241. *Studies in Polymorphism. Part VI. A Further Investigation of the Linear Rate of Transformation of Monoclinic into Rhombic Sulphur.*

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New measurements of the rate covering the range 0—80° afford strong evidence that the activation energy which determines the temperature coefficient of the reaction is of the same order as the heat of sublimation and not appreciably less than this as was formerly thought (Part V).

A possible reason for the very large pre-exponential factor (*ca.* $10^7 . \nu d$) is discussed. This is based on a suggestion by Garner that the transformation can proceed within small homogeneous elements of volume, *e.g.*, mosaic blocks, with a much smaller activation energy than the heat of sublimation, but that the latter amount of energy is required to bridge the discontinuity between one such element and the next, and is the rate-controlling factor. This idea receives some support from observations under the microscope which show that the advance of the interface is spasmodic, the interface continually surging forward locally at a greater rate than the average rate of advance.

The microscopic study has also shown that when the interface crosses the boundary between two differently oriented monoclinic crystals, it does so without change of orientation of the rhombic phase. The transformation is thus essentially a process of crystal growth in a solid medium.

Part V of this series (*J.*, 1940, 588) described measurements of the linear rate of transformation of monoclinic into rhombic sulphur at 20°, 30°, and 40°. It had originally been intended to study the rate at temperatures up to the transition point, but the work had to be suspended.

The present paper describes new measurements covering the range 0—80°, and also gives the results of a study of the nature and mode of advance of the interface at different temperatures under the microscope. This work has shown that some modifications to the conclusions drawn in Part V are necessary. First, the extension of the study to lower temperatures has yielded strong evidence that the activation energy determining the temperature coefficient is of the same order as the latent heat of sublimation, and not appreciably less than this as was thought. Secondly, the microscopic examination of the polycrystalline films, which has now been done under conditions permitting interference figures to be obtained, has shown that crystals presenting *b*(010) sections are by no means the most common, and that several other orientations are frequently represented.

Some of this work has been briefly reported [*Discuss. Faraday Soc.*, 1949, No. 5 (Crystal Growth), p. 149] but no details were given.

EXPERIMENTAL.

The methods described in Part V were used for the purification and degassing of the sulphur, and for the preparation of the films of the monoclinic modification, which were confined as before in stepped glass–mica–glass cells * and covered the same range of thickness (0·06—0·10 mm.). The method of measuring the linear rate over the range 10—80° was also essentially the same, but the projection apparatus was completely rebuilt to a design which gave much greater rigidity and incorporated several modifications making for greater convenience in operation. The projection unit (lantern, thermostat, and projection lens) was mounted on a trolley constructed of heavy-gauge angle iron, and running on rails so that the magnification on the screen could be readily altered or adjusted. The thermostat with all its necessary equipment was mounted on rollers running on a pair of secondary rails fixed across the top of the main trolley, so that it could be drawn to one side out of the path of the light. This enabled the lantern and lens to be used by themselves for projecting photographic records of the sulphur films, which was the basis of the method of measurement used in studying the transformation at 0° (see later).

In the earlier work, the slides were contained in an air-tight cell placed inside a larger cell in the thermostat (Part V, Fig. 2). The air-tight cell was used because it seemed possible that the fall of velocity at constant temperature observed with other substances, and attributed primarily to the development of a gap at the interface owing to the difference in the densities of the two forms (Parts III and IV), might have been partly caused by loss of material from the interface by evaporation.

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* In what follows, these cells with their sulphur films will be referred to simply as " slides."

Sulphur, however, showed no fall of velocity at all, and, as will appear later, there are strong reasons for thinking that this result was not connected with the fact that evaporation was prevented. Since also the double-cell arrangement was rather clumsy and inconvenient, and a slide placed in it took a long time to acquire the temperature of the thermostat (25—45 mins.), some modification of this part of the apparatus seemed desirable. Rough preliminary observations made on slides laid on a hot plate at 70° and 80° indicated that there was no significant difference in the mean rate of advance of the interface between slides that were completely unprotected and others on which the film edges were sealed with either a thick layer of sulphur or sealing wax. It was therefore decided that some relaxation of the precautions against evaporation could be accepted in the interests of greater convenience and an improved rate of heat transfer, and the following simplified design was adopted. A single cell of all-glass construction, having internal dimensions of $9 \times 1\frac{3}{4} \times \frac{3}{8}$ in., and with its open top ground flat, was firmly clamped at its upper end to a brass bridge running across the top of the thermostat. (The cell was specially made for this work by Messrs. C. J. Whilems, Barkingside, Essex.) At the bottom of the cell was placed a layer of a mixture of rhombic sulphur and calcium chloride in order to establish a dry atmosphere saturated with sulphur vapour. The slide was held by leaf springs in a very light box frame made of 50 : 50 nickel–iron alloy, and so constructed as to be a good sliding fit in the cell. (This alloy has approximately the same coefficient of expansion as glass, so there was no danger of fracture of the cell at higher temperatures.) At the top and to one side of the frame was attached a vertical brass tube which contained, and acted as guide for, the piano-wire handle of the inoculating brush, which was made and used in the same way as in the earlier apparatus. A further quantity of the sulphur–calcium chloride mixture, contained in a small flat box made of perforated zinc, was placed on top of the frame as it was being lowered into the cell. The upper end of the brass tube passed through a hole of the same diameter in a brass plate, faced underneath with rubber, which formed the lid of the cell and was bolted to it by means of suitably positioned screws and finger nuts after the frame had been inserted. A clamping screw passing through the edge of the plate, and bearing on the brass tube, enabled the vertical position of the frame in the cell to be adjusted. The top of the brass tube was kept closed by a small cork threaded over the projecting end of the wire handle of the inoculating brush, except when this was actually in use.

This slide holder proved to be very convenient to use at all temperatures, and it reduced the time equired for a slide to reach thermostat temperature to 15—20 minutes.

A further modification to the apparatus was the addition of a " Londex " timer, operated by a synchronous motor, to switch on the projection lamp at regular intervals. This timer could be set to make contacts of any required duration at intervals of ½, 1, or 2 minutes. The timer was also arranged to operate an electromagnetic counter placed on the observation desk near the screen, so that the reading on the counter gave instantly the time for which the transformation had been in progress. This greatly facilitated the timing of the reaction—a particularly important consideration at the higher temperatures, where the more rapid movement of the interface demanded the most concentrated attention on the part of the observer. The counter readings were checked from time to time during an experiment against an accurate watch, so that any irregularity in the speed of the timer due to fluctuations in the mains frequency should not pass unnoticed. A master switch to the projection lamp was also mounted on the observation desk so that the lamp could be switched on for one or two seconds during an " off " period if the need arose to check any of the observations.

