CCXLIV.—*The Kinetics of the Oxidation of Hydrogen Sulphide. Part I.**

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IT has recently been shown (*Z. physikal. Chem.*, 1930, *B*, **10**, 273) that mixtures of carbon disulphide and oxygen exhibit similar properties to those shown by mixtures of hydrogen and oxygen at low pressures (*Proc. Roy. Soc.*, 1929, **122**, *A*, 610) : at any temperature

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* In discussion with Dr. L. Farkas, of the Kaiser Wilhelm Institut für physikalische und Elektrochemie, Berlin-Dahlem, after this paper had been written, it was ascertained that he also had obtained some of the results now described. So far as we can see, his results are in general agreement with ours, but only involve the induction period and the explosion. They will be published by him later in the *Zeitschrift für Elektrochemie.*

ignition only occurs between two pressure limits outside which the measurable reaction is very slight and apparently largely dependent on the vessel walls. By using clean vessels, fairly reproducible values for the pressure limits can be obtained, but the existence of sulphur deposits on the wall leads to much irregularity. In most cases, again, an induction period varying from seconds to minutes, in which no measurable change occurs, precedes the ignition, and this is markedly dependent on the nature of the wall surface. The facts would indicate an initiation of chains on the wall, and this idea is supported by the lack of explosion until far higher temperatures in the absence of wall.

Further investigation has shown that this reaction is of peculiar interest, and it seemed desirable to examine other processes of a similar type. Amongst those which suggested themselves, the oxidation of hydrogen sulphide was chosen. The kinetics of this exothermic reaction have never been examined in detail, though determinations of the ignition temperature of hydrogen sulphide in oxygen and in air have been made (see reference to Meyer and Freyer, Dixon and Coward, in Bone and Townend's " Flame and Combustion in Gases ").

The values of these ignition temperatures deduced from the experiments to be described agree satisfactorily with those of Dixon and Coward, at any rate in so far as ignition in oxygen is concerned.

EXPERIMENTAL.

Method.—The reaction was followed by the static method usually employed in measurements of this kind (Fig. 1). The reaction vessel *A* was enclosed in an electrically heated furnace *B*, and connected by means of capillaries to a capillary three-way tap *C*, and to a mercury manometer *M*, the dead space being negligible.

Condensation of water during the course of an experiment was prevented by wiring the capillaries with electrically-heated resistance wire, maintained at about 120°. The tap *C* was connected to vessels *DD* and *E* containing respectively hydrogen sulphide and oxygen, and *via* tap *G* to a mercury-vapour pump, manometers being suitably interposed. The reaction was followed by pressure changes recorded on the manometer *M*, which was not wired, the vapour pressure of the mercury thus being reduced, and reaction between hydrogen sulphide and mercury being diminished to negligible proportions. The temperature of the furnace was measured by a subsequently calibrated mercury thermometer, placed so that its bulb was in contact with the reaction vessel.

Several reaction vessels of different dimensions were employed in the work (see Table I); I, III, V, and VI were soda-glass cylinders

7·5—8·5 cm. in length and of 3·2 cm. internal diameter, VIII was 14 cm. long and of 1·5 cm. internal diameter, II was 12 cm. long but only 1·1 cm. in diameter, IV was identical with V but packed with 45 pieces of glass tubing each 5 cm. long, 2 mm. internal and 3 mm. external diameter; VII was also identical with V but packed with glass wool.

FIG. 1.

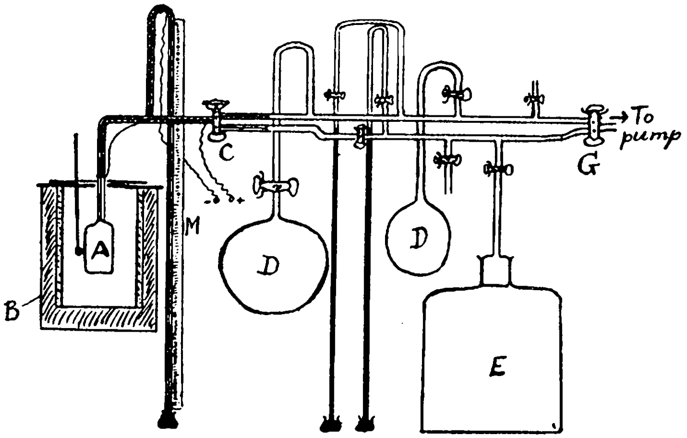


TABLE I.

No.	Width, cm.	Gaseous volume, c.c.	Surface area, cm.^{2}.	Surface/volume.
I	3·2	56	73	1·3
II	1·1	11·5	40	3·5
III	3·2	60	80	1·33
IV	3·2	45	350	7·8
V	3·2	56	73	1·3
VI	3·2	56	73	1·3
VII				
VIII	1·5	25	65	2·6

After the series of experiments in the smallest (narrow) vessel II had been completed, doubts arose as to whether here the dead-space had become relatively important. An entire repetition of the work in vessel VIII showed that the results in vessel II were quite valid, and indeed, as will be shown, gave assistance in their interpretation.

