THE REACTIONS OF CARBON WITH SULPHUR COMPOUNDS

PART 2.—THE REACTION OF HYDROGEN SULPHIDE WITH VARIOUS TYPES OF CARBON

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The hydrogen sulphide + carbon reaction has been studied by the flow method in the temperature range 1000-1600° K. Coconut charcoal reacts appreciably at 1000° K and the rate increases rapidly as the temperature is raised. For hydrogen sulphide pressures from 0·2 to 0·5 atm at 1200° K the experimental conversions to carbon disulphide (35·7-30·8 %) and to sulphur (4·0-2·0 %) are within 1 % of the theoretical equilibrium values. Above this temperature the maximum carbon disulphide yields are less than expected, e.g. only 55·5 % compared with a possible 69·7 % at 1600° K. It is probable that the rate of the forward reaction increases more slowly in this range and that some carbon disulphide is lost by the reverse reaction during the cooling of the gas stream. Under these conditions hydrogen sulphide is decomposed significantly into sulphur and hydrogen, but it is not yet clear whether the carbon disulphide is produced directly from hydrogen sulphide and carbon or through the intermediate formation of sulphur. Catalysis by sodium carbonate has been observed.

Other types of carbon decrease in reactivity towards hydrogen sulphide at 1300° K in the order: beechwood charcoal > coconut charcoal > B.C.U.R.A. reactive chars > coalite > anthracite > coke. Even coke, however, gives a 45·4 % yield of carbon disulphide at 1500° K. Measurements of B.E.T. adsorption, heat of wetting and water uptake indicate that the surface areas and pore radii of these materials cover the ranges 6-856 $m^2\ g^{-1}$ and 9-167 Å. Diffusion either inside or outside the pores is unlikely to be an important rate-determining factor at 1300° K in most cases, so it is understandable that the order of reactivities is broadly that of the surface areas.

The direct synthesis of carbon disulphide from hydrogen sulphide and carbon is thermodynamically possible at high temperatures. This conclusion emerged from a recent theoretical survey [1] (now taken to be part 1 of this series) of the various methods of converting hydrogen sulphide into carbon disulphide. It also appeared that the hydrogen sulphide + carbon reaction had not been studied previously. An investigation was therefore planned with the dual purpose of elucidating the fundamental aspects of an unexplored gas-solid reaction, and of assessing the feasibility of a new route for the industrial production of carbon disulphide.

The object of the work described in this paper was to find how closely the theoretical equilibrium yields could be approached in practice with various types of carbon ranging from activated charcoal to coke. Measurements of surface area and pore volume were also made, since structural changes are likely to affect the relative rates of reaction of such a wide series of materials.

Many experimental problems arise in work of this type with sulphur compounds. Among those to which attention has been paid are the preparation of pure hydrogen sulphide and its storage in cylinders, the construction of a reaction vessel for use at temperatures up to 1400° C and the development of a convenient analytical technique.

EXPERIMENTAL

The apparatus was similar in principle to that used for the reactions of the steam + carbon system.[2] Hydrogen sulphide, mixed with nitrogen as a carrier gas to control concentration and rate of flow, was passed through a vertical column of carbon granules kept at a known temperature. The products were analyzed by collection on solid adsorbents in detachable weighing tubes. Details are given below of the new techniques devised for problems peculiar to the hydrogen sulphide + carbon system; other aspects follow previous practice.

Preparation and storage of hydrogen sulphide.—As hydrogen sulphide is not available commercially, a separate vacuum apparatus was made to prepare this gas. A saturated solution of sodium sulphide was dropped slowly into 10 % sulphuric acid, both reagents, which were of A.R. grade, having been deaerated. The product was passed through water, sodium sulphide solution, calcium chloride, phosphorus pentoxide, a trap at − 78° C and finally collected as a solid in a trap protected by a metal sheath cooled in liquid oxygen. After any uncondensed gas had been pumped off, the liquid was distilled and the end fractions discarded. To check the purity, the vapour pressure was determined at temperatures measured by vapour pressure thermometers containing ammonia or carbon dioxide.[3] A satisfactory comparison with the best available data is shown in fig. 1. The pressure at the triple point was found to be 173 mm, which lies between the values of 170 and 174 mm, given respectively by Clark, Cockett and Eisner,[4] and by Giauque and Blue.[5]