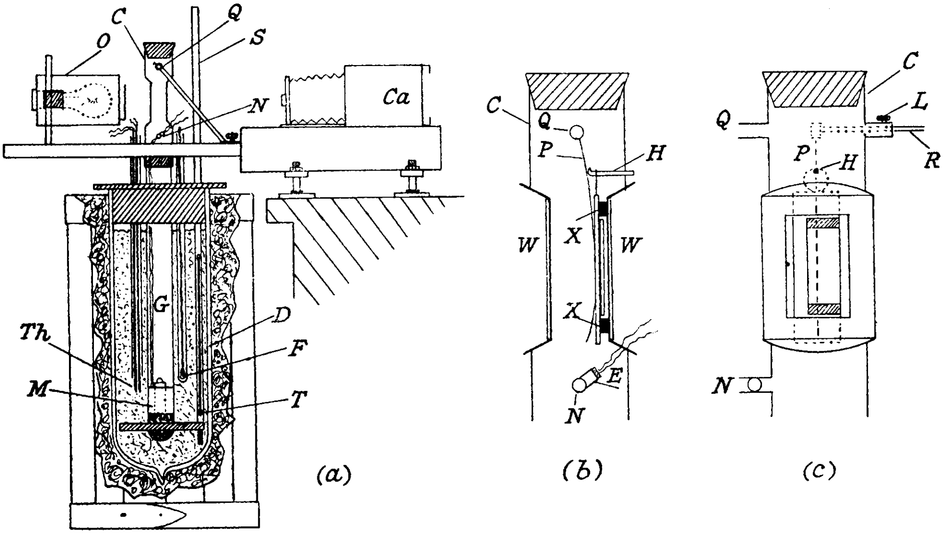
As in the previous work, the screen was ruled in vertical lines at distances apart equivalent to 0·25 mm. on the actual film, and horizontal lines at distances equivalent to 1·5 mm. divided the grid into 20 sections. The screen board was now, however, provided with vertical, lateral, and tilting adjustments by means of which the image of the edge of the film could be rapidly brought into coincidence with the zero vertical line at the start of an experiment. The time of crossing a vertical line in any section was taken, as before, as the mean of the time at which the image of the most forward part of the interface had just reached the line (time S) and that at which the most rearward part had just passed over the line (time F). On all slides the interface advance was followed to a distance of at least 1·5 mm. from the film edge, and in most cases to 2·0 mm. For reasons to be discussed later, the results obtained for the first 0·25 mm. were not used in calculating the mean rate.

The method of timing varied somewhat at the different temperatures to suit the different rates. At 30° the projection lamp was switched on for 15 seconds at intervals of 1 minute, the S times being noted at the odd minutes and the F times at the even minutes. At 50° and 80° the lamp was switched on for 10 seconds at ½-minute intervals (since the rate was appreciably greater than at 30°), and the S and F times were noted respectively at alternate periods of illumination. At these three temperatures it was possible by this procedure to keep track of the movement of the interface in all 20 sections without difficulty. In the work described in Part V, both S and F times were noted during every period of illumination, but these periods, though made as short as possible, were not constant, for the lamp was switched on by hand and was kept on as long as was needed to make the observations. The more regular timing given by the present method is obviously to be preferred on general grounds, and for the three temperatures in question, any error in the mean times introduced by taking S and F readings at alternate periods was negligible in comparison with the variance of the results. In any case the intervals between periods of illumination were half those in the previous work. At 60° and 70° the rate was near its maximum, and it was considered necessary to take both S and F readings together. It was not then possible to follow the movement in all 20 sections in the same run; at first only 5, and, with more practice, 8 sections could be dealt with. Each slide was therefore inoculated and studied in two separate halves, *i.e.*, half the slide was inoculated, and the movement of the interface followed in 8 sections, and then the other half of the slide was treated similarly. The periods of illumination were of 10 seconds at ½-minute intervals.

At 10° the movement of the interface was too slow to be followed in the above manner, since it would have involved continual observation of the screen for 7—9 hours. The following method was therefore adopted. The gridded screen was replaced by a sheet of drawing paper with a vertical line ruled on it. The screen board was adjusted so that the vertical line coincided with the image of the film edge, and the transformation started by inoculation in the usual manner. When the interface had advanced an actual distance of about 0·25 mm., its position was recorded on the drawing paper by tracing with a pencil. When it was estimated that the interface had advanced on the average about 1·5 mm. (between 7 and 9 hours), its position was traced again. Both tracings were made starting from the same end of the interface, and the times were taken as those at which the tracings were half completed. Twelve slides were studied in this way, giving a total length of interface equal to those studied at the higher temperatures. Each traced record was then divided into 20 horizontal sections of width equivalent to 1·5 mm. on the actual film, and the advance in each section, represented by the mean distance between the two pencil lines, was determined by means of a transparent scale. (The mean position of a line was taken as the average of its most forward and most rearward points.) Since the time interval between the two tracings varied somewhat from slide to slide, the results were multiplied by appropriate factors to convert them into values of the interface advance for a period of 10 hours. The results could then be averaged and treated statistically.

Since only the two tracings were made at 10°, the results did not enable a time–distance graph to be drawn for this temperature. Moreover, only 240 values of the rate (20 on each of the 12 slides) were obtained, as compared with about 1200 at other temperatures (though the same " area of transformation " was of course studied). Since, however, these results were the last to be obtained, and it was already known that the rate at both higher and lower temperatures was linear, it seemed unnecessary to collect the data for a time–distance graph, whilst the number of values appeared to be adequate to give a satisfactory measure of the variance of the rate.

FIG. 1.



In all the above experiments heat rays from the projection lamp were absorbed by passing the beam through (1) a plate of Chance heat-absorbing glass placed between the lantern condenser and the thermostat, and (2) a 2% solution of copper sulphate contained in a glass cell in the thermostat. The residual heating effect of the beam on the sulphur films was tested by means of a slide in which a very small copper–constantan thermocouple (made by thinning down the wires with acid) was embedded in the sulphur. This slide when placed in the usual position in the slide holder, with the thermocouple at the centre of the beam, and exposed to the light at the intervals and for the periods given above, showed a maximum rise of temperature of 0·1° during illumination, and this could be regarded as negligible.

Measurements at 0°.—At this temperature the rate was extremely slow (1·5 mm. in about 50 hours), and neither of the methods described above would have been suitable. The principle of the method adopted was to store a number of previously inoculated slides in a vessel surrounded by an ice–water bath, withdraw and photograph them at 12 hour intervals, and subsequently project the negatives on to a gridded screen on which the successive positions of the interface could be read off. The apparatus is shown in Fig. 1; *G* was a wide glass tube containing calcium chloride at the bottom to maintain a dry atmosphere, and just above this was a rack *M* in which six slides could be supported in a vertical position. No precautions against evaporation were thought necessary at this low temperature. The slides used for this work differed slightly from those used at other temperatures in that they were built up, not from two 3 in. × 1 in. plates (microscope slides), but from one of these and a smaller plate measuring 2⅛ in. × ¾ in. The reason for this will appear later. Furthermore, each slide, before being placed in the apparatus, was inserted in a light frame made of copper foil, with a large wire ring soldered to the upper end. By engaging a hook on the end of a long rod with this ring, the slide could be lowered into its position in the rack *M* and also raised to be photographed (see later). The upper end of *G* was attached by means of a wide rubber band to a metal tube *C* provided with glass windows on opposite sides (*W*, *W*, Fig. 1, *b*), and closed at the top with a rubber stopper as shown. In line with the windows were a 100-watt opal lamp in a metal housing *O*, carrying a filter of heat-absorbing glass, and a quarter-plate camera *Ca*. When it was required to photograph a slide, a current of dry nitrogen was passed through *C via* the side tubes *N* and *Q*, the stopper at the top was removed (the stream of nitrogen preventing the ingress of moist air), the long hooked rod, mentioned above, was passed down into *G*, and the slide was thereby raised (with the smaller of its two glass plates facing the camera) and hung on the bracket *H* by passing the wire ring over this (Fig. 1, *b* and *c*). The hooked rod was then removed, and the stopper replaced. The two ends of the larger plate of the slide were next brought into contact with the metal strips *X*, *X* by a gentle pressure of the spring wire *P* applied by turning the rod *R* and locking it with the screw *L*. (During the previous operations this rod had been drawn to one side, so that the spring wire did not interfere with the hanging up of the slide on the bracket *H*.) In this position the film of sulphur was in focus on the camera plate. When the photograph had been taken, the slide was lowered to its position in the rack *M* by reversing the above operations. The whole process of raising a slide, photographing it, and returning it to the rack took less than a minute. To facilitate the operation, the bottom of *G* was illuminated by means of the flash-lamp bulb *F* while it was in progress (Fig. 1, *a*).

