

Chemistry. — *On the Behaviour of amorphous Carbon and Sulphur, compared with the Behaviour of Diamond and of Graphite and on the Carbonsulphide of CIUSA.* By J. P. WIBAUT and E. J. VAN DER KAM. (Communicated by Prof. A. F. HOLLEMAN).

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§ 1. Introduction.

In previous investigations¹⁾ on this subject has been shown that by heating mixtures of pure amorphous carbon and sulphur at 500—600° C. in sealed tubes, "sulphurous carbons" are formed which contain 15—25 % sulphur and which show the same appearance as the amorphous carbon before the treatment. When these substances were heated at 600° C. in a vacuum, about 50 % of the combined sulphur was splitted off, at higher temperatures still more of the sulphur separated, but finally, after heating at 1000—1100°, there result sulphurous carbons which still contain 2—3 % sulphur. If these substances are exposed to the action of gaseous hydrogen at 500—700°, nearly the whole quantity of fixed sulphur is eliminated as sulphide of hydrogen.

The experimental results led us to the conception that at least the strongly held sulphur in this sulphurous carbons is fixed to the carbon by valency forces. However, since WIBAUT and LA BASTIDE²⁾ did not succeed in isolating any carbon-sulphur compound of definite composition from this sulphurous carbons (except carbondisulphide), it could not be decided if there were present in this sulphurous carbons one or more carbonsulphides of definite composition. It should be possible to settle this question if the pressure of the sulphur vapour above such substances could be measured at a constant temperature for varying compositions of the solid phase.

Before starting experiments on these lines, we thought it advisable to investigate a carbonsulphide in which the sulphur atoms are doubtless bound by primary valency forces. CIUSA³⁾ obtained by decomposition of tetraiodothiophen a black, carbonlike substance, which he called thiophen graphite, and to which the formula $(C_4S)_x$ was ascribed.

We have not been able to prepare a substance of the composition C_4S by this method ; the sulphur content of our preparations was too low and there was always a small content of iodine. An approximate estimation of the pression of the sulphur vapour above such a specimen at 500° was made with a glass-spring manometer ; the vapour pressure was between 5 and

¹⁾ Rec. des trav. chim. des Pays-Bas **41**, 154 (1922); these Proceedings Vol. **24**, 92 (1921).

²⁾ Rec. des trav. chim. des Pays-Bas **43**, 731 (1924).

³⁾ Gazz. chim. **55**, 384 (1925).

7 cm mercury, an exact estimation was impossible as it was very difficult to eliminate absorbed gases from these substances, without simultaneously eliminating a part of the fixed sulphur. In view of this experimental difficulties the plan of making an extensive investigation of the vapour pressure of our sulphurous carbons, was given up.

Another point of interest was to make experiments with the crystalline modifications of carbon : diamond and graphite.

In a diamond crystal the valencies of the carbon atoms are completely saturated. If the fixation of sulphur by amorphous carbon is caused by unsaturated valencies of the carbon, it was to be expected that diamond powder should not be able to combine with sulphur. It may be said at once that we found that pure finely powdered diamond did not fix any sulphur at 500° or at 600°. Nor did highly purified Ceylon graphite fix any sulphur at 600°.

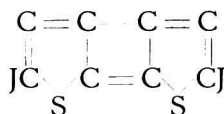
On the other hand we have found considerable differences in the quantities of sulphur fixed by different kind of amorphous carbon. We will first give a description of the experiments and afterwards a discussion of the results.

EXPERIMENTAL PART.

§ 2. *Preparation of sulphurous carbons.*

I. *From tetraiodothiophen according to CIUSA.*

CIUSA (3) heated tetraiodothiophen in a sealed tube at 340° ; iodine was liberated and a black, carbonlike substance resulted containing iodine and sulphur in the atomic ratio 1 : 1. For this reason CIUSA ascribes to this amorphous substance the formula



When this substance was heated in a current of carbon dioxide "at beginning red heat" the iodine was split off and an amorphous substance resulted, thiophengraphite; CIUSA found for the composition of this substance 37.57 % S and 54.71 % C. (C₄S requires 40 % S and 60 % C.).