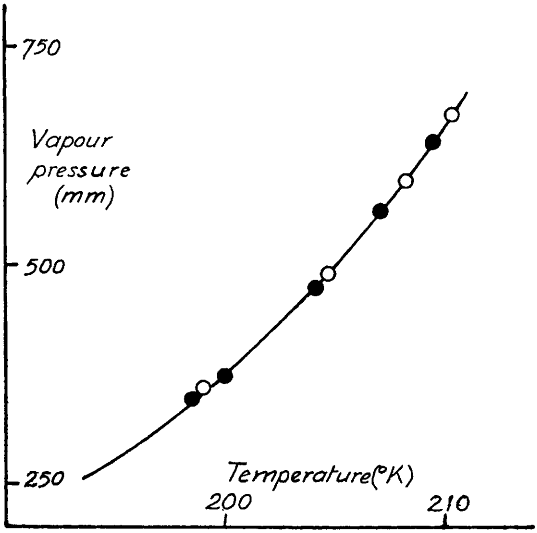

FIG. 1.—Vapour pressure of H_2S : ○ freshly prepared ; ● after four weeks in the cylinder ; —— Clark, Cockett and Eisner,[4] and Giauque and Blue.[5]

When about 200 g of pure hydrogen sulphide had been collected, it was distilled into a small steel cylinder previously evacuated and cooled to − 78 °C. This cylinder was fitted with an " on-off " valve and connected to the preparation system through a detachable metal cone. After the cylinder had been filled, a bellows-sealed needle valve was substituted for the cone in order to regulate the gas supplied to the flow apparatus. No corrosion difficulties were experienced and the purity of the gas, as may be seen from fig. 1, was not affected by storage in the cylinder even for 4 weeks.

Reaction vessels.—The transparent Vitreosil vessel of internal diameter 3·6 cm shown in fig. 2*a* was tried first. The gas entered through the annular space between the 8 mm diameter inlet tube and the loosely fitting silica rod which kept the carbon in place. A thermocouple in the central sheath gave the temperature of the reaction zone, and any changes in gaseous composition occurring above the carbon were minimized by the rapid withdrawal of the products through a 2 mm diam. capillary. One silica vessel was used successfully at 1127° C, but others failed at much lower temperatures and none lasted very long because chemical attack and devitrification soon made them brittle.

Triangle Impervious Mullite No. 671 (Morgan Crucible Co.) and Thermal Mullite 525 (Thermal Syndicate Ltd.) were both found to be extremely serviceable even at the highest temperatures attained. Mullite, however, cannot be shaped, so the ideal design of the silica vessel cannot be reproduced in this material. Of the various possibilities tested, that illustrated in fig. 2*b*, proved to be the most satisfactory. The carbon was supported by a block of cement at the top of the inlet tube, which contained a silica rod and was sealed to the 3·2 cm diam. outer tube by a rubber bung below the furnace. Ground-glass joints were fixed by cement covered with cellulose paint at the exit and by rubber tubing at the inlet. The space above the carbon was reduced to a small annular volume by a closed-end mullite tube filled with cement. Since the thermocouple could not easily be mounted internally, it was placed against the outside of the reaction vessel.

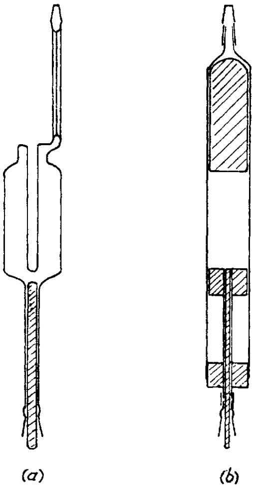

FIG. 2.—Reaction vessels: (*a*) silica.; (*b*) mullite.