The hydrogen sulphide was prepared by digesting a mixture of calcium sulphide and magnesium chloride with water (Moser, " Die Reindarstellung von Gasen "). After bubbling through water, it passed through potassium bisulphate, was dried by phosphoric oxide, and finally was frozen out in liquid air and fractionated twice.

Results.—Preliminary. Although the results of the investigation are not definitive and the kinetics of the reaction cannot yet be precisely formulated, the main characteristics of the process are sufficiently well established to justify description.

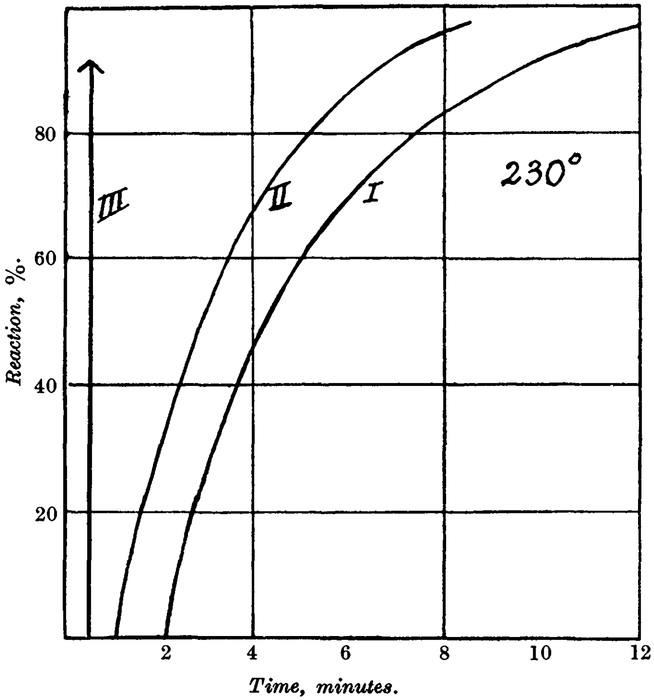
After earlier experiments had shown that hydrogen sulphide–oxygen mixtures sometimes exploded at about 220°, whereas at 190° there was scarcely any pressure change, the reaction was studied in the relatively wide vessel I. At first, the gases were used in the ratio $H_2S : 2O_2$, which would suffice for the oxidation of sulphur to trioxide, and, although " end-points " and analyses indicate that the reaction proceeds according to the equation $2H_2S + 3O_2 = 2H_2O + 2SO_2$, yet the excess of oxygen would appear to facilitate its progress.

The procedure was as follows : Hydrogen sulphide to the desired pressure was introduced into the previously evacuated reaction vessel, the temperature of which was constant to within 1° ; at the temperatures employed, *i.e.*, 200—300°, it was not noticeably decomposed over long periods. Oxygen was then introduced, the pressure read, and subsequent changes observed on the manometer. In all the experiments performed, an induction period, in which no change could be detected, succeeded the introduction of the oxygen. This period varied in extreme cases between a few seconds and some minutes. A very slight rapid increase of pressure (1—3 mm.) was then noticed, followed by either an explosion or a decrease in pressure which could be followed. The decrease in pressure consequent upon an explosion was usually approximately 52% of the original hydrogen sulphide pressure; that produced by the measurable reaction was not in general appreciably different, although occasionally it varied in an apparently anomalous manner, a fact which has made certain comparisons of data difficult. These variations in pressure decrease could be explained by the occurrence of varying amounts of some surface process in the different cases; and, in addition, subsidiary reactions, such as the interaction of hydrogen sulphide and sulphur dioxide or partial oxidation of the hydrogen sulphide itself, giving hydrogen and sulphur dioxide, might cause deviations from the general rule. Although a small quantity of sulphur was always formed in the oxidation, whether it occurred explosively or not, its amount did not seem to warrant the belief that it was the direct product of an important intermediate reaction. It is, of course, probable that a complicated series of changes occurs, each having different rates, the net effect of which produces the pressure change corresponding to the equation given above, *i.e.*, 50% of the original hydrogen sulphide pressure, but it seems likely that the slight difference from this theoretical pressure decrease is of subsidiary origin. This matter will be further examined.

The preliminary experiments in vessel I were carried out between

210° and 260°. At the lower of these temperatures explosion was never observed, and the measurable change, which occasionally did not occur at all, only proceeded slowly after an induction period of several minutes. At 220°, on the other hand, mixtures at a higher total pressure than about 450 mm. exploded, the induction period being somewhat erratic. The pressure above which explosion always occurred decreased with increasing temperature, falling from approximately 400 mm. at 220° to 210 mm. at 240° and 170 mm. at 260°.

FIG. 2.