We did not succeed in preparing a substance of the empirical composition C₄S notwithstanding several modifications in the mode of heating of the tetraiodothiophen were tried. In our experiments not only iodine but also sulphur was splitt off. The best result was obtained in the following manner : 5 grams tetraiodothiophen were put in a glass tube which was evacuated and then sealed off ; the glass tube was heated during 8 hours at 400° in an electrical furnace. The liberated iodine was removed from the reaction product by extraction with carbon tetrachloride ; the resulting black powder was put again in a glass tube, together with a spiral of silver

wire. The tube after having been evacuated and sealed off, was heated at 400° ($\pm 10^{\circ}$) during thirty days without interruption. The resulting product was again extracted with carbontetrachloride and dried. In this manner two preparations were obtained, black amorphous powders, which will be indicated by the letters T_1 and T_2 .

Analysis	T_1 :	28.4 % S ;	2.9 % J
	T_2 :	31.3 % S ;	1.7 % J

Though the composition of these substances differs widely from the values calculated for C_4S , we have used them for several experiments, as it may be assumed that in these preparations the sulphur is fixed by chemical bounds to the carbon atoms.

II. *From amorphous carbon and sulphur.*

The amorphous carbon was prepared by heating previously outgassed sugar carbon in a vacuum at 1000° as described by WIBAUT and LA BASTIDE (l.c.) (anal.: 0.22 % ash, C 99.55 %, 99.76 %; H 0.40 %, 0.48 %).

Samples of 5 grams of this carbon were mixed with 5 grams finely powdered sulphur and the mixture was heated in sealed glass tubes at a constant temperature in the manner described in the paper just quoted. When the heating was finished the content of the tube was extracted during 7—10 days with boiling toluene, till no more sulphur was dissolved by the toluene. The resulting amorphous powders, which had the appearance of the original amorphous carbon were analysed and used for several experiments¹⁾. In table 1, the amorphous carbon which served for the preparations is indicated by the letter C and the sulphurous carbons which were obtained from it by the letters C_1 , C_2 , C_3 and C_4 .

III. *From activated amorphous carbon and sulphur.*

The activated carbon was prepared by heating lumps of sugar charcoal at 900 — 960° with limited supply of air according to BARTELL and MILLER²⁾. The activated carbon had a black velvety appearance. (Analysis: C 98.9 %, H 0.3 %, ash 0.31 % ; the ash contained no ferric oxyde).

As the activated carbon is very hygroscopic it was necessary to dry the sample by heating at 1000° , immediately before use ; the cooled sample was mixed as quickly as possible with sulphur and put in the reaction tube. Notwithstanding these precautions the tube, after being heated at 500° , contained some hydrogen sulphide, which was formed from water absorbed by the carbon sample. The tubes were therefore first heated at 500° during 24 hours, opened and sealed off again and afterwards heated at 600° .

In table 1 the sample of activated carbon is indicated by the letter A and the sulphurous carbons obtained from it by the letters A_1 — A_4 .

¹⁾ The determination of the sulphur content of the sulphurous carbons described in § 2, I, II and III and in § 3 has been done by oxidising with nitric acid in a sealed tube according to CARIUS. All the analyses were done in duplicate.

²⁾ Journ. Am. Chem. Soc. **44**, 1866 (1922).

IV. *Experiments with diamond powder and sulphur.*

Diamond splitters, which are obtained as a by-product by the cleaving of diamonds were powdered in mechanically driven iron mortars ; a very fine white powder was obtained which contained 0.067 % of ash. We desire to express our thanks to Mr. J. VAN ZUTPHEN from the "Diamantbewerkeren Koperen Stelen Fonds", who very liberally put a sample of diamond powder at our disposition and to Mr. QUELLE who supervised the preparation of the diamond powder in the laboratory of the institution just mentioned.

As for the experiments with diamond powder only small quantities were available, we have first tried an analytic method for determining the sulphur content of sulphurous carbons which was adopted to the use of small samples. The CARIUS method cannot be applied on diamond powder, more over the gravimetric determination of little quantities of barium sulfate is tedious. We have used the method of TER MEULEN and HESLINGA ¹⁾ in which the sample of substance is burned in moist oxygen, the sulphur dioxide formed is absorbed by hydrogen peroxyde solution and the sulphuric acid titrated with $\frac{1}{50}$ n. natriumcarbonate. In adopting this method to the analysis of our sulphurous carbons, some precautions must be taken. We thank Prof. TER MEULEN and Miss RAVENSWAAY for their kindly help and advice by this experiments.

