CCCLXXIX.—The Conditions of Reaction of Hydrogen with Sulphur. Part IV. The Direct Union of Oxygen and Sulphur.

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In two papers recently published on the reaction of hydrogen with sulphur, and its catalysis by oxygen (this vol., pp. 695, 1689), evidence was furnished suggesting that the work done in detaching a molecule of hydrogen sulphide adsorbed on the surface of the liquid sulphur was equal to that done in subliming a molecule of S_2 , and it followed from the theoretical considerations there developed (*loc. cit.*, p. 1700) that an equal amount of work should be expended in removing a molecule of sulphur dioxide similarly adsorbed on the

It was therefore considered of interest to examine the surface. reaction of oxygen and sulphur with a view to test if possible the theoretical prediction, and the results of this investigation are given in the present communication. Whilst the reaction proved to be more complicated than had originally been expected, and developed a very interesting feature when the influence of pressure was studied, the predictions of the theory advanced in the previous papers have received striking confirmation. Thus it was predicted that the reaction of oxygen and sulphur at the surface of the latter would have a temperature coefficient of 1.48. Actually it has been found that oxygen combines with sulphur by way of two independent simultaneous surface reactions, one of which has the predicted temperature coefficient of 1.48, whilst the other has a temperature coefficient of 1.77. The nature of this second surface reaction is discussed at the end of this paper.

The reaction of oxygen and sulphur has been studied by Bodenstein and Caro (Z. physikal. Chem., 1909, 75, 30), who drew the conclusion that it is practically completely confined to the surface of the sulphur. No trustworthy data were, however, obtained on the influence of pressure and temperature on the reaction, factors of prime importance in obtaining an insight into the mechanism of the reaction.

EXPERIMENTAL.

The experimental arrangement adopted was the dynamic flow method used in the investigation of the reaction between hydrogen and sulphur (Part I, *loc. cit.*). This method has proved itself extremely trustworthy so long as great care is taken in keeping constant the rate of flow of gas through the sulphur bulb, and the temperature of the bath. In the first place, air, freed from carbon dioxide and water vapour, was passed through the sulphur bulb, and the variation in the velocity of sulphur dioxide formation with temperature studied between the limits of 235° and 385° .

The effect of variation of oxygen pressure was next investigated at the three temperatures 245° , 265° , and 285° by passing various oxygen-nitrogen mixtures of known concentration over the liquid sulphur and measuring the rate of sulphur dioxide formation.

Finally, by using bulbs of different dimensions and adding varying quantities of sulphur, the effect of surface extent was investigated.

The velocity of formation of sulphur dioxide was determined by allowing the effluent gases to pass at constant flow rate through a known volume of standard iodine solution, the time taken to discharge the colour of the latter being observed, with the help of starch solution, added as indicator as the end-point was approached. To establish equilibrium in the apparatus, it was generally found $5 \circ 2$

necessary to allow the gas to stream through the reaction chamber maintained at the desired temperature, for about two hours, the rate of gas flow being kept constant. At the end of this interval, the time of discharge of the iodine colour became constant, and from it the rate of production of sulphur dioxide in the reaction bulb could be calculated, since at equilibrium the weight of the latter carried over by the gas stream per second, and absorbed by the iodine, is equal to its rate of formation in the reaction chamber. The strength of iodine solution employed varied from 10 c.c. of N/1000iodine, diluted to 200 c.c., to 10 c.c. of N/20-iodine, similarly diluted, according to the rate of sulphur dioxide formation to be measured. In no case was the time of discharge allowed to fall below six minutes, and if it did so, stronger iodine solutions were taken.

The efflowing gases contained in some cases a considerable percentage of sulphur dioxide, and it was necessary to correct for the pressure in the bulb according to the formula

$$P = p - \frac{63 \times 10^6 x}{136 + 126 \times 10^4 x},$$

developed in Part II of this series (*loc. cit.*), where P =actual oxygen pressure in the reaction chamber, p = pressure of oxygen in gas flowing into the reaction chamber, and x =rate of formation of sulphur dioxide in grams per second.