FURNACES AND TEMPERATURE CONTROL.—A Nichrome furnace was used initially, but most of the measurements were made with a Globar furnace containing four rods with a heated length of 41 cm. The temperature varied over the reaction zone by 4° in the first furnace and 8° in the second. Automatic control of the single chromel/alumel or platinum/platinum-rhodium junction to within ± 2° was provided by a photocell circuit of the type previously described.[2]

ANALYSIS.—The products were hydrogen sulphide, carbon disulphide, sulphur and hydrogen. Some sulphur condensed, but much persisted in the gas stream as a fine powder which was removed by 10-14 mesh calcium chloride. The other components, which were not affected by this reagent, could then be diverted into the analysis section.

First, hydrogen sulphide was adsorbed on slightly moist A.R. copper phosphate * granulated to 28 mesh and backed by calcium chloride. A trace of moisture was essential, since Wright's statement [6] that copper phosphate does not take up hydrogen sulphide unless prepared by a special method was confirmed for the dry material. Next, carbon disulphide, which passes without loss over both used and unused copper phosphate, was determined on thoroughly dried active charcoal.[7] Finally, hydrogen was oxidized by excess air over platinized asbestos at 150° C and weighed as water on calcium chloride.

Since the rate of formation of sulphur could be calculated from the hydrogen and carbon disulphide values, only two of the three weighings were required for a complete analysis. However, the satisfactory consistency of the hydrogen sulphide figures with the known rate of flow (previously calibrated with copper phosphate) and the estimated rates of reaction provided a useful check. It also suggested that no appreciable errors were caused by combination of sulphur with the material of the reaction vessel or by loss of hydrogen through the walls. The gases were usually diverted for a sufficient time to give increments greater than 0·100 g in each tube and thus an accuracy of 1 % by weighing to the nearest 0·001 g. All the recorded results are the average of two observations made during the same experiment.

CARBON STRUCTURE.—Table 1 summarizes the physical properties of the various forms of carbon which were studied. The coconut charcoal (Sutcliffe Speakman Ltd.) is a steam-activated sample without metallic additions; it differs from that previously used for the steam and carbon dioxide reactions. Kramers [8] has described the reactive chars. The anthracite was group I, Llandebie (S. W. Division, National Coal Board).

It has been suggested that the B.E.T. technique does not give the true surface area of certain types of carbon for which higher values are obtained from the heat of wetting in methanol.[9] Some pores accessible to methanol at room temperature may contract sufficiently at liquid-air temperature to exclude argon or nitrogen. Surface area measurements were therefore made by both methods.

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* The authors are grateful to Dr. T. M. Walters for suggesting this reagent.

All the B.E.T. data were interpreted according to the usual equation,[10] except those for the two charcoals to which the modification of Joyner, Weinberger and Montgomery [11] for narrow pores was applied. This correction, which assigned pore radii of 3·2 and 9·0 Å to the coconut and beechwood charcoals respectively, increased the estimated area by about 50 %. The recorded results are the mean of values consistent to within 3 % obtained with argon and nitrogen, assuming these molecules to occupy 14·4 and 17·0 Å^2 respectively.

TABLE 1

	surface area			pore volume (cm^3 g^{-1})	pore radius (Å)	particle diameter (cm)	bulk density (g cm^{-3})
	B.E.T.	CH$_3$OH (m^2 g^{-1})	average				
coconut charcoal	856	194	856	0·450	10·5	0·21	0·399
beechwood charcoal	285	150	285	0·125	8·8	0·15	0·335
reactive char A	32	83	83	0·110	27	0·07	0·563
reactive char B	33	61	61	0·221	72	0·08	0·579
anthracite	0	15·1	15·1	0·045	60	0·14	0·922
coalite	7·1	9·8	8·5	0·071	167	0·43	0·629
coke	5·7	6·1	5·9	0·044	149	0·17	0·563

Heats of wetting were determined at 25° C, with an average deviation of 3 % by using thermistors (Standard Telephones Ltd., F 2311/300) in the manner described by Hutchinson.[12] Methanol was purified by refluxing for 3 h with potassium hydroxide and then distilling, followed by a similar treatment with calcium oxide. The conversion factor was taken to be 10 m^2 per calorie.[13]

The average areas shown in the third column were chosen as follows. Arithmetic means were calculated for coalite and coke, since the two methods gave consistent results for these materials. The smaller B.E.T. values obtained with anthracite, on which no adsorption of argon or nitrogen could be detected under the conditions of the other measurements, and also with the reactive chars, were thought to be influenced by the contraction of the pores and were therefore discounted. For both charcoals, however, the heat of wetting gave the lower areas. Their pores are evidently rigid, but perhaps some are too small to be penetrated rapidly by the methanol molecule, which has rather larger van der Waals' dimensions (4·7 × 4·0 Å) than argon (3·8 Å) or nitrogen (4·1 × 3·0 Å).[14, 15] The B.E.T. method was therefore assumed to give a more reliable estimate of the surface area of the charcoals.

