess of basic lead acetate was added with vigorous and continued shaking. Under these conditions any sodium mercaptides present would be converted to lead mercaptide which would dissolve in the benzene. The benzene layer was allowed to rise, and was separated in a separatory funnel. A portion thereof was shaken in a test-tube with dilute sulphuric acid[2]. Had lead mercaptide been present a white precipitate of lead sulphate would have formed.

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[1] This hypothesis is subject to confirmation when a larger sample can be obtained.

[2] Methods of Faragher, Morrell and Monroe: Ind. Eng. Chem. 19, 1281 (1927).

No such precipitate was obtained.

As a confirmatory test a composite sample of the absorption solutions from the five runs in Series III was again taken as described above, and the H_2S and sulphides were precipitated with acidified cadmium chloride solution as before. The filtrate was then treated with alkaline cadmium chloride solution containing 32 g. $CdCl_2$/litre in the presence of free ammonia, as specified in Chapter 2 (a). This solution precipitates both sulphides and mercaptans; and since the former compounds had already been removed by precipitation in the presence of acid it followed that a further precipitate at this stage would have proved the presence of mercaptans. No precipitate was obtained.

It was therefore concluded that the gas produced was free from mercaptans.

In further tests the purity of the gas evolved was estimated by the method used by previous workers, namely direct absorption in iodine solution. For this purpose the gas generated was used without preliminary treatment. A 50 ml. burette with wide-bore outlet tube was sealed off at its zero mark for use as the absorption apparatus. It was filled with water which had previously been saturated with H_2S at room temperature. The evolution flask was charged with a mixture of 25 g. sulphur with 100 g. oil and was heated as in previous experiments. The H_2S evolved was allowed to escape freely for thirty minutes to ensure that

the system was thoroughly purged. The gas was then collected by downward displacement of the water, the apparent volume being 50 ml. Iodine solution (N/10) was admitted to the burette with precautions against air leakage and with shaking to facilitate absorption. With continued absorption the iodine solution was drawn up further in the burette, and when the level remained stationary the volume was noted.

Found: Apparent volume of gas unabsorbed by iodine solution from 50 ml. sample : 0.7 ml.
Repeat: (approximately thirty minutes after previous experiment): 1.1 ml.

These results correspond to a purity of 98.6% and 97.8% respectively by volume.

To apply pressure correction use was made of the levelling tube of a Hempel gas apparatus. The tube was connected by rubber tubing to the absorption burette, iodine solution being used for levelling as well as for absorption. These arrangements were prepared in advance so that the experiment could be carried out as soon as possible after the last described experiment. The gas was collected as before by downward displacement and the volume taken was 50 ml. at atmospheric pressure. The iodine absorption was repeatedly agitated and finally the liquid in the tubes was levelled and the residual volume noted at the same pressure and at the same room temperature.

Found: Volume of evolved gas unabsorbed by iodine solution from 50 ml. sample, after pressure correction: 0.9 ml.

This corresponds to a purity of 98.2% by volume.

Heating of the gas evolution flask was continued for a further hour, and the estimation was then repeated with the same procedure and with pressure correction. By this time the gas was noticeably less pure, fumes being visible. The estimation showed a large reduction in purity.

Found: Volume of evolved gas unabsorbed by iodine solution from 50 ml. sample, after pressure correction: 8.0 ml.

This corresponds to a purity of 84% by volume.

(iv) Examination of Light Oil Distillate: It appeared desirable to examine the distilled oil recovered in the course of the evolution of H_2S not only because of its possible importance as a by-product but also because of the information which it might give as to the course of the main reaction. The oil subjected to these tests was that produced in Series III. As mentioned above the oil was recovered only from Runs 3, 4 and 5. The oil layer was pipetted from the surface of each absorption solution, together with a little of the solution to make recovery more complete. The mixture was allowed to settle in a narrow burette which was used in the manner of a separatory

funnel. In this way good separation was possible. The total oil recovered from Series III was 6.13 g. Despite the smallness of the sample it proved possible to obtain the data required.

The density was first determined by direct weighing of a sample measured at 24°C by means of a graduated pipette.

Found: Density of recovered oil at 24°C :

0.820 g. per ml.

Instead of determining the initial boiling point alone the distillation range at atmospheric pressure was obtained by using semi-micro technique. A miniature distillation apparatus was made from a $\frac{3}{4}$" test-tube. The delivery tube was taken to a narrow graduated tube, acting as receiver, which was water-cooled. The sample of oil taken weighed 3.485 g. Its volume was 4.25 ml. Heating was by careful use of a low flame.

The initial boiling point was 60°C. Distillation was continued up to 220°C. By this time the remainder of the sample was becoming carbonised and heating was stopped. The following table summarises the results:

Distillation of Recovered Oil

Oil taken: 4.25 ml.

Temp. °C.	Vol. Distilled, ml. per 10° Rise in temp.	Total Vol. Distilled, ml.
60	-	-
70	0.30	0.30
80	0.20	0.50

Temp. °C.	Vol. Distilled, ml. per 10° Rise in temp.	Total Vol. Distilled, ml.
90	0.40	0.90
100	0.35	1.25
110	0.15	1.40
120	0.15	1.55
130	0.10	1.65
140	0.10	1.75
150	0.10	1.85
160	0.10	1.95
170	0.10	2.05
180	0.10	2.15
190	0.30	2.45
200	0.30	2.75
210	0.35	3.10
220	0.35	3.45
	Residue, by difference,	0.80 ml.

(Note: Tube graduated at intervals of 0.1 ml. Second decimal by estimation).

By using samples of one drop of oil for each test, and mixing on a watch-glass illuminated from below, it was found that the oil mixed readily with petroleum ether, benzene, carbon disulphide and carbon tetrachloride. It did not mix with water or 95% alcohol.

Use of this observation was made by preparing a small quantity of a solution of the oil (20% by volume) in pure benzene for further tests. A sample thereof was shaken vigorously with acidified cadmium chloride solution. There was no precipitate, indicating the absence of H_2S. A further sample was shaken with alkaline cadmium chloride solution. A slight haze appeared to form, but on standing this was found to consist of oil which had been temporarily

emulsified in the presence of the ammonia, and no precipitate was present. The oil therefore contained no mercaptans.

Another portion of the solution was allowed to stand for two days in contact with mercury. There was very slight darkening indicating the presence of a trace of elementary sulphur[1].

In view of the comparatively low initial boiling point of the oil, it was considered desirable to ascertain whether thiophene (B.P. 84°C) was present. To a small sample was added a solution of isatin[2] in ether, with shaking. Cold, concentrated sulphuric acid was added. There was no blue colouration within one hour. Thiophene was therefore not present in the oil.

(v) Use of Spent Oil for the Reaction: With a view to the ultimate industrialisation of the process the work based on refined oil was supplemented by the preparation of H_2S from a mixture of sulphur and spent lubricating oil. The spent oil was of the same grade as that specified in the main investigation, but it was first subjected to use in a motor-car engine in the course of 1,000 miles travel and then recovered by draining.

The oil was slightly darker in colour than the original oil. Its behaviour was observed by heating a sample

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[1] Method of Ormandy and Craven, modified by Faragher, Morrell and Monroe, loc. cit.

[2] Kingzett: "Chemical Encylopaedia", 6th Ed. p. 986, Bailliére, Tindall & Cox, London.

of 200 ml. in a Pyrex beaker. As the temperature rose above 80°C there was very slight frothing due to moisture. At approximately 150°C fumes were visible, and were given off more heavily as the temperature was raised above 200°C. Heating was continued to 290°C, and the oil was held at this point for fifteen minutes to drive off any low-boiling material. There was no visible separation of carbon and it was not found necessary to filter the oil.

The oil thus treated for removal of low-boiling fractions was used for the evolution of H_2S. The apparatus and procedure were the same as described in respect of the preparations with refined oil, with the exception that the absorption vessels were filled with a larger quantity of absorption solution, namely 950 ml., so that the total gas evolved could be absorbed in one charge of the solution. On the basis of the experience gained in the previous experiments a total sulphur ratio of 25% on the weight of oil taken was regarded as a suitable proportion which would yield a residue sufficiently fluid to allow any coke to be readily separated. The sulphur (modified as before) was added in three stages, using the same technique as before. The estimation of the H_2S absorbed was done gravimetrically by precipitation with alkaline cadmium chloride solution. The total time of gas evolution (i.e. excluding heating up and cooling down time on each run) was approximately 3½ hours. The temperature range in which the gas was mainly evolved was

160° - 290°C. Details of the preparation are as follows:

SERIES IV

Wt. of spent oil 70.23 g.

Sulphur added.

Run No. 1	7.02 g.	(10% wt/wt of oil)
Run No. 2	7.02 g.	(10% " " ")
Run No. 3	3.51 g.	(5% " " ")
Total S added	17.55 g.	(25% " " ")

Weight of H_2S evolved	15.24 g.
Weight of S evolved as H_2S	14.34 g.
% " " " " " "	81.7%
Weight of Residue	63.51 g.
Total Sulphur content of residue (by oxygen bomb)	3.94%

The general course of experiment was similar to that observed when using refined oil. As before the light oil distillate was not evolved in the early part of the preparation. The oil was distilled only in the second and third runs. It was separated by the same technique as before and 2.8 g. were recovered. It had the same density as before (0.820 g. per ml. at 24°C). Like the previous sample it gave negative results when tested for the presence of hydrogen sulphide, mercaptans, and thiophene, but contained traces of elementary sulphur, due presumably to solution of particles of sublimed sulphur. It was slightly darker than the oil

recovered in the previous experiments, but dissolved in the same solvents. The slight dark suspension was observed in the absorption solution as before.

No special difficulties were encountered in the preparation, and the opinion was formed that spent oil, if pre-treated to remove moisture and volatile fractions, should be a suitable material for the proposed success.

(vi) Preparation of Crystalline Sodium Sulphide: While the main object of the present study was the preparation of hydrogen sulphide it was desirable to take the work a step further with a view towards the most likely initial method of industrial utilisation, namely the production of sodium sulphide. If sodium hydroxide is used as the absorption solution in a suitable system sodium sulphide is available for use either directly or for production of a concentrated solution for disposal. The more satisfactory alternative, however, would be recovery as solid. This preparation was therefore carried out on the laboratory scale.

A composite sample of 400 ml. of the dilute absorption solutions preserved from the foregoing evolution experiments was filtered and evaporated in a Pyrex beaker until the solution reached saturation. On cooling a mass of fine interlocked crystals was obtained, slightly yellowish in colour.

This product did not have the characteristic appearance of the tetragonal, colourless, crystals of $Na_2S.9H_2O$ which were being sought. It was clear that the conditions

were not correct for the crystallisation of this hydrate.

Renewed study of the literature showed that hydrates of sodium sulphide of the constitution $Na_2S.H_2O$ and $Na_2S.5\frac{1}{2}H_2O$ are formed between 95°C and 50°C, which is the transition point[1]. Clearly, therefore, it was necessary to crystallise as far below this temperature as possible. The crystals were redissolved and the usual procedures for rapid cooling were tried, but difficulties were encountered. Ultimately a reliable and simple method was used. The solution which was evaporated down as before was crystallised to a compact mass of the lower-hydrated crystals, which were cooled to room temperature. The crystals were then dissolved in a minimum of water at 40° - 45°C and the solution set aside to crystallise slowly. The crystals were dried on several thicknesses of filter paper.

The crystals thus obtained were almost colourless and detached specimens showed a characteristic tetragonal form. The yield was 26 g., without utilisation of the mother liquors. The chemical nature of the product was then formally confirmed. The flame test gave strongly the characteristic sodium colour. A solution of the crystals gave with silver nitrate a black precipitate insoluble in the presence of dilute nitric acid or in excess ammonium hydrate.

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[1] Sanfourche and Liebaut: Bull. Soc. chim. 31, 966 (1922) through Thorpe, "Dict. of Applied Chemistry", 4th Ed. Vol. X p. 890, Longmans Green & Co., London.

Finally a sample of the crystals was heated in a crucible. A portion of the water of crystallisation came off readily at first and with stronger heating fusion took place with formation of a characteristic melt which could be poured from the crucible at low red heat and cooled to a solid mass of faint yellowish-pink colour.

(vii) Determination of Bromine Addition and Substitution Values: In order to obtain further information regarding the theoretical mechanism of the reaction between sulphur and oil a study was made of methods for establishing whether compounds relatively more unsaturated than the original material were being formed. Bielenberg[1] had used iodine absorption for this purpose, but later workers, including particularly Johansen[2] have pointed out that with iodine both addition and substitution reactions occur and that the estimation does not distinguish between them in any way.

By using bromine instead of iodine, with a special procedure, it is possible to distinguish quantitatively between the two types of reaction. The original method using bromine was introduced by McIlheny[3]. It is based on the observation that for each atom of hydrogen replaced by bromine in a substitution reaction one molecule of hydrogen bromide is formed, estimation of which gives the extent of substitution.

