77. *The Kinetics of the Reaction between Hydrogen and Sulphur. Part II.* (1) *Formation and Characteristics of the Unimolecular Layer of Hydrogen Sulphide on the Glass Surface.* (2) *Independence of the Reaction of the Presence of Oxygen, Moisture, and Sulphur Dioxide.*

By Ernest E. Aynsley and Percy L. Robinson.

In a preceding communication (this vol., p. 58) hydrogen and sulphur have been shown to combine in glass vessels, homogeneously, at a velocity proportional to the concentration of hydrogen and to the square root of that of the sulphur throughout the range 280—343° and 153—382 mm. pressure of hydrogen (measured at 15°). This has been repeatedly confirmed and found to hold also for pressures between 20 mm. and 686 mm. (measured at 15°) (Table I). The static method employed is capable, with these materials, of a precision rare in measurements of reaction velocities, and permits the reaction to be examined with hydrogen pressures as low as 1 mm. At low pressures, the measurements disclosed the unexpected fact that the surface of the reaction vessel becomes covered with a unimolecular layer of hydrogen sulphide formed heterogeneously thereon, and thereafter, ceases to exert further influence on the reaction. The experiments here described throw some light on the mode of formation of this film, and demonstrate the tenacity with which it adheres to the glass. It appears that hydrogen sulphide is only slightly adsorbed by glass when not actually formed on the surface, but that such adsorption does not contribute appreciably to the formation of the unimolecular film just mentioned.

Table I.

Sulphur concentration = 0·245 mg./c.c.; p = hydrogen pressure (mm. Hg), measured at 15°; v = velocity of H_2S formation, g./sec./c.c. of gaseous volume × 10^{10}.

Temp.	p.	v.	$10^{14}v/p$.	Temp.	p.	v.	$10^{14}v/p$.	Temp.	p.	v.	$10^{14}v/p$.
301·0°	686	20·18	294	311·5°	382	22·70	594	322·0°	20	2·40	1200
301·0	382	11·50	301	311·5	20	1·14	570	343·0	686	256·80	3744
301·0	20	0·65	325	322·0	686	75·80	1105	343·0	382	150·20	3931
311·5	686	39·00	569	322·0	382	44·20	1157	343·0	20	7·70	3850

Results obtained by a dynamic method have been interpreted (Norrish and Rideal, J., 1923, **123**, 1689) as showing that oxygen has a complicated catalytic influence on the combination of hydrogen with sulphur, exerting a strong poisoning effect on the gaseous reaction at all temperatures. Our own experiments, however, leave no doubt that, under static conditions at least, the established characteristics of the homogeneous reaction remain unaltered by oxygen. Actually, the oxygen is quickly converted into sulphur dioxide, and, provided the glass surface presented be small, this gas remains in the system unchanged. In the presence, however, of a considerable surface, it reacts slowly and heterogeneously with hydrogen sulphide to form steam and sulphur. Furthermore, neither oxygen nor sulphur dioxide has a detectable effect on the velocity of the reactions producing hydrogen sulphide at temperatures about 340°, and steam is also without appreciable influence.

I. *The Unimolecular Layer of Hydrogen Sulphide on the Glass Surface.*

The gas-distributing apparatus employed differed from that previously used by us (*loc. cit.*) only in having ground-glass instead of rubber joints for attaching the reaction bulbs, and a McLeod gauge in addition to one of the barometer type. The hydrogen was deoxygenated, washed, and dried exactly as before, and the sulphur was of similar quality to that already employed. The pressures of hydrogen in the bulbs were measured with an accuracy of ±0·01 mm.; the sulphur was weighed on a microbalance with a precision of ±0·005 mg. The hydrogen sulphide present after the reaction was estimated with a certainty of ±0·02 mg., for which purpose 0·001*N*-iodine solution was employed with a correspondingly dilute thiosulphate solution for back titration, both solutions being freshly prepared and standardised against potassium dichromate at each estimation.