The pore volumes V were determined by the method of Bond, Griffiths and Maggs,[16] so that the average pore radii r could be estimated from the relation,

$$r = 2V/S,$$

where S is the surface area.[17] It is noteworthy that the small radii found for the pores in the charcoals are consistent with the above interpretation of the surface area results.

RESULTS AND DISCUSSION

COCONUT CHARCOAL.—THE APPROACH TO EQUILIBRIUM.—Table 2 shows the the results obtained with 50 g charcoal at a series of temperatures and rates of flow * with hydrogen sulphide at a constant initial pressure of 0·2 atm. At the three temperatures at which both the silica and mullite vessels were used, there is agreement to within about 1 % between the two sets of data. This suggests that both designs removed the gases without any large change in composition, and that the temperature of the charcoal in the mullite vessel was satisfactorily measured by the external thermocouple. The last column of table 2 gives the equilibrium yields calculated from the equations:

$$K_1 = \frac{[CS_2][H_2]^2}{[H_2S]^2} = \frac{x^2(x-y)P}{2(n_1-x)^2(n_1+n_2+\frac{1}{2}x)}, \qquad (1)$$

$$K_2 = \frac{[CS_2]}{[S_2]} = \frac{x-y}{y}. \qquad (2)$$

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* measured at 20° C and 760 mm.

P is the total pressure of 1 atm and n_1 moles of H_2S, mixed with n_2 of N_2, are assumed to produce $\frac{1}{2}(x - y)$ moles of CS_2 and $\frac{1}{2}y$ moles of S_2. The required equilibrium constants were taken from table 3 of part 1, or calculated from the previously assumed $\Delta E_0°$ values. Methane formation may be neglected, since the amount present at equilibrium is less than 0·1 % of the hydrogen sulphide under the present conditions.

TABLE 2.—PERCENTAGE CONVERSION OF H_2S AT VARIOUS TEMPERATURES (coconut charcoal, 0·20 atm H_2S)

temp. (°K)		reaction vessel	rate of flow (cm³/min) 200	400	600	calc. equilib.
1000	CS_2	silica	1·5	2·0	2·0	15·0
	S_2		9·0	9·0	8·1	1·3
1100	CS_2	silica	17·7	15·2	12·6	27·0
			24·0*	15·0*	16·5*	
	S_2		8·1	8·8	9·1	2·4
			—	7·5*	11·5*	
1200	CS_2	silica	35·7	33·5	32·6	36·5
	S_2		4·0	7·3	7·2	4·0
1300	CS_2	silica	40·4	40·4	39·0	47·0
		mullite	40·0	38·5	38·0	
	S_2	silica	4·1	5·6	5·9	5·6
		mullite	4·1	5·1	4·1	
1400	CS_2	silica	45·0	45·0	46·0	57·5
		mullite	45·0	46·0	45·0	
		silica	50·5*	49·9*	—	
	S_2	silica	7·0	7·3	6·5	7·6
		mullite	8·5	7·0	8·0	
		silica	5·0*	5·9*	—	
1500	CS_2	silica	50·5	50·5	50·5	64·5
		mullite	48·5	52·0	53·0	
	S_2	silica	12·0	9·6	9·4	9·5
		mullite	10·3	8·5	7·0	
1600	CS_2	mullite	—	54·5	55·5	69·7
	S_2		—	10·0	7·5	11·2

* charcoal impregnated with sodium carbonate.

