

Chemistry. — "*On the behaviour of Amorphous Carbon and Sulphur at High Temperatures and on Carbon-Sulphides*". By Dr. J. P. WIBAUT. (Communicated by Prof. A. F. HOLLEMAN).

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§ 1. *Introduction.* In 1919 Dr. A. STOFFEL and the author of this paper published an inquiry into the sulphurous compounds of coal ¹⁾. The result was briefly as follows:

A method was elaborated to determine the sulphur combined with iron (pyritic sulphur) and the sulphur present as organic compounds separately. It was then examined how these anorganic and organic sulphur compounds dissociate during the coking of coal, i.e. the heating with exclusion of air at temperatures of 1000° and higher. It then appeared among other things that during the coking the organic sulphur compounds partly yield sulphuretted hydrogen and volatile organic sulphur compounds, but that a large proportion of the organically bound sulphur from the coal is retained in the coke in the form of a sulphur-carbon compound, which does not lose its sulphur content at the temperature of 1000°. In gas coke, which mostly contains 1—1,5 % of sulphur, this sulphur appeared to be present for the greater part in the form of a carbon-compound, and only for a smaller part to be fixed by the anorganic components (ash components) of the coke. Comparative experiments on the coking of ash-containing coal-samples and of coal-samples that had been freed from mineral admixtures (ash), taught that during the coking of coal, part of the sulphur which is combined with iron as pyrite in the coal, is fixed by carbon in the coke. It seems, therefore, that carbon can combine with sulphur in some way or other at high temperature.

This find was very surprising, and not devoid of importance for the technics of coke-manufacture. About the same time PARR and POWELL ²⁾ published a research on the same subject, which did not appear as a magazine article, and did not come under our notice until later. The investigators followed another method of research; their results on the whole agree with ours. In two recent papers

¹⁾ Rec. trav. chim. **38**, 132 (1919).

²⁾ A Study of the Forms in which Sulfur occurs in Coal. University of Illinois Bulletin. Vol. XVI. N^o. 34 (1919).

POWELL¹⁾ communicates the result of further researches. In this the behaviour of the sulphur compounds during coking is examined in details for different kinds of coal, in which the already mentioned results were confirmed and extended.

It seems, however, to me that also questions of more general importance present themselves in connection with these reactions. In what way is this compound of sulphur and carbon formed, in which evidently a complex is formed that is very resistant with regard to heating? A preliminary experiment had already taught me that through quick heating of sugar carbon with sulphur a carbon-like sulphurous substance is obtained, which can be made red-hot without losing its sulphur content. Accordingly the mutual behaviour of two simple substances as sulphur and carbon is not yet known in detail. Hence I have begun an investigation purposing to examine the behaviour of amorphous carbon and sulphur on heating, and study more closely the products that arise from these two components. Though this investigation is not yet entirely completed, I feel obliged in view of POWELL's publications, to communicate already now the experiments carried out by me.

§ 2. In order to obtain reproducible results, it was desirable to experiment with an amorphous carbon as pure as possible, which was obtained in a well-defined way.

Finely powdered sugar-carbon obtained through moderate heating of sugar, was extracted with boiling hydrochloric acid, after which the ash-content was 0.30 %. Through extraction with hydrofluoric acid this ash-content is only little diminished. This carbon was heated at 900—1000° in a porcelain tube for 7 hours. The generated gases were pumped off by means of an oil-pump, in a vacuum of $\pm 1,7$ mm. This preparation was analysed, and then again heated at 970—1020° for three hours in a vacuum of 0.6 mm.; during the last hour of this heating experiment there was no generation of gases any more. The evacuation was continued during the cooling. The analysis of this carbon was performed as follows: a weighed quantity of substance was heated in a porcelain boat at 400—450° and 1 mm. for one hour; after having been cooled in vacuum, the boat was quickly placed in a weighing bottle, reweighed, and at once conveyed to the combustion tube. Such amorphous carbon is very hygroscopic; the content of absorbed water determined in this way, was 1.83 %. The analysis of this carbon dried in vacuum

¹⁾ Journ. Ind. and Engin. Chem. **12**, p. 1069, 1077 (1920).

at 400° showed 98,35 % C. 0,75 % H., and 0,30 % ash. After one hour heating at 600—660° at 2 mm.: 98,68 % carbon, 0,53 % hydrogen, 0,30 % ash. When the rest is estimated as oxygen, and when this content of oxygen is attributed to absorbed water, which has not been removed in spite of the heating at 600° in vacuum, the dried preparation has the following composition: ash 0,30 %, carbon 98,68 %, absorbed water 0,49 %, hydrogen (chemically bound) 0,48 %.