Hydrogen pressure = 1·35 mm. measured at 15°. Sulphur concentration = 0·245 mg./c.c.

	Velocity of H_2S formation, g./sec./c.c. of gaseous vol. × 10^{10}.	
Temp.	Found.	Calc.
343°	0·66	0·53

The data (above) show that at pressures of the order of 1 mm. the hydrogen sulphide formed exceeds the amount calculated from the velocity established for the homogeneous reaction occurring between 20 and 686 mm. of hydrogen. This increase arose from a second distinct reaction which was proved, quantitatively, to be heterogeneous, since it increased by no less than 400% in packed vessels. Quantitative response to precisely known changes in the area of glass surface, brought about by packing the bulbs with clean-cut, quill tubing, was next observed. The results (Table II) were obtained after the first hour of heating, the yields being from the new surface reaction alone, which were computed by deducting from the total amount of hydrogen sulphide produced that formed in the homogeneous reaction. It is clear that the velocity of the new reaction is initially directly proportional to the surface area. It was, however, independent of sulphur concentration over the considerable range studied, as shown by the data in Table III.

TABLE II.

The new reaction in relation to the area of glass surface.

Reaction temp. = 343°. Hydrogen press. = 1·26 mm. at 15°. Sulphur conc. = 0·245 mg./c.c.

Area of glass surface, sq. cm.	Yield of H_2S in the first hour from total surface, g. × 10^6.	Yield of H_2S/hour/sq. cm. of surface × 10^{10}.
1655	71	429
936	43	459
180	9	500

TABLE III.

Hydrogen press. = 1·26 mm. at 15°. Vol. of reaction vessel = 290 c.c. Reaction temp. = 343°.
Period of heating = 1 hr. Total area of glass = 936 sq. cm.

Weight of sulphur, mg.	Total yield of H_2S in first hour, g. × 10^6.	H_2S from homogeneous reaction, g./hr. × 10^6 (calc.).	H_2S from surface reaction, g./hr. × 10^6.
71	95	52	43
1·72	48	8	40
1·28	53	7	46

A notable feature of the reaction is the fact, brought out in Table IV, that the amount of hydrogen sulphide produced in the surface reaction ceases to increase after about the first hour. In this time an amount of hydrogen sulphide has been produced which is of the same order as that required to cover the whole of the glass surface with a film of gas one molecule thick. This conclusion has been reached from the following considerations :

TABLE IV.

Hydrogen press. = 1·26 mm. at 15°. Total glass area = 936 sq. cm. Reaction temp. = 343°.

Time of heating, mins.	Total yield H_2S, g. × 10^6.	H_2S from homogeneous reaction, g. × 10^6 (calc.).	H_2S from surface reaction, g. × 10^6.
15	41	13	28
30	65	26	39
60	95	52	43
90	117	78	39
120	148	103	45

Weight of film = 0·042 mg. Area of glass surface = 936 sq. cm. Then, if the hydrogen sulphide molecule has a mean cross-section of $0\cdot773 \times 10^{-15}$ cm.^{2} (Rankine and Smith, *Phil. Mag.*, 1921, **42**, 601, 615),

$$\text{area of film one molecule thick} = \frac{42 \times 10^{-6} \times 6\cdot1 \times 10^{23} \times 0\cdot773 \times 10^{-15}}{34} = 582 \text{ sq. cm.}$$

From this result it would appear that the film of hydrogen sulphide is 582/936, *i.e.*, 0·6 molecule thick. This value lies near to unity, and since there is nothing inherent in the method which prevents it from having any value whatsoever, it may be taken as signifying that the film is unimolecular.