In Table I are given the results of the investigation of the effect of temperature on the rate of sulphur dioxide formation. It is shown below that the velocity of sulphur dioxide formation is proportional to the oxygen pressure, and accordingly, in column 4, the observed velocities, in column 2, have been corrected for the lowering of oxygen pressure in the reaction bulb, being scaled up

TABLE I.

Influence of Temperature.

Pressure of oxygen in inflowing gas -0.21 atm. (air). Rate of flow of gas -136 c.c. per hour. Reaction bulb I. Internal radius 2.6 cm.

	Obs. velocity	Pressure of	Corrected			
Tem-	of SO, forma-	oxygen in	velocity.		Reciprocal	
per-	tion. Gms.	reaction bulb.	Gms. per	Temp.	of obs.	$\log_{10}SO_2$
ature.	per sec. $\times 10^8$.	Atmospheres.	sec. $\times 10^8$.	coeff.	temp.	velocity.
235°	34.2	21.0	$34 \cdot 2$	1.67	0.001969	-6.4660
245	56.7	20.75	57.3	1.61	0.001931	-6.2418
265	$145 \cdot 8$	20.3	150.8	1.69	0.001859	-5.8220
285	$364 \cdot 2$	19.3	$395 \cdot 9$	1.69	0.001792	-5.4024
305	860.0	17.3	1049	1.45	0.001730	-4.9792
325	1543	14.7	2204	1.17	0.001672	-4.6568
345	1931	13.4	3017	1.19	0.001618	-4.5204
365	2232	12.4	3781	1.12	0.001567	-4.4224
385	2387	11.9	4217	1.00	0.001520	-4.3750

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TABLE II.

Influence of Pressure.

Rate of flow of gas 136 c.c. per hour. Reaction bulb I. Internal radius 2.6 cm. Temperature.

	2	45°.	26	35°.	285°.	
Pressure of inflow- ing gas.	Pressure of oxygen in bulb. % Atm.	Vel. of SO_2 formation. Gms./sec. $\times 10^8$.	Pressure of oxygen in bulb. % Atm.	Vel. of SO_2 formation. Gms./sec. $\times 10^8$.	Pressure of oxygen in bulb. % Atm.	Vel. of SO ₂ formation. Gms./sec. $\times 10^8$.
7	6.9	15.72	70		/0	,
10	•••		9.7	64·0	$9 \cdot 2$	179.0
21	20.7	56.7	20.3	145.8	19.4	$364 \cdot 2$
34			33.0	228.9		
42.6	42.1	112.3	41.3	288.3	39.5	725.6
58.1	57.5	129.5	56.6	342.5		
59.4					$55 \cdot 4$	907·0
78.6	78.0	$146 \cdot 1$	77.7	420.7	73.8	1111
99	98.2	168.5	97.0	484.8	Sulphur vapour * exploded.	

* Above a pressure of 0.75 atm. at 285° the sulphur vapour and oxygen in the bulb exploded with considerable violence, and at the same time a blue flame began to play over the sulphur. These explosions sometimes occurred at lower temperatures and pressures and upset completely the equilibrium in the bulb, necessitating restarting of the experiment.

TABLE III.

Effect of Surface.

Rate of flow of gas -136 c.c. per hour. Pressure of oxygen -0.21 atm. (air).

Dimensions of Vessels. Reaction vessel I: Internal radius 2.6 cm. Total area of glass surface including H_2 delivery tube 92 sq. cm. Reaction vessel II: Internal radius 3.96 cm. Total area of glass surface including H_2 delivery tube 220 sq. cm.

