12. *The Kinetics of the Reaction between Hydrogen and Sulphur. Part I. Reaction at 265—350° and 290—820 mm.*

By Ernest E. Aynsley, Thomas G. Pearson, and Percy L. Robinson.

The investigation of the reaction between hydrogen and sulphur by Bodenstein (*Z. physikal. Chem.*, 1899, **29**, 315) and Norrish and Rideal (J., 1923, **123**, 696) failed to disclose its essential characteristics; we (*Nature*, 1933, **131**, 471) find it to occur in two ways, homogeneously in the gaseous phase, and heterogeneously at the surface of molten sulphur. Each reaction has a uniform temperature coefficient over the range of temperature investigated, and a velocity which is independent of the area and the nature of the glass surface and uninfluenced by hydrogen sulphide or nitrogen. The homogeneous reaction, therefore, is one of the simplest syntheses disclosed by kinetic studies.

The work of Hautefeuille (*Compt. rend.*, 1867, **64**, 610) and of Pélabon (*ibid.*, 1897, **124**, 686) has been discussed by Bodenstein (*loc. cit.*), who, using glass bulbs containing excess of sulphur, obtained equilibrium constants, and deduced the velocity of hydrogen sulphide formation between 234° and 356°. The temperature coefficient per 10° rose from 1·34 at the lower temperature to 1·77 at the higher. Nevertheless, he believed the reaction to be essentially homogeneous and confined to the gaseous phase. His velocities were proportional to the concentration of hydrogen and roughly to the square root of that of the sulphur, for, although he was really dealing with two concurrent reactions, his area of sulphur surface was sufficiently small to render the homogeneous reaction dominant.

Norrish and Rideal's criticism of Bodenstein's method, *viz.*, that hydrogen sulphide liberated by the sulphur on solidification vitiated his equilibrium measurements, seems scarcely warranted in view of the small amounts employed; the criticism, however, that the variable temperature coefficient indicated more than one reaction and that there was no information regarding the possible effect of the glass surface, is pertinent. To avoid difficulty from the solubility of hydrogen sulphide in molten sulphur, Norrish and Rideal employed a dynamic method. They used mixtures of hydrogen and nitrogen, and obtained curved lines on plotting the logarithms of the reaction velocity for the two hydrogen pressures (0·810 atm. and 0·304 atm.) against temperature. The differences of these velocities plotted against temperature gave a straight line, which was interpreted as indicating only a homogeneous reaction between sulphur and hydrogen at 0·506 atm., a reaction at the glass surface, believed to be common to each series, being regarded as independent of pressure. It is doubtful, however, whether Norrish and Rideal worked with hydrogen alone. Moreover, cylinder nitrogen invariably contains oxygen, which would probably not be completely removed by their method of purification, and the curvature must, in our judgment, be ascribed to such traces of oxygen and not to the incidence of a surface reaction. Indeed, we have shown this effect to be eliminated by rigorous removal of oxygen. Their results for the concentrations under consideration differ from ours also in respect of (1) an alleged heterogeneous reaction on the glass, of which we have found no trace, and (2) the heterogeneous reaction at the surface of molten sulphur, which they failed to observe.

During the progress of the present investigation, Kassel (" Kinetics of Homogeneous Gas Reactions," pp. 159—162) has criticised Norrish and Rideal's treatment of their data, and has drawn attention to the absence of experiments with pure hydrogen. These matters are discussed at greater length below, and general difficulties attending dynamic methods are pointed out.

EXPERIMENTAL.

Purification of Materials.—Hydrogen was prepared from arsenic-free zinc and hydrochloric acid, and gave a negative Marsh test. As our experiments indicated the necessity for the complete removal of oxygen, the following methods were used : (i) passage through heated platinised asbestos, and then through almost colourless, alkaline pyrogallol; (ii) treatment with chromous chloride and amalgamated zinc (Carter and Hartshorne, J., **1926**, 363; Hartshorne and Spencer, *J. Soc. Chem. Ind.*, 1926, **45**, 474). Reaction velocities with hydrogen purified by each method were the same, except at the lowest temperature, 280°, where that from pyrogallol gave a value higher, in a 49 c.c. bulb, by 0·5 c.c. of 0·001*N*-iodine, which is sufficient to disturb the strict linearity of the $d \log [H_2S]/dT$ function. With hydrogen treated with chromous chloride, this linearity was maintained.

These methods, except passage through platinised asbestos, were also employed for the nitrogen mixtures. The gases were washed with aqueous potash to remove acid spray coming from the chromous chloride, and passed through potash pellets and phosphoric oxide immediately before use.

Nitrogen. Cylinder nitrogen, containing 6% of oxygen, was treated with alkaline pyrogallol either alone or followed by chromous chloride.

Sulphur. Roll sulphur was refluxed in a Pyrex flask under dry carbon dioxide for several days, black material separating. It was distilled thrice in carbon dioxide and twice in pure nitrogen, with rejection of appreciable head and tail portions, and finally fractionated five times in a vacuum.

TABLE I.