I. 54 *mm.* H_2S, 115 *mm.* O_2.
II. 76 *mm.* H_2S, 160 *mm.* O_2.
III. 102 *mm.* H_2S, 200 *mm.* O_2.

The induction period appeared to decrease for any particular temperature with increase in pressure, and at any particular pressure with increase in temperature.

The " order " of the measurable reaction, as deduced from the influence of total pressure upon its rate, appeared to be low, even at pressures just below that required for ignition. Fig. 2 indicates this, the order here being rather more than unity.

The Measurable Reaction.

"*Total Order.*"—The preliminary experiments described above were repeated in a similar vessel III. The pressure above which explosion occurred at any given temperature agreed roughly with that previously found, though measurements were not strictly reproducible. Ignition could never be observed below 220°. The reaction which occurred below about 200° did not appear to be precisely that which occurred above this temperature. At the lower temperatures the decrease in pressure for complete reaction was considerably in excess of that noticed at the higher ones, was especially variable, and seemed to arise much more slowly. If disturbing wall effects are involved, it is very likely on the basis of our observations that they will become prominent in this region of lower temperature. The "order" of the measurable reaction which comes into prominence above about 200° in the region of pressure required for explosion appeared to increase from less than

TABLE II.

Temperature 261°.

(1) $\left.\begin{array}{l}\text{50 mm. H}_2\text{O}\\ \text{103 mm. O}_2\end{array}\right\}$

Time.	Press. decrease, mm.	%.
0′ 26″	expans.	—
0 30	0	0
0 48	6	22·2
1 2	10	37·0
1 31	15	55·5
2 18	20	74·0
3 0	23	85·1
3 30	24	89·2
4 30	26	96·3
10	27	100

(2) $\left.\begin{array}{l}\text{29 mm. H}_2\text{S}\\ \text{60 mm. O}_2\end{array}\right\}$

Time.	Press. decrease, mm.	%.
0′ 50″	expans.	—
1 25	2	13·3
1 50	4	26·6
2 3	5	33·3
2 18	6	40·0
2 38	7	46·7
3 8	8	53·3
3 40	9	60
5	11	73·3
8	13	86·7
20	15	100

(3) $\left.\begin{array}{l}\text{28 mm. H}_2\text{S}\\ \text{55 mm. O}_2\end{array}\right\}$

Time.	Press. decrease, mm.	%.
1′ 0″	expans.	—
2 45	6	40
5	10	66·7
7	12	80
11	13·5	90
14	15	100

Temperature 240°.

(1) $\left.\begin{array}{l}\text{74 mm. H}_2\text{S}\\ \text{144 mm. O}_2\end{array}\right\}$

Time.	Press. decrease, mm.	%.
1′ 50″	expans.	—
1 55	0	0
2 4	5	11·9
2 25	10	23·8
2 52	15	45·8
3 30	20	47·6
4 22	25	69·6
7 5	35	93·4
10 30	40	95·2
13 0	41	97·8
18 0	42	100

(2) $\left.\begin{array}{l}\text{50 mm. H}_2\text{S}\\ \text{103 mm. O}_2\end{array}\right\}$

Time.	Press. decrease, mm.	%.
1′ 0″	expans.	—
4 15	0	0
4 31	3	11·5
4 48	5	19·2
5 40	10	38·4
6 50	15	57·6
8 50	20	76·8
11 20	24	92·3
12 25	25	96·1
14 45	26	100

unity at 220° to rather more than two at 280°, although the somewhat variable rate of the process did not enable a precise value to be obtained. Table II gives examples of the course of the reaction at different temperatures and pressures, and Table III summarises some evaluations of the order, in the estimation of which, by computing the effect of total pressure upon the period of half-change, or by comparing the ratio $t_{3/4}$ to $t_{1/2}$, the values of these respective times were measured from an origin at the end of the induction period when the net pressure change was zero. This procedure may not be quite legitimate, depending really upon what is occurring during the induction period, but for our present purpose it is adequate, and will be employed whenever periods of half-change are to be compared.

TABLE III.

	Pressure, mm.				
Temp.	H_2S.	O_2.	Induction period.	$t_{\frac{1}{2}}$.	Order.
220°	200	394	1′ 30″	5′ 0″	0·45
	103	209	1 35	3 25	
222	157	306	1 40	4 25	1·3
	104	204	2 20	3 55	
230	80	161	1 57	2 0	2·4
	60	123	2 0	3 10	
232	101	205	1 30	1 30	2·1
	50	107	1 52	3 37	
240	75	144	1 28	1 49	1·45
	50	102	3 40	2 12	
261	50	103	0 30	0 50	2·5
	29	60	1 10	1 40	
	28	55	1 10	2 0	
280	36	73	0 30	0 46	2·1
	20	41	1 15	1 25	