The ice–water mixture surrounding *G* was contained in the large Dewar vessel *D*, which was embedded in slag wool in a large wooden drum. The top of the Dewar vessel was closed with a thick wooden cover in two halves, one of which could be easily removed for addition of fresh ice. Thermal insulation was very good, however, and replenishment was only needed at long intervals. The ice–water mixture was stirred from time to time with the hand stirrer *S*, the stem of which was hollow and contained a thermometer *T* which could be read when the stirrer was at the top of its stroke.

The Dewar vessel also contained two copper–constantan thermocouples *Th*, and a similar thermocouple was soldered to the slide rack *M*, the leads to it entering the apparatus through *E* (Fig. 1, *b*). By connecting the latter couple with one of those in the Dewar vessel, the rise of temperature of *M* resulting from the replacement of a slide after it had been photographed could be determined, the thermal E.M.F. being read on a sensitive galvanometer. This rise proved to be only about 0·5°, and the temperature returned to 0° in about 5 minutes. Even if the temperatures of other slides in the rack were affected to a like extent, it can be shown that the effect on their rates integrated over the whole run would be negligible. The zero of the galvanometer was checked from time to time by putting it in circuit with the two couples *Th* in the Dewar vessel.

The temperatures to which the slides rose during the brief and infrequent periods (see above) required to photograph them were not determined, but calculations show that the effect on the average rate for a run could not have exceeded about 3%, which is quite without significance for the estimation of the apparent activation energy to the nearest 1000 cals.

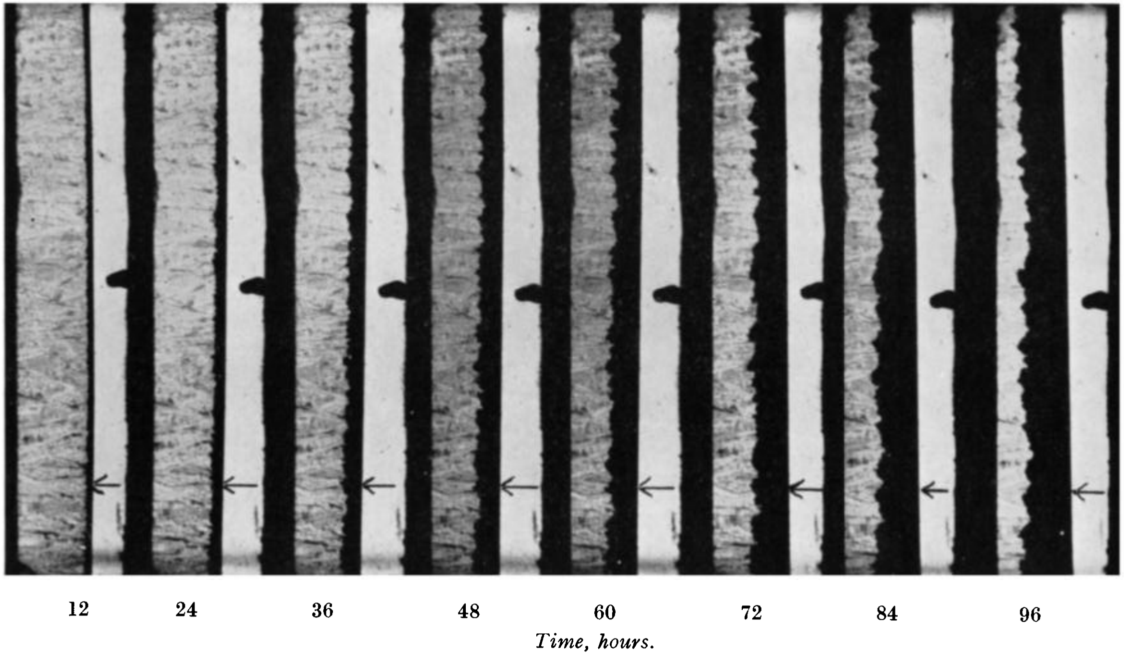
The window *W* (Fig. 1, *b*) nearer to the camera was masked (this is not shown in the figure) so that only a vertical strip of the sulphur film sufficiently wide to include comfortably the whole movement of the interface in a run was projected on to the photographic plate. The image of this strip registered with an opening of similar shape in a three-ply board forming the back of the camera. The dark slide containing the plate was held against this board by guides and leaf springs so that it could be shifted sideways to bring different sections of the plate opposite the opening. By means of this arrangement, eight records of successive positions of the interface could be taken on the same plate. Fig. 2 is a reproduction of a positive print of a typical negative. The comparatively regular advance of the interface will be noted.

To measure the advance, the negatives were projected by means of the optical system of the projection apparatus used for the higher temperatures on to a gridded screen ruled with vertical lines at a distance apart equivalent to 0·1 mm. on the actual film, and divided into horizontal sections equivalent to 1·5 mm. For this purpose the thermostat was drawn to one side out of the path of the light (see above) and the negative was supported in a special holder in front of the lantern condenser. This holder was a brass plate faced with baize, against which the gelatin side of the negative was lightly pressed by two large leaf springs. The light passed through an oblong opening in the middle of the plate, this opening being only large enough to illuminate one of the strip records on the negative at one time. The negative was moved in the holder so as to bring the eight records in sequence opposite the opening, correctly registered with respect to one another, and so that the image of the edge of the film coincided with the zero vertical line on the screen. This registration was facilitated by the presence of a mark on the step of the slide which had been made previously with Indian ink (see Fig. 2). Final adjustments were made by using the vertical, tilting, and lateral controls on the screen board, referred to above. For each record, the mean advance in each of the horizontal sections was taken as the average of the most forward and most rearward points on the interface as measured on the vertical scale lines. Estimates of these positions could be made to 0·05 mm. (actual). Thus the only difference in timing the reaction as compared with the procedure at higher temperatures was that here the measurements gave the linear advance in 12 hours, which averaged 0·345 mm., whereas at higher temperatures (except 10°) the measurements were times taken to advance by 0·25 mm. In both cases the width of of the horizontal sections was the same, namely 1·5 mm.

The method of starting a run at 0° was as follows. Six slides were prepared, and the monoclinic phase caused to crystallise, as in the work at higher temperatures. At intervals of 5 minutes each slide was inoculated by means of a brush of the same type as that used in the projection apparatus, and immediately lowered to its place in the rack *M*. Zero time was taken as the time of inoculation, but this was not important since, as in the work at higher temperatures, the first stage in the advance of the interface was ignored when calculating the mean rate.

Microscopic Study of the Transformation.—As indicated in Part V, the rather thick films used for the velocity determinations were not suitable for a complete optical study under the microscope. Owing

FIG. 2.



Photographic record of advance of interface at 0°. The arrows indicate the film edge. The rhombic phase appears dark.

to the high birefringence of sulphur, films of this thickness between crossed Nicols gave only " high white " polarisation effects, necessitating the use of special compensators of high relative retardation for the recognition of the " fast " and " slow " directions, whilst the fact that the films were confined between two microscope slides prevented the use of objectives of high numerical aperture (and therefore small working distance) so that interference figures could not be obtained. Moreover the details of the manner in which the rhombic phase grows, which it was one of the main objects of the present investigation to study, are not easy to make out on a thick film owing to the small depth of focus of high power objectives.

The microscopic study was therefore carried out on films of the order of 0·01 mm. or less in thickness, prepared by melting a little sulphur between a slide and a cover slip. As with the thicker films, care was taken not to exceed 123° when doing this. Owing, however, to the greater rate of heat loss from the thinner films through the thin cover slips, it was necessary to modify the procedure for crystallising out the monoclinic form as follows, in order to avoid the formation of very small crystals. When the sulphur had melted, a microscope slide was placed over the preparation so as to cover all but one edge of the cover slip. After time had been allowed for the additional slide to become warm, the hot-plate temperature was lowered to about 115°, and a platinum point run along the uncovered edge. A good proportion of large crystals was thus obtained, many of which filled or nearly filled the field of the microscope when the $\frac{1}{4}$-inch objective was used (equivalent diameter about 0·3 mm.). Inoculation of these films was conveniently effected by running the corner of a razor blade covered with powdered rhombic sulphur along an edge. (The type of inoculating brush used with thicker films was too coarse to penetrate.)