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[1] Bielenberg: Braunkohlenarchiv, 4, 40 (1923).
[2] Johansen: Ind. Eng. Chem. 14, 288 (1922).
[3] McIlheny: J. Am. Chem. Soc. 21, 1084 (1899).

McIlheny's method requires certain experimental safeguards, but if these are maintained the method gives reliable results. Details and apparatus have been specified by several modern authorities, including the Institute of Petroleum[1]. The procedure followed in the present study was that given by Snell and Biffen[2].

Special flasks are prescribed for the determination, to prevent loss of hydrogen bromide. The flasks used were of 250 ml. capacity and were conical. They were furnished with ground glass stoppers projecting well above the flask for easy manipulation. The mouth was flared above the ground joint, so that when the stopper was in position a space was available to hold the necessary reagent as a seal.

The following reagents were prepared:

Standard Solution of Bromine, (0.33N) containing 26.6 g./litre with pure carbon tetrachloride as solvent.

Potassium Iodide Solution, containing 250 g./litre.

Potassium Iodate Solution, containing 21.4 g./litre.

In each of the following determinations the same reagents and precisely the same procedure were used. A sample of approximately 0.8 g. was weighed in the special flask and dissolved in 10 ml. pure carbon tetrachloride. Exactly 20 ml.

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[1] Modified McIlheny Method, I.P. - 9/42, Institute of Petroleum, London.

[2] Snell & Biffen: "Commercial Methods of Analysis", p. 346, McGraw-Hill, New York.

standard bromine solution were added and the flask was immediately stoppered. A small quantity of the potassium iodide solution was placed in the flared mouth of the flask. The flask was allowed to stand at room temperature for two minutes, and was then cooled by standing in ice-water. The stopper was carefully removed, so that the potassium iodide solution was sucked into the flask, which was re-stoppered and shaken in order that gases might be absorbed. A further quantity of potassium iodide solution, making up a total of 25 ml., was now added to the flask, with shaking. The reaction liberated iodine. This was titrated with N/10 sodium thiosulphate, starch indicator being used near the end point.

After the end-point had been recorded 5 ml. potassium iodate solution were added. This solution reacted with any hydrogen bromide present as follows:

$$KIO_3 + 5KI + 6HBr \longrightarrow 6KBr + 3I_2 + 3H_2O$$

Thus a further quantity of iodine was liberated, which was again titrated and gave a second end-point. The entire test was repeated with only the solvent and reagents present. The "blank" values so obtained were allowed for in the calculations.

The estimations were carried out using three samples, namely:-

(a) Original oil, before reaction with sulphur.

(b) Liquid portion of residue, after reaction with sulphur in Series III evolution experiments

described above, and

(c) Light oil distillate, recovered from absorbers in Runs 3 - 5 in Series III.

Sample (b) was not suitable for the estimation in the form in which it was obtained from the evolution flask, because it contained sulphur compounds which might interfere. A sample was therefore prepared for the test by distilling the residue under vacuum at a temperature of 150° - 200°C. The distillate obtained was a brownish-yellow oil of density 0.860 g./ml. at 23°C and was free from sulphur.

In the control (blank) estimation it was found that no additional thiosulphate was required for the second titration. This indicated that the reagents and solvent were free from hydrogen bromide and compounds which would produce it under the experimental conditions.

The results are given in the following table. The bromine addition and substitution values are calculated as the weight in grams of bromine added or substituted respectively when reacted with 100 g. of the oil.

BROMINE VALUES

	Material	Bromine Addition Value	Bromine Substitution Value
(a)	Original Oil	Nil	2.40
(b)	Oil from Residue	21.78	1.42
(c)	Oil from Absorbers	15.98	19.30

It should be noted that in these estimations no hydrogen bromide is formed in the addition reactions. When it is formed in the substitution reactions it is clear that for every molecule of HBr found an atom of bromine has substituted in the hydrocarbon structure. For this reason it is necessary, in calculating the bromine addition value, to deduct from the total bromine absorbed twice the weight of bromine found as hydrobromic acid.

The results obtained show that the oil from the residue, and also the oil from the absorbers, are considerably more unsaturated in character than the original oil. This observation will be further discussed later.

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(1) PREPARATION OF TIMBER PRESERVATIVE FROM RESIDUE.

To complete the present investigation from the viewpoint of the proposed industrial process it was necessary to find a practical method of utilising the residue obtained as by-product from the reaction. It will be recalled that this may take one of two forms, namely a hard coke-like mass or alternatively an asphaltic material fluid while hot and somewhat viscous when cooled, with a proportion of coke in suspension, according to the experimental conditions. Earlier workers had applied analogous asphaltic residues for road construction and other such purposes, and in the petroleum industry sulphur has been used in special processes to modify the properties of asphalts. For example by using the reaction between sulphur and unsaturated naphthenic extracts resulting from solvent refining processes, McKinney, Mayberry and Westlake[1] produced a range of artificial high-sulphur asphalts ranging from "medium-stiff" to "hard-tough", with H_2S as a by-product.

In the present study it was found possible, by the technique already described, to obtain from the evolution process a residue more fluid at ordinary temperatures than those previously described.

It was reasonable to consider that its properties might be applied to a purpose which, in the South African environment, might be more desirable than the production of

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[1] McKinney, Mayberry and Westlake: Ind. Eng. Chem. 37, 177 (1945).

artificial asphalt.

In previous years the writer had carried out industrial work on the production of several wood preservatives using various accepted materials including creosote, pentachlorphenol solutions, and the metallic naphthenates. In observing the properties of residues obtained in the present study analogies with previous experience strongly suggested the possibility of utilising the residues in timber preservation.

Overseas practice in the application of sulphur for such a purpose has been confined mainly to its use in molten form. Thus Kobbe[1] described a process in which wood (particularly railway sleepers) could be impregnated with sulphur at 140° - 150°C. In a previous paper[2] the same worker had discussed the advantages of this type of process in hardening and preserving wood against different causes of decay. In South Africa English[3] has reported work in which local timbers were impregnated with sulphur in the presence of 5% naphthalene and proved resistant to termite and fungus attack in tests in which untreated controls were attacked. Such treatments, while effective in some applications, do not appear to make the most economical use of the sulphur, and also apply it in a form in which it is not very toxic.

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[1] Kobbe: U.S. Patent No. 1,599,135 of 1926.
[2] Kobbe: Chemical Trade Journal, 75, 520 (1924).
[3] English: J.S.A. Inst. Eng. 27, 127 (1929).

In the present work use was made of the fact that the sulphur is present in the residue in a form in which it can be mixed with solvents which have already been proved to be efficient vehicles in the manufacture of wood preservatives and in which elementary sulphur is not highly soluble. The remaining sulphur compounds present in the residue are all non-volatile below 270°C, because of the conditions under which they are produced in the process. This thermal stability would ensure permanence in the timber in actual use, while another advantage would be the insolubility in water.

The residue used in these experiments was a composite sample of that from Series I and the residues left from the other evolutions and tests. The mixed residue contained 5.48% total sulphur. The residue was first warmed to 70°C and was allowed to stand for 24 hours at this temperature in an oven. This treatment sufficed to settle out any coke lumps present, and the supernatant material could readily be removed by decantation. This decanted portion was used for the further experiments.

In a series of tests it was found that this residue could be diluted in the cold with a wide choice of solvents. In particular it mixed[1] with benzene and with creosote. Among the petroleum solvents it mixed readily with power

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[1] The term "mixed" is used here not in a rigorous sense but to indicate that the solvent named formed a satisfactory practical vehicle for the material. The complex nature of the asphaltic material must be borne in mind.

kerosene. These observations were specially important in that the last-named solvent and mineral turpentine are the main accepted fractions used successfully at present as solvents for other wood preservatives on account of their rapid penetration into the timber. Power kerosene was selected as the solvent for the rest of the work, and will henceforth be referred to as "the solvent".

To obtain a mixture of sufficiently low viscosity to be handled as easily as creosote, or other existing preservatives in non-aqueous vehicles, the residue was diluted with the solvent in the proportion of 2 parts solvent: 1 part residue, both by weight. The resulting preservative was filtered through cotton wool and used for the remaining experiments.

In preliminary tests the preservative was applied to thin pieces of planed pine wood by brushing. It flowed readily and was absorbed from the surface, leaving the wood an amber-brown colour similar to that produced by creosote. The test was repeated except that the wood was immersed in the preservative for ten minutes, removed and allowed to drain. The sample was then cut across the grain. It was found that the preservative had penetrated approximately 10 mm. along the grain from the ends, and approximately 2 mm. from the other surfaces.

The main series of tests was now undertaken, using samples of officially identified South African-grown timber

from the Forest Products Research Institute. The timbers used were:

Pinus insignis

Pinus pinaster

Pinus patula

Pinus taeda

Eucalyptus saligna

Eucalyptus rostrata.

The planed samples measured 11 cm. x 7.7 cm. x 12 mm. each. For the purpose of the experiments each was cut into two similar and comparable pieces by sawing lengthwise (i.e. with the grain). This gave six samples each 11 cm. x 3.8 cm. x 12 mm. and six similar controls.

Under industrial conditions the preferable method of application of the preservative would be the "full cell" method in which a vacuum is first applied (to remove much of the air from the cells of the wood) followed by impregnation under pressure. In the absence of the special facilities needed for this work the present tests were done by the "open tank" method[1]. The samples were placed in a Pyrex beaker and covered with the preservative, which was heated in an air-bath to 90°C and held at this temperature for an hour. This expanded the air in the cells and caused much of it to escape.

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[1] These methods of application are discussed by Cartwright and Findlay: "Decay of Timber and its Preservation", p.259, H.M. Stationery Office, London.

Heating was then stopped, and the wood was allowed to cool naturally, the preservative being drawn in during cooling and replacing the air removed. The samples were left in the preservative for one hour from the cessation of heating and then removed and allowed to drain and to become almost surface-dry by natural evaporation.

The treated samples were of dark brown colour slightly oily to the touch, and generally similar in appearance to wood treated with creosote. When cold the samples had a characteristic and pungent smell, which would possibly add to the effectiveness against attack by the higher insects, and also, by slight volatility, might affect fungi adjacent to the treated wood.

The treated pieces were then placed in soil for practical test. The situation chosen was one rich in decaying timber. Each piece was marked for identification and was placed with approximately two-thirds of its length underground. The six untreated controls were similarly exposed, care being taken to keep them sufficiently apart from the treated samples to avoid errors due to possible volatilisation of the preservative.

It is expected that about two years of exposure will be required to obtain definite results in these tests against fungal attack and decay. Meanwhile it is intended to prepare a duplicate set of treated test pieces and controls and to expose them to attack by borer beetle, Italian beetle, or termites.

It may be pointed out that, where such a procedure

is desirable, the proposed wood preservative may be rendered additionally effective by admixture of other known preservatives. This would provide an economical method of manufacture, since the supplementary preservative could be used in lower proportion than if it were applied alone.

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CHAPTER THREE

THEORETICAL DISCUSSION

In 1946 Westlake[1] wrote: "One thing is certain ... the structure of sulphur is intimately involved in the mechanism of sulphurization, and any step in the solution of one problem is an advance in the solution of the other". The observations made in the present study have emphasised the importance of this viewpoint, from which the many and complex phenomena encountered in the field of sulphur research may gradually be explained and correlated.

This discussion will accordingly deal with the following aspects of the study:

(a) The nature and probable course of the reactions, and

(b) The significance of the observations in the light of certain physico-chemical properties of sulphur.

(a) The nature and probable course of the reactions: In the present state of our knowledge the mechanism of the reactions between sulphur and saturated aliphatic hydrocarbons in the temperature range with which this study has been concerned, is inadequately understood. Even in the allied field - the reactions between sulphur and unsaturated compounds - which has been more intensively studied over many years, there

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[1] Westlake: Chem. Reviews, 39, 235 (1946).

is as yet no accepted body of explanatory theory. The subject of rubber vulcanisation constitutes what is probably the main individual problem in this latter field. It has been the object of research for over a century, and yet "its mechanism remains obscure up to the present day".[1]

Although no explanation is available of the full course of the reaction between sulphur and paraffin wax, or the other heavy hydrocarbons with which the present work has been concerned, there can be little doubt that in its initial stage the reaction is one of dehydrogenation, with the formation of double bonds and relatively unsaturated compounds. Much evidence in support of this view is to be found in the literature discussed in this study. Nellensteyn and Thoenes[2] reached the conclusion that the main reaction consisted of dehydrogenation. Bryce and Hinshelwood[3] considered further that "the primary reaction for all the hydrocarbons is assumed to be the removal of a hydrogen atom, with the formation of alkyl and HS radicals". Similar opinions were expressed by Dunlap[4] and by other workers. In other fields the effectiveness of sulphur as a dehydrogenating agent has also been successfully applied on an experimental basis. The best example is probably the method used by Vesterberg[5] for the

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[1] Westlake: loc cit.
[2] Nellensteyn and Thoenes: Chem Weekblad, 29, 582 (1932).
[3] Bryce and Hinshelwood: J. Chem. Soc. 136, 3379 (1949).
[4] Dunlap: Chem. Met. Eng., 34, 298 (1927).
[5] Vesterberg: Ber. 36, 4200 (1903).

preparation of retene by heating abietic acid with sulphur to approximately 200°C, with evolution of H_2S as a by-product. The effectiveness of sulphur as a dehydrogenating in this type of reaction has been fully discussed in recent years by Adleson and Bogert[1]. Plattner has also shown how dehydrogenation by means of sulphur can be used as a valuable research tool in numerous reactions[2].