Only a 2 % yield of carbon disulphide is produced at 1000° K, but the reaction becomes faster as the temperature is raised. At the lowest rate of flow at 1200° K, 35·7 % of the hydrogen sulphide is converted to carbon disulphide and 4·0 % to sulphur, in close agreement with the theoretical figures of 36·5 % and 4·0 % respectively. Above this temperature, however, the maximum yield falls below the theoretical value and at 1600° K, for example, is only 55·5 % compared with 69·7 %. There are four possible explanations of such a discrepancy: the rate does not increase much with rise of temperature because (i) the carbon itself becomes unreactive or (ii) control by diffusion intervenes; (iii) carbon disulphide and hydrogen reform hydrogen sulphide and carbon during the cooling of the gases; (iv) the data used for the thermodynamic calculations are in error. Only the first of these possibilities could account for an increased conversion if the surface reaction was catalyzed. Some experiments, denoted by an asterisk in table 2, were therefore made with charcoal impregnated with 3 % by weight of sodium carbonate. This substance, which is known to facilitate the formation of carbon disulphide from sulphur and carbon,[18] was shown to catalyze the hydrogen sulphide reaction by working first in the lower part of the temperature range. Thus at 1100° K the original charcoal did not produce more than 17·7 %

of carbon disulphide compared with 27·0 % expected at equilibrium, but the impregnated material gave 24·0 %. Since the addition of sodium carbonate also raised the yield at 1400° K from 45·0 % to 50·5 %, the discrepancy with the theoretical figure of 57·5 % must be attributed, at least in part, to a lack of reactivity of the carbon. A contribution by the reverse reaction cannot, however, be excluded.

As a further test of the thermodynamic predictions, measurements were made with various initial pressures of hydrogen sulphide at 1200° K, the temperature at which equilibrium appeared to be achieved. Table 3 shows that the yields of both carbon disulphide and sulphur closely approach the calculated values at each pressure as the rate of flow is reduced.

TABLE 3.—PERCENTAGE CONVERSION OF H_2S AT VARIOUS PRESSURES
(coconut charcoal at 1200° K)

H_2S pressure (atm)		rate of flow (cm³/min)										calc. equilib.
		80	120	160	200	240	320	360	400	480	600	
0·20	CS_2	—	—	—	35·7	—	—	—	33·5	—	32·6	36·5
	S_2	—	—	—	4·0	—	—	—	7·3	—	7·2	4·0
0·25	CS_2	—	—	34·8	—	—	33·3	—	—	32·6	—	34·8
	S_2	—	—	4·0	—	—	6·6	—	—	6·4	—	3·9
0·33	CS_2	—	32·6	—	—	31·0	—	30·0	—	—	—	32·5
	S_2	—	3·9	—	—	4·9	—	5·0	—	—	—	3·8
0·50	CS_2	30·8	—	29·2	—	29·1	—	—	—	—	—	29·8
	S_2	2·0	—	4·2	—	4·6	—	—	—	—	—	3·3

Two points have now been established, (i) carbon disulphide can be produced by the reaction of hydrogen sulphide with carbon at high temperatures; (ii) the position of equilibrium is correctly predicted by theory. Many of the results, however, differ considerably from equilibrium, so it is worth enquiring whether any evidence for the course of the reaction can be obtained by analyzing the deviations.

THE COURSE OF THE REACTION.—The yields of sulphur in table 2 are in reasonable agreement with the equilibrium figures above 1200° K but are noticeably greater at the lower temperatures. This fact suggested that the decomposition of hydrogen sulphide,

$$2H_2S = S_2 + 2H_2 \tag{3}$$

might be important, so experiments to isolate this reaction were made in the absence of carbon. The number z of moles decomposed at equilibrium was also calculated from the equation

$$K_3 = \frac{z^3P}{(n_1 - z)(n_1 + n_2 + \frac{1}{2}z)}, \tag{4}$$

using the recent values of the equilibrium constant given by Evans and Wagman.[19] Table 4 shows both the experimental and theoretical results.

