415. *The Kinetics of the Reaction between Oxygen and Sulphur. Part I. Aspects of the Reaction at 240—280°.*

By Leonard A. Sayce.

In the first kinetic study of the oxidation of sulphur to its dioxide, Ewan (*Z. physikal. Chem.*, 1895, **16**, 315) found that the velocity was proportional to the square root of the oxygen pressure, but Bodenstein and Caro (*ibid.*, 1909, **75**, 30) considered it to vary directly with this pressure and also, roughly, with the surface of liquid sulphur, and concluded that it was restricted mainly to that surface. Using a flow method, Norrish and Rideal (J., 1923, **123**, 3202) found that oxidation occurred equally well on the glass walls of the vessel and on the surface of liquid sulphur; *viz.*, that the velocity per unit area was the same on each of these surfaces. According to them, this pointed " to the probability of a liquid film covering the whole of the glass surface and identical in composition with the surface film of the liquid sulphur itself." They further deduced that above 0·4 atm. of oxygen the reaction common to both surfaces " 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 atm. of oxygen."

The last authors' experiments were repeated with considerable refinements, but the results were so discordant as to be quite inconclusive; consequently, a " static " method involving better control of the conditions was adopted, but the difficulty arose that, under certain conditions, a reaction occurred during the cooling of the reaction vessel which actually produced more sulphur dioxide than was formed during the heating stage. This frigescent reaction * was sometimes accompanied by a blue flash. Ultimately, however, a method was found which avoided the interference of these phenomena with the measurement of the products appropriate to the temperature and time of heating.

The results obtained, whilst contradicting those of Ewan, harmonise with those of later workers in so far as they demonstrate the heterogeneity of the reaction. They show, however, that Bodenstein and Caro were wrong in supposing the reaction to be restricted to liquid sulphur. The reaction upon glass was, however, found to be many times slower than that upon liquid sulphur and not, as Norrish and Rideal assert, of similar velocity. Similar heats of reaction upon the two surfaces did, nevertheless, suggest a similarity in mechanism.

Experimental.

The Dynamic Method.—Norrish and Rideal (*loc. cit.*) passed a stream of air over sulphur in a modified Claisen flask at constant temperature, the rate being adjusted by a screw-clip, and the oxide in the effluent estimated by iodine. The difficulty of such regulation has been commented upon by Aynsley, Pearson, and Robinson (this vol., p. 58), and to avoid it, a semi-automatic device, maintaining a constant speed of aspiration, was used. The improved reaction vessel of the last authors was adopted, and special precautions were taken to maintain uniform bath-temperature. To ensure, as far as possible, equilibrium conditions of surface and concentration, the gas flow was maintained at a constant rate for several hours before measurements were made. The range of temperature used was 237—308°. Despite precautions, about 100 experiments afforded only gravely inconsistent results, from which, by selection, a curve similar to that of Norrish and Rideal (*loc. cit.*, Fig. 1) might be constructed; there was, however, no reason to believe that it was especially representative of the reaction. The evident inconsistency of the dynamic method is in part attributable to the removal of sulphur from the heated zone and its fortuitous condensation in the neck of the vessel. This method was therefore replaced by a static one carried out in sealed bulbs, whereby differences of temperature in the system are avoided, and a study of the reactions with both gaseous and liquid sulphur is possible, as shown in the reaction of sulphur with hydrogen (Aynsley, Pearson, and Robinson, *loc. cit.*; Aynsley and Robinson, this vol., p. 351).

The Static Method.—In these experiments, Pyrex bulbs containing powdered purified sulphur (Aynsley and Robinson, *Chem. and Ind.*, 1935, **54**, 392) in contact with dry or moist

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* A frigescent reaction is one initiated by cooling.

oxygen at pressures between 25 and 760 mm. were heated during 5—125 minutes at temperatures between 200° and 280° and subsequently cooled, either rapidly or slowly, by quenching in air, cold water, or other media. The product was almost wholly sulphur dioxide, which was determined iodometrically; more than a trace of the trioxide was found only in a few exceptional cases marked by excessive reaction. For reasons which will become evident later, it will suffice to record in detail only the results of experiments carried out in studying the influence of the sulphur concentration, and merely to summarise the other results.