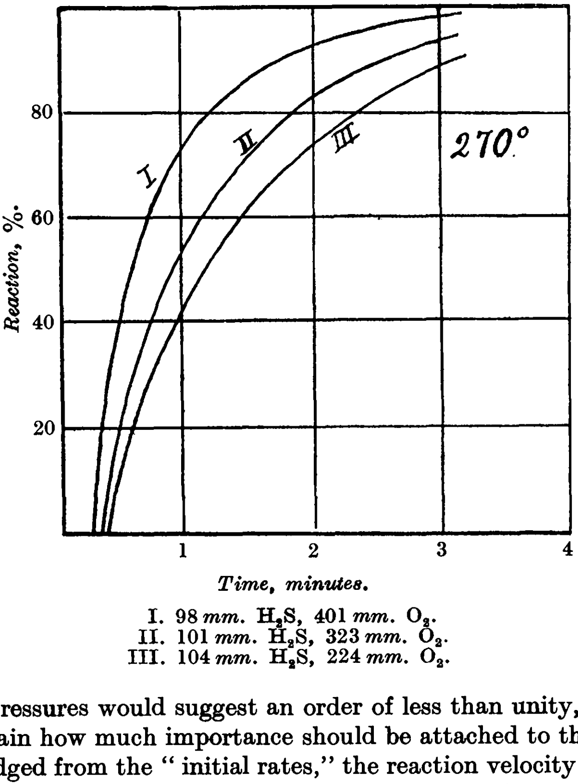
Influence of Separate Reactant Concentrations.—In the earlier experiments the separate influence of the respective reactants upon the rate of the reaction was not in general investigated, although a few experiments indicated that excess of oxygen accelerated the reaction markedly and often led to explosions which would otherwise not have occurred. This was examined in the vessel VIII. In measurements of this kind it is necessary always to have a volume of oxygen at least twice as great as that of hydrogen sulphide; the end-point in these circumstances does not vary appreciably. Fig. 3 shows the course of three experiments from which the accelerating effect of oxygen is apparent.

The experiments in vessel VIII are probably more trustworthy, and are summarised in Table IV, which shows, for differently constituted mixtures at different pressures and temperatures, (1) the period of half-change and (2) the induction period for each run. Here again the half-value periods are measured from an instant at the end of the induction period.

Although detailed study of these results discloses many anomalies, yet several facts are clear : the time for half-change at any temperature and total pressure always decreases as the proportion of oxygen increases, and always increases as the proportion of hydrogen sulphide increases. The total order of the process as measured from the influence of total pressure upon $t_{\frac{1}{2}}$ would appear to vary between 1 and 2 as a rule, attaining the higher values at the higher temperatures and pressures. At the lower temperatures the data at higher pressures would suggest an order of less than unity, but it is not certain how much importance should be attached to this result.

FIG. 3.

Effect of oxygen.



I. 98 *mm.* H_2S, 401 *mm.* O_2.
II. 101 *mm.* H_2S, 323 *mm.* O_2.
III. 104 *mm.* H_2S, 224 *mm.* O_2.

As judged from the " initial rates," the reaction velocity seems to be roughly proportional to the second power of the oxygen concentration, and is either independent of, or inversely proportional to a small power of, the hydrogen sulphide concentration. The latter alternative provides an explanation for the relatively low total order.

If it be assumed that the reaction velocity is given by $k[H_2S]^x[O_2]^y$, typical values of x and y are given in Table V.

TABLE IV.

Press., mm., $H_2S : O_2$. Temp.	50 : 100.	50 : 150.	50 : 200.	50 : 300.	75 : 200.	100 : 200.	100 : 300.	100 : 400.	150 : 300.	200 : 400.
200°	7′ 25″, 2′ 0″					8′ 26″, 45″		†*ca.* 6′ 0″		*ca.* 18′, (?) 1′ 0″
240						3 30 , 40 3 30 , 52			*ca.* 12′, 30″	10′ 0″, 35″
246	2 11 , 55			43″, 30″		2 6 , 30	1′ 25″, 25″	36″ 22″	2′ 49″, 25	3 26 , 10 5 , 20
250	2 21 , 1 10 2 20 , 50		56″. 24″	32 , 16	1′ 9″, 30″	2 27 , 35 2 0 , 25	43 , 25	29 , 14	1 50 , 28	3 45 , 20
260						1 12 , 35			1 5 , 25	*, 12 *, 12 *, 10
270	1 15 , 45	35″, 25″	30 , 15			54 , 23		*, 7	1 17 , 17	*, 7
280	1 30 , 15 1 0 , 30 54 , 32 1 15 , 18 58 , 32 50 , 12 52 , 27	30 , 15	15 , 10 17 , 15 15 , 14 25 , 12	50 : 400. *, 3″ *, 3″	28 , 14	48 , 19 38 , 17 39 , 15 40 , 12	24 , 8 24 , 10 23 , 10	*, 2, * * * * *	*, 10 *, 8 *, 10 *, 5	*, 5 *, 3 *, 2 *, 2 150 : 400. *, 2″

* Indicates explosion.

† At $H_2S = 100$ mm.; $O_2 = 500$ mm.

TABLE V.