Accepting the view that the initial stage of the reaction consists of dehydrogenation there remains the problem of tracing the fate of the unsaturated compounds that would be formed. The results of prior work are incomplete on this subject. Rasmussen, Hansford and Sachanen[3] bubbled n-butane through molten sulphur in the temperature range 300° - 400°C. The exit gas stream contained much H_2S but no olefines. Other workers also failed to recover unsaturated compounds from hydrocarbons subject to dehydrogenation by sulphur. Brooks and Humphrey[4] endeavoured to convert paraffin wax to a naphthene by dehydrogenation with sulphur, but when they distilled the resulting reaction mixture under vacuum they obtained paraffin wax of the same melting point as the original material. When they heated a saturated petroleum oil with sulphur the oil distilled under vacuum from the reaction mixture contained no olefine groups. They con-

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[1] Adleson and Bogert: Chem. Reviews, 24, 135 (1939).
[2] Plattner: Die Chemie, 55, 131 and 154 (1942). These valuable papers list 260 references covering dehydrogenation by sulphur, selenium and platinum.
[3] Rasmussen, Hansford and Sachanen: Ind. Eng. Chem. 38, 376 (1946).
[4] Brooks and Humphrey: Ind. Eng. Chem. 9, 747 (1917).

cluded that unsaturated compounds could not be made in this way because of the readiness with which sulphur reacts with unsaturated hydrocarbons.

On the other hand Friedmann[1] obtained a small yield of a dialkyl thiophene from the asphaltic residue formed in a reaction between n-octane and sulphur at about 280°C. By dehydrogenating cycloparaffins with sulphur Friedmann[2] also obtained some evidence of the formation of cyclic unsaturated compounds. Thus with cyclohexane as the starting material he obtained indications of the formation of cyclohexene and cyclohexadiene. Dunlap[3] suggested that under the conditions existing in internal combustion engines any free sulphur present would react with the lubricating oil to form H_2S and a diolefine. The latter product might in turn polymerise to form the gummy deposit found in engines. Nellensteyn and Thoenes[4], however, considered that polymerisation did not occur in their experiments. Bryce and Hinshelwood who reacted ethane, propane, n-butane and n-hexane respectively with sulphur vapour, stated that the principal products appeared to be hydrogen sulphide and unsaturated hydrocarbons.

In the present study strong evidence was obtained of the formation of unsaturated hydrocarbons as a result of

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[1]Friedmann: Ber. 49, 50, 1344 and 1551 (1916).
[2]Friedmann: Petroleum Zeitschrift: 11, 978 (1916).
[3]Dunlap: loc. cit.
[4]Nellensteyn and Thoenes: loc. cit.

the reaction between the high-boiling hydrocarbon material used and sulphur. Starting with highly refined oil which showed no addition value with bromine, products were obtained to which bromine added definitely and in considerable proportion. It was found possible to separate the unsaturated compounds formed into two broad groups, namely (i) those compounds that were distilled off at atmospheric pressure in the course of the preparation of H_2S and were recovered from the absorption system, and (ii) those remaining in the asphaltic and partly coked residue. These were recovered by vacuum distillation. The wide distillation range of the compounds included in group (i) indicates clearly that the distillate is a mixture. It is also probable that the distillate (ii) obtained under vacuum from the residue does not contain all the remaining unsaturated compounds and that the final residue still contains higher-boiling portions thereof.

The bromine addition values obtained (grams bromine added per 100 g. of sample) show a rise from zero in the case of the original oil to 19.30 for the oil recovered from the absorbers and 21.78 in respect of the oil recovered from the asphaltic residue. In comparing these results it should be borne in mind that small differences are not significant. The Institute of Petroleum[1] gives accuracy to about one unit in the value obtained, and the accuracy of the present method

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[1]Institute of Petroleum (Modified McIlheny Method): loc. cit.

is probably similar. Thus the difference between 19.30 and 21.78 is insufficient to be significant in itself.

The difference between either of these values and that of the original oil, however, is great, and affords strong evidence of the formation of unsaturated compounds in the course of the reaction.

The contrast between the two distillates is demonstrated by the difference in the substitution values (grams bromine substituted per 100 g. sample). Here the oil distilled from the residue has a substitution value of 1.42, which is not significantly different from the value given by the original oil (2.40); while the oil from the absorbers has the much higher substitution value of 15.98. This is further evidence that the two distillates are different mixtures. As far as can be ascertained from the available literature these two distillates appear to be the first samples of their kind prepared at atmospheric pressure by the reaction between sulphur and high-boiling saturated hydrocarbons. They were prepared under controlled and reproducible conditions, and were recovered in quantities sufficient for examination.

It was not within the scope of the present study to carry this portion of the work beyond this point, and the findings are recorded with the recommendation that the method of bromine value determination should be used in future work as a valuable means of following this and similar reactions.

Once it has been demonstrated that unsaturated compounds are formed in the reaction the question arises why it has been possible to obtain these compounds in the present work when such difficulties were previously encountered in their recovery.

It will be recalled that prior investigations have mainly utilised experimental methods, or proportions of material, which yielded what may be termed an "exhaustive" reaction. In the laboratory scale investigations the reaction was mostly carried out for long periods and often under pressure, with high temperatures in some instances. In the experiments of an industrial or semi-industrial character the conditions were chosen mainly so as to obtain the highest possible yield of gas, with almost complete coking of the residue. Under such conditions it appears that any unsaturated compounds formed must have reacted further and were consequently not found, or found only as traces, at the end of the experiments.

The conditions under which the gas was prepared in the course of the present study were different. The sulphur was first modified so that it did not become viscous during the experiment. This prevented the local formation of coke and lumps rich in sulphur early in the reaction with consequent local overheating and destruction of intermediates. The sulphur was also added in stages, each of which involved a short run at moderate temperatures (approximately 160° - 290°C). The sulphur was added in relatively small

proportions (5 - 10% on the oil taken). Thus, for example, in Runs 1 and 2 of Series III in the gas preparation experiments there was present a total of only 15% of sulphur on the weight of the original oil. It is likely that during these runs the reaction consisted largely of a dehydrogenation of the original oil, with formation of H_2S and unsaturated hydrocarbon compounds. As they accumulated the compounds began to distil over and to appear in the absorbers. Doubtless portions of the unsaturated compounds reacted further, but it is probable that their distillation was facilitated by the lowered partial pressure resulting from the simultaneous evolution of other gases. This would not occur in the closed systems used in some of the prior work.

A further difference in the conditions was that the reaction was deliberately carried out as to obtain as little as possible of the resultant carbon in the form of coke, and as much as possible in the asphalt. These milder conditions, again, assisted in preserving some of the intermediates.

In the light of these facts it now becomes possible to view the production of H_2S as the result of two broad groups of reactions, proceeding at first consecutively and later side by side. The first would from this viewpoint be the formation of H_2S by dehydrogenation of the paraffin chains or of the saturated cyclic compounds (as in the case of the lubricating oil used in the present work). This initial reaction would yield unsaturated compounds as by-products.

The second mechanism would consist in the production

of H_2S and other products as a result of reactions between these compounds and the free sulphur present, or with other sulphur-containing compounds produced, including hydrogen sulphide. The end-products of these reactions would be the complex and relatively stable sulphur compounds still left in the residue at the conclusion of the experiment.

This hypothesis provides a bridge between much of the prior work in the present field and links it with the results of other research relating to the reactions between sulphur and unsaturated hydrocarbons. The theoretical aspects of such reactions cannot be dealt with here in detail, but certain facts require discussion. With hexylene Spanier and von Engler[1] noted a vigorous reaction in a sealed tube at 210°C for 24 hours, with production of a large volume of H_2S, a brownish-yellow distillate, and a coke-like residue. When Foragher, Morrell and Comay[2] heated solutions in petroleum naphtha of alkyl sulphides, alkyl disulphides and other organic sulphur compounds (excepting thiophene) they obtained H_2S as the main decomposition product. Jones and Emmet-Reid[3] observed that the end products are much the same whether an unsaturated hydrocarbon is treated with S, H_2S, or RSH. They found that with ethylene sulphur gives H_2S which may react with more ethylene to form ethyl mercaptan. This in

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[1] Spanier & von Engler: loc. cit.
[2] Foragher, Morrell and Comay: loc. cit.
[3] Jones and Emmet-Reid: J.A. Chem. Soc. 60, 2452 (1938).

turn adds to ethylene to form ethyl sulphide. Such a chain of reactions could account for much of the sulphur not evolved as H_2S in the experiment as a whole since they utilise both sulphur and H_2S. They would also account for the occurence of mercaptans in the H_2S prepared by various prior workers when the reaction was completed at somewhat higher temperatures and over lengthy heating periods. Conversely in the gas prepared in the course of the present study the absence of mercaptans could be explained by the absence of experimental conditions favouring these reactions.

With cyclic hydrocarbons Meyer and Hohenemser[1] found that cyclohexene and sulphur reacted to give cyclohexyl mercaptan and cyclohexyl sulphide. They explained the latter reaction as a dehydrogenation followed by addition of the H_2S formed to cyclohexene.

It should be noticed that even if the reactions do follow a course resulting in mercaptans not all the sulphur so reacting will be lost from the viewpoint of H_2S evolution, since the mercaptans may sometimes decompose[2] with further formation of H_2S.

These and numerous other reactions may involve the unsaturated compounds in the H_2S evolution process contemplated in the present study. Some indication of the number and

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[1] Meyer and Hohenemser: Helv. Chim. Acta. 18, 1061 (1935), through Westlake: loc. cit.
[2] Malisoff and Marks: Ind. Eng. Chem. 23, 1114 (1931).

variety of the compounds that may result from such combinations and re-combinations may be obtained from the papers already referred to and in the literature relating to rubber chemistry. For the present purpose it is sufficient to note that the compounds in the form of which the remaining sulphur persists in the asphaltic or carbonised residues are probably derived from such secondary reactions rather than directly from the saturated compounds constituting the original material.

Before leaving this subject it is important to point out that the complexity of the products which may be formed by reaction of unsaturated hydrocarbons with sulphur and many of its compounds tends to obscure the fact that in the preparations with which the present study is concerned the main product is nevertheless observed to be hydrogen sulphide. Examples of such preparations have been referred to elsewhere in this work, and can only be briefly mentioned here. Nellensteyn and Thoenes[1] obtained good yields of H_2S when using Edeleanu extract, which is rich in unsaturated hydrocarbons, and the reaction commenced at 124°C - lower than in the experiment using saturated compounds. Bielenberg[2] found that H_2S was readily evolved when he heated sulphur with "yellow oil" (containing unsaturated compounds)

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[1] Nellensteyn and Thoenes: loc. cit.
[2] Bielenberg: loc. cit.

and observed first indications of the gas at 130°C. McKinney, Mayberry and Westlake[1], who prepared asphaltic products by the action of sulphur on unsaturated extracts recovered in the course of petroleum refinery, obtained H_2S as a by-product from about 140°C. Thus we find that not only is H_2S readily prepared in this manner but that the initial temperature of evolution appears to be lower than in similar experiments with saturated compounds.

No adequate explanation of these observations has been found in the literature. It is possible that the first step is addition of sulphur without degradation or elimination of H_2S. This would correspond to the formation of crosslinks as postulated in certain rubber vulcanisation theories. Such a view is supported by experiments carried out by Armstrong, Little, and Doak[2] in the temperature range 120° - 140°. With methyl - 4 - nonene less than 1% of the sulphur used was evolved as H_2S in that range. With increasing temperature decomposition of the sulphur compounds would commence with the evolution of part of the sulphur as H_2S, accompanied by dehydrogenation reactions on the analogy of the Vesterberg reaction. Thereafter the H_2S could react with the unsaturated hydrocarbons to give mercaptans and other sulphur compounds as already discussed. This hypothesis would imply that with long-continued reaction and higher temperatures the efficiency

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[1] McKinney, Mayberry and Westlake: loc. cit.
[2] Armstrong, Little and Doak: loc. cit.

of the process (from the special viewpoint of evolution of free H_2S) would fall, with final formation of complex sulphur compounds of a more stable character, such as are associated with asphalt formation.