Fall in Velocity of Hydrogen Sulphide Formation with Time.

Temp. = 290°.

Duration of heating, hrs.	1	2	3	4	5	6
Velocity of H_2S formation, g./sec. $\times 10^8$	2·36	2·03	1·89	1·84	1·75	1·61

Dynamic Method.—The method first used was identical with that of Norrish and Rideal, but this procedure was considerably modified for the following reasons. (i) The velocity of hydrogen sulphide formation diminishes with time, owing to the transfer of sulphur from the body to the neck of the flask; this is illustrated by Table I and is more marked the higher the temperature. (ii) The colorimetric estimation of hydrogen sulphide is untrustworthy through (*a*) the rapid atmospheric oxidation of the alkaline sulphide, (*b*) the difficulty of matching intensities, the colour of the suspension being brown when produced by excess lead and greyish-black by excess sulphide. (iii) It is difficult to maintain a constant streaming rate of hydrogen by a screw clip on rubber tubing.

Apparatus and manipulation. Our new Pyrex reaction vessel (Fig. 1) allowed hydrogen to enter at C, pass down the annulus P into the bulb A, and emerge *via* the annulus Q to D. The inner tube, F, expanded at G, served as a reservoir for replenishing the parallel-sided well, B. After being cleaned and dried, the vessel was charged with sulphur, evacuated, filled with hydrogen and emptied several times to remove oxygen, and again evacuated. The sulphur was boiled twice in a vacuum, dissolved gases being removed. After being cooled, the vessel was refilled with hydrogen and incorporated in the system, the tube, beyond tap T_2, being connected to a source of hydrogen. The system was swept out over-night with hydrogen and afterwards evacuated through both T_1 and D. The sulphur was just melted and, by adjustment of hydrogen pressures, assumed the position indicated in Fig. 1; after cooling, it remained solid in *G* even with the vessel in the heating bath. The well was replenished by melting the sulphur and allowing sufficient to flow into it. The reaction vessel was submerged in the bath of fused sodium and potassium nitrates to the depth indicated, the exposed portion being cooled by an air current directed into an aluminium cup. Temperatures within ± $0{\cdot}25°$ of those required were maintained by manual control.

Tests showed that iodine is removed from $0{\cdot}02N$- and weaker iodine solutions containing 10 g. of potassium iodide per litre by a hydrogen stream, but not from such solutions when starch is present. The estimation of iodine by the thiosulphate titration, against a white background, gave end-points accurate to ± $0{\cdot}1$ c.c. of $0{\cdot}001N$. Standard solutions less concentrated than $0{\cdot}1N$ were prepared and checked immediately before use. The ultimate standard employed was pure potassium dichromate.

FIG. 1.

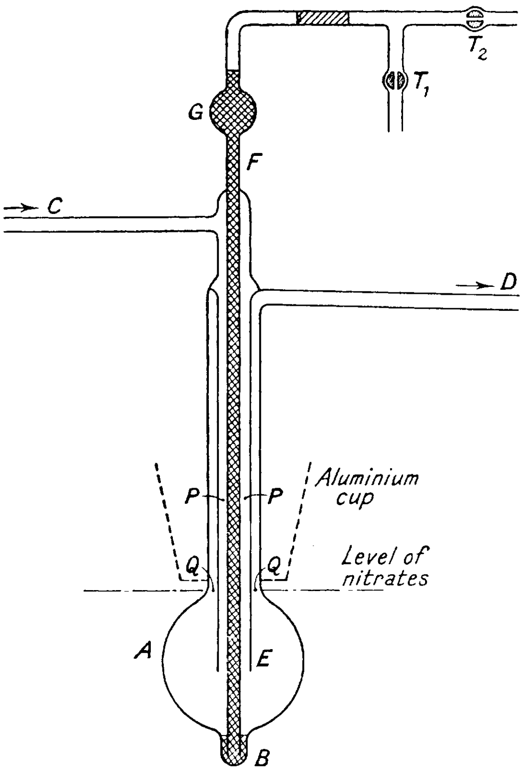
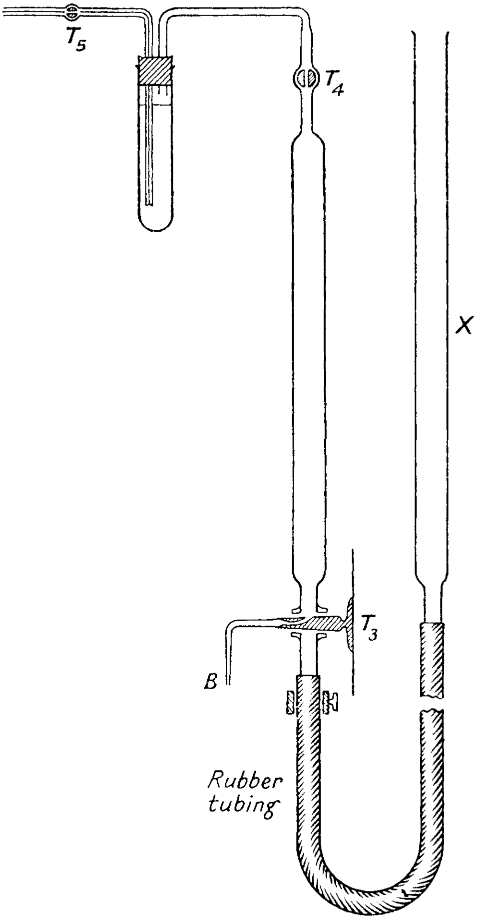


FIG. 2.