The characteristics of this newly observed heterogeneous reaction lead to certain deductions of interest. In the first place, as it is independent of the sulphur concentration, whilst the gaseous reaction is related thereto, the two processes necessarily proceed independently, and furthermore, the hydrogen sulphide formed in the gaseous phase is evidently not adsorbed at the surface in a way which interferes with the mechanism of the surface reaction. Since the latter is independent of the concentration of sulphur vapour and related to the surface area, it is undoubtedly between sulphur adsorbed on the surface and molecules of hydrogen striking the surface. The reaction presents a similarity to the one we (*loc. cit.*) have already shown to occur between a surface of liquid sulphur and hydrogen, but differs in its complete cessation when sufficient hydrogen sulphide has been produced to form a unimolecular film. At a surface of liquid sulphur there is no such inhibition of the reaction by its products, and hydrogen sulphide continues to be formed so long as liquid sulphur is available. The difference appears to be due to the strong adsorption of hydrogen sulphide at a glass surface on which it is formed, and, on the other hand, to its relative freedom to leave a surface of liquid sulphur by evaporation into the gaseous phase. There is, however, probably no fundamental difference between the two reactions; otherwise it would be difficult satisfactorily to account for the fact that the ratio of effective collisions of hydrogen molecules on the virgin film to the same area of liquid sulphur is practically unity under similar conditions.

FIG. 1.

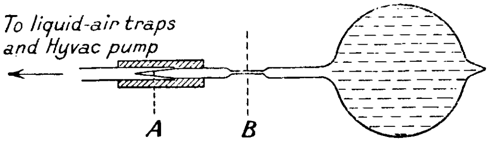
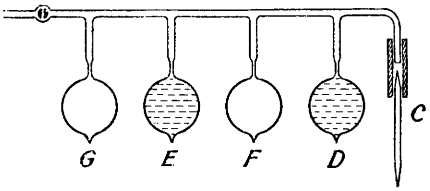


FIG. 2.



Since the adsorbed sulphur gives rise to only a single layer of hydrogen sulphide molecules, it seems certain that the glass surface is originally covered by a sulphur film at least one molecule thick. As, however, the hydrogen sulphide molecules are retained on formation, it seems improbable that the foundation layer of sulphur is more than a single molecule thick. That sulphur in the presence of hydrogen should completely cover the surface is in keeping with the fact that the latter is not adsorbed and does not compete for the surface. The molecules in the sulphur film may be polyatomic but are more probably diatomic at the temperatures under consideration, in which case the residual fragment of the molecule, after the abstraction of a single atom from it in the course of the reaction, may either evaporate and leave its place to be occupied by the newly-formed hydrogen sulphide molecule, or remain as a foundation upon which the hydrogen sulphide rests. An alternative view is that the sulphur atoms, present in small quantity in the vapour, are preferentially adsorbed by the glass surface (compare Langmuir's study of the oxygen films formed on a hot tungsten surface), in which case there is no residual sulphur after combination. In either event, the adsorbed sulphur is probably specifically oriented in respect to the surface and, since the reactions on the film and on liquid sulphur appear to be identical, support is lent to the idea that the surface of liquid sulphur is composed of specifically disposed molecules.

That the unimolecular layer of hydrogen sulphide is strongly held by the surface on which it is formed, was demonstrated by carrying out the synthesis in a packed bulb of the form shown in Fig. 1, and afterwards breaking the tip *A* under a vacuum in a heavy rubber tube and rapidly evacuating the bulb through liquid-air and other protective traps by means of a Hyvac pump, until a good vacuum was obtained and, finally, sealing off the bulb at *B*. In these circumstances, an amount of hydrogen sulphide was retained in the bulb which was 70% of that required to cover the available surface with a unimolecular layer. It was clearly desirable to know whether hydrogen sulphide as such was adsorbed to any extent by a clean glass surface, and as this normal adsorption did not appear to have been previously investigated, presumably on account of manometry difficulties, some measurements were made at 0·25 mm. pressure. For this purpose, pure, dry hydrogen sulphide at atmospheric pressure in the tube *C*, Fig. 2, was allowed to expand in an evacuated system consisting of two packed bulbs, *D* and *E*, and two unpacked bulbs, *F* and *G*. After being sealed off, the packed bulbs contained more hydrogen sulphide per unit of available volume than the unpacked, the excess being, however, only 20% of the amount required to cover the surface with a unimolecular layer. In similar circumstances, sulphur dioxide showed no excess in the packed bulbs and is presumably not adsorbed under these conditions.