The experiment with diamond powder was done as follows :

A mixture of 0.300 gram diamond powder and 0.300 gram sulphur was heated in a sealed tube during 24 hours at 500° ; when the cooled tube was opened, there was a very slight pressure. After sealing again the tube was heated during 24 hours at 600°. The contents of the tube were extracted twice with 100 ccm boiling toluene, the remaining diamond powder had quite the same appearance as the original sample. A sample was burned according the method just mentioned ; we did not find any sulphur, while a sulphur content of 0.2 % would have been detected with certainty.

V. *Experiments with Ceylon graphite.*

A sample of Ceylon graphite which had an ash content of 4.7 % was purified in the following manner.

The sample was successively treated with fused kalium hydroxyde, boiled with hydrochloric acid, heated in a current of dry chlorine at 500—600°, washed with distilled water, extracted with hot hydrofluoric acid, again washed and dried ²⁾. After this treatment the sample consisted of small shining scales.

Analysis : ash 0.02 %, C 99.6 %, H 0.3 %.

A mixture of 5 grams of this graphite with 5 grams sulphur was heated first during 24 hours at 500° and then during 24 hours at 600°. After

¹⁾ H. TER MEULEN en J. HESLINGA. Nieuwe methoden voor elementair analyse (Delft, 1925).

²⁾ Cf. DUMAS and STAS, Ann. Chim. et Phys. (3) 1, 26 (1840).
BURNS and HULETT, Journ. Am. Chem. Soc., 45 574 (1923).

extracting the content of the tube as described before, the graphite was tested for sulphur by the method used in the experiments with diamond. There was no sulphur present in the graphite.

The results of the experiments with the carbon preparations C and A with diamond powder and graphite are compiled in table 1 :

TABLE 1.

Number of experiment	Preparation of carbon	Temperature and duration of heating	Sulphur content of sulphurous carbon (after extraction)
1	C	24 hours at 500° then 24 hours at 600°	C ₁ 19.4 ‰
2	C	24 hours at 500° then 24 hours at 600°	C ₂ 19.1 ..
3	C	48 hours at 500°	C ₃ 14.7 ..
4	C	48 hours at 350°	C ₄ 3.05 ..
5	A	24 hours at 500° then 24 hours at 600°	A ₁ 9.8 ..
6	A	24 hours at 500° then 24 hours at 600°	A ₂ 9.65 ..
7	A	48 hours at 500°	A ₃ 9.5 ..
8	A	48 hours at 350°	A ₄ 9.6 ..
9	Diamond powder	24 hours at 500° then 24 hours at 600°	0 ..
10	Graphite	24 hours at 500° then 24 hours at 600°	0 ..

It will be seen from table 1 that the quantity of sulphur that is fixed, depends *ceteris paribus* on the properties of the carbon specimens. With purified sugar carbon (preparation C) the quantity of fixed sulphur varies with the temperature of heating ; the quantity of fixed sulphur at 350° is about $\frac{1}{6}$ of the quantity fixed at 600°. It may be remarked that the experiments at 600° show a very good concordance with the experiments described in the paper with LA BASTIDE (l.c.) when one takes in mind that in these two investigations different samples of purified sugar carbon have been used.

The activated sugar carbon (preparation A) fixes much less sulphur than the carbon-preparation C ; it is remarkable that the quantity of sulphur fixed by this activated carbon seems to be independent of the temperature of heating between 350 and 600°.

It should be kept in mind that the influence of temperature alone on the phenomenon cannot be seen from these experiments, as in the experiments

at 500° and 600° a different pressure of sulphur vapour prevailed in the sealed tubes.

§ 3. *Behaviour of the sulphurous carbons when heated in a vacuum.*

With the purpose of getting more information about the nature of the forces by which the sulphur is bound in the sulphurous carbons described in § 2, I, II, III, these substances were heated in a high vacuum at different temperatures, and the sulphur content of the remaining product was determined. A weighed quantity (1—6 grams) of sulphurous carbon was put in a porcelain boat, which was placed in a quartz tube near to the sealed bottom. The open end of the horizontal quartz tube was connected with two U-tubes provided with taps; the tubes were connected with a mercury diffusion pump and the apparatus was evacuated. When high vacuum prevailed in the apparatus, an electrical furnace, which had been heated previously on the desired temperature, was pushed over the quartz tube and the U-tubes were cooled in liquid air. In this manner the decomposition products were rapidly removed from the hot reaction tube, and the sulphur which was split off could not recombine with the carbon. The temperature was measured by means of a galvanometer and a thermocouple; the junction was kept at the outer wall of the quartz tube in front of the middle of the porcelain boat. Each heating experiment was continued during 6 hours (the temperature being kept constant at about 5°) while pumping continued and the U-tubes were kept in liquid air during the experiment. Then the furnace was removed from the quartz tube, and pumping and cooling of the U-tubes was continued till the quartz tube was at room temperature. The stop cocks of the U-tubes were closed and the tubes taken from the liquid air. The U-tubes were washed with dry ether and the ethereal liquid tested with an ethereal solution of triaethylphosphine; traces of carbondisulphide could be detected in this manner. Then the U-tubes were washed with carbon disulphide, and after evaporation of this liquid the remaining sulphur was weighed. The content of the porcelain boat, which always had the appearance of amorphous carbon was analysed. The quantity of combined sulphur in the carbon, augmented with the quantity of free sulphur found in the U-tubes corresponded approximatively with combined sulphur present in the original preparation; in these experiments only small quantities of carbondisulphide were formed, this substance was not estimated quantitatively.