Regular and accurately known streaming velocities were given by a Hempel burette (Fig. 2) fitted with a fine jet at *B*. The velocity of aspiration was governed by regulating T_3 so that the gas in the burette increased uniformly with time, and, finally, the volume of the gas employed in the run was measured at atmospheric pressure. Since alteration from 50 to 100 c.c. per hour in the streaming rates did not change the velocity of the reaction, the convenient rate of 75 c.c. per hour was adopted.

The reaction vessel was swept out for 12 hours at approximately the velocity and slightly below the temperature to be employed in the run, and finally for 2 hours under precisely these conditions, with hydrogen which had passed (i) through 1 m. of alkaline pyrogallol, (ii) over 10 cm. of heated platinised asbestos, (iii) through 25 cm. of potash pellets, followed by 50 cm.

of phosphoric oxide. The velocities recorded are means of six or more individual determinations of which the set of six (Table II) is representative.

TABLE II.

Temp. 599·9° Abs. Duration of run, 60 mins.

Vol. of H_2 collected in burette, c.c.	75·1	75·0	75·2	75·3	75·1	75·2	
0·01*N*-Iodine used, c.c.	11·9	11·8	11·8	11·8	11·9	11·8	
Velocity of H_2S formation, g./sec. × 10^8	56·2	55·7	55·7	55·7	56·2	55·7	Mean 55·9

It was known (see below) that the reaction velocities varied with the area of liquid sulphur, and the values below were those obtained with 1·02 sq. cm. area of liquid in (*a*) hydrogen at atmospheric pressure and (*b*) a mixture of hydrogen and nitrogen (not treated with chromous chloride). When the logarithms of the velocity are plotted against $1/T$, the data of Table III (a) give an almost straight line, whilst those in Table III (b) give a curve.

TABLE III.

Velocities of H_2S *Formation.*

(*Surfaces of liquid sulphur and of glass constant.*)

(a) *In pure hydrogen.*

Temp., Abs.	538·7°	553·7°	569·0°	584·3°	599·9°	621·3°
Total press. of H_2 plus S vapour at temp. of expt., mm.	779	774	767	784	784	777
Mean velocity of H_2S formation, g./sec. × 10^8	1·42	3·63	8·50	22·9	55·9	189·0

(b) *In hydrogen–nitrogen mixture* (40 : 60 *by vol.*).

Temp., Abs.	538·7°	553·7°	569·0°	584·3°	599·9°	621·3°
Total press. of H_2 plus S vapour at temp. of expt., mm.	752	756	762	758	766	754
Mean velocity of H_2S formation, g./sec. × 10^8	0·76	1·51	3·76	8·40	18·9	64·7

The glass surface was increased by 500% by packing with round-ended lengths of Pyrex rod, not touching the liquid. (Runs with shorter rods partly covering the liquid surface showed a diminished velocity.) The gaseous volumes of both the packed and the empty reaction chamber were identical, and the following velocities show that the additional surface is without effect :

Temp. 569° Abs. Area of liquid sulphur pool constant.

Condition of vessel.	Mean rate of H_2S formation, g./sec. × 10^8.
Without glass rods	15·8
Packed with glass rods clear of sulphur pool	15·7
,, ,, ,, partly covering sulphur pool	12·2

To investigate the behaviour of liquid sulphur, a Pyrex Claisen flask was charged with 1 g. of sulphur, from which gas was removed by boiling in a vacuum. The sulphur solidified on the bottom in a circular pool, the area of which could be ascertained with reasonable accuracy. After a maturing period of 12 hours at just below 296°, runs were made at this temperature. Successively larger amounts of sulphur were used but, as anticipated, a quantitative correlation was not obtained. With the larger quantities, however, the velocity was roughly proportional to the area, but as this became less, the ratio of the velocities approached unity, owing to the contribution of the homogeneous reaction (see below).

Relation of Velocity to Area of Liquid Sulphur.

Temp. 569° Abs. Volume of reaction vessel = 65 c.c.

Area of liquid sulphur pool, sq. cm.	Mean rate of H_2S formation, g./sec. × 10^8.	$\frac{\text{Rate}}{\text{Area of pool}}$.
1·13	6·5	5·75
2·69	8·6	3·20
8·76	17·4	1·99

Comparative experiments in identical flasks proved the reaction velocity to be the same in Pyrex, Monax, or soft glasses.

Our dynamic study of the combination of hydrogen and sulphur points to two distinct reactions: (i) homogeneous, and (ii) heterogeneous at the surface of the liquid. It shows, further, that quantitative investigation of the individual velocities of the two reactions is impossible by this method and indicates, in conflict with Norrish and Rideal's observations, that the velocity is independent of the area of glass surface and varies with the area of the liquid sulphur.

