109. *The Kinetics of the Reaction between Hydrogen and Sulphur. Part III.* (i) *Reaction at* 350—412° *and* 50—150 *mm.* (ii) *Behaviour of Sulphur on a Hot Glass Surface.*

By Ralph P. Cook and Percy L. Robinson.

(i) Up to 350°, and from a few mm. to 1 atm. of hydrogen, the reaction with sulphur is homogeneous and has a velocity proportional to the concentration of hydrogen and the square root of the concentration of sulphur (Aynsley, Pearson, and Robinson, J., 1935, 58). Below this pressure range, a reaction on the glass is detectable, which, however, ceases immediately it has covered the surface with a unimolecular layer of hydrogen sulphide. At pressures greater than a few mm., the amount of hydrogen sulphide produced heterogeneously, even in packed vessels, is too small for independent recognition (Aynsley and Robinson, J., 1935, 351). The cessation of the heterogeneous reaction was ascribed to the occupation of the surface by molecules of hydrogen sulphide, and it was anticipated that at higher temperatures this layer would be wholly, or in part, desorbed, and a continuous reaction would proceed on the cleared surface. It has been necessary, in connexion with other work shortly to be published, to extend our knowledge of the hydrogen–sulphur reaction up to the highest temperature at which it could be accurately measured, which, unfortunately, was only 412°, on account of the velocities there experienced, but the onset of a continuous heterogeneous reaction has not been observed.

The experimental procedure was similar to that previously described. Over the extended temperature range the velocity remains proportional to the hydrogen concentration (Table I*a*) and to the square root of the sulphur concentration (Table I*b*). The reaction rates over a period of 5 minutes' actual heating were obtained by using two identically charged bulbs, one being heated for 3 and the other for 8 minutes, and taking the difference. The reaction is also independent of the area of the glass surface (Table I*c*).

Table I.

(*a*) *Effect of hydrogen concentration.*

Vol. of bulb = 218 c.c. Weight of sulphur = 0·0534 g. Time of heating = 5 mins.
Temp. = 675° Abs.

Press. of hydrogen at 15°, mm.	51	102	153
Rate of H_2S formation, g./c.c./sec. × 10^{10}	398·0	806·5	1199·0
Ratio of rates	1·00	2·03	3·01

(*b*) *Effect of sulphur concentration.*

Vol. of bulb = 218 c.c. Press. of H_2 = 153 mm. (at 15°). Time of heating = 5 mins.
Temp. = 675° Abs.

Wt. of sulphur, g.	0·0534	0·1000	0·1500
Rate of H_2S formation, g./c.c./sec. × 10^{10}	1199	1676	2036
(Rate/$\sqrt{[S]}$) × 10^{11}	519·0	530·0	525·6

(*c*) *Effect of glass surface.*

Vol. of bulb, c.c.	Wt. of S, g.	Press. of H_2, mm. (at 15°).	Glass surface, sq. cm.	Abs. temp.	Rate of H_2S formation, g./c.c./sec. × 10^{10}.
218	0·0534	153	175	675°	1199
218	0·0534	153	895	675	1220

Table II, corrected for the fall in concentration of sulphur during the reaction, shows that the plot of the logarithm of velocity against $1/T$ (see fig.) continues the straight line

Table II.

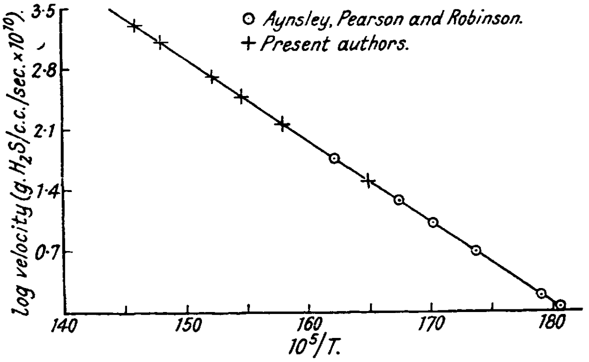
Velocity and temperature.