The Influence of Sulphur Concentration.—*Air cooling.* The results are shown below :

Temp. 260°; O_2 pressure 100 mm. at 260°; bulbs cooled in air.

Period of heating (mins.)	10	10	10	10	15	30	45	10	10
Wt. of sulphur (mg.)	1·825	2·167	3·200	4·574	4·300	4·531	4·168	(a)	(b)
SO_2 formed (mg.)	1·38	1·34	1·39	1·36	1·36	1·57	1·50	7·20	7·81

(a) Pool of liquid sulphur 1 cm. diam.
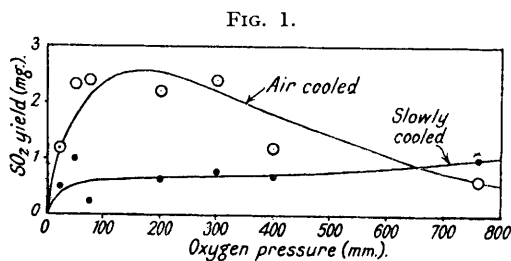(b)   ,,   ,,   ,,   ,,   2 cm.   ,,

6·6 Mg. of sulphur give saturated vapour in a 50 c.c. bulb at 260°; below this amount, *i.e.*, in the absence of liquid, the yield of sulphur dioxide appears to be independent of sulphur concentration and to be only slightly affected by time of heating. On several occasions, some seconds after removal from the heating bath to the air, a blue flash occurred in the bulbs, but the effect was unaccompanied by any apparent increase in the yield of sulphur trioxide.

Rapid cooling. The results obtained are shown below :

Temp. 260°; O_2 pressure 100 mm. at 260°; bulbs cooled in cold water.

Period of heating (mins.)	10	10	20	40	45	45(a)	40(b)
Wt. of sulphur (mg.)	4·995	4·671	4·882	3·443	3·621	3·166	5·195
SO_2 formed (mg.)	0·48	0·86	0·86	0·80	1·06	5·90	3·82

In experiments designated (a) and (b) the bulbs were removed from the bath, cooled in cold water, and reheated, the reheating and cooling being repeated three times. No flash was

FIG. 1.

observed in (a), but (b) showed a faint flash at the first cooling and a vivid flash at the second cooling. In both cases the flash occurred approximately 3 seconds after the bulb had been immersed, and it appeared to fill the bulb. From these results the frigescent reaction appears to be largely independent of sulphur concentration and time of heating.

To summarise the results of over 200 experiments : the frigescent reaction (1) occurs when a mixture of sulphur vapour and oxygen at 200—280° is cooled rapidly; (2) is greatest when the vessel is cooled in air, less when in water or kerosene, and least when the cooling takes several hours; (3) is at a maximum with oxygen pressures of 100—300 mm. (Fig. 1); (4) is uninfluenced by the initial temperature between 240° and 280°, but falls off rapidly below an initial temperature of 240°, becoming very small below 220°; (5) is rather irregular in extent.

The frigescent reaction, despite its association with chemi-luminescence, appears to differ radically from the phosphorescent combustion of sulphur studied by Emeléus (J., 1928, 1942), which is inhibited by sulphur dioxide and is apparently a homogeneous reaction, and from the low-pressure oxidation studied by Semenoff and Rjabinin (*Z. physikal. Chem.*, 1928, *B*, **1**, 122), who initiated it electrically, and by Ritchie and Ludlam (*Proc. Roy. Soc.*, 1932, *A*, **138**, 635), who initiated it at hot surfaces. Further, the experimental procedure precluded the catalysing effect of traces of ozone.

The New Static Method.—A study of the main reaction evidently required conditions which eliminated the frigescent reaction, and after much preliminary work a method was devised which attained these fairly successfully. It depends upon the sudden abstraction of the reaction products from the heated zone and their rapid cooling.