No. of reaction	Weight of sulphur in bulb.	Area of liquid sulphur surface.	Total in- ternal area (glass + liquid sulphur).	Velocity of SO ₂ formation. Grams per	Velocity.
vessel.	Grams.	Sq. cm.	Sq. cm.	sec. $\times 10^{6}$.	Total area.
I	1	4.5	92	148	1.61
11	1.8	7.06	219.6	363.8	1.66
II	4.5	11.3	219.4	360.4	1.64
II	8.8	16.0	219.3	358.9	1.63
II	47.4	$32 \cdot 1$	211.6	350.8	1.66
II	120.8	45.3	197.7	346.3	1.75

to the oxygen pressure of the inflowing gas, -0.21 atm. This gives a series of comparable figures which can be used for the calculation of the temperature coefficients of the reaction shown in column 5, which will be seen to remain sensibly constant between the temperatures 235° and 305°. Above this latter temperature, however, they rapidly diminish, suggesting that some disturbing factor here

becomes of importance to the course of the reaction. This disturbing action on the sulphur dioxide reaction was traced to the secondary formation of sulphur trioxide, which was found to become apparent at temperatures above 305°. Thus, at 305°, no trace of sulphate



formation could be detected on collecting the effluent gases in caustic soda solution, for half an hour, and testing with barium chloride solution, whereas similar tests carried out at higher temperatures always indicated the presence of sulphate in rapidly increasing quantity as the temperature was raised. No quanti-

tative measurements were carried out on the production of sulphur trioxide at these higher temperatures (> 305°), all future measurements on the sulphur dioxide reaction being carried out between the temperatures 235° and 305° , where the secondary oxidation to sulphur trioxide, if it occurs at all, is too insignificant to cause any appreciable error.



In Fig. 1, the logarithms of the velocities are plotted against the reciprocal of the absolute temperatures, the dotted curve indicating the theoretical sulphur dioxide reaction if we imagine secondary sulphur trioxide formation to be absent. It will be seen that below 305° the relationship is approximately linear, corresponding to a nearly constant temperature coefficient.

The data of Table II, showing the effect of oxygen pressure on the sulphur dioxide reaction, are graphed in Fig. 2, from which it will be seen that whilst the velocity of the reaction is in all cases pro-

portional to the oxygen pressure, very marked breaks occur in the straight lines at the oxygen pressure of 0.413 atmosphere, without any appreciable variation for the three temperatures investigated. These breaks, which formed a most unexpected feature of the investigation, can only be taken as evidence of the heterogeneity * of the hitherto apparently homogeneous sulphur dioxide surface Each of the broken straight-line curves may be split up reaction. into two straight lines as has been done in Fig. 3, along one of which the reaction velocity finally reaches a maximum constant value with increase of oxygen pressure, whilst along the other it continues to increase, in a linear manner with pressure.

The figures of Table III show beyond all doubt that the total reaction is a surface reaction to such an overwhelming extent that any gaseous reaction is entirely negligible. Thus the ratio of velocity to total area is the same for flasks of widely different dimensions, whilst the velocity is independent of the weight of sulphur present (except in so far as it decreases the extent of total surfaces), and of the area of the liquid sulphur surface. In this connexion, it should be mentioned that sublimed sulphur contains much absorbed sulphur dioxide and hydrogen sulphide, and that until this is removed by continually heating the sulphur to ca. 300° in a vacuum figures independent of the weight of sulphur in the bulb will not be obtained. When these preliminary precautions were taken, reproducible results were always obtained.

It follows therefore that the heterogeneity of the sulphur dioxide formation must be confined to the surface and we are forced to the conclusion that the formation of sulphur dioxide can take place on the surface of the sulphur and of the vessel by way of two independent reactions, whilst the ratio in which the sulphur dioxide formation is divided between these two reactions must be independent of the nature of the surface-that is, whether liquid sulphur or glasssince variation in the liquid surface produces no appreciable change in the total quantity of sulphur dioxide formed. This fact points to the probability of a complete liquid film covering the whole of the glass surface, and identical in composition with the surface film of the liquid sulphur itself. This liquid sulphur film made itself apparent by the interference colours developed on the walls of the reaction vessel when it was rapidly withdrawn from the heating bath, and in the dendritic growth of sulphur crystals which formed on the walls as they cooled.

^{*} The term heterogeneity is not used here, and in what follows, in the sense usually implied in catalysis, but rather as indicating that the sulphur dioxide reaction observed in the surface of sulphur is not simple, but the sum of two (or more) simple surface reactions.