Vol. of bulb = 218 c.c. Conc. of sulphur = 0·0534/218 g./c.c. Hydrogen press. = 153 mm. (at 15°).

Abs. temp.	606°	633°	647·5°	656·7°	675°	688·1°
Rate of H_2S formation, g./c.c./sec. × 10^{10}	34·1	152·8	335·4	546·8	1199·0	1941·5

given in Part I, Fig. 3, and indicates an identical temperature coefficient (1·9) and heat of activation (43·3 kg.-cals.). Evidently the kinetics of the reaction remains unchanged; in particular, there is no increase in the heterogeneous contribution.

(ii) The observations described in Parts I and II and above are contrary to those which led Norrish and Rideal (J., 1923, **123**, 696) to state that "as a result of experiments carried out using flasks of different internal surface area it was found possible to show that the surface action" (which in their case was believed to be considerable and continuous) "is directly proportional to the area of the internal surface of the reaction chamber, and thus independent of the quantity of sulphur present." They used a flow method and found "that on removing the reaction flask suddenly from the bath, the whole internal surface was covered with a thin film of liquid sulphur which quickly solidified to a coating of feathery crystals." When we first encountered the difficulty of accepting the original work, Dr. Norrish kindly sent us one of his own flasks showing the coating described, and with it we repeated many times the operation of sudden removal from the bath, but were forced to conclude that the liquid film seen by Dr. Norrish arises from the condensation of sulphur vapour upon the walls of the vessel. The distribution of the condensate thereon is changed by any irregularity in cooling: for instance, the sulphur can be made to separate entirely on one side of the flask, by suitably cooling that region, and to leave the other side quite free. Of more importance than the liquid which separates on cooling, however, is the question whether, as alleged by Norrish and Rideal, a liquid film is present on the glass surface during the time the flask is at the reaction temperature. To investigate this, we have heated sulphur in (i) a stream of hydrogen and (ii) closed vessels with hydrogen and alone, and have used soft, Monax, and Pyrex glasses for these purposes. In the first case, the apparatus was similar to that of Norrish and Rideal (*loc. cit.*) except that the heating liquid, colourless paraffin, was in a large, lagged, Pyrex beaker provided with two narrow windows in the asbestos covering, to serve severally for the illumination and the observation of the reaction vessels and their contents.



The flask, through which hydrogen was passing, was submerged in the bath so slowly that the whole surface was successively covered with liquid sulphur which, evaporating from the bottom, condensed just above the level of the bath liquid. At the temperatures employed, 260—310°, the sulphur at the bottom of the flask failed to wet the glass, with which it assumed a contact similar to that shown by mercury and other non-wetting liquids. The lower edge of the ring of liquid adhering to the neck, where it was but little below bath-temperature, presented a like contact. Between the pool in the bottom and the material in the neck, the glass was free from a visible film, the presence of which could have been readily recognised because, unlike the liquid, sulphur vapour is, even at these temperatures, light in colour. After a time, sulphur collected to such an extent in the neck that it flowed down as pensile drops which, in their passage, did not spread out over the glass, and left upon the surface narrow, dark brown smears that became fainter by evaporation, broke into small globules, and finally disappeared. These smears served to indicate the dark colour which a liquid film such as that postulated by Norrish and Rideal would assume at these temperatures and thereby render itself readily recognisable if present.

Closed vessels, containing sulphur either in a vacuum or with hydrogen, slowly lowered into the bath so that their surfaces were successively covered with liquid showed no evidence of a liquid film when equilibrium was reached, the whole of the sulphur being then in a pool at the bottom.

Neither long periods of maturing at the working temperatures, nor changes in the type of glass affected this behaviour.

These observations bear out our previous conclusion that glass is not " wetted " by sulphur at these temperatures, a view which has gained further support by the recent work of Sayce (J., 1935, 1767) on the kinetics of the oxidation of sulphur.

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