Even after prolonged heating at 1000° in vacuum a small quantity of hydrogen is retained in this preparation. This hydrogen content lies, however, near the limit of the errors of the analysis. Apart from the ash-content, the preparation consists, therefore, practically of amorphous carbon. The ash almost entirely dissolved in hydrochloric acid, and contained but very little iron-oxide.

The following experiments were made with this amorphous carbon K_1 : 24 grammes of K_1 were mixed with 8 grammes of pure sulphur; the mixture was placed in a porcelain tube, which was shoved horizontally into an oven heated at 510° C. The temperature of the oven was raised in an hour to 760°, and in the following 90 minutes to 975°. From 600° to the end of the experiment there developed some sulphuretted hydrogen. After cooling much sulphur was found in the colder part of the tube, which had been condensed there. The black carbon-like mass was again placed in a porcelain tube, and this was slowly heated in a vertical oven. At 800° very little sulphuretted hydrogen began to develop; the temperature was carried up to 1000° in two hours, and kept at 1000° for half an hour, then the H_2S -generation had ceased and the heating was discontinued. A sulphur determination in the carbon-like powder showed: 1,98 % S.

16 grammes of P_1 were extracted for a long time with boiling toluene; after evaporation of the toluene no sulphur remained behind. 2,03 % was found for the sulphur content of the extracted product. Hence extraction with toluene does not reduce the sulphur content of P_1 . Extraction with carbon disulphide did not lead to the purpose, as it appeared impossible to remove the last rests of carbon disulphide from the extracted product.

I then tried whether through heating in vacuum, in which the receiver was cooled with liquid air to condense gaseous compounds that might possibly be formed, a sulphurous substance could be isolated from this preparation. It appeared, however, in several experiments that even prolonged heating in vacuum reduced the sulphur-content of P_1 hardly perceptibly; hence a volatile sulphur

compound is not formed. The following figures give an idea of the course of such an experiment.

A porcelain boat with 3.09 grammes of P_1 was placed in a porcelain tube, which was open on one side, and was connected there with the oil-pump. The tube was heated in an electrical oven (thermo-element on the outside of the tube).

Time	Temp.	Pressure	} There is formed a little sulphuretted hydrogen.
1.30	620°	1.5 mm.	
3.15	840	1.7 „	
3.45	910	1.5 „	
5.10	1010	2 „	
5.45	900	2 „	

Left to cool with evacuation; the sulphur-content of the thus obtained product P_2 was 1.94 %.

2.38 grammes of P_2 heated anew in vacuum:

11.15	400°	1 mm.	
2	940	1 „	
3	980	1 „	
4	1030	1.5 mm.	there still arise traces of H_2S .
5	1060	1.5 „	
6.10	990	1 „	

Left to cool with evacuation. The product P_3 thus obtained contains 1.87 % of sulphur.

It appears from these experiments that the sulphur content of P_1 decreases very little by prolonged heating at about 1000° C. and 1.5 mm., the decrease of the last experiment lies near the limit of the errors of the analysis. The total analysis of the preparation P_1 , which had been dried at 600° and 2 mm. for an hour gave: 0.27 % ash, 96.1 % C, 0.33 % H, 2.00 % sulphur, together 98.70 %.

Besides absorbed water this preparation contains, therefore, still a hardly appreciable quantity of hydrogen.

§ 3. Behaviour towards oxidizers and towards hydrogen. In order to get a better insight in the nature of this compound of carbon and sulphur the behaviour of this preparation towards oxidizing and towards reducing agents was examined.

2 grammes of P_1 were shaken with 100 cc. of water and 3 cc. of bromine for four hours on the shaking apparatus at the ordinary temperature. After this operation 3.6 mgr. of sulphur was oxidized

to sulphuric acid, hence 9% of the sulphur present in the 2 grammes of P_1 . In a duplicate experiment 13.5% of the sulphur was oxidized. In this product the sulphur was, therefore, oxidized only for a small part or at least very slowly by bromine water at the ordinary temperature. When on the other hand a mixture of charcoal with 2% sulphur was treated in the same way with bromine, the sulphur present was quantitatively found back as sulphuric acid, as was to be expected.