The 65 c.c. Pyrex vessel *A* (Fig. 2) was sealed to a T-piece *C*, with a thin diaphragm of glass *D* separating *A* from *C*. After cleaning and drying, it was charged with sulphur through *B*, which was subsequently constricted close to the bulb and attached to a train for exhaustion and filling with oxygen. The oxygen, generated by electrolysis of dilute sulphuric acid, was

passed successively over solid caustic potash, hot palladium–asbestos, and phosphoric oxide. After exhaustion, the sulphur was distributed as a fine sublimate by suitable heating, the oxygen was admitted to an appropriate pressure, and the bulb was sealed off at B. As shown in Fig. 3, the vertical arm of the **T**-piece carried the glass plunger G, held in place by means of wired-on
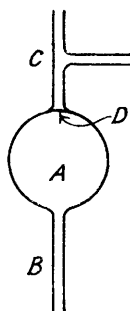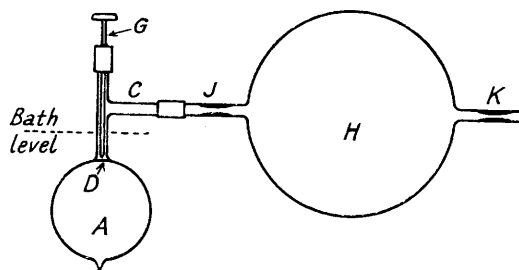
FIG. 2.

FIG. 3.

pressure tubing, which formed a gas-tight but slightly flexible joint. The pointed lower end of the plunger rested lightly upon the diaphragm D. The horizontal arm, C, of the **T**-piece was connected by way of a constricted tube, J, to a vessel, H (capacity approx. 700 c.c.), which was connected to a pump through the constricted tube, K. When ready, bulb A was submerged, as shown, in a well-stirred bath of fused alkali nitrates maintained at the required temperature. Vessel H was thoroughly evacuated and sealed off from the pump at K, and at the end of the heating period diaphragm D was broken by a smart blow on G; A and H were thus placed in communication and reached pressure equilibrium almost instantly, about nine-tenths of the gaseous content of the former being transferred to the latter, which was immediately sealed off at J.

One of the tips of H was broken under $0.01N$-iodine, and by back titration with thiosulphate the sulphur dioxide present was estimated. Finally, the volumes of the bulbs A and H and of the tube connecting them (v, V, and v', respectively) were measured, and the total yield of sulphur dioxide calculated from the value of $X(vt/T + V + v')/V$, where X = mg. of SO_2 found in H, and t and T are the absolute temperatures of H and A respectively. The reaction was studied between $240°$ and $280°$, since outside these limits it was inconveniently slow or fast.

Influence of period of heating. With oxygen and sulphur concentrations constant (180×10^{-6} g./c.c. and saturated vapour, respectively) the amount of sulphur dioxide produced is proportional to the period of heating (Table I and Fig. 4) : every curve intersects the ordinate in the neighbourhood of 1 mg. of sulphur dioxide—presumably a vestige
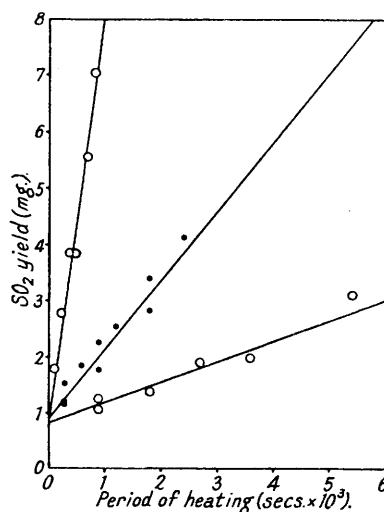
FIG. 4.

TABLE I.

Temp. $240°$.

Period of heating (secs.)	900	900	1800	2700	3600	5400		
SO$_2$ formed (mg.)	1·25	1·06	1·36	1·89	1·97	3·09		

Temp. $260°$.

Period of heating (secs.)	300	300	300	600	900	900	1200	1800	1800	2400
SO$_2$ formed (mg.)	1·52	1·19	1·16	1·84	1·76	2·26	2·53	2·80	3·39	4·12

Temp. $280°$.