For study of the interface movement at different temperatures, an electrically heated stage was used. This consisted of a circular brass plate, 3 in. in diameter and $\frac{1}{16}$ in. thick, recessed underneath over most of its area to a depth of $\frac{1}{32}$ in. to accommodate an evenly spaced nichrome-ribbon heating element wound on mica. At the centre of the plate was a hole for the passage of the light, tapering from $\frac{1}{4}$ in. diameter on the lower surface to $\frac{1}{8}$ in. at the top, so as to fit the convergent beam from the condenser. A copper–constantan thermocouple was screwed to the under-side of the plate as near as possible to the edge of the central hole. A circular sheet of mica covering the under-side of the plate, and attached to the edge of it by small screws kept the heating element and thermocouple leads in place when the stage was not in use. The whole assembly was attached directly to the stage of the microscope (a Swift " Lapidex ") by finger screws passing through four equidistant holes near the periphery. These holes allowed a little lateral movement so that the hot stage could be centred (this being done by focusing on the central $\frac{1}{8}$ in. aperture, a low-power objective being used) before the screws were finally tightened. The heads of two adjacent screws were recessed to take a pair of stage clips. The leads from the heating element and thermocouple were led upwards to a small terminal panel fixed just in front of the microscope, leaving sufficient slack to permit the microscope stage to be turned through one complete revolution. The cold junction of the thermocouple circuit was kept at 0° in melting ice in a Dewar vessel, and the temperature was read to $\frac{1}{2}$° on a high-resistance millivoltmeter. This had been previously calibrated by observations on the melting of a series of substances of known m. p. in powder form placed between a slide and a cover slip. Different calibration graphs had to be used for the low-power and the $\frac{1}{4}$ in. objectives (the latter was the highest power used with the hot stage) for the close proximity of the latter to the object had a considerable cooling effect, and with it, the millivoltmeter reading corresponding to a given temperature was higher than when a low-power objective was used, the difference increasing with rise of temperature. From the smoothness of the calibration graphs and the reproducibility of m. p.s, the accuracy of the stage was found to be rather better than $\pm 1°$.

The advantage of this type of hot stage was that owing to its small thickness ($\frac{1}{16}$ in. plus the thickness of the mica cover sheet) the slide was not raised very much above its normal position in relation to the condenser, so that interference figures could still be obtained, though with some slight sacrifice of numerical aperture. Its temperature could be rapidly altered, and yet readily held constant over long periods by hand control of a rheostat in the heating circuit.

Photomicrographs of the interface were taken by means of a Kodak 35-mm. camera. This was supported on a bridge between two rigid pillars, one on each side of the microscope, which were firmly secured to a wooden baseboard to which the microscope was clamped. The bridge was pivoted about one pillar and was clamped to the other. By releasing this clamp, therefore, the bridge could be swung out of the way, thus permitting ordinary visual observation down the microscope. Two procedures were used : (1) the subject having been found by direct observation, the bridge with the camera focused on infinity was rapidly swung into position, clamped, and the exposure made; (2) the ordinary microscope eyepiece was replaced by a viewing eyepiece attachment incorporating a half-reflecting prism, which could be moved out of the path of the light by a wire cable control. With this, the bridge and camera were in position from the start, and the subject was observed through the viewing eyepiece up to and if necessary during the moment of exposure. If the maximum intensity of illumination was required, as when photographing a fast-moving subject, the prism was thrown out of position just before opening the shutter. The viewing eyepiece attachment was supplied by Messrs. Cooke, Troughton and Simms, Ltd.

With this apparatus and a Cooke 48-watt high-intensity lamp as illuminant (with a heat-absorbing glass filter) records of the interface could be made at exposures as small as 1/200 sec., when using a $\frac{1}{4}$ in. objective and ordinary light. With crossed Nicols and the same objective, exposures of 1/50 to 1/25 sec. were required. Some interesting records of the movement of the interface were also made with a 16-mm. Ciné camera mounted on the bridge in place of the Kodak, and further work on this method of study of polymorphic transformations is in progress.

The Temperature at the Interface.—The transformation of monoclinic to rhombic sulphur is an exothermic process, and it was therefore considered necessary to try to ascertain whether under the experimental conditions the temperature at the interface was significantly higher than the temperature of the thermostat. In this connection we acknowledge with gratitude the assistance of Dr. P. M. Davidson, of the Physics Department, University College of Swansea. On the basis of the accepted principles of heat flow in a solid medium, and taking account of the fact that a real solid is an assemblage of atomic oscillators and not a continuum, Davidson obtains the following expression for the temperature rise, θ, at a plane heat source of infinite length and finite width moving perpendicular to the plane, in a solid medium extending indefinitely in all directions :

$$\theta = \frac{Q}{\pi k}\left[\frac{D}{2}(1 - \ln\left(\frac{DV}{8K^2}\right) - 0{\cdot}5772)\right]$$

where Q is the heat generated by unit area of the plane per second, V is the linear velocity, k is the thermal conductivity of the medium, D is the width of the plane source, and $K^2 = k/(\text{spec. heat} \times \text{density})$ for the medium. The conditions in the sulphur films used for the rate measurements could be regarded as approximating to those just stated, because the width of the interface was very small in relation to its length, and (if it is taken as the thickness of the film *) did not exceed 1/10 to 1/20 of the thickness of the glass slides confining the sulphur. The expression was therefore applied on the assumption that the actual temperature rise would lie somewhere between that for an all-glass medium and that for an all-sulphur medium. The results for 70° (at which V is near its maximum) were : θ (all glass) = $0{\cdot}5 \times 10^{-2}$ °c. ; θ (all sulphur) = 10^{-2} °c. It thus appeared that the effect was negligibly small. However, it was thought desirable to check this conclusion independently, and the following experiment was therefore carried out. The mixture of sulphur and calcium chloride was removed from the bottom of the glass cell of the slide holder, and dry mercury poured in to a depth of about 1½ inches. A slide was prepared in the usual manner, inserted in the nickel–iron frame, and lowered into the cell until its lower end was just above the mercury surface. After it had attained the temperature of the thermostat, it was inoculated, and then lowered further so that the lower half was immersed in the mercury. This half was therefore surrounded by a considerable quantity of a medium of good thermal conductivity and capacity at the thermostat temperature, and conditions for the dissipation of the heat of transformation were optimum. After the interface in the non-immersed upper part of the slide was seen to have advanced about 1·5 mm., a tracing of this part was made on the screen. Immediately afterwards, the slide was withdrawn from the mercury, and a tracing of the position of the interface in the lower half made. No significant difference in the rates for the two halves as indicated by these tracings was found. The experiment was done at a bath temperature of 60°, *i.e.*, just below the temperature of maximum velocity where the heating effect should be most marked, and it was repeated twice with the same result.

RESULTS AND DISCUSSION.

Table I and Fig. 3 give the average time (t)–distance (s) results (at 0°, time-average distance), including for completeness those reported in Part V (with some small corrections which a

TABLE I.