To throw some light on this problem research is now required on the reaction between sulphur and some of the higher-boiling unsaturated hydrocarbons. Most of the reported work till now has been concerned with gaseous or low-boiling olefins, asphaltic materials of unknown composition, and unsaturated compounds associated with or analogous to rubber. It is suggested that melene, ($C_{30}H_{60}$, M.P. 62°C) may be a useful starting point for such an investigation. When the present study was drawing to a close methods of preparing this compound from beeswax were being considered; but it is possible that purer material could be obtained from a petroleum source. Alternatively the olefin cerotene ($C_{26}H_{52}$, M.P. 58°C) could be obtained from the same source.

It has been customary in some of the prior work to submit the final residues from the reactions to combustion analysis, and on the basis thereof to suggest an empirical formula for the material. When the present work was undertaken it was intended to follow this practice. Study of the literature, however, and practical experience in the laboratory indicated that such estimations would give an unreal appearance of constant chemical composition to residues which are essentially complex mixtures, and which alter in composition with changes in the time and conditions of

working. In preference the oxygen bomb method was used for the determination of sulphur content, a figure which was of value in estimating the extent of conversion to H_2S and in other respects. In some of the prior work considerable precautions were taken to eliminate variables and sources of error before making the combustion analysis, and in some instances constancy of composition has been claimed for some portion thus isolated. However, it appears from work reported earlier in this study that even repeated extractions by solvents do not remove all the sulphur from mixtures with carbon, and that in fact portions remain absorbed even at high temperatures[1]. Accordingly various formulae suggested in the literature in regard to the residue or portions thereof should be used with care in the light of these difficulties and limitations.

A variable which must be mentioned in relation to the present discussion is the effect of heating alone on the hydrocarbon compounds used for the reaction in the present study. One must consider whether the unsaturated compounds found may be the result not of dehydrogenation by sulphur but rather of "cracking" or thermal decomposition of the raw materials as is so frequently encountered in petroleum technology. That thermal "cracking" cannot play any important part in the main reaction is clear from the moderate temperatures employed. "Cracking" temperatures listed in the

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[1] Wibaut: Z Anorg. Chem. 211, 398 (1933).

literature in relation to petroleum range from about 400°C upwards, usually in conjunction with high-pressure conditions. For typical paraffins such as methane ethane, propane, and n-butane Egloff and Parrish[1] have reported initial decomposition temperatures ranging from 400°C - 675°C. It will also be recalled that at the start of the present work the behaviour of the oil on being heated in the absence of sulphur was specially observed, and it was found that even at 270°C only slight fumes were produced.

The effect of thermal decomposition may be greater in regard to the unsaturated compounds formed as intermediates. Egloff and Parrish[2] found lower temperatures of initial decomposition for olefines than for the corresponding paraffins, ranging from 325°C to 400°C. There is little information available relating to pyrolysis of the heavier unsaturated hydrocarbons but the possibility of their thermal decomposition under the experimental conditions cannot be excluded. Such pyrolysis would be an additional reason for the complete or partial absence of such compounds from some of the previous experimental residues and by-products. Under the experimental conditions of the present study such decomposition would have little effect on the over-all yield of H_2S, since a considerable excess of oil is present, but it could account for a portion of the original oil that disappears in the course of the reaction.

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[1] Egloff and Parrish: Chem. Reviews, 19, 158 (1936).
[2] Egloff and Parrish: loc. cit.

(b) The significance of the observations in the light of certain physico-chemical properties of sulphur:

Much of the prior work in the field of the present study was carried out before 1935. Since then the important studies of Warren and Burwell[1], Lark-Horovitz and Miller[2], Gingrich[3] and Chia-Si Lu and Donohue[4], have provided the experimental basis for a new conception of the sulphur molecule. The determination of the viscosity of sulphur by Bacon and Fanelli[5] and the elucidation by Fanelli[6] of the effects of certain reagents and impurities on the viscosity are closely related to this work. It is only in recent years, therefore, that an adequate basis has existed for theories of sulphur structure and the chemical behaviour of sulphur.

A vast amount of work has been done in the past on sulphur allotropy and crystallisation. At this point a summary of the main forms reported may be helpful, in view of scattered literature and confusing nomenclature. Apart from the clearly defined main crystalline forms rhombic sulphur ($S\alpha$) and monoclinic sulphur ($S\beta$) a number of other crystalline forms have been reported. These have been named by various workers either according to their shape (e.g. triclinic)

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[1] Warren and Burwell: J. Chem. Physics, 3, 6 (1935).
[2] Lark-Horovitz and Miller: Physical Rev. 51, 61 (1937).
[3] Gingrich: J. Chem. Physics, 8, 29 (1940).
[4] Chia-Si Lu and Donohue: J. Am. Chem. Soc. 66, 818 (1944).
[5] Bacon and Fanelli: J. Am. Soc. 65, 639 (1943).
[6] Fanelli: Ind. Eng. Chem. 38, 39 (1946). In this section all unspecified discussion of the work of Bacon and Fanelli refers to these papers.

or according to the discoverer's name, or according to an arbitrary system of numerals.

The present discussion will be more concerned with liquid sulphur. The main molecular forms or molecular modifications reported are:

$S\lambda$: This is liquid sulphur at or near its melting point, whether derived from rhombic or from monoclinic sulphur.

$S\pi$: This modification is reported to exist in the liquid mainly at about 170°C and in the rapidly chilled solid. It is distinguished by solubility in CS_2 at - 80°C, when rhombic sulphur is almost insoluble.

$S\mu$: This is amorphous sulphur, insoluble in CS_2.

To each of these modifications different molecular sizes have been ascribed in the literature, the respective formulae being S_8, S_6, and S_4. From this viewpoint liquid sulphur when heated above its melting point consists of varying mixtures of the molecular species in equilibrium. The molecular weight of both rhombic and monoclinic sulphur has been determined by various methods, including the lowering of freezing point in solvents, and has been found to be identical, i.e. the molecule is S_8.

Attempts have been made in the past to interpret the chemical behaviour of sulphur in terms of its allotropy

and in terms of the molecular changes believed to take place in the liquid state. Reference has already been made to the work of Erdmann[1] on "thiozonides". This work was founded on the belief that an additional highly reactive molecular modification (S_3) exists in liquid sulphur at temperatures in the region of 160°C. In relation to the reaction between sulphur and certain unsaturated hydrocarbons van Iterson[2] and Dannenberg[3] put forward theories in which S_μ was regarded as the effective reagent. Erdmann's theory is no longer accepted, and the theories mentioned above, and other of a similar nature, have not stood up to experimental test.

In brief, the modern view of the sulphur molecule is that it is a puckered 8 - atom ring, the bond angle being 105° and the S-S distance 2.12 Å. With increasing temperature between the melting-point and about 163°C the rings open into long chains, the tangling of which accounts for the rise in viscosity above this temperature. Above about 188°C the splitting of the chains into shorter segments gives lower viscosity values. It is not known with certainty to what temperature the S_8 molecule persists, but there is evidence for the appearance of S_2 molecules only well above the boiling point. Under these circumstances much of the earlier work on intermediate molecular modifications may have to be

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[1] Erdmann: Annalen, 362, 133 (1908).
[2] van Iterson: Intern. Ass. for Rubber Cultiv. 7, 239 (1918) through A. Chem. Abs. 13, 386 (1919).
[3] Dannenberg: Kautschuk, 3, 104, 108 (1927) through Westlake, loc. cit.

reconsidered.

It seems that the stage has been reached in the study of sulphur and its compounds where a new start must be made on the basis of the structural evidence and other data provided by modern research techniques. In making this new start the results of past work and thought must not necessarily be abandoned, but in many instances will require reconsideration and re-interpretation.

It is from this viewpoint that the work of Bacon and Fanelli, and later Fanelli working independently, is of such importance. These workers have lifted the theory of the behaviour of liquid sulphur out of the confusion of past observations and related it clearly and logically to structural changes and to sulphur chemistry generally.

In the present study the proposed industrial process was linked as closely as possible with the results of modern work and thought in this field; and while a full theoretical investigation was not in the scope of the project it was found possible to make certain observations of theoretical value.

In those portions of the work which touched, from time to time, on part of the ground covered by Bacon and Fanelli, and by Fanelli himself, the observations made have confirmed the observations reported by these workers. These observations were numerous and cannot be detailed here, but they have been made clear in the text. They cover such important common ground as the purification of sulphur, the

behaviour of impure sulphur on heating, the effect of the halogens on sulphur viscosity, and the modification of viscosity behaviour. In addition the results obtained by the use of the mechanical viscometer gave support, within the limitations of the method, to the results obtained by these workers, using the capillary-tube method.

With such a large area of agreement as starting point it was found possible to extend the theoretical observations in several directions. One was the introduction of different materials. Thus it was shown that sulphur in the form of gasworks residues behaved similarly to the sulphur samples previously used in which other impurities were present. Here again the theoretical and industrial aspects are closely related, since this observation may point the way to new methods of processing or utilising this material.

The observation of an induction period[1] in the evolution of free hydrogen sulphide from the reaction between sulphur and certain high-boiling hydrocarbons requires detailed discussion, since it constitutes new evidence in support of some of the chemical and physical theories postulated. It will be recalled that Bacon and Fanelli proved that the presence of organic matter caused a lowering of the viscosity of sulphur when heated, and that its effect could be ascribed to the formation of hydrogen sulphide and

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[1] For a formal statement of this observation see p. 92.

hydrogen persulphides. The formation of hydrogen persulphide in this way was not directly demonstrated; but the addition of hydrogen sulphide itself or of liquid hydrogen persulphide, was shown to produce the same effect. Finally the phenomenon of viscosity lowering was explained in terms of the breaking-up and isolation of smaller segments of the sulphur chains by means of hydrogen atoms in terminal positions.

In the present work a step was taken towards direct proof of this theory of persulphide formation. During the induction period thereaction probably proceeds by the mechanism of simple dehydrogenation as discussed above. The resulting H_2S however, does not appear as a gas during this period, and definite gas evolution starts only about 40°C above the usually accepted initial temperature of about 150°C. If the temperature is not allowed to rise too high, and if the sulphur is allowed to solidify undisturbed, it is recovered as a disc or block which does not outwardly show more than slight discolouration, and very slight smell of H_2S. On breaking the sulphur, however, there is unmistakable evolution of H_2S, which can be demonstrated by various tests.

This phenomenon can be explained in one way only, namely that during the induction period the H_2S has been mainly sequestered in the liquid sulphur. In its initial stages this may consist of the formation of a solution saturated at the particular temperature concerned, but this

view does not account for the accumulation and retention of the gas on cooling. We are fortunate in having accurate data on the solubility of H_2S in sulphur near the temperatures concerned. Fanelli[1] showed that the solubility of H_2S at 126°C (i.e. slightly above solidifying temperature) is only 0.057 g./100 g. sulphur, as compared with 0.139 g./100 g. sulphur at 139°C. Thus one would expect the dissolved H_2S to be readily given up as the solution cools further to solidification.

The persistence of the gas in the solid, its absence from the surface and its evolution from newly broken surfaces strongly support Fanelli's theory that hydrogen persulphides are, in fact, formed. From this viewpoint the absence from the surface can be readily explained as being due to decomposition of the unstable persulphides in contact with the atmosphere, with deposition of sulphur. It is of much interest that the phenomena encountered by Fanelli after saturating the sulphur with H_2S are thus paralleled by the behaviour of the sulphur itself after controlled heating in the temperature range of the induction period.

It is probable that little of the gas goes into solution in the oil during this stage. This was shown by the fact that the oil itself, when left in a closed vessel below test paper, did not cause darkening.

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[1] Fanelli: Ind. Eng. Chem. 41, 2033 (1949).

It should be noted that in the description of the induction period observation, given earlier in this work, mention is specially made of the test-method, namely darkening of lead acetate paper. It is quite possible that if more sensitive tests are found or applied the presence of traces of H_2S above the oil will be demonstrable, since the phenomenon is partially one based on solution. The retardation of H_2S evolution as a gas during the induction period is not necessarily absolute suppression. The phenomenon must be regarded as a relative one, characterised by the shifting of initial temperature of regular H_2S evolution as a gas, by the very slight darkening of the reactants, and by the properties of the resulting solid sulphur, as described above.

It was further observed that during the induction period a viscosity increase in the sulphur was not prevented as was largely the case when sulphur had been pre-heated with oil to a higher temperature, cooled, and then heated again through the same temperature range. It seems that the reaction which causes the change in viscosity behaviour - whatever it may be - does take place, but is not rapid during this period. If the theory set out above is valid then this observation can be explained in terms of the gradual building up of the concentration of persulphides, with progressive "sealing-off" of the terminal positions of the sulphur chains by hydrogen. Such a reaction might provide the means for following the process quantitatively and obtaining informa-

tion - at present lacking - on the nature and properties of the chains.