Period of heating (secs.)	120	240	360	480	600	720	840
SO$_2$ formed (mg.)	1·76	2·75,	3·84	3·84	5·09	5·54	7·04

of the frigescent reaction survives rapid cooling. This was unavoidable and, since it must be allowed for, some measure of it, more accurate than extrapolation of the results of Table I, was desirable. A number of bulbs containing various concentrations of oxygen saturated with sulphur vapour were therefore heated for one minute at 240°, 260°, and 280°, respectively :

|	Temp. 240°.					Temp. 260°.				Temp. 280°.	
O_2 concn. (g. $\times 10^{-6}$/c.c.)	45	90	361	496	631	90	270	451	631	90	361
SO_2 formed (mg.)	0·710	0·506	0·675	0·675	0·675	0·913	0·944	0·976	0·978	0·740	1·518

At 240° and 260° the formation of sulphur dioxide is practically independent of oxygen concentration, and mean values are taken. At 280°, the influence of the oxygen concentration is considerable and corrections were computed for a range of concentrations. These were applied to each subsequent observation by deducting one minute from the period of heating and the appropriate amount from the sulphur dioxide formed.

TABLE II.

Temp. 240°; period of heating 5400 secs.; O_2 concn. 180×10^{-6} g./c.c.

S (mg.)	1·120	1·305	2·990	3·174	3·390	3·990	4·385	4·500	17·820
SO_2 formed/sec.	17·0	27·7	26·4	26·4	30·9	30·9	30·9	37·8	36·7

Temp. 260°; period of heating 900 secs.; O_2 concn. 180×10^{-6} g./c.c.

S (mg.)	0·433	0·788	1·422	1·768	2·462	3·620	3·722	5·045	5·045
SO_2 formed/sec.	33	40	57	51	48	158	68	106	192

S (mg.)	5·775	6·865	8·453	8·530	9·042	29·030	42·590	51·650	62·560
SO_2 formed/sec.	163	169	192	199	169	177	177	213	229

Temp. 280°; period of heating 300 secs.; O_2 concn. 180×10^{-6} g./c.c.

S (mg.)	2·750	7·442	12·300	20·730	71·450
SO_2 formed/sec.	483	688	937	895	913

Influence of concentration of sulphur vapour. The concentration of oxygen still being kept constant, that of sulphur was varied on both sides of saturation. Times of heating giving

FIG. 5.
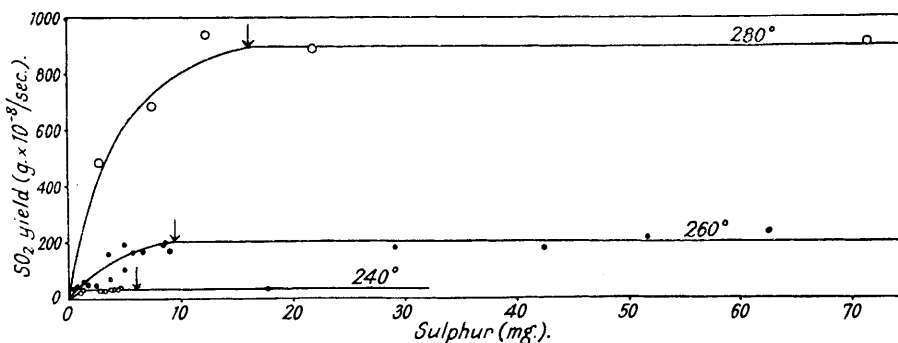
convenient quantities of sulphur dioxide were chosen but, for purposes of comparison, the results (Table II, Fig. 5) are given in yields (g. $\times 10^{-8}$) per second. On the graphs obtained, the vertical arrows indicate the amount of sulphur (assumed to be S_8) required to maintain saturation at the end of the heating period.