Behaviour towards hydrogen.

In a preliminary experiment 0.90 gramme of P_1 were spread out in a thin layer in a porcelain boat, and slowly heated in a current of pure dry hydrogen. Up to 500° no formation of sulphuretted hydrogen could be found; this began at about 550° . In two hours the temperature was raised from 550 to 750° ; in this temperature range sulphuretted hydrogen was slowly but regularly developed. About $\frac{1}{3}$ of the sulphur originally present in the P_1 was converted to sulphuretted hydrogen.

In a second experiment 2 grammes of P_1 were heated in a hydrogen current; at 430° sulphuretted hydrogen began to evolve. When 650° was reached, this temperature was kept constant, till the regular generation of sulphuretted hydrogen diminished. The heating at 650° had then been continued for 5 hours. The temperature was then raised to 750° , which gave rise to the formation of some more sulphuretted hydrogen. After the heating at 750° had been continued for four hours, only very little sulphuretted hydrogen was slowly developed, after which the experiment was stopped. The quantity of sulphuretted hydrogen formed corresponded to 0.0281 gr. sulphur or 70% of the quantity present in 2 grammes of P_1 . 1.945 grammes of carbon were recovered, which contained 0.47% sulphur. Hence 23% of the sulphur present in P_1 has remained behind in the carbon that is left.

In a third experiment 2 grammes of P_1 were heated for some days in a hydrogen current. The temperature was between 500 — 700° for 9 hours, and between 700 — 800° for 11 hours. Throughout the experiment sulphuretted hydrogen was regularly generated. The remaining carbon still contained 0.29% sulphur; it is, therefore, possible to convert practically all the sulphur from P_1 to sulphuretted hydrogen by prolonged heating in hydrogen at 500 — 800° .

To verify whether really a particular action of hydrogen should be assumed here, 1 gramme of P_1 was heated in a current of pure dry nitrogen at 900 — 990° for 8 hours; this appeared to have reduced the sulphur content only little. The percentage of sulphur found

in the remaining product was 1.75 %. It follows from this last experiment that the formation of sulphuretted hydrogen does not take place in this manner, that primarily sulphur vapour is split off, which reacts with the hydrogen. For if the sulphur combined with the carbon had an appreciable vapour tension at 900°, the generated sulphur vapour would be carried along by the nitrogen current, and then it would be possible to remove nearly all the sulphur from the carbon by heating in a nitrogen current, which is not the case. In the action of hydrogen on P_1 we have, therefore, to do with a specific action of the hydrogen, hence with a chemical reaction.

§ 4. I then examined more closely the conditions under which, and the temperatures at which this fixation of sulphur by amorphous carbon takes place. These experiments have not yet led to a satisfactory insight into the proposed problem, and should, therefore, be considered as provisional. A series of experiments was arranged as follows:

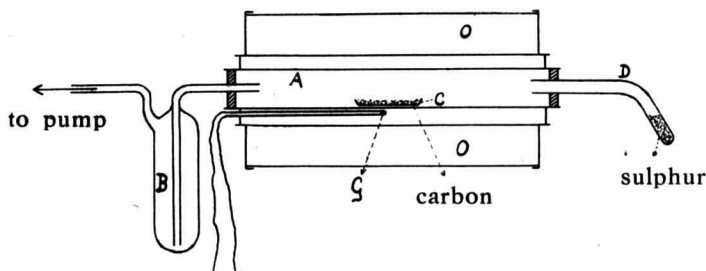
1.5–2 grammes of a mixture of 75 % amorphous carbon K_1 and 25 % sulphur was put in a porcelain boat, this boat was placed in a porcelain tube, which was in an oven heated beforehand at a definite temperature. The oven was then kept at this temperature for an hour, pure nitrogen flowing through the tube during this time; then the tube was cooled in a nitrogen current. This experiment was made at different temperatures (all above the boiling-point of sulphur), viz. at 500–510°, at 610–590°, 670–710°, 900–940°.

Most sulphur distilled from the boat for the greater part already at the beginning of the experiment. In the experiment at 500–510° no H_2S -formation was observed; it was, however, observed in the experiments at 610–590° and at the higher temperatures.