In other experiments it was found that if viscosity-reducing agents such as iodine, bromine, and chlorine, are first added to the sulphur the induction period cannot be observed and free H_2S is first evolved at about the usual temperature. It will be recalled that in terms of Bacon and Fanelli's theory the halogens reduce the viscosity of sulphur by the same mechanism as previously discussed, excepting that the terminal positions in the sulphur chains are filled by iodine, bromine, or chlorine atoms. Thus the present observation could be explained by the fact that, with these positions already occupied by the halogen there is little (if any) formation of hydrogen persulphide and the H_2S is detected as a gas. If this explanation is correct the present observation further strengthens the view that in the previous experiments the concentration of the H_2S in the sulphur was by reaction to persulphides rather than by solution alone.

It will be recalled that the sulphur recovered after the induction period experiment is only slightly darkened, and that the oil was only slightly more amber-coloured than at the start. The contrast between these products and the usual dark residues serves to emphasize the relationship between the phenomena now under consideration and the theoretical mechanism of H_2S production discussed earlier in this chapter. It seems very probable that here the hydrogen sulphide, and

ultimately the persulphide, have been formed as a result of dehydrogenation of the saturated hydrocarbons - a reaction involving no formation of free carbon which would darken the products. Thus it appears that by confining the reaction to conditions approximating to those of the induction period experiment it might be possible to recover and study the unsaturated compounds formed before they are further attacked by the sulphur.

The further observation was made that when a small portion of the induction period preparation was deliberately overheated the induction period phenomenon could no longer be demonstrated. To this can be added the fact that in none of the preparations carried out with direct heating was an induction period encountered. Here again the physical and chemical behaviour must be studied as parts of the same pattern, and not as isolated phenomena. The immediate darkening of the overheated portion, i.e. the appearance of free carbon, provides the clue to the fact that here the reaction has gone definitely beyond the stage of dehydrogenation. Here the unsaturated compounds have already become involved. There is insufficient information in the literature to found a full theory of what happens thereafter, but we may be guided by the fact that, as mentioned earlier, H_2S has been very readily evolved in many experiments as a result of reaction between sulphur and unsaturated hydrocarbons, as well as from the heating of many organic sulphur compounds. It

is suggested that once the unsaturated compounds are involved production of H_2S in the mixture is so increased that equilibrium conditions in the formation of the persulphides are rapidly attained and further evolution is observed as free H_2S. In this connection it must be remembered that in all these phenomena very small quantities of hydrogen persulphides are involved. In Bacon and Fanelli's experiments with persulphides 5% was added, but under experimental conditions so much of this unstable material was lost that they state that at the end of the experimental period the amount of persulphide present must have been "a minute portion of the original amount". Nevertheless its effect was clearly observed.

In the present experiments in which chlorine and bromine had been added as viscosity-reducing agents, a sluggish period in the evolution of free H_2S was observed between about 190°C annd 240°C, and between about 180°C and 230°C respectively. With iodine as viscosity-reducing agent no such period was observed. It is not considered that this is a sign of any further physical change, but rather the result of well-known reaction between H_2S evolved and the excess of the halogens concerned, resulting in the formation of the respective acids, deposition of sulphur and possibly formation of sulphur chloride or bromide. These reactions would slow down the apparent rate of gas evolution until the excess of halogen had reacted. The absence of any

similar observation in the case of iodine may lend support to the modern view that sulphur iodide cannot in fact be prepared directly. It also seems unlikely that hydrogen iodide could be formed under these experimental conditions. On the other hand Fanelli pointed out that the persistence of iodine in liquid sulphur on heating, and the profound changes caused by its presence, are evidence of combination. This issue must remain open at the present time. Much of the experimental work discussed in this chapter was repeated with paraffin wax in place of oil, so that the results would be of wider interest and significance than if confined to the oil alone.

It remains to discuss briefly the significance of the observations made in the present study in relation to certain reported results and apparent contradictions in literature. It will be recalled from the review of prior work that there have been wide variations in the reported temperatures of initial evolution of H_2S. In the light of the observations made these apparent contradictions are seen to be reconcilable. Where the evolution conditions favoured the occurrence of an induction period the apparent initial temperature of evolution would be higher, and conversely. An apparent exception to this explanation is found in Gruse and Stevens[1] who state that Paul obtained H_2S from vaseline/sulphur mixtures at an initial temperature of 80°C.

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[1] Gruse and Stevens: "Chemical Technology of Petroleum", 2nd. Ed. p. 163, McGraw Hill, New York.

However, on checking back to the original paper it was found that the statement is an error, and that in fact Paul[1] reported that the sulphur began to dissolve at 80°C. Other apparent contradictions relate to the composition of the final residues and the by-products. These are mostly reconcilable when differences in materials and technique are considered, and when the process is visualised as proceeding by way of both dehydrogenation and more complex successive reactions involving unsaturated compounds.

Some of the work of Scudder and Lyons[2] (to certain aspects of which reference was made earlier) can also be better explained in terms of the present observations. The effectiveness of finely divided lampblack as a so-called catalyst is seen as a case of viscosity reduction in the sulphur, resulting in more satisfactory evolution conditions and less local overheating and destructive carbonisation. The high temperatures of initial evolution of H_2S reported are seen to be due to the method of testing. These temperatures were recorded when the gas first gave a precipitate in the cadmium chloride absorption vessel. In each preparation this would imply that the air must be displaced from the evolution flask and delivery tube before the H_2S reaches the cadmium chloride solution. To this must be added the fact that before the gas can enter the solution

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[1] Paul: Seifensieder Zeitung, 42, 868 (1915).
[2] Scudder and Lyons: loc. cit.

through the tube a slight pressure must be developed. These errors are cumulatively sufficient to account for the difference in temperatures observed, as compared with observations in other studies where test paper or a similar sensitive method was used.

Finally it is desirable to call attention to the fact that analogies exist between the evolution of H_2S in the manner discussed in this study and its appearance in the gases resulting from the heating of coal containing sulphur and sulphur compounds. It does not appear that the results of the extensive research in this latter field have been utilised in this respect. Valuable analogies are also to be found in work relating to the heating of oil shales. As a starting-point for future workers who wish to study these aspects of the matter certain references are given in the bibliography.

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CHAPTER FOUR

PRACTICAL DISCUSSION AND PROPOSED PROCESS

It is the purpose of this chapter to consider the results of the study in the light of problems likely to be encountered on an industrial scale, and to propose a process as starting point for the future design of a pilot plant.

The subject will be discussed under the following headings:

(i) Materials for Process.

(ii) Main Processing Problems.

(iii) Proposed Process and Flowsheet.

(i) Materials for Process: The study has shown that sulphur and heavy lubricating oil are suitable materials for the reaction on which the proposed process would be based. In transferring the observations to the industrial field it is important to point out that if it were essential to use these materials in substantially pure form the process would have little chance of large-scale success. The study has shown, however, that the reaction is practicable with the use of relatively impure materials, and that in fact the presence of traces of organic impurities in the sulphur is desirable since they lower the viscosity of the sulphur in the temperature range in which the reaction commences. Consequently it should be possible to use relatively impure forms of sulphur which would be less adaptable to other in-

dustrial uses. Under prevailing conditions of sulphur scarcity throughout the world this fact may be of fundamental importance in the industrialisation of the process.

Similarly in regard to lubricating oil there would in practice be no likelihood of using high-grade oil for the process. It is proposed that the lubricating oil to be used should be the spent lubricating oil drained periodically from internal-combustion engines and other machines. Some of this oil is at present recovered and refined for further use; but transportation and other difficulties prevent its full utilization in this manner and a large proportion is still wasted or applied to relatively unimportant uses. The use of this alternative form of lubricating oil is of great practical importance, and for this reason a typical sample of spent oil was included in the series of evolution experiments already described. While it is possible that under special circumstances other suitable oil may be economically available in South Africa (e.g. as a by-product from some refining process) such supplies cannot, at this stage, be relied upon. The present discussion, therefore, does not assume their availability.

In relation to spent oil supplies the question of impurities present must be briefly considered. Mainly as a result of work on the operation of automobile engines, and the oils drained from them, very much information is already available on this aspect of the problem. This

information was studied as part of the background of the present work, but considerations of space preclude detailed discussion here. The references given below[1,2,3,4] will be helpful to future workers in this connection. In brief, the impurities encountered in spent oil are mainly the following:-

(a) Finely divided foreign matter such as dust drawn in while the engine is running, as well as traces of metal resulting from wear of the engine.

(b) Water, due to condensation of vapour from the combustion gases or from outside under cold conditions. The latter is rarely of importance under South African conditions.

(c) Diluents derived from the fuel of the engine. The relatively high temperature at which engines operate prevents the continued accumulation of such low-boiling fractions in the oil and they are largely evaporated through the sump vent pipe.

(d) Breakdown products from the decomposition of some of the oil under engine conditions. These products are commonly known as "carbon" and "gum" and though present in only small

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[1] Flowers, McBerty, and Reamer: Ind. Eng. Chem. 17, 481 (1925).
[2] Broughall: Chem. and Ind. 46, 1096 and 1112 (1927).
[3] Bassett: Chem. and Ind. 50, 527 (1931).
[4] Dickenson: Ind. Eng. Chem. 11, 187 (1933).

proportions they give the drained oil its well-known dark appearance.

Spent oil is being successfully reclaimed for re-use in engines, and though the respective merits of new and reclaimed oil as lubricants are still under discussion there is no doubt that existing methods of treating spent oil can provide material of sufficient purity for the present purpose. The purifying procedure need not be elaborate. Known and relatively simple techniques are readily available for preparing the oil. Dirt and water may be removed by filtration, settling, and/or centrifuging. Light fractions present in the oil as a result of crank-case dilution or cracking may be removed by heating. Further filtration with filtration aids may be used for clarification if desired, but in view of the fact that free carbon is formed in the proposed process it appears unnecessary to carry the preparatory process so far.

In recent years the practice of using so-called "additives" to give special properties to lubricating oils has become widespread, and in consequence traces of these additives may also be found in some batches of spent oil. Apart from additives used in high-pressure lubricants (e.g. transmission greases), which would not be encountered in relation to the present work, the main additives likely to be found in small proportion in spent engine oil would be those added to minimise oxidation and others of a detergent character intended to hold sludge in suspension and minimise

corrosion. Both types are largely destroyed in the course of use in the engine. Some of these additives have been discussed by Prutton and Musgrave[1] and cannot be listed here in detail. Such additives, if and when encountered, would have to be borne in mind in the pilot-plant investigation[2].

(ii) Main Processing Problems: The study indicated that the main problems likely to be encountered in practice would be the following:

(a) The poisonous nature of the product and the consequent hazards in process operation: These hazards are dealt with in the following chapter. In relation to the design of a suitable process it is necessary here to point out that a process which might be otherwise satisfactory will not be suitable for industrial use if the resultant hazards cannot be substantially provided against.

(b) Materials of construction: In the laboratory the apparatus used was mainly of Pyrex glass, supplemented in special instances by stainless steel. On a larger scale the choice of suitable materials of construction would be made difficult by the corrosive properties of both molten sulphur and hydrogen sulphide. Apart from these difficulties provision must be made for heating the evolution apparatus, with added risks of further corrosion in the higher temperature range.

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[1] Prutton and Musgrave: Chem. Eng. Prog. 45, 17 (1949).
[2] See also: Symposium on Additives for Petroleum, Ind. Eng. Chem. 41, 886 (1949).

Detailed data on the behaviour of alternative materials of construction in the presence of sulphur have been recently published by West[1], and should be used in the design of plant. While cast iron and steel are widely utilised in the handling of sulphur they are by no means ideal as they are corroded in the presence of moisture, particularly where aeration is also present. However in relation to the proposed process it is probable that these materials could be usefully applied wherever care can be taken to avoid both moisture and aeration[2].

Of the alternative metals which are more resistant than cast iron and steel it is recommended that use be made of aluminium and/or stainless steel. Aluminium is not corroded by either molten sulphur or by sulphur vapour. Panelli[3] in his laboratory tests observed no corrosion of aluminium by liquid sulphur at 210° and at 410°C. West[4] reports successful tests with aluminium on an industrial scale, but calls attention to the limitations of this material for the construction of processing vessels, due to its low melting point. From our present viewpoint, therefore, aluminium would be unsuitable for the strongly heated portions of the plant but suitable elsewhere. It may be found that

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[1] West: Chem. Eng. 58, 276 (1951).
[2] See also a study of corrosion in the Frasch Process by Shock & Hackerman: Ind. Eng. Chem. 41, 1974 (1949).
[3] Panelli: Ind. Eng. Chem. 38, 39 (1946).
[4] West: loc. cit.

the corrosion resistance of aluminium can be simultaneously maintained with the mechanical strength of steel by using some of the modern forms of "aluminium-clad" steel.