Influence of glass surface. Vessels packed with short lengths of Pyrex tubing were adjusted in size to have the same free space. Sufficient sulphur was added to ensure saturation finally, but at the same time to avoid a significant surface of liquid. The oxygen concentration employed was 180×10^{-6} g./c.c. The results (Table III and Fig. 6) make it evident that the reaction is heterogeneous.
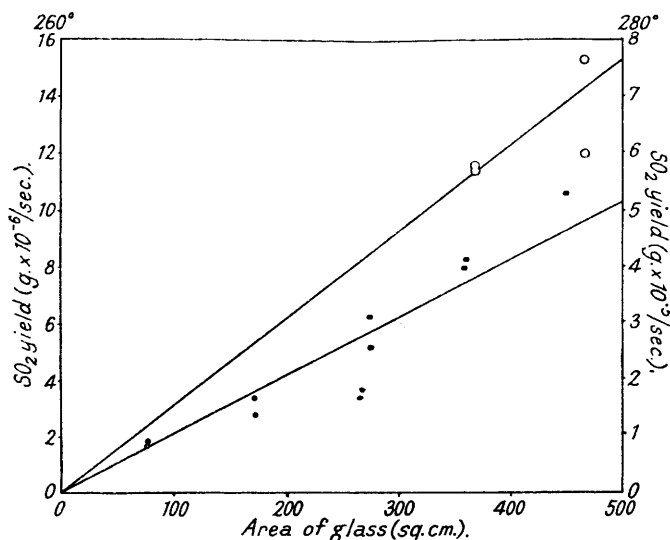
TABLE III.

Temp. 260°.

Glass surface (sq. cm.)	78	173	173	266	268	276	276	360	363	451
SO_2 formed (g. $\times 10^{-8}$/sec.)	185	278	334	334	361	624	511	793	818	1058

Temp. 280°.

Glass surface (sq. cm.)	78	370	370	468	468
SO_2 formed (g. $\times 10^{-8}$/sec.)	905	5660	5790	7640	5990

FIG. 6.

Influence of concentration of oxygen. Saturated vapour was used, and the oxygen concentration was varied. The heating periods, *viz.*, 90 mins. at 240°, 15 mins. at 260°, 5 mins. at 280°, were adjusted to give convenient yields and, the reaction being heterogeneous, the results (see below and Fig. 7) are corrected for surface area, being brought to that for a standard 65 c.c. bulb. Oxygen concentrations are given in g. $\times 10^{-6}$/c.c., and rates of sulphur dioxide formation in g. $\times 10^{-8}$/sec. :

Temp. 240°.				Temp. 260°.				Temp. 280°.			
O_2 concn.	SO_2 formed.	O_2 concn.	SO_2 formed.	O_2 concn.	SO_2 formed.	O_2 concn.	SO_2 formed.	O_2 concn.	SO_2 formed.	O_2 concn.	SO_2 formed.
45	20	361	80	90	67	451	614	45	260	406	2135
45	13	361	63	90	59	451	550	90	511	451	2250
90	19	451	82	180	185	496	640	135	666	496	2855
90	25	451	87	180	221	496	662	180	905	541	3260
90	16	451	103	180	222	541	648	225	1042	541	3530
180	35	541	87	270	320	541	626	270	1414	631	4150
180	39	541	103	270	286	541	775	316	1883	631	4340
270	60	631	156	361	388	613	808	361	1560		

Influence of surface of liquid sulphur. Two series, at 240° and 260°, with liquid sulphur present, showed that the yield of sulphur dioxide depends upon the area of the sulphur surface but not upon the mass of sulphur. The results (Table IV and Fig. 8) were therefore unaffected

TABLE IV.

Temp. 240°.

Sulphur surface (sq. cm.)	0	3·1	3·8	6·2	8·0	8·0	9·1
SO_2 formed (g. $\times 10^{-8}$/sec.)	40	85	105	109	106	103	91

Temp. 260°.