For convenience of further discussion we shall designate the two independent surface reactions by the letters A and B, "A" referring to that reaction which reaches a constant maximum velocity with increase of pressure.



TABLE IV.

Pressure of oxygen	Ve form Gms.	locity c nation a . per sec	of SO ₂ t 245°. . $\times 10^{8}$.	Ve form Gms.	locity of nation at per sec.	${{{\rm SO}_2}\atop{{ m 265}^\circ}.}\atop{ imes 10^8}.$	Vel form Gms.	locity of ation at per sec.	${{{\rm SO}_2}\atop{{\rm 285}^\circ}.}\atop{ imes 10^8}.$
in reac-	Total			Total			Total		
bulb.	reac.	A reac.	B reac.	reac-	A reac-	B reac.	reac.	A reac.	B reac.
Atm.	tion.	tion.	tion.	tion.	tion.	tion.	tion.	tion	tion.
0.20	54	31	22	140	71	69	367	150	217
0.40	$10\bar{6}$	63	44	280	$14\tilde{1}$	139	731	300	431
0.60	131	65	66	353	145	208	959	312	647
0.80	153	65	88	423	145	278	1174	312	862
1.00	175	65	110	492	145	347	1393	312	1081
								5 o*	

The A and B reactions have been plotted in Fig. 3, for temperatures 245°, 265°, and 285°, by splitting the corresponding composite curves of Fig. 2. This was done by producing the upper segments of the curves of Fig. 2 backward to cut the ordinate, and measuring the slopes of the lines so produced. Straight lines of the same slope drawn to pass through the origin gave the B reaction curves of Fig. 3. The A reaction curves were then obtained by subtracting the B curves from the corresponding composite curves of Fig. 2.

The data from the curves in Fig. 3 have been tabulated in Table IV, and from any corresponding sets of figures in this table the temperature coefficients of the two reactions may be obtained. They are better obtained graphically, however, by taking the square root of the ratio of the slopes of corresponding pressure-velocity curves in Fig. 3.

Thus, if η represents the temperature coefficient calculated for a 10° rise, we have, for the A reaction,

$$\eta_{245}^{285} = \sqrt{\frac{\text{Slope of A reaction curve at } 285^{\circ}}{\text{Slope of A reaction curve at } 265^{\circ}}} = 1.47$$

 $\eta_{245}^{285} = \sqrt{\frac{\text{Slope of A reaction curve at } 265^{\circ}}{\text{Slope of A reaction curve at } 245^{\circ}}} = 1.49$

Similarly, for the B reaction,

$$\eta_{265}^{285} = 1.765$$
 and $\eta_{245}^{265} = 1.775$.

Hence, denoting the temperature coefficients of the A and B reactions, respectively, by η_A and η_B , we have

 $\eta_{\rm A} = 1.48$ and $\eta_{\rm B} = 1.77$.

The temperature coefficients of the two reactions, while differing widely from each other, thus remain constant over the temperature range investigated. It follows from this that the constant temperature coefficient observed for the total reaction between 235° and 305° , and tabulated in Table I, was to some extent accidental, since the total reaction is the sum of two surface reactions of different temperature coefficients. When, however, as in Table V, the total reaction is calculated from the figures for the A and B reactions at 245° and 0.21 atm.* oxygen pressure, by means of their respective temperature coefficients, good agreement with the total observed reaction up to 305° is obtained, after which the discrepancy between theoretical and observed values gradually increases, due, as has already been shown, to the secondary formation of sulphur trioxide.

* The experimental figures for any other pressure serve equally well.

TABLE V.