The Static Method.—By carrying out the reaction in bulbs wherein any desired quantity of sulphur may be used, the difficulties caused by the removal of sulphur from the reaction zone, inherent in the dynamic method, are avoided. Especially, the static method allows of working with less than saturated sulphur vapour and, indeed, is only limited by the accuracy obtainable in the evaluation of the reaction products, which, in the present instance, is very high. The reaction was therefore studied in glass bulbs (i) in the gaseous phase alone, (ii) with liquid also present, and (iii) with various volumes and against different areas of glass.

The Homogeneous Reaction.

Glass bulbs, provided with two limbs, were cleaned and closed at one end. After the appropriate weight of sulphur had been added, a capillary was formed on the other limb, and they were attached by rubber to a vacuum train. The train was swept out over-night with hydrogen, and the bulbs were evacuated and filled with hydrogen four times to remove air. The pressures were measured on the manometer, and the bulbs were sealed off under conditions which led to inappreciable changes in pressure on removal. The bulbs were held below the surface of the fused nitrates, and, since the bath is slightly cooled by this operation, the liquid was in such a condition that when equilibrium was reached, the bath and its contents were at the required temperature. The bulbs were cooled in air, washed, and opened beneath standard iodine solution, which entered in a sufficient quantity to react with the hydrogen sulphide; the contents were then washed into a beaker. Control experiments showed that the operation of opening and washing could be accomplished without diminution in the iodine titre. The estimation was concluded by titrating unused iodine with standard thiosulphate.

TABLE IV.

Effect of Sulphur Concentration.

Vol. of standard bulb = 61 c.c. Hydrogen press. = 357 mm. (at 15°).

Temp. = 574° Abs. Duration of run = 60 mins.

Wt. of S in bulb, g.	0·0120	0·0085	0·0055
Rate of H_2S formation, g./sec. $\times 10^8$	6·52	5·53	4·44
Rate $\times 10^9/\sqrt{[S]}$	594	599	598

Vol. of standard bulb = 49 c.c. Hydrogen press. = 382 mm. (at 15°).

Temp. = 595° Abs. Duration of run = 60 mins.

Wt. of S in bulb, g.	0·0190	0·0150	0·0120	0·0090
Rate of H_2S formation, g./sec. $\times 10^8$	27·2	24·2	21·7	19·0
Rate $\times 10^8/\sqrt{[S]}$	197	197	198	201

Sulphur Concentration.—Table IV shows that, for two temperatures, the velocities are proportional to the square root of the sulphur concentration.

TABLE V.

Effect of Hydrogen Concentration.

Duration of run = 60 mins.

Temp., Abs.	Press. of H_2 in bulb at reaction temp., mm.	Rate of H_2S formation, g./sec. $\times 10^8$.	Ratio of pressures.	Ratio of rates.
573°	760	5·34	2·50	2·48
	304	2·15		
593	787	19·28	2·50	2·51
	315	7·67		

Hydrogen Concentration.—A set of bulbs of uniform volume (49 c.c.) were charged with 0·0120 g. of sulphur, and half were filled with hydrogen at 382 mm. (15·0°) and half at 153 mm. (15·0°). The bulbs were heated, some at 300° and others at 320°, with results (Table V) which prove the velocity of hydrogen sulphide formation to be directly proportional to the pressure of hydrogen.

TABLE VI.

Effect of Hydrogen Sulphide.

Vol. of reaction bulb = 49 c.c. Wt. of S added = 0·0190 g.

Temp. = 594·6° Abs.

Period of heating bulb, hrs.	1	4	6
Titre, c.c. of 0·001*N*-I_2	55·3	199·9	283·4
Wt. of H_2S formed, g. × 10^5	94	340	482
k, calc.	491	485	489

It is evident that a certain amount of sulphur and hydrogen is used up during the course of the reaction so that a slight allowance should be made for this, and, as the effects on the velocity of the reaction of both the sulphur and the hydrogen concentration are known, it is possible to apply this correction. Throughout the investigation, however, the decrease in the concentration of reactants was usually only 1—2% in any run, and therefore the means of the initial and final concentrations of hydrogen and sulphur were employed as the effective concentrations to which the velocities were related.

Effect of Hydrogen Sulphide.—Since the velocity of hydrogen sulphide formation is proportional both to the concentration of hydrogen and to the square root of that of the sulphur, then, provided the velocity be uninfluenced by the accumulated hydrogen sulphide, if x is the amount of hydrogen sulphide formed after time t,

$$dx/dt = k(\sqrt{[S] - x})([H_2] - x)$$

This on integration gives

$$k = \frac{2}{t\sqrt{[H] - [S]}} \tan^{-1} \frac{(\sqrt{[H] - [S]})(\sqrt{[S]} - \sqrt{[S] - x})}{([H] - [S]) + (\sqrt{[S]} \,.\, \sqrt{[S] - x})},$$

an expression amenable to experimental verification.