In table 2 the results of this experiments are compiled. In the second column the letter and the original sulphur content of the sulphurous carbon which served for an experiment, is given. In the 3^d, 4th and 5th column are given the sulphur contents of the sulphurous carbons which remained after heating at the indicated temperature. The sulphurous carbons in the 5th column are indicated by letters and indexes.

In experiment I the preparation C_1 containing 19.4% sulphur was heated during 6 hours at 600° ; a part from the residue containing 6.5% sulphur was heated at 800° , the sulphur content of the residue was then 4.8%; part of this residue was then heated at 1000° , after which a substance with 3.0% sulphur remained. In experiments 2, 3, 4, 7 and 8 the sulphurous carbons were first heated at 600° during 6 hours; without interrupting the experiment the temperature of the furnace was brought to 1000° and kept constant there for another period of 6 hours, the remaining sulphurous carbon was then analysed. In experiments 5 and 10 the substance was first heated at 600° , the residue analysed and parts of this residues heated at 1000° . In experiments 6 and 9 the substance was first heated at 800° during 6 hours, the residues were analysed and parts of it heated again at 1000° . After the heating at 1000° the *U*-tubes contained little quantities of carbondisulphide in all experiments (in N^0 . 4 only traces). After the heating at 800° also carbondisulphide was found, but not after the heating at 600° in experiments 5 and 10; in experiment 1 where 6.2 gram of sulphurous carbon was used, a trace of carbondisulphide was formed after the heating at 600° . This is in accordance with our previous results, where we found that from a sulphurous carbon containing 21% sulphur only traces of carbondisulphide were splitt off at 600° , while at 800° and 1000° some more of this substance was separated. (Compare WIBAUT and LA BASTIDE l.c.).

TABLE 2.

Number of experiment	Number and S content of sulphurous carbon	Sulphur content after heating in a high vacuum during 6 hours at:		
		600°	800°	1000°
1	C_1 19.4 %	6.5 %	C''_1 4.8 %	C'_1 3.0 %
2	C_2 19.1 ..			C'_2 2.1 ..
3	C_3 14.7 ..			C'_3 2.7 ..
4	C_4 3.05 ..			C'_4 1.4 ..
5	A_1 9.8 ..	8.1 ..		A'_1 4.6 ..
6	A_2 9.65 ..		6.1 %	A'_2 4.5 ..
7	A_3 9.5 ..			A'_3 4.3 ..
8	A_4 9.6 ..			A'_4 2.5 ..
9	T_1 { 28.4 .. S 2.9 .. J		{ 14.0 .. S 0.9 .. J	T'_1 4.8 .. S traces J
10	T_2 { 31.3 .. S 1.7 .. J	{ 27.45 .. S 0.85 .. J		T'_2 5.2 .. S traces J

It is seen from table 2 that the greatest part of the sulphur from preparations C_1 is splitt off at 600° in a high vacuum, obviously this part of the sulphur is loosely bound; a smaller part of the sulphur is firmly bound for after heating at 1000° in vacuum a carbon with 2—3% sulphur results. On the other hand in the preparation T_2 (which has been prepared from tetraiodo-thiophen and wherein the sulphur atoms are beyond doubt bound in thiophen-rings), only a small proportion of the sulphur is split

off at 600°. One might conclude that in preparation C₁ only a small part of the sulphur is fixed by primary valencies of the carbon atoms.

It is interesting that in the sulphurous carbon A₁, which is prepared from activated carbon and sulphur, the sulphur is firmly bound, only 17 % of the sulphur being separated at 600° in a vacuum.