Temper- ature.	Obs. vel. of SO ₂ formation. Gms./sec. $\times 10^8$.	Observed apparent temperature coefficient.	Vel. of SO_2 formation calc. as sum of A and B reactions. Gms./sec. $\times 10^8$.	Calculated apparent temperature coefficient.
235° 245 265 285 305	$34 \cdot 2 \\ 57 \cdot 3 \\ 150 \cdot 8 \\ 395 \cdot 9 \\ 1049$	1.67 1.61 1.63 1.62	$\begin{array}{r} 35.6 \\ 56.7 \\ 146.8 \\ 393.0 \\ 1087 \end{array}$	1.59 1.61 1.63 1.66
$325 \\ 345 \\ 365 \\ 385$	$2204 \\ 3017 \\ 3781 \\ 4217$	1·45 1·17 1·12 1·06	3000 8752 25,800 77,200	1.66 1.71 1.72 1.73

The facts relating to the reactions of hydrogen and oxygen with sulphur at the surface of the latter, considered in this and the previous papers of this series, may now be summarised as follows :

(1) The surface reaction of hydrogen and sulphur is independent of the pressure of the hydrogen (Part I, *loc. cit.*).

(2) It is catalysed by the admixture of small percentages of oxygen with the hydrogen, but, when the quantity of oxygen is increased, the catalysis passes through a maximum, finally falling off to a complete poisoning effect, when the hydrogen contains more than 10 per cent. of oxygen (Part II, *loc. cit.*).

(3) At the same time sulphur dioxide is formed at a rate proportional to the oxygen pressure (Part II, *loc. cit.*).

(4) When the oxygen percentage is greater than that required to poison the hydrogen sulphide reaction, sulphur dioxide formation is still proportional to the oxygen pressure.

(5) A break in the curve connecting the velocity of sulphur dioxide formation with oxygen pressure, however, indicates that at these higher oxygen pressures, sulphur dioxide formation proceeds by two distinct surface reactions, having definite but different temperature coefficients, one of which becomes independent of oxygen pressure at about 0.4 atm. of oxygen, whilst the other remains proportional to oxygen pressure up to 1 atmosphere of oxygen.

(6) The temperature coefficient of the hydrogen sulphide reaction is 1.48, leading to a heat of activation of 25,750 cals. at 300°. This heat of activation is nearly equal to the heat of sublimation of a molecule of S_2 from the surface (28,000 cals.), and is half the heat of activation found for the gaseous hydrogen sulphide reaction, 51,460 cals. at 300°.

(7) The assumption was made that in the former two cases we are measuring the work done in detaching a molecule of H_2S or S_2 from $5 \circ 2$

the surface by the breaking of one bond, whilst in the latter case we are measuring the work done in dissociating the S_2 molecule, by breaking two bonds. The hypothesis predicts that the work done in detaching a molecule of sulphur dioxide from the surface should be of the order 26,000 cals. This has been found to be so in the present paper for the A sulphur dioxide reaction, the heat of activation calculated from the temperature coefficient (1.48) being 25,750 cals. at 300°. For the B reaction, however, the heat of activation is 37,450 cals. at 300°.

The facts enumerated above may all be harmonised by an extension of the theory advanced in Part III (loc. cit.) of this series. It was there postulated that since the vapour of sulphur at 260-300° consists almost completely of S8 molecules, the sulphur surface in equilibrium with it must be very largely composed of S₈ molecules These molecules are probably highly saturated and non-polar, also. and therefore incapable of the adsorption of hydrogen or oxygen. A small number, however (constant for a given temperature), may at any moment be considered to be activated to a polar form. For example, if the saturated S₈ molecule is a closed ring, it may be activated by the rupture of a bond, possibly as a result of collision, the free ends then being available for hydrogen or oxygen adsorption. If pure hydrogen be in contact with the sulphur surface, all the polarised sulphur molecules will immediately become attached to hydrogen, hydrogen sulphide formation occurring by the evaporation of the hydrogen molecule with the sulphur atom, with the concomitant rupture of a sulphur linking. The activated sulphur molecules, by reason of their high polarity, must be supposed to attach hydrogen extremely rapidly, so that at any moment all but a small fraction of the sulphur molecules available for hydrogen adsorption are occupied. This mechanism results in the surface formation of hydrogen sulphide being independent of hydrogen pressure except for very low pressures. Admixture of oxygen with the hydrogen atmosphere results in the displacement of some hydrogen from the surface, and owing to the preferential adsorption of the former, the hydrogen is completely displaced from the surface when the gaseous atmosphere contains more than 7-10 per cent, of oxygen according to the temperature, resulting in a complete poisoning of the hydrogen sulphide reaction. It has already been shown how this gradual replacement of hydrogen by oxygen on the surface can also explain quantitatively the catalytic and poisoning activity of the latter (Part II, loc. cit.).