Three bulbs with 0·0190 g. of sulphur and hydrogen at 382 mm. (at 15·0°) were heated at 321·6° for 1, 4, and 6 hours respectively, and the hydrogen sulphide formed was determined. These quantities (Table VI) show that hydrogen sulphide up to 15·7% by volume is without effect on the velocity of the reaction at this temperature and pressure.

Effect of Glass Surface.—By introducing glass rods into a 63 c.c. bulb, its capacity was reduced to the standard 49 c.c., and the glass surface was increased five-fold. Rods with rounded ends were used in order to preserve the fire-polished surface. In one series, 0·0120 g. of sulphur, insufficient to leave any liquid at 301°, was employed, and in another 0·0300 g., enough to provide a slight residue of liquid at 322°. The results show that the rate is independent of the surface :

	Wt. of H_2S formed, g./sec. × 10^8.		
Temp., Abs.	(*a*) Without rods.	(*b*) With rods.	Diff., %.
574°	5·62	5·57	− 0·89
595	28·60	28·70	+ 0·35

Influence of Volume.—Runs in bulbs of volume ranging from 47 to 225 c.c. with uniform concentrations of both sulphur and hydrogen were made at several temperatures and the velocities were proportional to the volume. Corrections may thus be applied for bulb volume.

Temp., Abs.	Press. of H_2 at 15·0°, mm.	Vol. of reaction bulb, c.c.	Wt. of S, g.	Wt. of H_2S formed, g./sec. × 10^8.	Wt. (g. × 10^{11}) of H_2S formed per sec. per c.c. of gaseous vol.
595°	382	49	0·0120	21·7	442
		225	0·0551	99·3	441
616	382	49	0·0120	73·6	150
		225	0·0551	336·7	150
563	153	49	0·0120	1·1	22·4
		225	0·0551	5·0	22·2
595	153	49	0·0120	8·4	171
		225	0·0551	38·2	170

Temperature Coefficient of the Homogeneous Reaction.—Velocities were measured at temperatures between 280° to 343° at two concentrations of hydrogen, and, except at 280°, with one concentration of sulphur (0·0120 g. in a 49 c.c. bulb); since this amount of sulphur would have given some liquid at this temperature, less solid was used, and the velocity obtained was scaled to correspond to that from the normal concentration (0·0120 g./49 c.c.) by multiplying it by the square root of the ratio of the two concentrations, thus making this result comparable with the others.

Temp., Abs.		553°	558°	563°	574°	584·5°	595°	616°
Wt. of H_2S formed, g./sec. × 10^{10}/c.c. of gaseous volume, at a hydrogen pressure (measured at 15°) of	382 mm.	2·77	3·89	5·49	11·47	22·66	44·23	150·2
	153 mm.	1·13	—	2·22	4·63	9·06	17·16	59·36

Plots of the logarithms of the velocities against the reciprocal of the absolute temperature (Fig. 3) proved to be parallel straight lines, and point to a single reaction of which the temperature coefficient is 1·90 per 10°, and the heat of activation 43·3 kg.-cals.

Influence of Minute Traces of Oxygen in the Nitrogen–Hydrogen Mixtures.—Hydrogen and nitrogen (40 : 60, by vol.) which had each passed through 1 m. of alkaline pyrogallol were mixed and, immediately before entering the reaction bulbs, were bubbled slowly through two 1 m. lengths of alkaline pyrogallol followed by the usual drying tubes. Results, Table VII, gave, when the logarithms of the velocities were plotted against $1/T$, a curve (*A*, Fig. 4) which, by comparison with the straight line from pure hydrogen (*i.e.*, line 153 mm. in Fig. 3), indicated an increase in the velocity which was very pronounced at the lower temperatures but vanished at the highest temperatures. (The slightly low values at the higher temperatures are due to interaction between the hydrogen sulphide and the sulphur dioxide, whereby the apparent yields are lessened—see Part II.) This led to further treatment for the removal of oxygen. In the first case the above mixture was allowed to stand in the gas-holder over alkaline

FIG. 3.

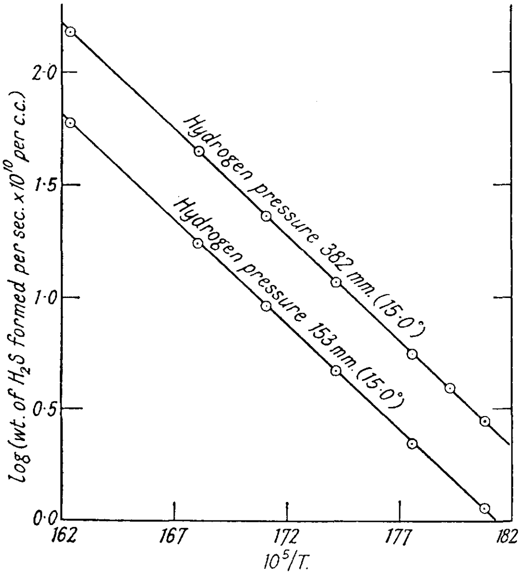


FIG. 4.