Comparing the preparations A₁ and A₄ which have been prepared by heating activated carbon with sulphur at 600° and at 350° respectively, it is seen that the sulphur is more loosely bound in A₄. Notwithstanding the activated carbon fixes the same quantities of sulphur when heated either at 600° or at 350°, it appears that the manner in which the sulphur is combined, is different in both cases.

§ 4. *The Action of hydrogen on the sulphurous carbons.*

It has been shown by POWELL¹⁾ and in our former papers (l.c.) that hydrogen reacts with sulphurous carbons at higher temperatures, whereby the sulphur is eliminated in the form of hydrogen sulphide.

We have made comparative experiments with the sulphurous carbons described in § 2, on their behaviour towards hydrogen.

1500 cc hydrogen (15°, 760 mm) were passed at a constant rate over 0.350 gram of sulphurous carbon, which was heated at a constant temperature; the quantity of hydrogen sulphide in the outlet gases was determined. In table 3 are recorded the results of this experiments; the sulphurous carbons are indicated by the same letters as in tables 1 and 2.

TABLE 3. Action of hydrogen on sulphurous carbons at 400° C.

Number of experiment	Number and S-content of sulphurous carbon	Sulphur eliminated as H ₂ S in percentage of original sulphur
1	C ₁ (19.4 % S)	22.8; 24.6
2	C ₂ (19.1 .. S)	22.0; 23.8
3	A ₁ (9.8 .. S)	2.6; 3.6
4	A ₂ (9.65 .. S)	3.1; 3.7
5	T ₁ (28.4 .. S)	9.5; 9.1
6	T ₂ (31.3 .. S)	7.4
7	C ₃ (14.7 .. S)	26.7
8	C ₄ (3.05 .. S)	31.7
9	A ₃ (9.5 .. S)	20.1
10	A ₄ (9.6 .. S)	20.7; 21.9

¹⁾ Journ. Amer. Chem. Soc. **45**, 1 (1923).

It is to be seen from table 3, that the results of duplicate experiments differ somewhat, but these differences are much smaller than the differences between different sulphurous carbons. It is obvious that these sulphurous carbons are attacked at different rates by hydrogen; *ceteris paribus* the sulphur is eliminated at a greater rate from the sulphurous carbons which are prepared from purified sugar carbon, then from those which are prepared from activated sugar carbon (compare experiment 1 and 2 with 3 and 4). The sulphurous carbons prepared from tetra-iodothiophen (T_1 and T_2) stand between the preparations just mentioned.

The sulphurous carbons which are prepared at 500° or at 350° , either from purified sugar carbon or from activated sugar carbon are more rapidly attacked by hydrogen than the sulphurous carbons which are prepared at 600° (compare exp. 7 and 8 with 1 and 2 or 9 and 10 with 3 and 4).

In another series of experiments we have exposed to the action of hydrogen at 600° the sulphurous carbons which had remained after the heating at 800° or at 1000° in vacuum. Preliminary experiments had shown that at 400° or at 500° only very small quantities of hydrogen sulphide were formed from these substances. In table 4 the results of the experiments are recorded (the numbers of the preparations are the same as in table 2).

TABLE 4. Action of hydrogen on sulphurous carbons at 600° C.

Number of experiment	Number and S-content of sulphurous carbon	Sulphur eliminated as H_2S in percentage of original sulphur
1	C'_1 (4.8 % S)	23.0; 22.7
2	A'_1 (4.6 .. S)	11.3
3	A'_2 (4.5 .. S)	12.8; 13.2
4	T'_1 (4.8 .. S)	10.2
5	T'_2 (5.2 .. S)	11.25
6	C'_4 (1.4 .. S)	10.7

5. Discussion of the results.

It follows from our experiments that only "amorphous carbons" are able to fix sulphur, while the crystalline modifications of carbon do not possess this property. It seems probable that at least a part of the sulphur in these sulphurous carbons is combined to the carbon-atoms by valency forces; these valency forces are therefore available in amorphous carbon, but not in diamond or graphite. This conclusion is in accord with recent views on the nature of amorphous carbon. DEBYE and SCHERRER¹⁾ concluded from

¹⁾ Physik. Zeits. 18, 301 (1917).

an examination by X-rays that amorphous carbon was merely graphite in a powder form ; this conclusion was supported by KOHLSCHÜTTER ¹⁾ who founded his opinion on the chemical and physical properties of different species of graphite and amorphous carbons.