Temp.	Pressure, mm. H$_2$S.	O$_2$.	Initial rate, mm. per sec.	x.	y.
250°	50	100	0·13		1·26
	51	201	0·31		1·1 } 1·2
	50	304	0·45		
270	53	110	0·24		1·55
	53	150	0·42		1·2 } 1·4
	53	219	0·625		
280	99	200	0·60		} 1·8
	100	300	1·26		
250	50	200	0·31		
	75	201	0·33	0	
	100	200	0·24	−0·4 } −0·4	
250	100	400	0·91	−0·8	
	201	400	0·5		
280	51	202	0·68		
	75	201	0·72	0·14	
	100	202	0·60	−0·65 } −0·14	

The Influence of Nitrogen.—The effect of adding nitrogen to the reaction mixture was also studied, although for experimental reasons it could not be used in as great a proportion as exists in air. The measurable reaction appears to be slightly retarded under these conditions, the end-point not being affected (see Table VI).

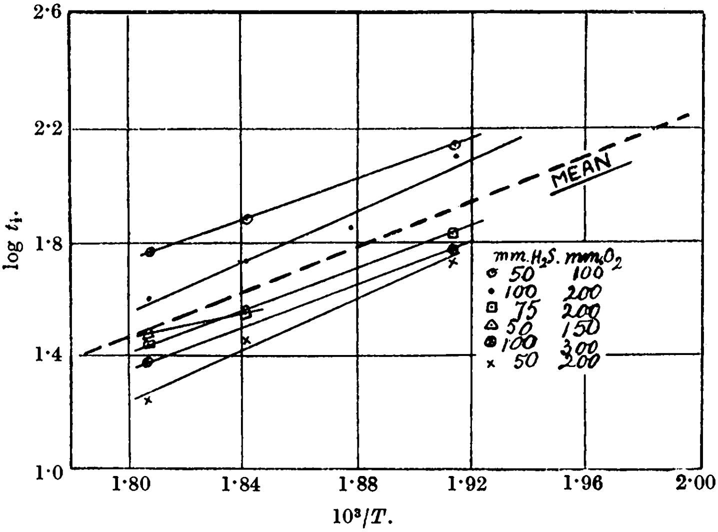
TABLE VI.

Temp.	Pressure, mm. H$_2$S.	O$_2$.	N$_2$.	Induction period.	$t_{\frac{1}{2}}$.
230°	91	184	—	1′ 30″	1′ 26″
	90	180	—	1 30	1 30
	92	187	195	1 34	3 0
	90	180	400	2 40	4 0
270	50	98	—	0 30	0 55
	50	103	205	0 35	1 13
	49	99	400	0 45	1 3
290	31	64	—	0 30	0 28
	31	60	—	0 30	0 30
	31	62	152	0 38	0 42
	31	60	300	1 30	1 15

Temperature Coefficient.—An estimate of the temperature coefficient, and of the heat of activation of the process, has been made, although if a chain process be involved it is, of course, difficult to attach any precise significance to these quantities. The ease of explosion at the higher pressures in the wider vessel makes it impossible to obtain sufficient data here, but in the narrower vessels VIII and II averages can be made. The results in the former case are shown in Fig. 4. The values obtained in the two cases for the heat of activation are 18,000 and 17,600 cals. respectively, and, although extensive averaging makes this close agreement fortuitous, yet there is no doubt as to the order of magnitude.

Influence of the Vessel Dimensions.—Decisive evidence as to the nature of the measurable reaction was obtained by studying it in narrow and in packed vessels (II, IV, and VII). In vessel II no explosion of hydrogen sulphide and oxygen could be observed at 300°—some 80° above the lowest explosion temperature in the wider vessel. At 220° as a rule hardly any change could be noticed with total initial pressures of 300 or 600 mm., although occasionally a slow reaction did occur. At higher temperatures and pressures, the decrease in pressure accompanying complete reaction was rather less than that in the wider vessel, *i.e.*, approximately 49% of the original hydrogen sulphide pressure. At all temperatures, narrowing the vessel considerably diminished the reaction velocity. The majority of the results are summarised in Table VII, in which they are placed alongside those in the wider vessels. It is noteworthy that the slight increase of pressure after the induction period, which was almost always observed in the wider vessels, was usually absent here.

FIG. 4.



It will be seen from this table that the reaction occurring in the narrower vessel has an order which, though difficult to estimate, is low, and lies between 1 and 2. The frequent failure to react at the lower pressures is not, however, accounted for on this basis.

Table VII also gives values of the induction periods (I.P.) observed in the various cases.

TABLE VII.

Comparison of periods of half-life and of induction periods in vessels II (*narrow*) *and* III (*wider*).

— Indicates no appreciable reaction. * Indicates explosion.