Hydrogen sulphide is appreciably decomposed even in the empty reaction vessel. At the two lower temperatures equilibrium is approached only after the longest time of contact, but at 1200° K it is established under all conditions. Comparison with table 2 indicates that sulphur is produced more rapidly at 600 cm³/min, both at 1000° and 1100° K, in the presence of charcoal than in its absence. Evidently the decomposition of hydrogen sulphide is catalyzed by the charcoal surface and controls the production of sulphur. When the conversion of hydrogen sulphide to carbon disulphide is only a small fraction of the equilibrium value, as it is below 1200° K, the yield of sulphur is correspondingly greater and approaches the value expected in the absence of carbon. At higher temperatures more carbon disulphide is formed, so the sulphur approximates to the equilibrium figure for the hydrogen sulphide + carbon system.

Between 1100 and 1300° K an increasing fraction of the hydrogen sulphide is converted to carbon disulphide as the rate of flow is reduced. This is the normal effect of varying the time of contact, and is to be expected whether the carbon reacts with the hydrogen sulphide or with the sulphur. Above 1300° K the yield becomes substantially independent of the contact time, so some factor must limit the rate of reaction at the lower rates of flow. Either control by diffusion outside the granules or the deposition of carbon during the cooling of the gas stream might have such an effect on either reaction mechanism. At very high temperatures there is also the possibility that hydrogen sulphide might be decomposed before reaching the carbon; this decomposition would occur to an increasing extent at the lower rates of flow, and would hinder the production of carbon disulphide if hydrogen sulphide reacts more rapidly with the charcoal than sulphur does.

TABLE 4.—PERCENTAGE DECOMPOSITION OF H_2S
(empty silica vessel)

H_2S pressure (atm)	temp. (°K)	rate of flow (cm^3/min) 200	400	600	calc. equilib.
0·20	1000	7·1	5·0	3·3	7·6
0·20	1100	13·0	8·5	5·5	14·0
0·20	1200	24·0	22·0	22·0	22·7

H_2S pressure (atm)	temp. (°K)	rate of flow (cm^3/min) 80	120	160	240	320	360	480	calc. equilib.
0·25	1200	—	—	23·5	—	22·0	—	23·5	21·3
0·33	1200	—	21·0	—	22·5	—	23·0	—	19·7
0·50	1200	17·2	—	20·0	17·3	—	—	—	17·6

Although it is clear from the above discussion that the decomposition of hydrogen sulphide is an important contributing reaction, the mechanism of the overall process appears to be too complex to be elucidated without a full kinetic investigation.

COMPARISON OF DIFFERENT TYPES OF CARBON.—While the behaviour of hydrogen sulphide with other types of carbon involves fundamental questions of some importance, any possible industrial application would be greatly facilitated if the reaction could be shown to occur with a material more readily available than coconut charcoal. Comparative experiments were therefore made with the other forms of carbon described in the experimental section. Hydrogen sulphide at 0·20 atm pressure was passed at a series of rates of flow over 50 g of each substance in the mullite reaction vessel at 1300° K. Some measurements were repeated at 1500° K. The results are summarized in table 5, where the various types of carbon are arranged in order of decreasing reactivity as measured by the carbon disulphide yield at the highest rate of flow

Beechwood charcoal is the most reactive substance under all conditions. The 44·2 % yield of carbon disulphide at the lowest rate of flow at 1300° K is very close to the theoretical equilibrium figure of 47·0 %. At 1500° K, however, the conversion is only 51·7 % compared with a possible 64·5 %, and so resembles that of coconut charcoal in rising less rapidly than expected with increase of temperature. The catalysis experiments discussed in an earlier paragraph suggested that the surface reaction played some part in determining the yield obtained from coconut charcoal at 1400° K. This conclusion is supported by the higher yields observed with beechwood charcoal at 1300 and 1500° K, though the importance of the reactivity of the carbon appears to decline with increase of temperature. Such a trend is consistent with control either by diffusion or by the reverse reaction. Both reactive chars produce slightly less carbon disulphide than the charcoals, but the difference is more marked at the lower temperature as might be expected from the above analysis. The relative inertness of coalite, anthracite and coke at 1300° K is illustrated by the fact that these materials give much smaller conversions which fall rapidly as the time of contact is decreased.