However RUFF, SCHMIDT and OLBRICH ²⁾ think that true amorphous carbons exist in which the atoms are not arranged in the graphite lattice, they concluded from their investigation of different kinds of amorphous carbon, that some of these varieties pass into graphite only at temperatures as high as 2000°. Their conclusion is that in typical amorphous carbons there exist at the surface (included the capillary surfaces) atoms the valency forces of which are not fully saturated by neighbouring atoms and which possess therefore "free valencies".

GARNER and MAC KIE ³⁾ point out that these surface atoms in such amorphous carbons may possess different degrees of unsaturation. The high value of the heat of adsorption for small amounts of adsorbed oxygen supports this idea.

RHEAD and WHEELER ⁴⁾ have shown in a very interesting investigation on the mode of combustion of carbon, that oxygen may be fixed by amorphous carbon at temperatures between 300° and 600° ; according to these authors the fixed oxygen is present as a "loosely formed physico-chemical complex to which no definite formula can be assigned". As the temperature increases the fixed oxygen is released in the form of carbon monoxide and carbon dioxide. At a given temperature of decomposition only a part of the fixed oxygen is released ; if the temperature increases another part of the fixed oxygen is split off in the form of oxides of carbon.

It seems therefore that the forces by which the oxygen-atoms (or molecules) are held, are of different size ; GARNER and MC KIE point out that this behaviour is to be expected with a truly amorphous substance, wherein surface-atoms of different energy-content occur.

Our sulphurous carbons show many analogies with the oxygenated carbons of RHEAD and WHEELER.

In the sulphurous carbons prepared from non activated amorphous carbon most of the sulphur is loosely bound ; this is that part of the sulphur that is split off in a vacuum at 600°; another part however is still held at 800° or even at 1000°. Obviously the forces by which the carbon-atoms are held in the sulphurous carbons of high sulphur content, are different in size. The same conclusion may be drawn from the splitting off of carbon-disulphide, which occurs over a range of temperatures.

That in our experiments most of the sulphur is liberated as free sulphur and not in the form of carbondisulphide, is in accordance with the fact that

¹⁾ Zeits. anorg. Chem. **105**, 35 (1919).

²⁾ Zeits. f. anorg. Chem. **148**, 313 (1925).

³⁾ J. Chem. Soc., 1927, 2451.

⁴⁾ J. Chem. Soc., **103**, 461 (1913).

C.f. LOWRY and HULETT, J. Am. Chem. Soc. **42**, 1408 (1920).

the affinity of carbon to sulphur is less than the affinity of carbon to oxygen. The fact that diamond powder and graphite are not capable to fix sulphur is in accordance with our hypothesis that this fixation is caused by unsaturated surface-atoms of the amorphous carbon; in the crystalline modifications of carbon a comparatively small number of free valency forces in the surface is available, as compared with amorphous carbons.

As the properties of an amorphous carbon may differ widely, according to different modes of preparation, it is quite conceivable that different carbons may show considerable quantitative differences in the behaviour towards sulphur, as we have found with the specimens of activated and non-activated sugar-carbon. However we are not able to explain why the influence of temperature on the phenomenon of sulphur fixation is so different for this two kinds of carbon.

In the sulphurous carbons which are prepared from tetraiodothiophen, the sulphur-atoms will beyond doubt form part of condensed thiophen-chains according to the supposition of CIUSA. It is interesting that the sulphur in this products is held more firmly than in the sulphurous carbons prepared from non-activated carbon, but less firmly than in those prepared from the activated carbon.

When these thiophen-carbons are heated at 1000° sulphurous carbons result, which show a close resemblance to the products prepared from activated carbon and sulphur after the same treatment (compare A_1' and A_2' with T_1' and T_2' in tables 2 and 4).

There seems no reason to suppose that in the sulphurous carbons T_1' and T_2' the sulphur-atoms are held only by surface-atoms. In this preparations there might be present a non volatible carbon-sulphide of low sulphur content, which seems a rather arbitrary hypothesis, or it might be supposed that the sulphur-atoms are dispersed in an irregular manner in the carbon lattice.

It would be interesting to investigate if there is a relation between the size of surface of different carbons and the quantity of sulphur that is fixed at a given temperature.

We express our thanks to Prof. Dr. A. SMITS who very kindly put at our disposition apparatus for vacuum work and a glass spring manometer, to Prof. H. TER MEULEN for his valuable help and advice in analytical difficulties and to Mr. J. VAN ZUTPHEN and Mr. J. QUELLE who put diamond-powder at our disposal.

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