	50 mm. H_2S; 100 mm. O_2.				100 mm. H_2S; 200 mm. O_2.				200 mm. H_2S; 400 mm. O_2.			
	Vessel II.		Vessel III.		Vessel II.		Vessel III.		Vessel II.		Vessel III.	
Temp.	$t_{\frac{1}{2}}$.	I.P.	$t_{\frac{1}{2}}$.	I.P.	$t_{\frac{1}{2}}$.	I.P.	$t_{\frac{1}{2}}$.	I.P.	$t_{\frac{1}{2}}$.	I.P.	$t_{\frac{1}{2}}$.	I.P.
220°	—	—	—	—	—	—	3′ 0″ 3 20 3 40 3 55	2′ 0″ 2 0 3 30 2 20	—	—	* * *	58″ 1′ 0 1 0
240	—	—	1′ 45″ 2 7 2 15	1 5″ 4 15 3 10	5′ 0″ 6 25	1′ 0″ 1 0	*	46	2′ 30″ 3 0 3 0 3 39 4 13	45″ 46 1′ 0 1 0 35	*	16
260	2′ 15″ 4 35	3′ 0″ 1 25	50 *	30 25	1 28 1 30 2 6	52 55 41	* * * *	10 11 15 16	1 24 1 33	21 35	* *	5 5
270	—	—	50	30	1 0	17	*	10	1 2 1 3 1 6 1 24	15 15 15 30	*	5
280			31 * *	20 18 29			*	8	1 0 48	10 20	*	3
298	1 25	25	*	20	28 37 38	10 7 25	*	5			*	2

The Explosive Reaction.

Table VIII summarises the average of the ignition pressures at the various temperatures in the wider vessels, from which it is possible to test the validity of the relationship, $\log p/T = A/T + E$, derived by Semenov for gaseous explosions, and tested by Sagulin for various explosion mixtures (*Z. physikal. Chem.*, 1928, *B*, **1**, 275). As Fig. 5 shows, the present data conform closely to this relationship, the value of A being approximately 2400.

FIG. 5.

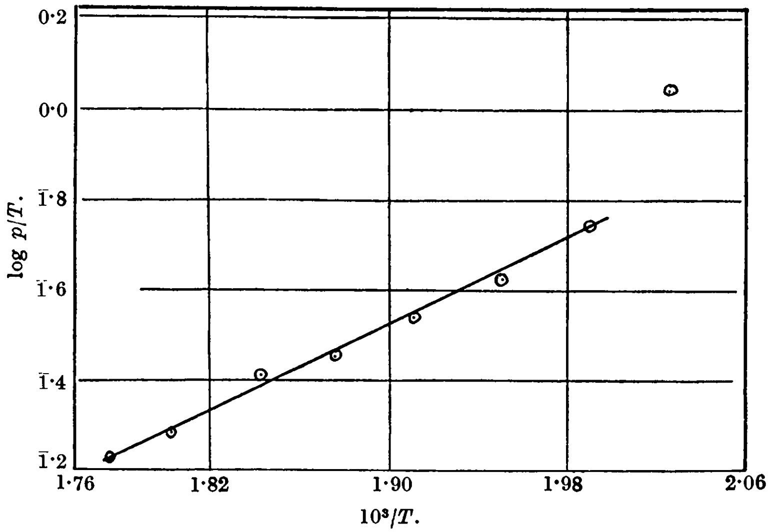


TABLE VIII.

Temp.	Abs. temp., T.	Explosion pressure, p mm.	$10^3/T$.	$\log p/T$.
210°	483°	>600	2·070	0·0942
220	493	500	2·028	0·0061
230	503	270	1·988	$\bar{1}$·7299
240	513	215	1·949	$\bar{1}$·6222
250	523	190	1·912	$\bar{1}$·5602
260	533	150	1·876	$\bar{1}$·4493
270	543	140	1·842	$\bar{1}$·4114
280	553	110	1·808	$\bar{1}$·2986
290	563	96	1·776	$\bar{1}$·2318

The exact interpretation of this result in the light of the facts already outlined is postponed until more precise data about the reaction have been obtained.

Like the measurable reaction, the explosion is also inhibited by nitrogen, to such an extent that it often gives way to a measurable combination. The effect, however, is not very marked. These experiments are peculiar in that, whereas the end-point in a measurable change is independent of the concentration of the diluent, on the other hand, the decrease in pressure accompanying an explosion is always considerably diminished by the presence of nitrogen, falling to some 42% of the original hydrogen sulphide pressure and even less in some cases. It is not yet certain whether this phenomenon is to be explained by a combustion of only part of the hydrogen sulphide or by the occurrence of different processes in the two cases; but later considerations (see p. 1824) favour the former explanation. Typical examples of the results with nitrogen are given in Table IX.

TABLE IX.

The influence of nitrogen (" wide " vessel III).