Time (t)*–distance* (s) *results.*

Temp.		*s* (mm.) at :										
	t (hrs.) =	12.		24.		36.		48.		60.		72.
0°		0·36		0·69		1·03		1·39		1·73		2·09
	Δ*s*		*0·33*		*0·34*		*0·36*		*0·34*		*0·36*	

	t (mins.) at :															
	s (mm.) =	0·25.		0·50.		0·75.		1·00.		1·25.		1·50.		1·75.		2·00.
20 †		36·8		71·5		110·5		154·8		201·5		245·2				
	Δ*t*		*34·7*		*39·0*		*44·3*		*46·7*		*43·7*					
30 †		17·2		37·6		54·5		73·5		93·8		112·0				
	Δ*t*		*20·4*		*16·9*		*19·0*		*20·3*		*18·2*					
30		20·6		40·6		59·0		75·8		95·1		107·4		122·2		136·5
	Δ*t*		*20·0*		*18·4*		*16·8*		*19·3*		*12·3*		14·8		14·3	
40 †		6·9		15·3		23·6		32·4		41·7		49·8				
	Δ*t*		*8·4*		*8·3*		*8·8*		*9·3*		*8·1*					
50		5·55		10·55		15·10		19·35		23·60		27·70		31·85		36·00
	Δ*t*		*5·00*		*4·55*		*4·25*		*4·25*		*4·10*		4·15		4·15	
60		4·40		7·90		11·10		14·15		17·20		20·15		22·95		25·65
	Δ*t*		*3·50*		*3·20*		*3·05*		*3·05*		*2·95*		2·80		2·75	
70		4·65		7·95		11·15		14·05		17·00		19·90		22·80		25·60
	Δ*t*		*3·30*		*3·20*		*2·90*		*2·95*		*2·90*		2·90		2·80	
80		24·8		37·8		48·7		58·6		68·1		77·3		84·7		93·9
	Δ*t*		*13·0*		*10·9*		*9·9*		*9·5*		*9·2*		7·4		9·2	

† Results of Elias, Hartshorne, and James, Part V.

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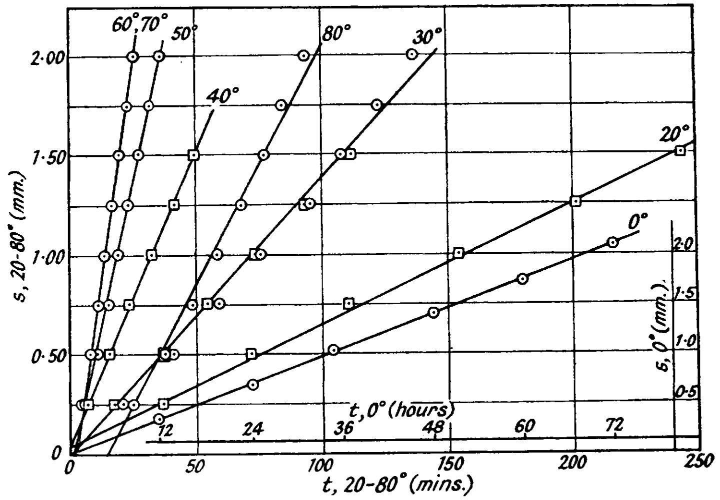
* Actually it is effectively greater than this owing to the fact that the advancing front is wedge-shaped (see later), but the increase is not serious near the temperature of maximum V (at which θ is also a maximum), since the wedge is narrow in this region.

revision of the previous calculations of the means has shown to be necessary). Each figure in the present work is based on 230—240 measurements, except those for 12 and 24 hours at 0° (220 measurements each), and for 1·75 and 2·00 mm. at 80° (196 measurements each). No results for 10° are given here, since, as already stated, only the mean rate of advance from about 0·25 to 1·50 mm. was determined. Attention is directed to the close agreement between the old and the new results at 30° up to $s = 1{\cdot}50$ mm., beyond which the former did not extend. In view of the considerable variance of measurements of this nature, this may be regarded as very satisfactory.

All the plots for the new results (Fig. 3) are very near to straight lines, as was previously found at 20°, 30°, and 40°. From 50° to 80°, however, the " best " straight lines extrapolate to the t axis, the value of the intercept increasing with rise of temperature and being especially large at 80°. The marked initial increase in rate which this represents is succeeded at all these temperatures by a slight upward trend (see Δt values in Table I), and a similar trend is apparent in the new results at 30° if the Δt values for 1·75 and 2·00 mm. are taken into account. It was suggested in Part V that results for the first 0·25 mm. might be somewhat unreliable, but the reasons advanced were mostly such as would account only for an apparent initial *decrease* in the rate which was shown by the s–t graphs at 20° and 40° (see Fig. 3). (It may be noted that the s–t graph for the intermediate temperature of 30° extrapolates very nearly to the origin.) At first sight it seems possible that the deviations from linearity now in question might have arisen from the use of the new slide holder (p. 1098). This could not have completely prevented evaporation of the *monoclinic* form since the atmosphere inside the cell was saturated with vapour with respect to rhombic sulphur. If therefore loss of material from the film in the region of the interface did in some way slow down the rate of transformation, it would be expected that the effect would be most marked in the initial stages when the interface was very near to the film edge, and that it would increase with rise of temperature, as was actually found. The following experimental evidence and general considerations show, however, that evaporation could have had little if any effect on the rate except possibly in the very early stages.

FIG. 3.



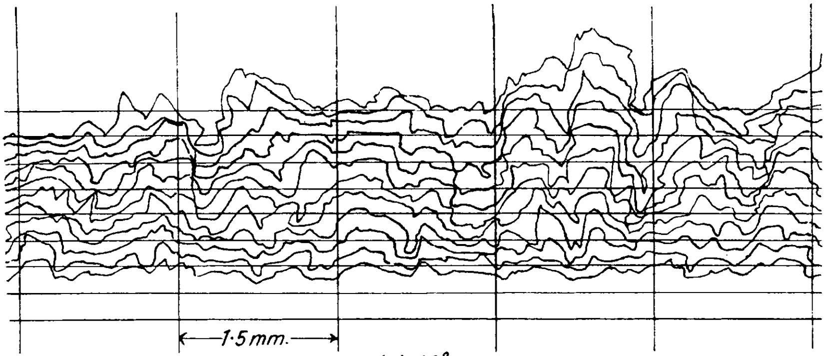
⊡ = *Results of Elias, Hartshorne, and James.*

(*The third point from the left on the* 0° *graph should be moved horizontally so as to be immediately above the* 36-*hour point on the time scale.*)

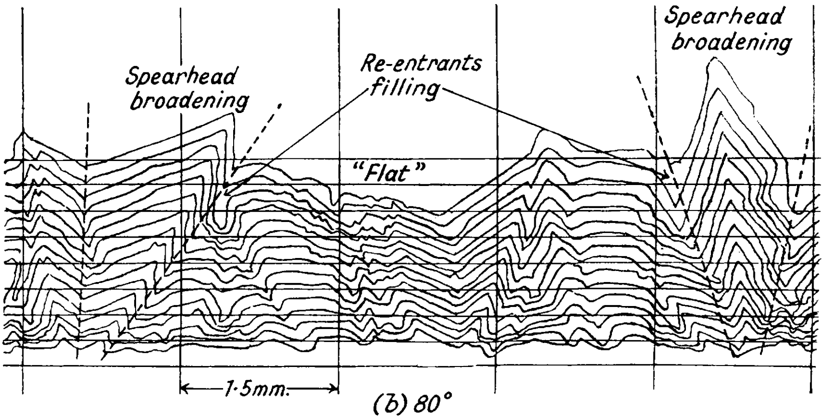
(1) Films, very much thinner than those used for the rate measurements, prepared between a slide and cover slip and observed under the microscope at 60—70°, show no apparent reduction in the rate of advance of the interface when the cover slip is stripped off and the sulphur is thus completely exposed to the atmosphere. (If evaporation were important, it would be expected to affect conditions at the interface much more in these thinner films than in those used for the rate measurements.)