It was therefore expected that when the oxygen pressure was increased beyond that required to poison the surface with respect to hydrogen sulphide formation, the rate of formation of sulphur dioxide

would become independent of oxygen pressure, since all the active sulphur molecules which previously adsorbed hydrogen would now be occupied by oxygen, and therefore the surface should be *saturated* with respect to oxygen.

The data of the present communication, however, do not fulfil this expectation, for the velocity of formation of sulphur dioxide continues to increase with the pressure of oxygen, far beyond the point at which the above hypothesis indicates that it should become constant. By assuming in addition, however, that oxygen molecules are able to activate some non-polar form of sulphur molecules in the surface by collision, and thereafter become adsorbed by them, the hypothesis can be extended to account satisfactorily for all the observed facts. The number of sulphur molecules activated by collision per second, and therefore the number of oxygen molecules adsorbed per second, would be proportional to the number of oxygen molecules striking the surface per second, and hence to the oxygen pressure over the sulphur surface. Thus the velocity of sulphur dioxide formation, limited by the velocity of oxygen adsorption, would be proportional to the oxygen pressure as found experimentally. We have up to the present considered only the S₈ molecules, which must constitute the major portion of the sulphur surface, at the experimental temperatures, since at these temperatures the sulphur vapour in equilibrium with it consists almost completely of S₈ complexes. It is apparent, however, since the existence of two sulphur dioxide surface reactions has been demonstrated, that at least two types of sulphur molecules must exist in the surface which can also adsorb oxygen proportionally to the pressure of the latter and give rise to sulphur dioxide. This conclusion is in harmony with the fact that liquid sulphur is known to be a mixture of at least two forms of sulphur— $S\mu$ and $S\lambda$ —existing in dynamic equilibrium with each other. In any sulphur surface, either on the glass walls of the vessel or on the sulphur liquid itself, one only of these forms will be deposited from the vapour state, and then in the liquid film subsequently give rise to the second modification. At a certain pressure of oxygen (about 0.4 atm.) the rate at which the second form is removed by formation of sulphur dioxide is equal to its rate of regeneration from the parent form of sulphur molecules. At this point the velocity of sulphur dioxide formation will become constant and independent of any further increase of oxygen pressure, since it is now limited by the rate of formation of the allotropic sulphur molecule. In this way we can account for the A surface reaction, which is at first dependent on oxygen pressure and finally, beyond 0.41 atm., independent of it. Furthermore, at the points O, P, and Q in Fig. 3, where the A reaction just becomes independent

of pressure, the velocity of sulphur dioxide formation by the A reaction is a measure of the velocity of allotropic change of the sulphur, as explained above, and by taking the ratio of these velocities we can obtain the temperature coefficient of this allotropic change. On calculation, this is found to be 1.49 between 245° and 265°, and 1.47 between 265° and 285°, giving a mean value of 1.48, identical with that of the A reaction, and the hydrogen sulphide surface reaction.

Simultaneously, the parent form of liquid sulphur, which is deposited from the vapour on to the glass and liquid sulphur surfaces, and therefore probably consists of closed S_a molecules, continues to give active adsorbing molecules on collision with oxygen molecules; consequently sulphur dioxide is produced at a rate proportional to the oxygen pressure as already described. This reaction constitutes the B reaction. Theoretically, if a sufficiently high oxygen pressure could be obtained in the bulb, the B reaction should also become independent of oxygen pressure, at the point where the rate of oxygen adsorption becomes equal to the rate of deposition of S₈ molecules from the vapour.

It will now be of interest to examine the A and B reactions from the point of view of their temperature coefficients.