Temp.	Press. (mm.) of			Result.*	Press. decr., % of H_2S.
	H_2S.	O_2.	N_2.		
250°	68	137	—	E	51
	70	142	—	,,	50
	70	148	204	,,	42
	70	137	201	M	55
	85	169	201	E	42
	86	176	298	,,	43
280°	29	59	—	M	54
	47	96	—	,,	53
	53	101	—	E	50
	51	104	99	,,	42
	52	108	191	M	54
	50	97	303	,,	52
	70	146	297	E	40
270°	58	98	—	M	60
	49	99	205	,,	58
	50	103	400	,,	55
	73	146	—	E	52
	70	141	193	,,	42
	70	143	353	,,	36
290°	31	64	—	M	52
	30	60	300	,,	52
	100	205	—	E	53
	100	197	200	,,	46

* E = explosion; M = measurable reaction.

Experiments were also made in the packed vessels IV and VII; no explosion could be observed in either vessel at 300°. At any given temperature and pressure, the reaction proceeded somewhat faster than in vessel II, but much slower than in vessels I, III, or V. A slight increase of pressure was observed after the introduction of the hydrogen sulphide into the tubular-packed vessel. This might conceivably have been caused by a partial catalytic decomposition of the hydrogen sulphide, but its effect on the process as a whole does not appear to be important.

A Phenomenon of " Successive Explosions."—That the hydrogen sulphide really inhibits the reaction is demonstrated in a striking way by the following discovery. It has already been stated that, in the widest vessels used, complete explosive combustion of the hydrogen sulphide occurred, provided the requisite pressures were used, above about 220°, whereas in the narrowest vessel no ignition could be observed at 300°. In vessel VIII ignition could be observed above about 260°, although not as a rule below about 270°, but under these conditions the explosion was never complete. In an explosion the hydrogen sulphide was oxidised to steam and sulphur dioxide, but all of it was not burnt in this way in any one explosion. In order to complete the combustion, one of two alternatives ensued after the primary ignition : either, after an appropriate induction period, a further explosion occurred, or, again after an induction period, a rapid measurable reaction was noticed, which proceeded in the same manner as it would have done had the products of the first explosion not been present. Under the proper conditions (primarily, increase in the proportion of oxygen) it has been possible to observe as many as five explosions of the same mixture, each preceded by an induction period which lengthened as the mixture was exhausted.* Examples of the phenomenon are given in Table X, in which M. R. denotes measurable reaction, and A. P. D. denotes additional pressure decrease.

TABLE X.

(1) Temp. 280°. H_2S 100 mm., O_2 400 mm.

Time.			Press. decr., mm.
0′	3″	Exploded	25
0	8	Exploded again	15
0	15	Exploded again	10
		Total	50

(2) Temp. 280°. H_2S 196 mm., O_2 404 mm.

Time.				Press. decr., mm.
0′	5″	Exploded		25
0	15	Exploded again		16
0	20	M.R. starts		
0	50	A.P.D.	10	
1	27	,,	20	
2	18	,,	30	
3	20	,,	40	
5	35	,,	55	55
			Total	96

(3) Temp. 280°. H_2S 146 mm., O_2 304 mm.

Time.				Press. decr., mm.
0	8	Exploded		34
0	12	M.R. starts		
0	37	A.P.D.	5	
1	33	,,	10	
8	0	,,	19	
20		Stopped at	42	42
			Total	76

It is clear from examples (1) and (2) in this table that the hydrogen sulphide must, to some extent at least, function as an interrupter of the reaction chains, and the occurrence of these successive incomplete explosions in the relatively narrow vessel further substantiates

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* The suggestion that the phenomenon of successive explosions here described arises by virtue of temperature gradients in the vessel *A* is for a variety of reasons considered improbable. The temperature of the furnace *B* was constant, except at the extreme ends, to 1—2° ; temperature gradients of this magnitude could hardly give rise to the effect observed, which is not in general noticed in other reactions of a similar nature examined in the same way. Further, the interpretation of the phenomenon seems a perfectly satisfactory one, in agreement with other characteristics of these chain reactions. The rise in temperature registered consequent upon an explosion was about 1°.

the original result that the reaction chains are broken at the vessel walls. We have here, furthermore, a probable interpretation of the influence of nitrogen previously mentioned, when it reduces the pressure decrease consequent upon explosions in the relatively wide vessels. It seems that the nitrogen, by breaking the reaction chains, behaves as a deactivator in the same way as, but less efficiently than, the vessel walls or the hydrogen sulphide itself. It should, however, be remembered that, whereas the deactivation by the wall or by nitrogen would in all probability be a physical process, interruption of the chains by the hydrogen sulphide might well be due to some chemical reaction.

The Induction Period and General Discussion.

For a consideration of the mechanism of the whole process, it is essential to discover the significance of the induction period. Different samples of the reactants appeared to have no noticeable influence upon this, and for this reason its explanation as a period during which some inhibiting impurity is being removed (as in the case of amino-compounds in the combination of hydrogen and chlorine) is considered improbable. The occasional variability observed in this connexion in the earlier experiments suggested that it involved some surface process. In a few experiments the order of introduction of the hydrogen sulphide and the oxygen was reversed, but no significant change resulted in either the induction period or the subsequent reaction. This result makes the alternative idea more probable, namely, that the process occurring in the initial stages after mixing is not fundamentally dependent upon the surface, since a change in the order of introduction would be expected to affect the rate at which adsorption equilibria are set up. But there is other evidence for the belief that the process occurring during the induction period takes place in the gas.