In all these cases the carbon recovered after the experiment had fixed no sulphur or very little. Compare with this the preparation of P_1 (§ 2), in which a larger quantity of mixture of carbon + sulphur was placed in an oven heated at 510°, which temperature was slowly raised to 975°; in this latter case the contents of the porcelain tube will have assumed the temperature of 510° less rapidly, and the sulphur could, therefore, be fixed by the carbon, before all the sulphur had been distilled out from the mixture.

The temperature at which the fixation took place in this experiment, cannot be ascertained. In the series of experiments mentioned in § 4 the small quantity of substance quickly assumed the temperature of the heated tube, the sulphur evaporated almost immediately after the boat had been pushed into the oven, the time during

which the sulphur vapour was in contact with the heated carbon was evidently too short for the fixation of sulphur by carbon to take place. For this reason some experiments were made in which the sulphur vapour was longer in contact with the carbon heated at a definite temperature.



In the middle of a porcelain tube *A* there is a boat *C* with about 2 grammes of amorphous carbon. The junction *G* of a thermocouple is on the outside of the porcelain tube at a level with the boat. *O* is an electrical oven. On one side a tube of sparingly fusible glass *D* was fastened air-tight in the porcelain tube. The bent part of this tube was partly filled with sulphur. On the other side the tube was in connection with a receiver *B*, which could be cooled during the experiment, and which was also connected with the vacuum pump. First the whole apparatus was evacuated to $\pm 2\text{ mm.}$, and then the heating was started. When the desired temperature had been reached, it was kept constant and — while evacuation was continued — the tube *D* was heated, so that the sulphur began to distill through the porcelain tube. In this way sulphur vapour flowed over carbon that was heated at a definite temperature. After the sulphur had been distilled over, the apparatus was left to cool in vacuum.

I. Carbon heated at $550^{\circ} \pm 6$ grammes of sulphur distilled over during 30 min. Original weight of carbon found back: it contained 0.91 % sulphur.

II. Carbon heated at $885^{\circ} \pm 4$ grammes of sulphur distilled over during 15 min., the product obtained contained 1.53% sulphur. In these experiments most of the distilled sulphur condensed in the colder part of the tube, a little in the receiver which was cooled in carbonic acid and alcohol. Formation of carbon disulphide (CS_2) was not observed. If any was formed which did not condense at -80° and 2 mm., the quantity must have been very small, because the greater part of the carbon was found back.

It accordingly appears from these experiments that sulphur is

fixed by carbon both at 550° and at 885° . The influence of time and temperature will be decided by further experiments.

5. The experiments described may be interpreted in different ways. The sulphur may have been absorbed by the carbon or fixed by chemical forces. Let us first consider the former case more closely. Amorphous carbon is an exceedingly efficient absorbent for various gases¹⁾, why should not sulphur vapour be absorbed? By absorption is understood a reversible phenomenon; the absorbed gas is condensed on the absorbent, and has remained unchanged in its chemical properties.

The fact that the carbon does not lose its sulphur-content at 1000° and 1 mm. pressure is not conclusive against the assumption of absorption. For if the absorption-isotherm has an asymptote in the axis of coordinates, it is possible that the last rests of absorbed substance (in this case 2 % sulphur) are practically not to be removed. The influence of the temperature and the time during which the sulphur vapour is in contact with the carbon, on the quantity of sulphur which is fixed, will have to be studied more closely to render it possible to draw a definitive conclusion in this respect. The behaviour of the fixed sulphur towards hydrogen, however, seems to me an argument in favour of the sulphur being fixed to the carbon by chemical forces. By the action of hydrogen on the sulphur-carbon complex sulphuretted hydrogen is formed. In this reaction it must be assumed that the hydrogen reacts with the solid phase. For the sulphur vapour tension of the sulphur-carbon complex is still very small at 900° , otherwise finally all the sulphur would be expelled in gaseous form by heating in a nitrogen current at that temperature. For the same reason the sulphur cannot be assumed to be in the carbon in a solid solution having a certain vapour-tension. In this case, too, it would be incomprehensible why the sulphur could be expelled by hydrogen, and not by nitrogen.

Also the fact that by treatment of the product P_1 with bromine water only a small part of the sulphur is oxidized, is difficult to reconcile with the idea of absorption.