TABLE 5.—PERCENTAGE CONVERSION OF H_2S WITH VARIOUS TYPES OF CARBON (0·20 atm H_2S)

		rate of flow (cm^3/min)			calc. equilib.
		200	400	600	
			1300° K		
beechwood charcoal	CS_2	44·2	43·0	41·0	47·0
	S_2	3·5	4·8	5·2	5·8
coconut charcoal	CS_2	40·4	40·4	39·0	
	S_2	4·1	5·1	4·1	
reactive char B	CS_2	38·0	36·0	31·0	
	S_2	4·9	6·2	9·3	
reactive char A	CS_2	35·6	33·0	27·0	
	S_2	7·8	5·8	5·4	
coalite	CS_2	28·7	22·8	19·0	
	S_2	11·2	6·3	5·9	
anthracite	CS_2	24·6	18·4	—	
	S_2	6·6	9·4	—	
coke	CS_2	23·9	16·0	12·4	
	S_2	7·0	7·1	8·1	
			1500° K		
beechwood charcoal	CS_2	51·7	52·7	51·7	64·5
	S_2	7·3	6·2	5·1	9·5
coconut charcoal	CS_2	50·5	50·5	50·5	
	S_2	10·5	8·5	7·0	
reactive char B	CS_2	46·0	49·4	51·7	
	S_2	14·4	9·5	6·8	
reactive char A	CS_2	49·3	51·2	50·1	
	S_2	12·0	10·7	7·0	
coke	CS_2	45·4	42·8	37·0	
	S_2	14·5	7·5	11·5	

At 1500° K, however, even coke, the least reactive of these substances, produces 45·5 % of carbon disulphide at the lowest rate of flow. This yield, moreover, is not greatly affected by reduction of the time of contact. The important practical point is thus established that most types of carbon will convert hydrogen sulphide to carbon disulphide in good yield provided the temperature is sufficiently high. As may also be seen from table 5, only small amounts of sulphur are produced.

It is of interest to consider what determines the relative reactivities of the various forms of carbon. Before the yields may be compared with the surface areas, however, allowance must be made for any other factors which might be important.

It may be calculated from the mass transfer data of van Heerden [20] that diffusion outside the carbon granules does not control the conversion. In the terminology of Hurt,[21] the height of the transfer unit is found to be only a few percent of the height of the reaction unit. The fraction f of the internal surface which contributes effectively to the reaction depends on the rate of diffusion inside the carbon granules. Wheeler's theory [17] should be approximately applicable in the form

$$f = (1/h) \tanh h, \qquad (5)$$

where h is defined by

$$h \tanh h = (a^2/18D\tau\rho V) \ln \{1/(1 - \alpha)\}, \qquad (6)$$

since the order of reaction with respect to hydrogen sulphide is more nearly the first than any other integral value.[22] All the pore radii r are small compared with the mean free path, so the diffusion coefficient D was calculated for Knudsen flow from the expression $2r\bar{c}/3$ where $\bar{c}$ is the average velocity of the hydrogen sulphide molecules. Tables 1 and 5 give the data used to evaluate the other quantities: τ, the time of contact in the empty reaction vessel; α, the fraction of hydrogen sulphide converted to carbon disulphide; ρ, V and a respectively the bulk density, pore volume and particle diameter of the carbon. At 1300° K all the f values are found to be greater than 0·7, so it would appear that the rate of diffusion through the pores does not limit the yields appreciably. This conclusion, however, is open to doubt for the more reactive materials; the closer equilibrium is approached, the less adequate theoretically is the neglect of the reverse reaction in the logarithmic term of eqn, (6) and the more likely is carbon deposition to reduce the experimental conversion.

Comparison of tables 1 and 5 shows that the order of reactivities is broadly that of the surface areas, though there are some exceptions in detail. Thus the first of each of the following pairs gives the higher yield but has the smaller area: beechwood (285 m^2) and coconut (856 m^2) charcoals; reactive chars B (61 m^2) and A (83 m^2); coalite (8·5 m^2) and anthracite (15 m^2). Both reactive char B and coalite have respectively larger pore radii (72 and 167Å) than reactive char A (27Å) and anthracite (60 Å), so the influence of diffusion might have been underestimated. This explanation, however, cannot hold for the charcoals, unless the heats of wetting are assumed to be more reliable than the B.E.T. measurements. It seems, therefore, that the area is an important variable, but that other factors, including catalysis and the nature of the surface, require further investigation.

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