Many grades of stainless steel now available perform well under the conditions visualised, but it is proposed that where this metal is required the standard 18-8 grade should be used from the viewpoint both of economy and of availability in a variety of sheet, rod and tube sizes. Of the special alloys it appears that higher chromium content confers greater corrosion resistance, but it is unlikely that the use of more expensive alloys would be justified.

Experience gained in the present study indicated the need for great care where welding is used in the fabrication of stainless-steel for the process plant. Not only must the welding rod be equally as resistant as the parent metal, but it is essential that precautions be taken not to alter the composition and physical character of the stainless steel adjacent to the weld by overheating and the like. In tests during the present study it was found that where such precautions had not been observed by the welder the metal adjacent to the weld behaved much the same as ordinary mild steel under working conditions and corrosion was rapid.

It may be mentioned that stainless steel is also now being manufactured in "clad" form, on a backing of mild steel. The stainless steel layer and the mild steel base are rolled together and are homogeneously attached, so that the valuable

properties of stainless steel can be made available at a much lower cost than the usual stainless plate.

For portions of the plant which will not be exposed to special corrosion risks or strong heating there is a much wider choice of well-known materials of construction which do not require detailed mention here.

(c) Problems arising out of the reaction conditions:

The main evolution reaction in the proposed process would be carried out industrially in the temperature range of approximately 160° - 290°C. The alternative methods of heating are discussed below.

The problem of heat transfer was a source of difficulty from the beginning of the laboratory study and it would be a major consideration in large-scale design and working. In this connection the observations reported on the behaviour of sulphur-oil mixtures on heating should be specially borne in mind when designing the plant. It was found that where the sulphur was added to the oil and heated indiscriminately there resulted a tough, coke-containing asphaltic layer on the bottom of the vessel, and that the rate of heat transfer, as a result, fell rapidly. Two methods of overcoming this difficulty were found. The one consisted in adding the sulphur in small quantities as the reaction progressed. In this way a sufficient concentration of hydrogen-sulphide (or possibly persulphide) was first built up to ensure that the successive portions of sulphur added thereafter would not assume the

viscous state at the bottom of the vessel. The other method consisted in pre-treating or modifying the sulphur before use in the reaction, by heating with a small proportion of oil so as to reduce its viscosity in the main heating range. Whichever method is used the induction period is also simultaneously avoided by these proposals.

The method of sulphur addition and other related problems will be referred to again when the proposed process as a whole is described.

It is possible that even with due precautions and care there will sometimes be sufficient carbonaceous deposit on the inner surface of the heating vessel to hinder heat transafer. This aspect will also be referred to when discussing the suggested plant arrangements more specifically.

The study showed that there was a tendency for the reaction mixture to foam up slightly due to effervescence at the most rapid stage of gas evolution. In the laboratory this was provided against by working with vessels only about one-third full. It is suggested that analogous precautions should be taken in the industrial plant.

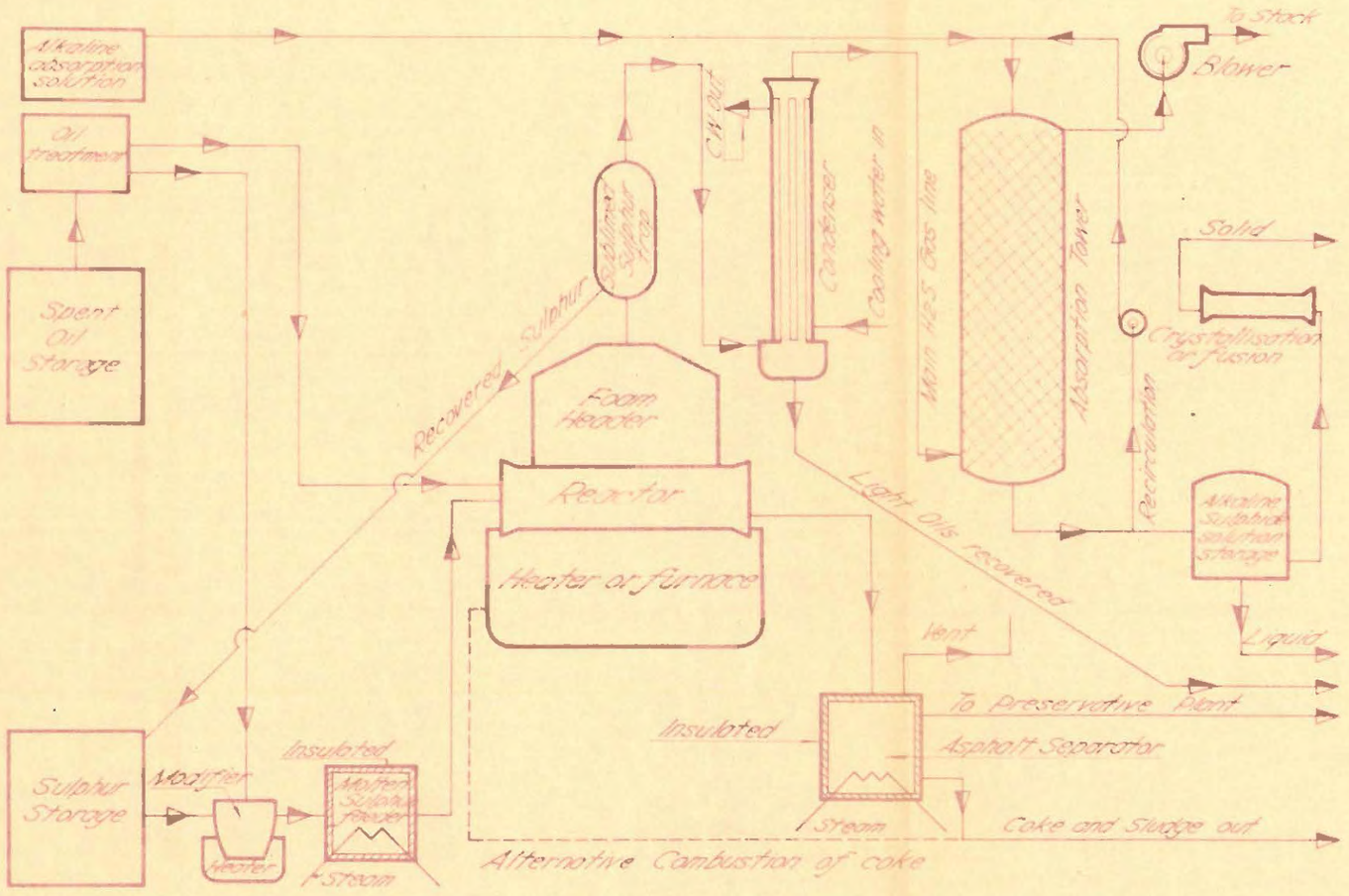
It was also found that adequate mixing was desirable. On the small scale this was achieved by the addition of successive increments of sulphur followed by rapid effervescence which helped to disperse the sulphur in the oil. On an industrial scale it would be desirable to supplement this method by some provision for mechanical mixing, which would also contribute

towards solving the problem of heat transfer.

At the end of the evolution reaction there will be encountered the difficult problem of removing the residue from the reaction vessel. The peculiar difficulties involved may be envisaged by referring back to the various sections of this study dealing with the properties of the residue. In brief the residue is a hot black asphaltic mass smelling of hydrogen sulphide. Where the process is used with a low proportion of oil the residue will tend to be coke-like in character, but where (as recommended in the proposed process) the oil is used in considerable excess, the residue will be semi-fluid.

It will be impracticable to work on the industrial scale any process which requires that this residue should be manually removed from the reaction vessels. Not only will the work be extremely distasteful to the operators but the risks of poisoning by the gas will be too great, even where protective appliances are available. There is also the additional risk of fire to be considered when the hot residue is handled in the presence of air. Accordingly it is proposed that provision be made for mechanical discharge and removal of the process residue and its subsequent useful application.

Among the remaining problems which are likely to be encountered in developing the process may be mentioned that of temperature observation and control. The technical means



Flowsheet of Proposed Process for Hydrogen Sulphide Production

of such control is already available in the form of distant-reading thermometers based on corrosion-resistant metal bulbs and capillary tube transmission systems, or alternative thermocouples. The difficulty in practice arises from the fact that the thermometer bulb becomes coated with a carbonaceous layer which insulates it from the reaction mixture. In the present study various methods of meeting this difficulty were tried, but none were wholly successful. It may be necessary to provide some means for withdrawal and cleaning while the plant is operating. Alternatively it may be possible to arrange that the mechanical mixing arrangement provided should also have a cleaning action in the vicinity of the thermometer bulb or the thermocouple. This requirement is stressed particularly because temperature control is critically necessary not only for the efficiency of the process but equally to prevent the process going completely out of the working range, with thermal cracking of the oil and ultimately fire or explosion.

(iii) Proposed Process: On the basis of the facts discussed above and of other observations made in the course of the study the following process[1] is proposed:

The raw materials, sulphur and spent oil respectively,

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[1] The proposed process is shown in the flowsheet attached.

are received into storage. It is assumed for this preliminary proposal that the sulphur is in such form as not to require preliminary purification. The oil is pre-treated to remove moisture, dirt, and sludge, by known methods, and the volatile contaminants (if any) are driven off by heating to approximately 280°C. The treated oil is conveyed to separate bulk storage. The proposed process may be worked in two alternative ways, namely on a batch basis or continuously. Using either method provision must be made for weighing or measuring and conveying the materials from storage to the processing plant.

It is proposed that the sulphur be pre-treated to improve its viscosity characteristics. The sulphur would therefore be given a preliminary heating in the presence of approximately 2 - 5% of oil, the sulphur being carefully melted, the oil added with stirring, and the temperature raised to approximately 220°C and held at that point for approximately five minutes. The molten sulphur would then be cooled to 150°C, pumped to an insulated and heated intermediate storage tank, and thence through steam-heated pipes to the reactor.

In the reactor the initial charge of oil will have meanwhile been pre-heated to approximately 160°C - 180°C. The stream of liquid sulphur is slowly introduced with agitation and with observance of all precautions from the viewpoint of safety. The reaction will commence immediately, with

evolution of hydrogen sulphide and formation of asphaltic-like by-products, which under the proposed conditions will remain sufficiently fluid to be agitated and moved further through the process without serious coke blockages occurring.

It is recommended that the process be carried out with a proportion of 20% - 25% of sulphur on the weight of oil used. This would give an economic yield of H_2S while still maintaining the advantages of a fluid residue and less coke formation. Allowing for losses on the large scale working the yield of H_2S should be about 75 - 80% on the weight of sulphur taken. It should also be borne in mind that the remainder of the sulphur would not be lost, but would be utilised with the residue as suggested elsewhere.

The reactor would be constructed of stainless steel and may take two alternative forms, according to whether continuous or batch operation is chosen. For continuous working the proposed reactor would consist of one or more horizontal tubular or cylindrical units passing through the furnace, and through the walls on either side. Within the reactor tubes or cylinders and for their full length, a shaft carries staggered or spiral blades which carry out the treble functions of mixing the materials, moving them forward as the reaction proceeds, and scraping the reactor tube wall to break down any accumulation of carbonaceous matter, thus dispersing it before it can affect substantially the rate of heat transfer. The slow stream of molten sulphur enters continuously at one end of the reactor as the mixture is slowly moved towards the

other end.

For the purpose of gas removal a wide slot or a series of large holes, is provided in the top of the reactor tube over almost its full length within the furnace. These openings are covered by a vertical hood or duct, rendered perfectly gastight by welding on to the reactor tube. The size of the hood or duct is thus approximately the length of the reactor tube and about half as wide. It continues vertically for a sufficient distance to act as a foam header for returning any entrained liquids to the reactor and for this purpose may be provided with baffles or similar devices. Thereafter the gas goes to the gas main.

The length of the reactor tube and the rate of movement are so chosen as to allow sufficient reaction time while the materials are passing through. This will be approximately 3 - 4 hours. Check tests at the outlet of the tube control this provision, and should unreacted material be found, the time of reaction is increased by slowing down the spiral conveyor mechanism and rate of feed of oil and sulphur.

The main by-product of the reaction (which will henceforth be termed "the residue") will be discharged as a hot liquid generally similar in appearance to molten asphalt, with some carbonised material, or coke, suspended in it. Under no circumstances should the hot stream be exposed to the atmosphere when it is discharged, owing to the risk of fire

and other hazards. It is proposed that it be run to a suitable covered storage tank, fitted with steam heating coils, and suitably vented. The reactor and furnace unit should be isolated from all other sections of the plant, and should be protected against fire and explosion risks by methods similar to those used in the petroleum industry.