The unimolecular layer which has been observed in this study of the hydrogen–sulphur reaction effectively prevents the surface from promoting further action between hydrogen and sulphur with pressures of the former up to 686 mm. (measured at 15°). The actual amount of hydrogen sulphide involved in the formation of the unimolecular layer is small even in packed bulbs, and undetectable except when the total yield is small. Thus the composite reaction at about 343° in the absence of liquid sulphur naturally appears to be homogeneous with hydrogen pressures from about 20 mm. upwards, exactly as we found it.

Unimolecular gas films on solids were first described by Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 1162), who showed that such an oxygen film changed the character of a hot tungsten surface by increasing its ability to hold cæsium atoms and completely removing its power to dissociate hydrogen molecules. Subsequent workers have investigated adsorption films on glass: Carver (*ibid.*, 1923, **45**, 63) found that toluene vapour most probably gives a unimolecular film, and a similar result has since been obtained by Crespí (*Anal. Soc. Fís. Quím.*, 1932, **30**, 520) for nitrous oxide; whilst, on the other hand, Evans and George (*Proc. Roy. Soc.*, 1923, **103**, 190), who employed a number of different gases, found the layers to be multimolecular, *viz.*, 39·9 molecules with ammonia and 3·5 with acetylene. Water vapour has also been described as giving a multimolecular layer. The question of the formation of unimolecular films in the case of glass was thus an open one, and consequently special interest attaches to the film of hydrogen sulphide now described, because it is not only definitely unimolecular, but has in addition specific chemical characteristics and, as does Langmuir's oxygen film on tungsten, profoundly alters the catalytic character of the surface which it covers.

II. *The Influence of Oxygen, Sulphur Dioxide, and Moisture on the Velocity of the Homogeneous Reaction between Hydrogen and Sulphur.*

Pyrex-glass bulbs containing appropriate quantities of sulphur were filled at known pressures with various mixtures of hydrogen and oxygen of definite composition. These mixtures were prepared by measuring the gases carefully, a McLeod gauge being employed for the lower range of oxygen pressures, and allowing them, before use, to mix thoroughly in a vessel attached to the all-glass distributing system. The amount of sulphur used, whilst sufficient to combine with the oxygen several times over, was always insufficient to leave liquid at the reaction temperatures, *viz.*, 290—343°. Both packed and unpacked bulbs were used. The reaction products were hydrogen sulphide and sulphur dioxide and, in addition, uncombined sulphur and hydrogen were present. The contents of the bulbs after reaction were treated with standard iodine in the manner already described (this vol., p. 58) and the resulting liquid was back-titrated with sodium thiosulphate to ascertain the amount of iodine reduced. The portion of the titre due to sulphur dioxide was found by filtering off the sulphur from the liquors after titration and estimating the sulphate present as barium sulphate, with parallel blanks on all the reagents employed. Oxidation with iodine, followed by filtration and precipitation with barium chloride, without reduction of the excess iodine with thiosulphate, gave identical sulphate results.

Separate experiments, which will be described elsewhere, showed that when mixtures of sulphur dioxide and hydrogen sulphide, at a total pressure up to approx. 45 mm. of the mixed gases, are treated with aqueous iodine, there is no perceptible reaction between the two gases. Hence the iodine titre is equivalent to the sulphur dioxide together with the hydrogen sulphide (Table V).

By varying the time of heating in different unpacked bulbs, it was shown that the oxidation of the sulphur takes place so rapidly that after a short heating the whole of the oxygen has been converted into sulphur dioxide, and subsequently the hydrogen–sulphur reaction proceeds at

TABLE V.

Reaction temp. = 322°. The figures in the table represent c.c. of 0·01*N*-iodine.