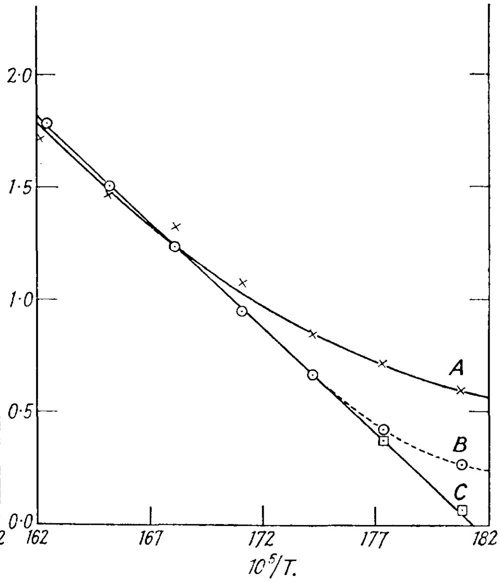


TABLE VII.

Influence of Minute Trace of Oxygen.

Press. of H_2–N_2 mixture = 382 mm. (at 15·0°). S concn. = 0·0120 g./49 c.c.

Temp., Abs.	Wt. of H_2S formed, g./sec. × 10^{10}/c.c. of gaseous volume, H_2–N_2 mixture having been treated		
	(*a*) ordinarily.	(*b*) with alk. pyrogallol.	(*c*) with chromous chloride.
553°	3·92	1·86	1·66
564	5·14	2·63	2·40
575	6·96	4·63	—
584·5	11·7	8·88	—
595	20·6	17·2	—
605·3	29·5	31·7	—
616	—	61·1	—
617	51·8	—	—

pyrogallol and, immediately before use, was passed through two 1 m. lengths of pyrogallol and a special form of gas-washer (Parker and Robinson, J., 1929, 1106). The results (*B*, Fig. 4) were now identical with those from pure hydrogen except at 290° and 280°, where a slight increase was still apparent. In consequence, each gas was individually passed through 1 m. of chromous chloride before mixing and, immediately prior to use, the mixture was passed through two 1 m. tubes containing the chromous chloride–amalgamated zinc reagent; the results (*C*, Fig. 4) were then almost identical with those from pure hydrogen at the lowest temperatures. Evidently the reaction is unaffected by nitrogen, which acts simply as a diluent.

The Heterogeneous Reaction on the Liquid Sulphur.

The contribution of the homogeneous reaction to the composite velocity now being known, the investigation of the reaction at the surface of liquid sulphur became possible. For this, vessels of identical volume, provided with wells so shaped that equal quantities of liquid presented different areas, were used. The volume of the liquid, as distinct from its exposed surface, was shown to be without effect on the reaction.

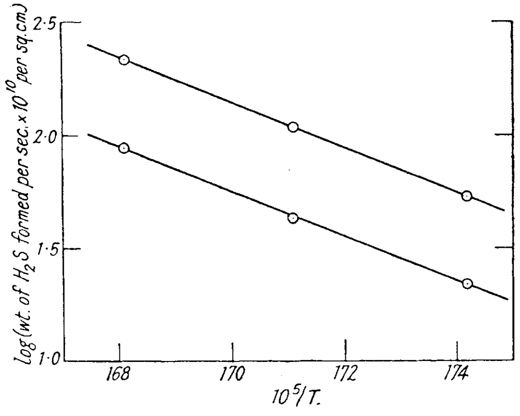
Hydrogen press. = 382 mm. (at 15·0°). Temp. = 584·5° Abs.

Wt. of S, g.	Surface area of pool, sq. cm.	Gaseous vol. above pool, c.c.	Wt. of H_2S formed from composite reactions, g./sec. × 10^8.
4·5	4·75	122·7	40·1
3·0	4·75	122·7	40·3

The homogeneous reaction was first measured in saturated sulphur vapour at appropriate temperatures and pressures. Subsequently, 4·5-g. lots of sulphur were weighed into bulbs. These were attached to the charging train, evacuated after several washings with hydrogen, and finally the sulphur was boiled in a vacuum to facilitate drying and degassing. Sulphur which had condensed on the sides of the bulb was subsequently returned to the well by warming with a Bunsen flame, so that the pool had a well-defined area. The vessels after cooling were filled with hydrogen, sealed, and heated, with precautions against alteration of the areas of sulphur surface when melting occurred.

The contribution of each reaction to the total velocity was computed by two methods : (i) the experimentally determined gaseous velocity, corrected to the particular volume undeı consideration, was deducted from the composite velocity; (ii) the simultaneous equations based on the composite velocities with either different areas of sulphur or different working volumes were solved.

FIG. 5.



Temp. = 584·5° Abs. Hydrogen press. = 382 mm. (at 15·0°).