Table IV shows how the induction period varies with temperature, pressure, and the composition of the mixture in vessel VIII. It is considerably shortened by increasing the proportion of oxygen in the mixture and somewhat lengthened by increasing that of hydrogen sulphide. For a given hydrogen sulphide–oxygen ratio, it is always noticeably decreased by an increase of the total pressure. The data already given show that addition of nitrogen lengthens it, and to a greater extent as the proportion of nitrogen increases. Narrowing the vessel acts in the same manner. Thus it seems almost certain that the process occurring during the induction is a gaseous one.

It is difficult to state whether the process occurring is of precisely the same nature as the subsequent chain reaction. One fact militates against this suggestion, namely, that in those cases where an increase in the total pressure causes an increase in the time for half-change, the induction period is not lengthened but markedly shortened by the increase in pressure.

The slight increase in pressure often observed after the induction period might conceivably be caused by a slight heating of the mixture consequent upon some primary reaction, but no change in temperature was recorded by the thermometer. Indeed, a rapid decrease of pressure in the initial stages of the reaction might be partially discounted by such a rise in temperature, and therefore the observed fall of pressure at the start might be rather illusory. How far the nature of the induction period complicates the matter is a question for further investigation.

The experiments in vessels of relatively large dimensions, whilst suggesting that the measurable change involves the same process as the explosion and passes continuously into the latter on increase of pressure, do not entirely preclude another interpretation of the facts. The relatively low order of the measurable process might have been thought to imply a surface reaction rather than one in the gas, involving reaction chains. The occurrence of explosion in a pressure region of predominantly surface reaction could then have been accounted for by supposing that reaction chains of the branching type are successfully propagated at a certain pressure by reaction centres which leave the wall. The somewhat erratic nature of the induction period preceding the explosion might appear at first sight to favour this idea, and the fact that for no apparent reason mixtures at the lower temperatures occasionally failed to react at all might be deemed to substantiate it.

The results obtained by using the different reaction vessels, however, make the conception of the measurable low-order reaction between hydrogen sulphide and oxygen as a surface reaction in entirety impossible, for the reaction is much retarded rather than accelerated by an increase in the surface exposed to the reacting gases. If a small percentage of the total reaction takes place on the surface, the true retardation of the non-surface process by the packing is all the greater. To regard it as a chain reaction which passes continuously into explosion would appear most reasonable. In this case the total order of the reaction would seem rather lower than that usually found for chain reactions. This result is, however, explained in that the reaction velocity is lowered by an increase in the hydrogen sulphide concentration. That nitrogen inhibits the progress of the reaction is not at all contrary to this idea, since it could behave as a physical deactivator of products carrying large amounts of energy.

Thus the general picture of the process appears to be roughly as follows. Some undetermined process occurs, probably in the gas phase, during the induction period; sufficient active products of some kind have by that time been produced to start a chain reaction; the propagation of the chains is favoured by impact of the products of an elementary change with oxygen, and collision with hydrogen sulphide molecules often interrupts the chain. From the nature of the experiments so far performed it is impossible to state the precise nature of the active products, radicals, etc., involved in the chain, nor is it possible to conjecture whether the hydrogen sulphide breaks the chain by reacting with hydrogen atoms, or sulphur atoms, or any other product which might be suggested. Further investigations of this and other analogous reactions are being undertaken with this problem in mind, but it is clear that any hypothesis must take into account the above-described effect of oxygen and hydrogen sulphide on the rate, and no differential equation has yet been found to connect the rate of reaction with the concentrations of these substances.

The measurable reaction appears to pass continuously into ignition as the pressure increases, *i.e.*, when the rate of loss of heat is not large enough to balance its rate of production.

The reaction is now being studied in silica vessels, in the hope that diminished variability will yield more conclusive data. The photochemical reaction is also being studied.

Summary.

The reaction between hydrogen sulphide and oxygen is a chain reaction at temperatures in the vicinity of the ignition points, *i.e.*, 220—300°. The propagation of chains appears to be favoured by excess of oxygen and diminished by excess of hydrogen sulphide.

The reaction is very markedly retarded by a decrease in the dimensions of the vessel in which it is occurring. It is concluded that the chains are interrupted by a physical deactivation at the wall and probably by a chemical reaction of activated products with hydrogen sulphide. Nitrogen also appears to retard the reaction by breaking reaction chains.

A peculiar phenomenon of successive incomplete explosions of the same reaction mixture which can be observed under certain conditions has been described.

The reaction or explosion is preceded by an induction period in which a process is involved which would appear to occur "in the gas."

The heat of activation of the principal process is of the order of 18,000 cals.

The conditions for explosion seem to comply with a relationship discussed by Semenov.

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