Sulphur surface (sq. cm.)	0	1·9	2·5	3·5	5·7	7·5	9·6
SO_2 formed (g. $\times 10^{-8}$/sec.)	225	322	369	336	408	469	724

by dissolution of sulphur dioxide in the sulphur. In the computations, allowance was made (as shown by broken lines in Fig. 8) for the reduction of the glass surface and of gas space by the liquid sulphur. A strong tendency to anomalously high yields of sulphur dioxide invalidated a considerable proportion of these series of experiments; but it is evident from Table IV that there is a great increase in the yield in the presence of liquid.
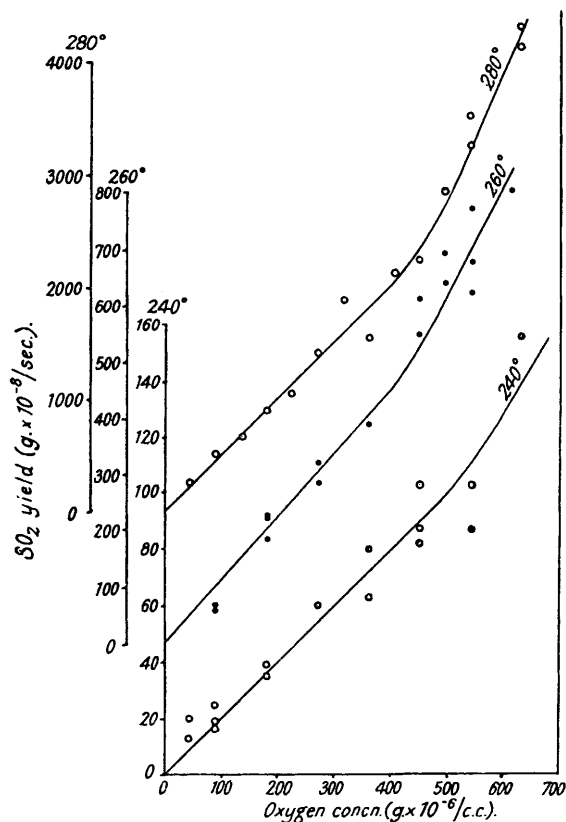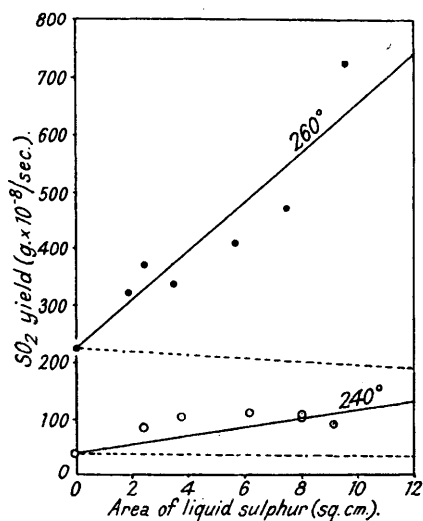
FIG. 7.

FIG. 8.

Oxygen concn.(g.x 10⁻⁶/c.c.).

Area of liquid sulphur (sq. cm.).

DISCUSSION.

It has been shown that the reaction between oxygen and sulphur cannot successfully be investigated by a flow method such as that described by Norrish and Rideal (*loc. cit.*), and further, that a simple static method is unsuitable on account of a production, during the cooling period, of sulphur dioxide which may actually be in excess of that formed at the temperature of the heating bath. The device for the sudden removal of the reaction products from the hot zone, thereby reducing the frigescent reaction to small and consistent values, has, however, enabled the normal reaction to be investigated. The results still showed slight discordance, possibly attributable, since reaction occurs at both the glass and the sulphur surface, to variations in the character of the former and error in estimating the latter. These uncertainties, however, were minimised by making a large number of observations.

Anomalously high yields of sulphur dioxide caused much trouble, especially at 280° and with packed bulbs, due presumably to the onset of a chain reaction. Sometimes the sulphur took fire on heating the bulb, but more often the abnormality was disclosed only by an amount of sulphur dioxide so great as to be readily recognisable.

That the reaction is inappreciably influenced by the presence of its products and the consequential change in the concentration of the reactants, is demonstrated by the recti-linearity of the graphs of Fig. 5.

In the experiments recorded in Table II there was no significant surface of liquid, and the curves (Fig. 5) indicate an upper limit of reaction velocity with regard to sulphur. The sulphur concentration cannot exceed saturation, beyond which point (shown by the arrows) the curves become horizontal. It is those portions to the left of the arrows which are here of especial significance.