Surface area of S pool, sq. cm.	Gaseous vol. above pool, c.c.	Yield of H_2S from composite reaction, g./sec. × 10^6.
4·75	122·7	0·401
9·84	129·7	0·476

If x and y are the number of g. of H_2S formed per sec. respectively in each c.c. of saturated sulphur vapour and on each sq. cm. of liquid sulphur surface; then

$$122{\cdot}7x + 4{\cdot}75y = 0{\cdot}401 \times 10^{-6}$$
$$129{\cdot}7x + 9{\cdot}84y = 0{\cdot}476 \times 10^{-6}$$

whence $x = 0{\cdot}286 \times 10^{-8}$ (Found : $0{\cdot}285 \times 10^{-8}$ g.)

and $y = 0{\cdot}108 \times 10^{-7}$

so the yield per sec. of the H_2S from a surface of 4·75 sq. cm. = $4{\cdot}75y = 0{\cdot}511 \times 10^{-7}$ g. (Found : $0{\cdot}519 \times 10^{-7}$ g.), and yield per sec. of H_2S from a surface of 9·84 sq. cm. = $9{\cdot}84y = 1{\cdot}06 \times 10^{-7}$ g. (Found : $1{\cdot}07 \times 10^{-7}$ g.).

The concordance (Table VIII) is good, and sufficient to permit an estimate of the velocity of the heterogeneous reaction at the surface of liquid sulphur. The results, plotted in Fig. 5,

TABLE VIII.

Heterogeneous Reaction.

Temp., Abs.	H_2 press., mm. at 15·0°.	Area of liquid pool, sq. cm.	Gaseous vol. above pool, c.c.	Rate of composite reaction, g. H_2S/sec. × 10^{10}.	Velocity of gas reaction for saturated S vapour, g./sec. × 10^{10}/c.c. of gaseous volume.		Surface yields, g. H_2S/sec. × 10^{10}.	
					Found.	Calc.	Found.	Calc.
595°	382	4·75	122·7	8220	58·4	58·8	1050	1010
		9·29	132·7	9760			2010	1970
584·5	382	4·75	122·7	4010	28·5	28·6	519	511
		9·84	129·7	4760			1070	1060
574	382	4·75	122·7	1880	13·1	13·2	262	251
		10·20	132·7	2300			551	539
595	153	4·75	122·7	3290	23·3	23·4	425	415
		9·29	132·7	3920			826	811
584·5	153	4·75	122·7	1600	11·3	11·4	217	198
		9·84	129·7	1890			430	410
574	153	4·75	122·7	767	5·4	5·4	104	105
		9·84	129·7	917			215	217

show that the reaction is proportional to the area of liquid sulphur and also to the hydrogen pressure. The temperature coefficient is 1·95 per 10°, and the heat of activation 45·5 kg.-cals.

Influence of Nitrogen.—Pure nitrogen does not affect the composite velocity (Table IX), and since it does not affect the homogeneous reaction, it follows that the surface reaction is also unaffected.

TABLE IX.

Influence of Nitrogen.

Press. of H_2–N_2 mixture (40 : 60 by vol.) = 382 mm. at 15·0°.

Temp., Abs.	Area of liquid pool, sq. cm.	Gaseous vol. above pool, c.c.	Composite reaction (g. H_2S/sec. × 10^9) with	
			H_2–N_2 mixture.	pure H_2 at corresponding press.
574°	4·75	122·7	78	77
584·5	4·75	122·7	159	160
595	4·75	122·7	324	329

Pyrex glass was adopted as standard in this work, but the results given below show that Monax and soft glasses may be used without affecting either the homogeneous or the heterogeneous reaction.

Press. of H_2 = 382 mm. at 15·0°. Area of S. pool = 1·08 sq. cm. Gaseous vol. above pool = 49 c.c.

Glass	Soft.	Monax.	Pyrex.
Composite reaction, g. H_2S/sec. × 10^9	151	151	157

DISCUSSION.

We have found the reaction between hydrogen and sulphur under the present conditions to proceed only in the gas phase, or at the sulphur surface. Neither reaction is influenced by glass or the presence of nitrogen or hydrogen sulphide. The effect of oxygen and sulphur dioxide will be dealt with in Part II.

The velocity of the homogeneous reaction (temperature coefficient 1·90; heat of activation 43·3 kg.-cals.) is proportional to the square root of the sulphur concentration and to the hydrogen concentration; hence

$$dx_1/dt = k_1[\mathrm{S}]^{\frac{1}{2}}[\mathrm{H}_2] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The velocity of the heterogeneous reaction (temperature coefficient 1·95; heat of activation 45·5 kg.-cals.) is proportional to the area of the surface of molten sulphur (A) and to the hydrogen concentration, and is independent of the vapour pressure of the sulphur; hence