These temperature coefficients, 1.48 for the A reaction and 1.77 for the B reaction, correspond to critical increments, calculated at 300°, of 25,750 cals. for the A reaction and 37,450 cals. for the B reaction. In Part III, reasons were given for expecting that the surface formation of sulphur dioxide would have a critical increment of 26,000 cals., corresponding, as explained there, to the breakage of one sulphur bond.* The critical increment of the A reaction above is in complete agreement with this prediction, and may therefore be taken as a measure of the work done in either

(1) preparing the new form of sulphur molecule from the parent form (S_8) by the rupture of one bond per potential sulphur dioxide molecule in some way, or

(2) activation of the new form by collision with an oxygen molecule, or

(3) detaching a molecule of sulphur dioxide from the surface as explained in Part III of this series.

All these processes, which together form a complete series, should have the same critical increment, namely, that required to break

* Although it might be considered somewhat speculative to associate the critical energy increment in any way with molecular structure, yet we believe that it has some connexion with the chemical conception of a bond; and the constancy of the energy value in a series of chemical actions of the sulphur molecule as shown in Table VI certainly does not disprove the conception, which we have found valuable as a guiding hypothesis throughout this work.

one sulphur bond, but only that of the slowest reaction would be measured by the temperature coefficient, since, as already explained in Part III, the temperature coefficient of a chain of linked reactions is that of the slowest reaction in the chain.

Thus, the above series of reactions might be represented as follows:



Each of the above suggested reactions involves the production of one free bond for each potential sulphur dioxide molecule, and therefore, according to our hypothesis, the expenditure of 26,000 cals. per mol. of sulphur dioxide produced. When the rate of removal of S_4 by reaction with oxygen shall have become equal to its rate of production from S_8 , the velocity of the sulphur dioxide reaction would become independent of the pressure of oxygen, and would be limited by the rate of production of S_4 , as we have found experimentally for the A surface reaction.

In harmony with the above scheme, the temperature coefficient of the allotropic change of the sulphur molecules has already been shown to be 1.48, leading to a critical increment of 25,750 cals. at 300°, as required by the hypothesis put forward.

The reaction kinetics of the B surface reaction open up the interesting problem of activation by molecular collision, which it is not possible to enter into fully at this point. It may be pointed out that the critical increment, 38,000 cals., observed is approximately one and a half times that observed for the A reaction and for the hydrogen sulphide surface reaction. The supposition might be made that we are here engaged in activating by oxygen collision a molecular system differing from those already considered, in that it involves the formation of one and a half free bonds for every potential sulphur dioxide molecule produced, and that the rate of activation governs the rate of sulphur dioxide production. The constancy in the energy value of the "half" sulphur bond is shown by the figures in Table VI, which are here collected from the various sulphur reactions we have dealt with in this series.

			No. of	
		Crit. in-	sulphur	
		crement at	bonds	
	Temp.	$300^{\circ} = c$	produced	Const.=
Reaction.	coeff.	cals.	$\times 2 = n$.	c/n.
$\frac{1}{2}(2H_2+S_2)$ gaseous *	2.19	51,460	4	12,865
$H_2 + S$ surface \dagger	1.48	25,750	2	12,875
$\frac{1}{2}(S_2 \longrightarrow 2S)$ gas dissoc. \ddagger		50,000	4	12,500
$\operatorname{Liq.} S \longrightarrow S_2 \text{ gas } \ \dots \dots \dots \dots \dots$		28,000	2	14,000
Latent heat of liquid sulphur per				
gmatom ¶				11,600
Allotropic change of liquid S	1.48	25,750	2	12,875
O ₂ +S surface A	1.48	25,750	2	12,875
O ₂ +S surface B	1.78	37,450	3 (?)	12,480
* Part I. loc cit				

TABLE VI.

+ Ibid.

[‡] Budde, Z. anorg. Chem., 1912, 58, 169. See also Part III, loc. cit.

|| Pollitzer, ibid., 1909, 64, 121.

¶ Person, Pogg. Ann., 1849, 70, 310, 386.