Where it is desired to work on a batch basis, i.e. discontinuously, the reactor tube or cylinder would be of much larger diameter, so as to carry a sufficient charge of material. It would thus be somewhat analogous to a horizontal boiler, but it would be provided with a central shaft and blades larger than but generally analogous to those of the continuous reactor. The ends of the reactor cylinder would project beyond the furnace walls, as previously described, and the feed and discharge arrangements would also be analogous, but on a discontinuous basis. The molten sulphur stream would preferably be introduced slowly at several points instead of at the one end only. The heating would be arranged on a set schedule, and some time before discharge the heating would be stopped, so that when the residue is discharged the reactor should not become overheated before the new charge is introduced.

The heating arrangements are a very important part of the process, and must be specially discussed. In the proposals made above the word "furnace" has been used for convenience, but the heating system may, in practice, take

one of several forms, the choice being influenced partly by local facilities and economic limitations. Where the heating method is a furnace it would be fired by coal, coke or gas, or possibly by oil where this is cheaply available. It would also be possible to burn the residue and recover SO_2 from the flue gases. The flames would not be allowed to heat the reactor tube directly, baffle walls being provided for protection. A series of suitable dampers and flaps would make it possible to divert the hot gases partly or wholly away from the reactor and by-pass them directly up the stack in case of need. The furnace proper would be built of brick, with firebrick lining and an arched or suspended firebrick roof.

Three of the main alternatives to furnace heating would be the use of superheated steam, Dowtherm heating, or electrical heating. Superheated steam could theoretically provide the necessary temperature which is inconveniently high for the use of saturated steam. It has great advantages from the view-point of safety, but the initial costs would probably be large. The Dowtherm heating system, and other analogous systems, circulate high-boiling organic liquids as the heating medium with a separate heater or boiler. Here, too, the installation costs are likely to be very high. Electric heating, though attractive in theory, would be too costly to run except in a few exceptional situations, or on a small scale. In this connection attention is called to the

possible use of induction heating rather than conventional methods of resistance heating.

Following on this stage of the process the products of the reaction would follow two separate paths, which will now be briefly discussed. The gas main would convey the raw gas from the reactor through a sulphur trap to a condenser which would be water-cooled, where the light oil distillates resulting from the process. It is not recommended that this distillate should be refluxed back to the reactor or returned to the main oil feed for recycling. Its boiling range makes it unsuited for this purpose, while its utility as a mixed solvent or as a starting-point for further fractionation is likely to be considerable. A further use for this distillate would be to add it to the solvent used in the production of timber preservative from the reactor residue.

The gas main should be of ample dimensions, and the trap must be arranged for ready removal of any sublimed sulphur for return to the process. After leaving the condenser the gas would be purified according to its intended end use. This purification may range from filtering and scrubbing to more complete purification, for example by activated carbon, but as such techniques are well-known they need not be discussed here. For most commercial applications this purification will not be necessary.

Though large-scale storage of the hydrogen sulphide in gasometers can be arranged it is suggested that the gas

should rather be utilised directly when produced. For example it may be applied for the manufacture of sodium sulphide by passage through suitable absorption towers countercurrent to the alkaline solution. The resultant solution may be marketed as such or concentrated and recovered in conventional forms, i.e. as crystals or fused solid. A blower situated just after the absorption tower draws the gas through and maintains a slight vacuum on the entire system, so that there can be no outward leakage of gas. The blower discharges to a high stack.

The hot residue from the reactor, as previously described, passes to an insulated and heated storage tank. There it is settled or filtered while warm and is available for the manufacture of timber preservative in a special section of the plant. For this purpose it is run into a mixing tank fitted with a stirrer. It is allowed to cool to atmospheric temperature and is mixed with the calculated amount of solvent, preferably power kerosene. Where it is desired to add additional active ingredients these may conveniently be added as concentrates at this stage.

The prepared preservative is filtered and pumped to storage for filling into drums or tins after analytical checks.

The whole process and plant thus proposed is adaptable to construction in the open, with either no roof covering or else under simple open-sided framed structures, and the materials and products may be handled almost entirely by pumps, blowers, conveyors and other mechanical equipment.

CHAPTER FIVE

HAZARDS AND SAFETY MEASURES

No account of this study would be complete without reference to the hazards involved in work with H_2S and indication of safety measures to be taken, for the guidance of future workers in this field.

It is customary for chemical text-books to refer briefly to the unpleasant smell of H_2S and its poisonous character, but its dangerous properties are seldom sufficiently stressed. In the present study every endeavour was made to take precautions against H_2S poisoning, yet there were many occasions on which the initial symptoms were felt, and experimental work had to be interrupted temporarily to avoid greater dangers.

Miner, Tilden, and Miller[1], in their account of health hazards, distinguish between acute and sub-acute poisoning by H_2S. The former causes asphyxiation and irritation of the eyelids (conjunctivitis) while the latter may result in bronchitis, pharyngitis, and depression of the central nervous system. First symptoms of mild poisoning are headache, sleeplessness, dullness, dizziness and weariness. The eyes,

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[1] Miner, Tilden, and Miller: "Chemical Engineers' Handbook", Ed. by Perry, 2nd Ed., p. 2938. McGraw-Hill, New York.

pharynx, bronchii and chest are affected later, and in severe cases gross depression, unconsciousness and death follow. Where exposure has been severe death occurs rapidly by direct respiratory paralysis. Where, on the other hand, exposure has been less or chronic, the lungs may be affected.

For the present study a special fume cupboard was built to minimise these hazards. It was of usual timber and glass construction, but the front was subdivided into three narrow sections, each of which had its own sliding sash. Thus each section could be used independently. A further important advantage was that the middle section could be kept closed, and manipulations could be performed by putting the arms through one or both of the sashes on either side of the closed one. Gas, electricity, compressed air and vacuum services were provided through holes drilled through the timber frame close to bench level. Similar provision was made for the introduction of nitrogen, chlorine, and ammonia for certain experiments. At the back of the fume cupboard, fixed to the wall, was a teak framework which was useful in supporting apparatus. Under ideal conditions this should rather have been a metallic frame or grid, but stainless steel or other resistant metal was not available. The fume cupboard was ventilated by means of a dust and corrosion-resistant fan situated axially in the vent pipe leading from the inclined roof of the cupboard. The fan was run for some time before and after working, and at night one of the doors was always

left slightly raised so that natural draught would prevent any unforeseen gas accumulation.

Additional precautions for emergency use included the provision of a gas-mask covering the full face, and an oxygen bottle.

It may appear strange that, with all these precautions, some of the symptoms of sub-acute poisoning were encountered. The explanation may be that in the ordinary course of experimental work the arms are moved into and out of the fume cupboard, apparatus is handled in and out and so on. The arm, with its covering of laboratory coat-sleeve, acts as a kind of piston, drawing out gas. In short periods of work the effect is unimportant, but in longer periods the local concentration and prolonged exposure can produce the first effects outlined above.

It is of interest to note, in this connection, Friedmann's graphic record of how he was forced to abandon certain work in this field. He states: "Hierzu kommt bei allen diesen Versuchen als bezonderes erschwerendes Moment hinzu, dass bei der grösstmöglichsten Vorsicht die sich verbreitenden Gerüche nicht nur für den, der damit arbeitet, sondern auch für die im gleichen Institut befindlichen Personen so unangenehm werden dass infolge allgemeinen Protestes nach kurzer Zeit die Fortzetzung dieser Arbeiten

geradezu unmöglich wird"[1].

In larger scale working the hazards are greater, and much attention has been paid overseas to the dangers of H_2S poisoning, particularly in relation to the operations of oil handling and processing. Among numerous papers mention may be made of Lehmann's[2] early work in Germany, and the investigations of the Bureau of Mines[3] in the U.S.A. The Bureau summarises its findings as follows, and gives the approximate concentrations at which acute and sub-acute poisoning respectively can occur:

1. Hydrogen sulphide is an exceedingly toxic gas.
2. Poisoning from gases presumably containing H_2S has been recorded at 25 places in refineries.
3. Thirty-eight per cent of all cases of poisoning reported have occurred in the receiving houses of refineries.
4. All individuals of whatever class, age, or nationality are susceptible to H_2S poisoning.
5. Acute poisoning by H_2S acts on the nervous system; it results in a respiratory paralysis that is followed by cardiac failure and death.
6. Acute poisoning can be produced by concentrations of 0.06% to 0.08% or more of H_2S.

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[1] Friedmann: Petroleum Zeitschrift, 11, 696 (1916).
[2] Lehman: Archiv für Hygiene, 14, 135 (1892).
[3] U.S. Bureau of Mines: Bulletin No. 231 (1925), Circular No. 7334 (1945) and other official pamphlets.

7. Sub-acute poisoning by H_2S is mainly one of irritation of the respiratory tract and depression.
8. Sub-acute poisoning can be produced by long exposure to concentrations as low as 0.0005%.
9. Fatal cases of sub-acute poisoning at a refinery should be rare, because the men would leave the irritating atmosphere.
10. Fatal cases of acute poisoning can easily occur, owing to the rapidity and type of action.
11. Pathological findings are typical of irritation.
12. Microscopic examination indicates destruction of the cell lining of lung alveoli.
13. Artificial respiration is necessary if breathing has ceased. The Schaefer or prone pressure method should be applied to victims.
14. Oxygen aids early recovery in cases of acute poisoning.

The Bureau of Mines recommended soda-lime as the absorbent in gas-masks where H_2S alone is present. Should other gases or vapours be present the additional use of active charcoal was advised. Even soda-lime, however, is inadequate in high concentrations of the gas. The Bureau found that when soda-lime absorbed 3% of H_2S the heat of reaction was enough to melt the solder on the canisters and scorch the

cotton-wool filters.[1]

Future workers in the field of the present study who may encounter these hazards are likely to be engaged either in laboratory operations or in the extension of the work to pilot-plant or large-scale working. In respect of laboratory work the precautions already referred to may readily be followed and supplemented. In respect of large-scale working the best precaution is the avoidance of local concentrations of H_2S in work-places. To achieve this the plant should be built in the open, with a minimum of conventional buildings. Where buildings are indispensable it should be constantly remembered that every joint, every valve and even every instrument in the installation is a possible source of leakage. The only form of gas-mask that can be fully relied upon for lengthy periods in dangerous concentrations of the gas is the air-hose mask, where air is pumped to the facepiece from an uncontaminated source.

To these provisions must be added precautions against the fire risk involved in handling hydrogen sulphide. These need not be dealt with in detail here, as they are analogous to established practices in other fields. It may be mentioned, however, that the fire risk can be greatly minimised by direct absorption of the H_2S for the production of

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[1] See also Mitchell and Davenport: U.S. Public Health Report 39, (1924) which gives a bibliography of eighty-four articles on H_2S poisoning.

such compounds as the alkali sulphides and sulphydrates as recommended above thus avoiding the need for intermediate storage of the gas and the risks of forming explosive mixtures by air leakages.

A valuable account of the precautions introduced at an installation in which dangerous concentrations of H_2S frequently arose from the handling of crude oil rich in sulphur compounds has been given by Willson[1]. At this plant instruments are read through a window from outside the building. A special watch is kept on sewer openings, tanks, pits and other places where pockets of gas may accumulate. At various points first-aid stations with oxygen inhalators are available, and all workers are trained in the nature of the hazards, their avoidance, and the treatment of poisoning.

Probably the greatest source of danger in working with H_2S is its insidious character as a poison. Chemists who work occasionally with the gas are sufficiently warned by the smell. Unfortunately after a short while the smell becomes less noticeable, so that one may readily be exposed without realising the danger in time. When operating on a larger scale, therefore, future workers are strongly advised to take the precaution of working in pairs.

Finally it should be stressed that the hazards of research or large-scale operations with H_2S should not deter

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[1] Willson: Oil and Gas Journal, 32, 13 (1934).

the chemist from continuing this work. The dangers are real, but as long as they are understood they can be readily provided against, and the resources of modern chemical engineering practice are adaptable to meet the large-scale problems involved.