(2) If it be assumed that the thickness of the transitional layer at the interface is of the order of the average distance between the molecules in the crystals, *i.e.*, *ca.* 10^{-7} cm., then the interface " fissure " in a film 10^{-2} cm. thick, such as those used for the rate measurements, must be about 10^{5} times as deep as its distance from wall to wall, which is of course very much less than the average intermolecular distance in the free vapour (*ca.* $3{\cdot}5 \times 10^{-5}$ cm. at 80°). It seems impossible that diffusion from such a fissure could appreciably affect the population of molecules undergoing transition except near the film surfaces, especially when it is remembered that the walls are not inert but are continuous sources of these molecules, and that air is present. The rate of advance of the leading edge of the rhombic phase deep down in the film (which is what is observed) should not therefore be appreciably affected.

FIG. 4.



(a) 30°



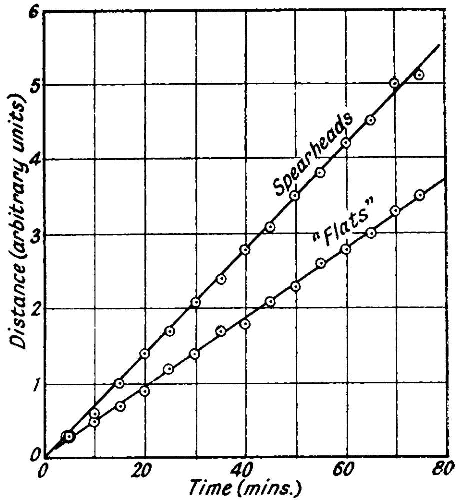
(b) 80°

Tracings of position of interface at 5-minute intervals.

(3) At 80° the advancing rhombic phase consists of large crystals which may be broadly divided into two groups according to their orientation : (*a*) those whose leading edge is approximately parallel to the film edge (for convenience these will be referred to as " flats ") ; (*b*) more rapidly advancing " spearheads," most of which, to judge from their profile angles, are probably pyramids bounded by {111}, and if so, show that there is a preferred tendency to grow in the direction of the *c* crystallographic axis (see Fig. 4, *b*). Measurements of the average rate of advance of these flats and spearheads in a film have been made over the range 0·25—2·00 mm. (for the interface advance as a whole) from tracings of successive positions of the interface at 5-minute intervals. Fig. 4, *b* shows a section of these tracings. The rate is strictly constant, as will be seen from the very good straight lines in Fig. 5, which are based respectively on measurements made on 6 flats and 7 spearheads. This indicated that the advancing fronts of *individual crystals* do move at a steady rate, though the *s–t* results for the interface as a whole show an upward trend over the same range (Table I). If this latter had been due to evaporation becoming less and less important as the interface receded from the film edge, it should have appeared also in the measurements on the single crystals.

The observations just described suggest at least part of the reason for this upward trend. As the interface advances, the more rapidly moving spearheads broaden at the expense of the flats, and so contribute more and more to the average rate measured in the direction normal to the film edge. In addition, sharp re-entrants tend to fill up by lateral growth. Both these features are exemplified in Fig. 4, *b*. To a lesser extent the same features appear at lower temperatures, and could account for the upward trends observed at 50°, 60°, and 70°, and in the later stages at 30°. Only in the range above the temperature of maximum rate (about 65°, see later), however, do the spearheads show such good development as those illustrated in Fig. 4, *b*. Fig. 4, *a* shows for comparison tracings of the interface made at 30°. Spearheads are present, but it will be seen that they are not so large as those in Fig. 4, *b*, and that they do not maintain their individuality and direction nearly so well.

FIG. 5.



It is very doubtful whether the above explanation can account for the very much more marked increase in the rate observed in the initial stage at these higher temperatures—particularly that at 80°—and no good reason can be given for it. It is possible that evaporation of the monoclinic form at the edge of the film impaired the efficiency of the inoculation process by reducing the areas of contact between the monoclinic crystals and the particles of rhombic sulphur scattered by the inoculation brush, so that the continuous interface took longer to form and "get going." Indeed, we formed the impression that there was a distinct lag in the visible response to the act of inoculation at 80°, though it was difficult to be sure of this, because owing to refraction and internal reflection effects at the edge of the glass slide which coincided with the edge of the film, the latter could not be focused on the screen very critically. A contributing factor might be a phenomenon similar to the abnormally slow rate of growth of very small dehydration "nuclei" on crystals of salt hydrates, found, *e.g.*, by Garner and Cooper (*Trans. Faraday Soc.*, 1936, **32**, 1739), though it must be remembered that this effect decreases with rise of temperature, whilst that now in question increases.

TABLE II.

Mean linear rate (*mm.*/*hr.*) *calculated in different ways.*

Temp.	(1). Mode of distribution curve of Δ*t* * values.				(2.) Mean of Δ*t* values.				(3.) Mean of reciprocals of Δ*t* values.			
	V_1.	log V_1.	Δ log V_1.		V_2.	log V_2.	Δ log V_2.		V_3.	log V_3.	Δ log V_3.	
0°	0·028	−1·55	0·63	1·11	0·027	−1·57	0·67	1·10	0·029	−1·54	0·65	1·10
10	0·119	−0·92	0·48		0·126	−0·90	0·43		0·130	−0·89	0·45	
20 †	0·36	−0·44	0·37		0·34	−0·47	0·39		0·36	−0·44	0·39	
30 †	0·83	−0·08			0·79	−0·10			0·86	−0·07		
30	0·85	−0·07	0·34		0·86	−0·07	0·33		0·94	−0·03	0·35	
40 †	1·83	0·26	0·29		1·75	0·24	0·29		1·98	0·30	0·26	
50	3·53	0·55	0·18		3·39	0·53	0·15		3·60	0·56	0·15	
60	5·36	0·73	0·02		4·77	0·68	0·01		5·16	0·71	0·01	
70	5·66	0·75	0·56		4·92	0·69	0·53		5·30	0·72	0·52	
80	1·54	0·19			1·43	0·16			1·60	0·20		

* Δ*t* = Time required to advance 0·25 mm.
† Results of Elias, Hartshorne, and James, Part V.

The Temperature Coefficient of the Transformation.—As the basis for the comparison of the rates at different temperatures, only the results for the *s* range 0·25—1·50 mm. (italicised in Table I) have been used, except at 0°, thus eliminating the uncertainties attached to the measurements at the extreme edge of the film. Over this range the deviations from linearity are negligible or very small at all temperatures, and, as in Part V, the rate has been assumed to be constant in calculating the means from the Δ*t* values. At 0° the measurements for the first stage of advance from the film edge were again ignored, but the *s* range used, 0·36—2·09 mm., was necessarily rather different owing to the different method of measurement used. Since, however, the *s–t* graph for this temperature was a very good straight line over its whole length (see Fig. 3), this was not thought to be important. As stated above, about 1200 Δt values (Δs values at 0°) were averaged at each temperature. This corresponds to the same length and advance of interface as was covered by the results in Part V, but there the Δt values for the first 0·25 mm. were included in the means. The means have now been recalculated. without using these initial measurements, in order to make them comparable with the newer results, though this has made little difference in the figures.

Table II gives the linear rates (V) expressed as (1) the reciprocals of the modes of the Δt distribution curves, (2) the reciprocals of the means of the Δt values, and (3) the means of the reciprocals of the Δt values. Fig. 6 shows a typical Δt distribution curve. These curves were the same at all temperatures in being skew towards the higher Δt values, and they exhibited no trend in the degree of skewness with change of temperature. The standard deviations and coefficients of variation have already been reported (*Discuss. Faraday Soc., loc. cit.*). Fig. 7 shows the plots of log V, expressed in the above three ways, against $1/T$. The standard deviations are shown on curve (3) by the short strokes above and below each point. It will be seen that, from the point of view of determining the temperature coefficient, particularly at the important low-temperature end of the curves, there is little to choose between them. This appears also from the Δ log V values in Table II. The closest agreement between the old and the new results at 30° is given by the modes (1), and this curve is also the smoothest, but the means of the reciprocal Δt values (3), *i.e.*, the means of the measured velocities, are probably the most fundamental functions of the results statistically.