I assume for the present that the sulphur is bound to the carbon by chemical forces, and propose to designate the carbon-sulphur compound formed in this way for the present by the name of carbon sulphide. Nothing can be concluded with regard to the composition

¹⁾ This holds at least for charcoal, animal charcoal and such substances. Whether also pure amorphous carbon is a good absorbent, does not seem to have been decided as yet.

of this carbon sulphide from the experiments described. A priori it does not even seem established that there is question here of one or more compounds of constant composition. Besides it seems possible that a fixation by chemical forces has to do something with surface phenomena. In LANGMUIR's experiments ¹⁾ on the fixation of oxygen by heated filament of carbon or tungsten one has to do with a very thin layer of oxygen, which is retained at the surface of the carbon or tungsten filament by chemical forces.

LOWRY and HULETT ²⁾ have shown that amorphous carbon (in their case not entirely pure) can fix oxygen at 25° in another way than by absorption. Even at 180° this oxygen could not be pumped off from the carbon, at higher temperatures the oxygen split off as CO and CO₂. Some years ago, RHEAD and WHEELER ³⁾ have shown that oxygen can be fixed by amorphous carbon at temperatures between 250° and 500°, and that on heating of this carbon-oxygen complex CO and CO₂ is formed. In these researches it has been established beyond doubt that the fixation of oxygen to the carbon takes place by chemical forces. The quantity of oxygen fixed in this way in LOWRY and HULETT's experiments, was 1.7—3.75 of the weight of the carbon, a quantity which is, therefore, of the same order of magnitude as in the sulphur-carbon complexes. An analogy between these solid carbon-oxides and the carbon-sulphides described in this communication is undeniable. Whether these carbon sulphides also on still higher and more prolonged heating split off the sulphur as volatile carbon-sulphide compounds, would have to be decided by further experiments.

It is possible that the sulphur atoms are bound by rest-valencies of the carbon atoms which have remained unsaturated after the combination of the carbon atoms to amorphous carbon. This rest-affinity will possibly not be the same for different preparations of amorphous carbon, but depend on the way in which the amorphous carbon has been obtained.

Led by this idea I have made similar carbon sulphides starting from sulphur and from sugar-carbon, which had been purified by being heated successively in a current of chlorine, a current of hydrogen and in vacuum. In this way similar, but quantitatively different, results were obtained. By heating of charcoal with sulphur first a large quantity of sulphuretted hydrogen was developed, and finally a carbonsulphide resulted containing 3,5 %.

¹⁾ Journ. Amer. Chem. Soc. **37**, 1154 (1915) and **38**, 2271 (1916).

²⁾ Journ. Amer. Chem. Soc. **42**, 1408 (1920).

³⁾ Journ. Chem. Soc. **101**, 831 (1912), **103**, 461.

sulphur; this sulphur-content could be reduced to 2,7 % by heating in vacuum, but remained then constant. Its behaviour towards oxidizers was perfectly analogous to that of the carbon sulphide described in § 2. These experiments, which are still to be confirmed by a new series will be described later.

§ 6. These carbon sulphides obtained synthetically present a close resemblance with coal-coke, for so far as the sulphur-content is considered. The sulphur fixed to carbon in coal-coke is very resistant to oxidizers and cannot be expelled by heating.

In a recent research POWELL¹⁾ has shown that the sulphur content of coke can be considerably reduced by leading hydrogen over the coke at 500—1000°, which caused the sulphur fixed to carbon to be transformed into sulphuretted hydrogen for a large part. His statement²⁾ that sulphur-free coke can combine with sulphur when heated in a mixture of hydrogen and sulphuretted hydrogen, and that there is equilibrium between the carbon-sulphide and the sulphur vapour, cannot be judged until the experiments have been further described.

In conclusion I will mention the product that STOCK and PRAETORIUS³⁾ obtained in their research on the carbonsubsulphide (C_3S_2). This carbonsubsulphide polymerizes to a black mass of unknown molecular weight. On heating this carbon-like substance to dark redness CS_2 and C_3S_2 escaped; but there remained a carbon-like mass that contained 39 % sulphur. A closer examination of such a product and its behaviour at prolonged heating will be of interest.

¹⁾ Journ. of Ind. and Engin. Chem. **12**, 1077 (1920).

²⁾ Ibid. **13**, 34 (1921).

³⁾ Ber. **45**, 3569 (1912).