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LITERATURE CITED AND SELECT BIBLIOGRAPHY

Adleson and Bogert: Chem. Reviews, 24, 135 (1939).
Anon: Modified McIlhony Method, I.P. - 9/42, Institute of Petroleum, London.
Armstrong, Little and Doak: Ind. Eng. Chem. 36, 628 (1944).
Bacon and Boe: Ind. Eng. Chem. 37, 469 (1945).
Bacon and Davis: U.S. Patents Nos. 1,374,897 and 1,374,898 of 1921.
Bacon and Fanelli: Ind. Eng. Chem. 34, 1043 (1942).
Bacon and Fanelli: J. Am. Chem. Soc. 65, 639 (1943).
Bacon: U.S. Patent No. 1,151,236 of 1915.
Bassett: Chem. and Ind. 50, 527 (1931).
Bell and Agruss: Ind. Eng. Chem., Anal. Ed., 13, 297 (1941).
Bernthsen: "Organic Chemistry", 1941 Ed. p. 332, Blackie & Son, London.
Bielenberg: Braunkohlenarchiv 4, 40 (1923).
Bindschedler and Rugeley: U.S. Patent No. 1,565,894 of 1925.
Bloxam: "Inorganic Chemistry", 10th Ed., p. 151, J. & A. Churchill, London.
Borgstrom and Emmet Reid: Oil and Gas Journal, 26, 352 (1927).
Brooks and Humphreys: Ind. Eng. Chem. 9, 746 (1917).
Broome and Thomas: J. Soc. Chem. Ind. 50, 424 (1931).
Broughall: Chem. and Ind. 46, 1096 and 1112 (1927).
Bryce and Hinshelwood: J. Chem. Soc. 136, 3379 (1949).
Cartwright and Findlay: "Decay of Timber and its Preservation", p. 259, H.M. Stationery Office, London.
Charitchkoff: Chem. Zeitung, 26, 731 (1903).
Chia-Si Lu and Donohue: J. Am. Chem. Soc. 66, 818 (1944).
Dannenberg: Kautschuk, 3, 104, 108 (1927) through Westlake Chem. Reviews, 39, 219 (1946).
Denison, Harle and others: Symposium on Additives for Petroleum, Ind. Eng. Chem. 41, 886 (1949).
Dickenson: Ind. Eng. Chem. 11, 187 (1933).
Drakeley: J. Chem. Soc. 111, 853 (1917).
Duffey, Snow, and Keyes: Ind. Eng. Chem. 26, 91 (1934).
Dunlap: Chem. Met. Eng. 34, 298 (1927).
Edgar and Calingaert: Ind. Eng. Chem. Anal. Ed., 2, 104 (1930).
Eggleston: U.S. Patent No. 1,018,040 of 1912.
Egloff and Parrish: Chem. Reviews, 19, 158 (1936).
English: J.S.A. Inst. Eng. 27, 127 (1929).

Ephraim: "Inorganic Chemistry", Edited by Thorne and Roberts, 4th English Ed. p. 521, Gurney & Jackson, London.
Erdmann: Annalen 362, 133 (1908).
Fanelli: Ind. Eng. Chem. 38, 39 (1946).
Fanelli: Ind. Eng. Chem. 41, 2031 (1949).
Fanelli: J. Am. Chem. Soc. 67, 1832 (1945).
Faragher, Morrell and Comay: Ind. Eng. Chem. 20, 527 (1928).
Faragher, Morrell and Monroe: Ind. Eng. Chem. 19, 1281 (1927).
Farr and McLeod: Proc. Roy. Soc. 97, 80 (1920).
Fletcher: Chemical News, 40, 154 (1879).
Flowers, McBerty, and Reamer: Ind. Eng. Chem. 17, 481 (1925).
Friedmann: Ber. 49, 50, 1344 and 1551 (1916).
Friedmann: Petroleum Zeitschrift: 11, 696 (1916).
Friedmann: Petroleum Zeitschrift: II, 978 (1916).
Galletly: Chemical News, 23-24, 162 (1871).
Gfeller and Schaefer: Schweizerische Apotheker Zeit. 10, 110 (1929).
Gingrich: J. Chem. Physics, 8, 29 (1940).
Glass and Emmet Reid: J. Am. Chem. Soc. 51, 3428 (1929).
Graefe: Z. für angewandte Chemie, 34, 509 (1921).
Gruse and Stevens: "Chemical Technology of Petroleum", 2nd Ed. p. 163, McGraw-Hill, New York.
Hagerman: Ind. Eng. Chem. 19, 381 (1947).
Hanley: Chem. Met. Eng. 24, 693 (1921).
Henwood, Garey, Goldberg and Field: J. Franklin Inst. 199, 685 (1925) through Chem. and Ind. 44, (New Series), 584 (1925).
Jaza and Blanke: Z. anorg. Chem. 210, 81 (1933).
Johansen: Ind. Eng. Chem. 14, 288 (1922).
Johnstone: Chemical News, 40, 167 (1879).
Jones and Emmet Reid: J. Am. Chem. Soc. 60, 2452 (1938).
Kellas: J. Chem. Soc. 113, 903 (1918).
Kingzett: "Chemical Encylopaedia", 6th Ed. p. 986, Bailliere, Tindall & Cox, London.
Kobbe: Chemical Trade Journal, 75, 520 (1924).
Kobbe: U.S. Patent No. 1,599,135 of 1926.
Kruyt: Z.physikal. Chem. 64, 486 (1909).
Lark-Horovitz and Miller: Physical Rev. 51, 61 (1937).
Lawrie: "Glycerol and the Glycols", p. 215 Chemical Catalog. Co., New York.
Lidoff: Chem. Zentr., 52, 22 (1882).

Malisoff and Marks: Ind. Eng. Chem. 23, 1114 (1931).
Markownikoff and Spady: Ber. 20, 1850 (1887).
McIlheny: J. Am. Chem. Soc. 21, 1084 (1899).
McKinney and Mayberry: U.S. Patent No. 2,354,868 of 1/8/44.
McKinney, Mayberry and Westlake: Ind. Eng. Chem., 17, 177 (1945).
McKinney, Mayberry and Westlake: Ind. Eng. Chem., 37, 177 (1945).
Mellor: "Comp. Treatise on Inorg. and Theoretical Chemistry", Vol. VI pp. 125, 127, and 128, Longmans Green & Co., London.
Merrington: "Viscometry", p. 68, Edward Arnold & Co., London.
Meyer and Hohenemser: Helv. Chim. Acta. 18, 1061 (1935).
Mikewska: Ind. Eng. Chem. 28, 970 (1936).
Miner, Tilden, and Miller: "Chemical Engineers' Handbook", Ed. by Perry, 2nd Ed., p. 2938, McGraw-Hill, New York.
Mitchell and Davenport: U.S. Public Health Report 39, (1924).
Moore and Cuthbertson: Ind. Eng. Chem. Anal. Ed. 2, 419 (1930).
Murray: U.S. Patent No. 2,052,892 of 1936.
Nellensteyn and Thoenes: Chem. Weekblad, 29, 582 (1932).
Paul: Seifensieder Zeitung, 42, 868 (1915).
Plattner: Die Chemie, 55, 131 and 154 (1942).
Powell and Eyring: J. Am. Chem. Soc. 65, 648 (1943).
Procter: "Leather Chemists Pocket Book", 3rd Ed. 114, E & F.N. Spon, London.
Prothière: Pharmaceutische Zeitung, 48, 78 (1903).
Prutton and Musgrave: Chem. Eng. Prog. 45, 17 (1949).
Rakusin: Petroleum Zeitschrift, 18, 581 (1922).
Rasmussen, Hansford and Sachanen: Ind. Eng. Chem. 38, 376 (1946).
Reimsch: Journal für praktische Chemie, 4, 136 (1838).
Rotinjanz: Physik. Chem. 62, 609 (1908).
Sanfourche and Liebaut: Bull. Soc. chim. 31, 966 (1922) through Thorpe, "Dict. of Applied Chemistry", 4th Ed. Vol. X p. 890, Longmans Green & Co., London.
Scheele: "Chemische Abhandling von der Luft und dem Feuer", Berlin Ed. p. 237, published 1793; originally published Upsala 1777; through Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. X, p. 122, Longmans Green & Co., London.
Scudder and Lyons: Proceedings Indiana Academy of Science, 40, 185 (1931).

Sedlaczek: Teer 24, 436 (1926).
Shock and Hackerman: Ind. Eng. Chem. 41, 1974 (1949).
Siebeneck: Petroleum Zeitschrift, 18, 281 (1922).
Snell and Biffen: "Commercial Methods of Analysis", First. Ed., pp. 171 and 346, McGraw-Hill, New York.
Spanier and von Engler: "Zur Kenntnis der Wirkung des Schwefels auf Kohlenwasserstoffe und des Schwefelgehaltes der Erdole": Dissertation, Karlsruhe, 1910; through Friedmann: Petroleum Zeitschrift, 11, 694 (1916).
Stormer: Trans. Am. Ceramic Soc. 11, 597 (1909).
Symes and Lantz: Ind. Eng. Chem. 1, 35 (1929).
Taylor: Mem. Manchester Phil. Soc. 79, 99 (1935).
Thacker and Miller: Ind. Eng. Chem. 36, 182 (1944).
Thiessen: Ind. Eng. Chem. 27, 473 (1935).
U.S. Bureau of Mines: Bulletin No. 231 (1925).
U.S. Bureau of Mines: Circular No. 7334 (1945).
van Iterson: Intern. Assn. for Rubber Cultiv. 7, 239 (1918) through Am. Chem. Abs. 13, 386 (1919).
Vesterberg: Ber. 36, 4200 (1903).
Warren and Burwell: J. Chem. Physics, 3, 6 (1935).
West: Chem. Eng. 58, 276 (1951).
Westlake: Chem. Reviews, 39, 219 (1946).
Wibaut: Z.anorg. Chem. 211, 398 (1933).
Willson: Oil and Gas Journal, 32, 13 (1934).
Yost and Russell: "Systematic Inorganic Chemistry of the Fifth and Sixth Group non-Metallic Elements", p. 279, Prentice-Hall, New York.

SELECT ADDITIONAL BIBLIOGRAPHY

Abegg, Auerbach and Koppel: "Handbuch der anorganischen Chemie", Vol. IV, (1), Hirzel, Leipzig.
Abrahams: "Asphalts and Allied Substances", 5th Ed. 2 Vols. 1945, D. van Nostrand Co., New York.
Anon.: "Standard Methods for Testing Petroleum and its Products", Institute of Petroleum, London.
Auden: "Sulphur and Sulphur Derivatives", Pitman and Sons, London.
Barr: "A Monograph of Viscometry", Humphrey Milford, London.

Borgstrom, Bost and Brown: "Bibliography on Sulphur Compounds in Petroleum, 1871 - 1929, American Petroleum Institute, New York.
Bouman: "Properties of Lubricating Oil and Engine Deposits", MacMillan and Co., London.
Brooks: "The non-Benzenoid Hydrocarbons", Chemical Catalog Co., New York.
Cross: "Handbook of Petroleum, Asphalt, and Natural Gas", Kansas City Testing Lab. Bull. 25, 1928.
Egloff: "Reactions of Pure Hydrocarbons" (A.C.S. Monograph No. 73), 1937, Rheinhold Publishing Corp. New York.
Ellis: "The Chemistry of Petroleum Derivatives", Vol. I, 1934; Vol. II, 1937; Vol. III, 1942, Rheinhold Publishing Corp. New York.
Ellis: "The Chemistry of Synthetic Resins", Rheinhold Publishing Corp. New York.
Georgi: "Motor Oils and Engine Lubrication", Rheinhold Publishing Corp., New York.
Glasstone, Laidler and Eyring: "The Theory of Rate Processes", 5th Ed. McGraw-Hill, New York.
Gurwitsch and Moore: "The Scientific Principles of Petroleum Technology", 2nd Ed. 1932, Chapman and Hall Ltd., London.
Hamor and Padgett: "The Technical Examination of Crude Petroleum and Petroleum Products", McGraw-Hill Book Co. Inc. New York.
Hildebrand: "Solubility of non-Electrolytes", 3rd Ed., Rheinhold Publishing Corp., New York.
Holtz: "The Origin and Decomposition of Organic Sulphur Compounds under Gasmaking Conditions", Johns Hopkins University Press.
Hurt: "Pyrolysis of Carbon Compounds", (A.C.S. Monograph No. 50) 1930, Chemical Catalog. Co. Inc. New York.
Kalichevsky and Stogner: "Chemical Refining of Petroleum", 2nd Ed., Rheinhold Publishing Corp., New York.
Lowry: "Chemistry of Coal Utilisation", 2 Vols., John Wiley and Sons, New York; Chapman and Hall, London.
Nash and Howes: "Principles and Practice of Motor Fuel Preparation and Application", 2 Vols., 1934, Chapman and Hall, London.
Nelson: "Petroleum Refinery Engineering", 2nd Ed., McGraw-Hill, New York.
Petrick and Gaigher: "A Contribution to the Study of South African Oil Shales", No. 2, (Bulletin No. 11), S.A. Fuel Research Institute, Pretoria.

Plant and Newling: "The Catalytic Removal of Organic Sulphur Compounds from Coal Gas", Institution of Gas Engineers, London.
Reid: "Science of Petroleum", 1938, 2 Vols., Oxford University Press.
Sachanen: "Conversion of Petroleum"; 1940, Rheinhold Publishing Corp. New York.
Weil and Lane: "The Technology of the Fisher-Tropsch Process", Constable and Co., London.

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