Determined.			Calculated.		
$H_2S + SO_2$.	SO_2, grav.	H_2S, by diff.	$SO_2 \equiv$ all O_2.	H_2S.	$H_2S + SO_2$.
86·6	64·8	21·8	63·2	21·4	84·6
84·3	62·9	21·4	62·5	21·1	83·6

precisely the velocity found when hydrogen and sulphur only are present (Table VI). Thus oxygen, up to about 7% by volume, and sulphur dioxide are without effect on the hydrogen–sulphur reaction. This result is in conflict with that of Norrish and Rideal (J., 1923, **123**, 1689), who found that oxygen exerts "a strong poisoning effect in the gaseous reaction between hydrogen and sulphur at all temperatures."

TABLE VI.

Volume of bulb = 223 c.c. Hydrogen press. = 384·6 mm. at 17°. Weight of sulphur present = 0·0546 g. Oxygen press. = 1·025 at 17°. Reaction temp. = 301°. The figures in the table represent c.c. of 0·001*N*-iodine.

Period of heating, mins.	$H_2S + SO_2$.	$SO_2 \equiv O_2$ (calc.).	H_2S, by diff.	H_2S, calc. from velocity of reaction.
15	38·0	24·7	13·3	13·5
30	48·9	24·7	24·2	27·1
60	78·1	24·7	53·4	54·2
120	132·2	24·7	107·4	108·3
180	185·7	24·7	161·0	162·5

In one hour, in unpacked bulbs, there is a barely detectable interaction between sulphur dioxide and hydrogen sulphide, whereas in packed bulbs appreciable reaction takes place between the gases, resulting in the formation of sulphur and steam. With an area of glass surface of 1600 sq. cm., about 9% of the hydride–oxide mixture reacts in one hour at 343°. Evidently the velocity of the reaction is low, and if it is assumed to be proportional to the area of the surface, it should be just perceptible in our unpacked bulbs. Actually, it could just be detected, as may be seen in the higher portion of Curve A, Fig. 4, Part I (*loc. cit.*). The demonstration of the heterogeneous character of this reaction confirms the work of Taylor and Wesley (*J. Physical Chem.*, 1927, **31**, 216), who, using a dynamic method, drew the same conclusion. With certain of their higher concentrations, Norrish and Rideal found the total yield of hydrogen sulphide to fall to nearly zero, an effect which, in our opinion, may be more simply explained by reference to interaction between sulphur dioxide and the hydrogen sulphide than by assuming a negative catalysis of the synthesis.

The reaction $2H_2S + SO_2 = 2H_2O + 3S$ involves the formation of steam, which, in the limited quantities present, does not appear to affect the hydrogen–sulphur reaction. To confirm this view, specific experiments were made with hydrogen containing 2% by volume of water vapour, and velocities were obtained which were identical with those already found when hydrogen which had been previously carefully dried over phosphoric oxide was used (see below):

Reaction temp. = 343°.

Treatment of hydrogen.	Velocity of H_2S formation, g./sec./c.c. of gaseous vol. $\times 10^{10}$.
Dried over P_2O_5	150·2
Containing 2% H_2O (by vol.)	150·1

SUMMARY.

1. The reaction between hydrogen and sulphur has been studied for the first time at pressures of the order of 1 mm., and it has been shown that (i) the characteristics of the homogeneous reaction previously described by us are maintained under these conditions; (ii) a heterogeneous reaction takes place at the surface of the glass but continues only until a unimolecular layer of hydrogen sulphide has been formed thereon. All the hydrogen sulphide formed is retained by this surface and the unimolecular layer has specific properties (cf. Langmuir's oxygen film on tungsten) and prevents further participation of the surface in the reaction.

2. The homogeneous combination of hydrogen and sulphur has been studied in the

presence of oxygen, sulphur dioxide, and moisture, and it has been shown that none of these gases has any effect on the velocity of the reaction.

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