FIG. 6.

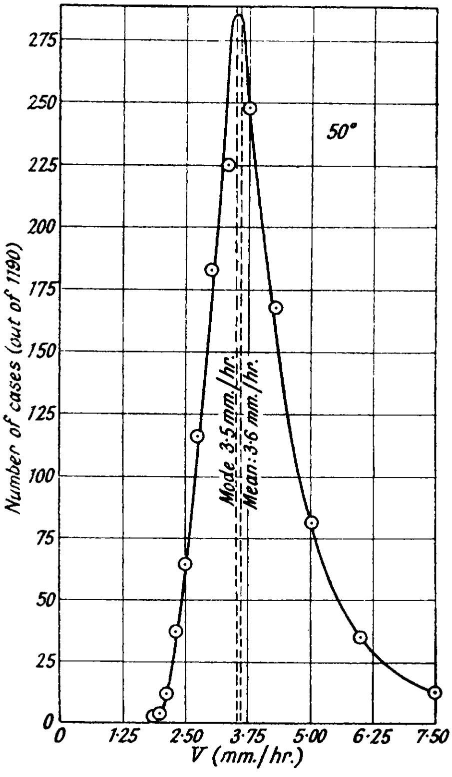
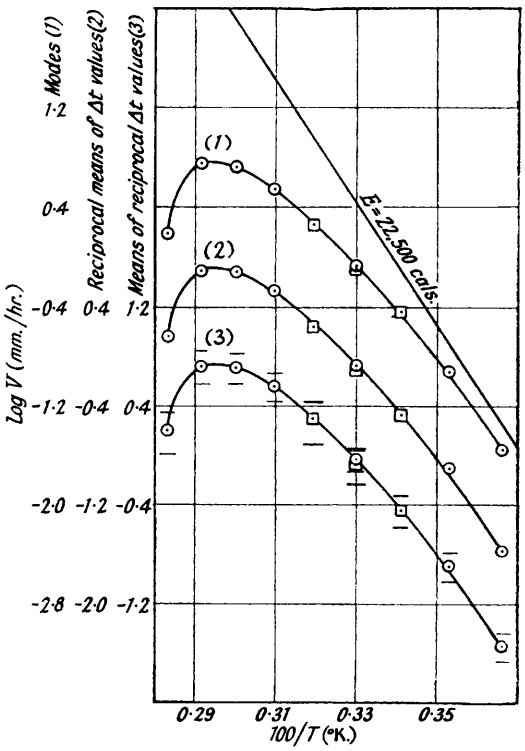


FIG. 7.



□ = *Results of Elias, Hartshorne, and James.*

The apparent activation energy (*i.e.*, the value corresponding to the slope of the log V–$1/T$ graph) over the limited range of temperature, 20—40°, covered in Part V was found to be practically constant at about 15,000 cals. The theoretical value for 20 to 30°, based on the assumption that the rate was given by the difference between the rates of evaporation of the two forms (or between rates of escape having the same temperature dependence as these) was found by the graphical method described in Part IV (*J.*, 1938, 1636) to be about 22,000 cals. [A rounded value of 1000 cals. for q, the mean heat of transformation, was used in this calculation. Using the more accurate figure of 730 cals., and calculating by means of the equation

$$\ln V - \ln [1 - e^{q(1/T_0 - 1/T)/\boldsymbol{R}}] = -\frac{E\alpha}{\boldsymbol{R}T} + \ln\frac{A\alpha}{2} \quad . \quad . \quad . \quad . \quad \text{(i)}$$

(see *Discuss. Faraday Soc.*, *loc. cit.*, p. 150, eqn. 6), we obtain 19,400 cals. as the value for the range 20—40°—still very much greater than the experimental one.] It was concluded from this that the true activation energy involved in the transfer of molecules from the monoclinic to the rhombic lattice was less than the heat of sublimation. The newer results show, however, that this conclusion was premature, at least in so far as it concerned the activation energy which determines the temperature coefficient of the transformation (see later). The apparent activation energy for the lower range 0—20° is 20,300 cals. on the basis of the modes (Curve 1, Fig. 7), or 20,000 cals. on the basis of the means (Curves 2 and 3), whilst the value calculated for this range by means of eqn. (i) is 20,500 cals., in very good agreement with these figures. In the Faraday Society paper (*loc. cit.*) it was shown that deviations from the requirements of eqn. (i) at higher temperatures such as that just cited for the range 20—40°, could be quantitatively accounted for on the assumption that the surface energy of the rhombic phase below the temperature of maximum velocity was slightly higher than normal, as was suggested by microscopic studies of the interface. It was also pointed out that deviations attributable to this cause would be small at lower temperatures. The good agreement between the observed and the calculated apparent activation energies for the range 0—20°, when E_a is taken as the heat of sublimation of the monoclinic form, may therefore be taken as evidence that the true activation energy is equal to, or nearly as great as, that which a molecule must acquire to enter the free vapour phase (it can hardly be greater than this).

The fact that all the curves in Fig. 7 appear to tend to a limiting slope corresponding to *ca.* 22,500 cals. supports this conclusion irrespective of the particular mechanism by which the molecules are supposed to be transferred from one lattice to the other. Stated in quite general terms, the reason why the rate of transformation passes through a maximum is that there is an increasing tendency for the reverse reaction to occur, *i.e.*, for molecules to pass from the stable to the unstable lattice, as the transition point is approached. As the temperature falls, the relative contribution of this reverse flow to the net rate of transformation progressively decreases, so that the slope of the log rate–$1/T$ graph tends more and more to that corresponding to the activation energy for the forward reaction. In the theory underlying eqn. (i), the forward and the reverse reactions are pictured as simple evaporation–condensation processes occurring through a transitional layer; in Dunning's nucleation theory (*Discuss. Faraday Soc.*, *loc. cit.*, p. 156), the reverse process is the overall tendency for nuclei below the critical size to disperse, some at least of the molecules so dispersed finding their way back to the unstable lattice.

Measurements of the rate at temperatures below 0° are required to settle definitely whether the curves are in fact approaching a limiting slope of the above value, and it is hoped to make such measurements in the near future.

In Part V the point was made that a direct comparison between scalar properties such as the heat of sublimation on the one hand, and activation energies derived from measurements of the linear rate of advance of the interface on the other, was not justifiable, since the measurements had a largely vectorial basis. This was based on the supposition that the monoclinic crystals were mostly oriented with $b(010)$ parallel to the plane of the film, and their c axes parallel or nearly parallel to the direction of growth of the rhombic phase. As appears below, it is now known from microscopic examination that the orientation of the monoclinic crystals in the films is much more varied than this and that, owing to the ragged contour of the interface (particularly at the lower temperatures), a given rhombic crystal advances along many different crystallographic directions in the same monoclinic crystal. The rate measured may therefore be assumed to be the average for a large range of relative orientations of the two forms, and the point in question thus seems now to be of little importance.

Dunning's Theory of the Temperature Coefficient (*ibid.*, p. 157).—Further consideration has been given to this theory which appears to account so elegantly for the effect of temperature on the rate over the whole range studied. The objections previously advanced, however, still seem to be important, and in particular it is felt that a theory which fails to take account of the obvious differences in the character of the interface above and below the temperature of maximum velocity must at best be incomplete. One of these objections, it will be recalled, was that the theory led to a value for the surface free energy which appeared to be far too small (4 ergs/cm.^{2}). It is of interest that the explanation proposed by the senior author for the deviations of the results from eqn. (i) (see above) is consistent with a much more probable value. The deviations up to 50—60° can be accounted for by a ϕ factor (ratio of the rate of escape of molecules from the finely serrated front of the rhombic phase to the rate for a plane surface) of 1·10. Taking the surface free energy as 100 ergs/cm.^{2}, which seems to be of the right order, since the value (International Critical Tables) for the liquid at the melting point is 60, and applying the Gibbs–Thomson equation, we find that this factor corresponds to a particle radius of between 10^{-5} and 10^{-4} cm. This is the order of the size of the smallest " teeth " visible under the microscope on the advancing front of the rhombic phase.