$$dx_2/dt = k_2A[\mathrm{H}_2] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Our knowledge of the equilibria in sulphur vapour is imperfect, and attempts to evaluate the equilibrium constants, and therefrom the partial pressure of the individual molecular species, involve some uncertainty (compare Preuner and Schupp, *Z. physikal. Chem.*, 1909, **68**, 129). Although, for this reason, a full interpretation of the data is necessarily tentative, points emerge for which considerable probability may be claimed. There is little foundation, for example, for Bodenstein's suggestion that the occurrence of the $\sqrt{S}$ function in the velocity equation implies the mechanism $H_2 + S \longrightarrow H_2S$, which, from other considerations, was also adopted by Norrish and Rideal. It rests on Bodenstein's assumption that the last step of the chain $S_8 \rightleftarrows 2S_4 \rightleftarrows 4S_2 \rightleftarrows 8S$ is the one which immediately precedes combination. Actually, $S_4 \rightleftarrows S_2$ may be responsible, and is the more likely for two reasons : (*a*) at the pressures used, the concentration of sulphur atoms is negligibly small, and (*b*) the reaction $H_2 + S \longrightarrow H_2S$ can only result from three-body collisions, which are too rare to account for the yields. The reaction $H_2 + S_2 \longrightarrow H_2S + S$, however, occurs without the intervention of a third body, little difficulty being presented by the removal of the liberated sulphur atom by collisions which will occur with other particles. Moreover, the absence of chains of appreciable length discounts the possibility of such mechanisms as

$$\begin{array}{ll} H_2 + S \longrightarrow SH + H, & HS + H_2 \longrightarrow H_2S + H \\ H + S_x \longrightarrow HS + S_{x-1} & H + S_2 \longrightarrow HS + S \end{array}$$

which alone, on the sulphur atom hypothesis, would account for the hydrogen sulphide formed. The evidence favours the sequence

$$\begin{array}{ll} 1. & H_2 + S_2 \longrightarrow H_2S + S \\ 2. & \begin{cases} S + S_x \longrightarrow yS_{(x+1)/y} \\ S + H_2 + M \longrightarrow H_2S + M' \end{cases} \end{array}$$

rather than a process initiated by sulphur atoms. It should be emphasised, however, that anything more than a tentative suggestion of the probable mechanism must await precise knowledge of the molecular constitution of sulphur vapour and its dependence on temperature and pressure.

It is impossible to state a mechanism for the heterogeneous reaction in the absence of any knowledge of the nature of the sulphur surface. A striking feature of the reaction is that the temperature coefficient is almost identical with that of the gas reaction, which probably indicates that the reaction is of the same type, and lends support to our contention that it is not between sulphur atoms but rather between S_2 molecules and hydrogen, since it is improbable that sulphur atoms are present in liquid sulphur. The fact that the reaction is independent of the concentration of sulphur vapour in the body of the vessel shows that it arises from sulphur " in the surface " or immediately released therefrom.

The mechanism previously proposed by Norrish and Rideal is based on data which we have been unable to confirm. There are, moreover, some points in their treatment of the results which are open to criticism.

(1) Their assessment of the vapour pressure of sulphur assumes that $[S_8]/[S]$ is independent of temperature, *i.e.*, that the heat of dissociation of gaseous S_8 is zero, which involves an error of 60 kg.-cals. and also involves the employment of $[S]^{\frac{1}{8}}$ instead of $[S]^{\frac{1}{2}}$.

(2) No allowance is made for the fall in concentration of hydrogen with rising temperature consequent upon the increase in sulphur concentration.

(3) They found the heat of activation of the gas reaction to be 52 kg.-cals., whereas " from the data of Preuner and Schupp it is possible to calculate a rather uncertain value for the heat of vaporisation of S_2 at 350° C., namely, 28 kg.-cals. The heat of dissociation of S_2 is somewhat better known, being 102·5 kg.-cals. Thus the heat of vaporisation of S atoms from liquid sulphur at 350° must be about 65 kg.-cals. Since it is very unlikely that the true reaction has a negative temperature coefficient, the suggestion that S atoms are involved must be dismissed " (Kassel, *op. cit.*).

The flow method suffers from serious difficulty when employed with a volatile material, such as sulphur, in that (i) useful investigation in the gaseous phase is limited to the saturated vapour only and (ii) the area of reacting surface, whether solid or liquid, is difficult to assess precisely.

Mr. E. A. O'Connor, of Queensland University, Brisbane, who has very kindly communicated to us the results of an independent investigation of the reaction by a dynamic method, has also failed to find evidence of a reaction at the glass surface.

SUMMARY.

1. The reaction between hydrogen and sulphur has been investigated by a dynamic and by a static method. The former is incapable of dealing fully with the problem, but the latter proved adequate.

2. Hydrogen and sulphur react (i) homogeneously, with a velocity proportional to the concentration of hydrogen and to the square root of that of sulphur (temperature coefficient 1·90; heat of activation 43·3 kg.-cals.); (ii) heterogeneously, with a velocity proportional to the concentration of hydrogen and to the area of liquid sulphur (temperature coefficient 1·95; heat of activation 45·5 kg.-cals.).

3. The following mechanism has been tentatively suggested for the gas reaction :

$$\text{(i)}\quad H_2 + S_2 \longrightarrow H_2S + S$$
$$\text{(ii)}\quad \begin{cases} S + S_x \longrightarrow yS_{(x+1)/y} \\ S + H_2 + M \longrightarrow H_2S + M'. \end{cases}$$

4. The work of Bodenstein and of Norrish and Rideal has been discussed.

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UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE.

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