The curve for 240° becomes horizontal considerably to the left of the arrow, and indicates that above approximately 2 mg. of sulphur (0·03 mg. per c.c.) further increase does not affect the velocity of reaction. The initial curved portion of the graph may correspond to the saturation of the glass surface with sulphur, and if so, it is kept fully reactive even by this concentration.

At 260°, the inflexion of the graph continues almost to the arrow, and results with packed bulbs show that the reaction has not lost its strictly heterogeneous character. The higher temperature has increased the reaction velocity and also decreased the amount of adsorbed sulphur in equilibrium on the glass surface. On both accounts a greater concentration of sulphur, attained only at about saturation, is required to maintain the glass surface at its full reactivity.

At 280°, a still greater concentration is necessary, so that even saturated vapour is insufficient for full reactivity of the surface. From this cause a falling off of the temperature coefficient is anticipated and was in fact found (see below).

Experiments with packed bulbs (Table III and Fig. 6) showed that the velocities at 260° and 280° were proportional to glass surface at these temperatures. The distribution of the points upon the graphs makes it difficult completely to exclude the possibility of a homogeneous component, but, if present, this would lead to intersection of the vertical axis, which is absent. Experiments at 240° with packed bulbs were not carried out because the reaction had already been shown to be completely heterogeneous at this temperature.

The graphs relating reaction velocity to oxygen concentration show a rectilinear relationship up to approximately 400×10^{-6} g./c.c. Above this there is, at 280°, a pronounced acceleration, and a similar, but smaller, effect is shown at 260°, whilst, even at 240°, there is a tendency in the same direction. Evidently, the reaction undergoes a change in character at higher oxygen concentrations and temperatures. Still higher temperatures and concentrations are known to cause the reaction to proceed explosively, and the frequent occurrence here recorded of anomalously high results is undoubtedly associated with this phenomenon. The curvature of the graphs is therefore ascribed to the development of a chain reaction, a tendency which is naturally more evident at 280° than below.

For the rectilinear portions of the graphs, *i.e.*, where oxygen concentrations are 0—400×10^{-6} g./c.c., the heat of activation is 46,430 cals. for the range 240—260° and 43,930 cals. for 260—280°, and the corresponding temperature coefficients are 2·37 and 2·13 respectively. The apparent fall in the heat of activation with temperature is believed to be due to the partial desorption of sulphur from the glass surface already adumbrated.

The reaction upon liquid sulphur is approximately 16 times as rapid as that upon glass. The full lines (Fig. 8) represent the total reaction, and the broken lines that on the glass surface. The full line for 260° represents observed values and gives the velocity of reaction as $45·9 \times 10^{-8}$ g./sec./sq. cm. Assuming the temperature coefficient at the liquid surface between 240° and 260° to be the same as that for the glass surface reaction, *viz.*, 2·37 per 10°, then the velocity on liquid sulphur at 240° becomes $8·2 \times 10^{-8}$ g./sec./sq. cm. This value is used to construct the full-line graph for 240° (Fig. 8), which fits the observed points reasonably well. Apparently the heat of activation of the two heterogeneous reactions is approximately the same. The notable difference in their velocities may therefore be due simply to a greater abundance of available sulphur molecules upon the liquid surface.

SUMMARY.

1. The reaction between oxygen and sulphur has been investigated at 240—280° by a static method, since the dynamic method was found unsatisfactory and previous results obtained with it were not confirmed.

2. Between 240° and 280° the reaction occurs only upon surfaces of liquid sulphur

and of glass, that upon the former being approximately **16** times as rapid as that upon the latter.   The existence of these radically different rates is difficult to reconcile with the " liquid film " of sulphur upon glass postulated by Norrish and Rideal.   The heat of activation of the glass surface reaction is 46,430 cals., and the evidence suggests a similar value for the sulphur-surface reaction.

3. The investigation was complicated by a newly observed vigorous reaction which occurs in the cooling reactants, and a special technique was necessary to prevent its products from vitiating the results of the ordinary thermal reaction.

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