There is, however, an alternative explanation of the high critical increment of the B reaction, namely, that the critical increment of the activation of a given sulphur molecule by oxygen collision is different from the critical increment of activation of the same sulphur molecule by collision with a similar sulphur molecule. All the reactions but the last in Table VI may be represented as depending on the production of polarised sulphur molecules by the mutual collision of unpolarised sulphur molecules or atoms. The last reaction, however, depends on the collision of oxygen and sulphur molecules.

The factors governing the magnitude of the critical activation increments in the two cases depend on consideration of the momentum and energy exchanges of the colliding molecules and will be discussed in another place. It may be pointed out here, however, that if the activation of a molecule by collision depends on the exertion of a certain minimum intermolecular force, then, no matter what the mass of the second colliding molecule may be, the same quantity of momentum must disappear in each case. Thus, for the three collisions S₂ against S₂, S₂ against O₂, and S₂ against H₂, if for simplicity we suppose the first colliding molecule (that is, the S_2) to be stationary and the second colliding molecule (that is, the S_2 , O_2 , or H_2) to move up to it with the same energy in the three cases (that is, at the same temperature), then the intermolecular forces exerted during collision will be very different in the three cases and will depend on the momenta and not the energies of the colliding The force exerted between the two sulphur molecules molecules. will be greater than that between the oxygen and sulphur molecules,

and both much greater than the force exerted between the hydrogen and sulphur molecules. Whilst in the former two cases the intermolecular forces exerted may be sufficient at a certain temperature to cause the distortion in the sulphur molecule which we call "polarisation" or "activation," that called forth in the latter, by reason of its much smaller magnitude, may be insufficient. \mathbf{It} will thus be clear that it is legitimate to imagine activation by oxygen collision when it does not take place at the same temperature by hydrogen collision. Furthermore, it follows from the above reasoning that, in order that the same intermolecular force may be exerted between two colliding sulphur molecules as between a sulphur and an oxygen molecule colliding, a greater energy exchange will take place in the latter case than in the former, that is, for the same minimum polarising force in the two collisions different critical increments are involved. It is possible, with certain plausible assumptions, to calculate the ratios of the critical increments for sulphur activation by different collisions from the ordinary laws of inelastic impact, and the results obtained are of the right order, but until something more definite is known of the actual magnitude of the sulphur complexes undergoing collision, such calculations can have little further value.

Summary.

(1) The reaction of oxygen and sulphur has been studied by a dynamic flow method between the temperatures of 235° and 385° . Between 235° and 305° it proceeds normally, with an apparent temperature coefficient of 1.63. Above 305° , the temperature coefficient falls off very rapidly owing to the secondary formation of sulphur trioxide.

(2) The reaction has been shown to be practically limited to the surface of the sulphur and the walls of the vessel, and to proceed as well on the latter as on the former, pointing to the existence of a liquid film covering the whole surface of the vessel.

(3) The reaction is proportional to oxygen pressure.

(4) At 0.41 atm. pressure of oxygen, a break occurs in the pressurevelocity curves, which indicates that the reaction on the surface is complex and made up of the sum of two surface reactions, one of which—the A reaction—becomes independent of pressure beyond the above oxygen pressure, whilst the other—the B reaction remains proportional to the oxygen pressure at least as high as 1 atm.

(5) The two reactions have been separated and their temperature coefficients obtained; these are :—

For the A reaction -1.48. For the B reaction -1.77.

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(6) The critical increments calculated from these temperature coefficients at 300° are

A reaction -25,750 cals. B reaction -37,450 cals.

The former fulfils a prediction of the hypothesis advanced in the earlier papers of the series.

(7) The assumption is made that the sulphur surface contains two types of sulphur molecules, which react along two different courses with the oxygen striking the surface, giving rise to the A and B reactions. The fact that the A reaction finally becomes independent of the oxygen pressure indicates that the rate of production of the second allotropic form of sulphur now limits the velocity of the reaction.

(8) The temperature coefficient of the interconversion of the two allotropic forms is shown to be 1.48 as required by the hypothesis advanced.

(9) A table is given of seven different sulphur reactions, showing that their critical increments are simple multiples of a constant quantity which is considered to be the half value of the work required to create one free sulphur bond.

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