Moreover, it seems that there is no case on record of the growth of a real crystal from its free vapour obeying Volmer's equation for two-dimensional nucleation quantitatively, the critical supersaturation for continued growth being always very much less, if detectable at all, than the equation demands (cf. Volmer's own investigation of the growth of crystals of iodine, phosphorus, and naphthalene; Volmer and Schultze, *Z. physikal. Chem.*, 1931, *A*, **156**, 1), and, as is well known, Frank (*Discuss. Faraday Soc.*, No. 5, p. 48) has accounted for this by the theory that real crystal faces have self-perpetuating growth steps due to screw dislocations.

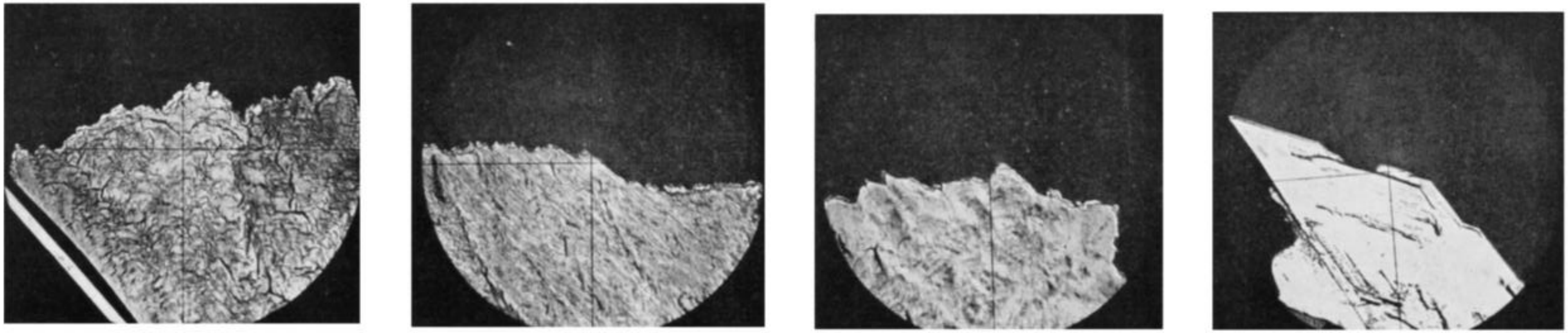
Specimens of Sulphur showing Abnormal Rates of Transformation.—During the measurements at 80° (the last temperature but one at which measurements were made), the stock of purified sulphur (A) which had been used up to then became nearly exhausted, and a new one (B) was prepared, exactly the same methods of recrystallisation and degassing being used as before. Slides prepared from this sample and studied at 80° behaved in a highly unusual manner. After advancing at about the normal rate for the first 0·25 mm., the interface developed a number of promontories which advanced at rates up to some 10 times the normal value, at the same time spreading sideways into the screen sections occupied by the more slowly moving parts. The sample of sulphur was again recrystallised and degassed, but slides prepared from this new product (C) showed the same abnormal behaviour. So too did slides prepared from a third sample of recrystallised and degassed sulphur (D) derived from an entirely different source of starting material, which in all cases was " Crystalline Sulphur " supplied by either Hopkin and Williams or British Drug Houses.

Various tests were made to ascertain whether this behaviour was due to the presence of impurities (*e.g.*, selenium), or to a high proportion of insoluble sulphur (which must be formed to some extent when the sulphur is melted in the degassing process), but the results were all negative or inconclusive. It was then noticed that specimens B, C, and D consisted of clear crystals, whilst A consisted of opaque lumps. This indicated that the former had crystallised from the melt directly as the rhombic form, the latter as the monoclinic form which had then undergone the usual transformation to the rhombic form. Specimen D was therefore put through the degassing process again, but in such a way as to ensure that it crystallised initially as monoclinic tulphur. (The specimen was melted except for a few crystals, which at that high temperature underwent transformation to the monoclinic form, and on cooling induced the crystallisation of this form alone.) After time had been allowed for the cooled specimen (E) to be transformed into rhombic sulphur, slides were prepared from it and these behaved in an entirely " normal " manner, *i.e.*, in each slide the interface advanced at approximately the same rate over its whole length, and the mean rates at 80° covered almost exactly the same range as did those for slides prepared from specimen A at this temperature. Specimen E was subsequently used for the measurements at 10°, and Fig. 7 shows that the results fit in well with those at 0° and 20°.

Comparisons of the melting behaviour of specimens B, C, and D with that of specimens A and E have since been made on the hot stage (previously described) under the microscope, and, to the accuracy possible with this apparatus (see above), show no evidence of any difference of chemical purity : B, C, and D all melted completely at about 115° (the metastable m. p. of rhombic sulphur), but most of the opaque particles of A and E were seen to undergo a phase transformation above the monoclinic–rhombic transition point (96°) and then melted at about 120° (the m. p. of monoclinic sulphur). Further, when B, C, and D were caused to crystallise from a melted film as monoclinic sulphur, this melted at the same temperature as A and E, whilst if the latter were crystallised from the melt in the rhombic form they melted at the same temperature as the original particles of B, C, and D.

The only ascertainable difference then between the " abnormal " specimens and specimens

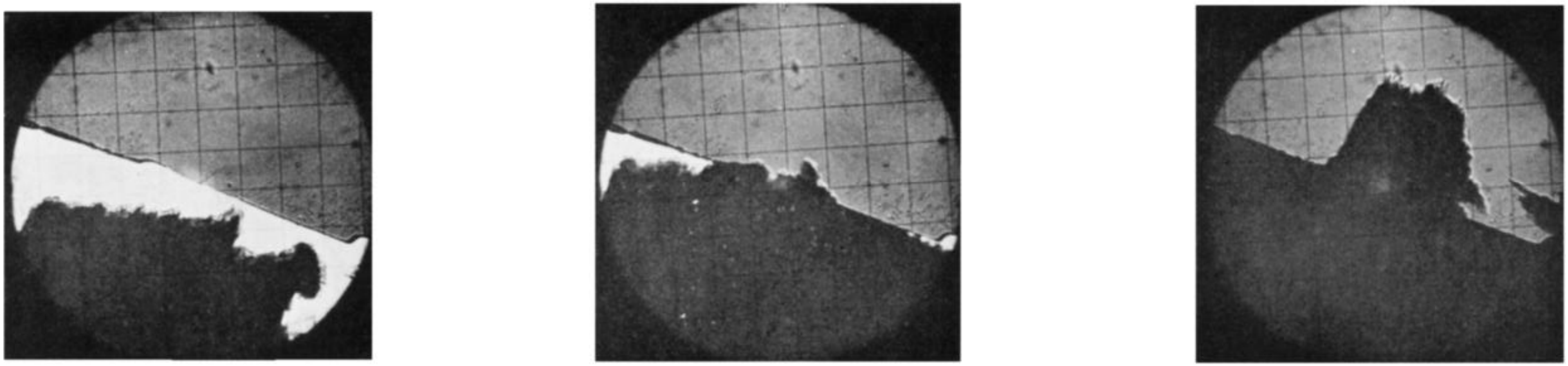
FIG. 8.



(*a*) 20°. (*b*) 40°. (*c*) 60°. (*d*) 80°.

Effect of temperature on the interface. (The monoclinic phase is shown in extinction.) Scale × 185.

FIG. 9.



(*a*) (*b*) (*c*)

Interface crossing the boundary between two monoclinic crystals. (1 grid square = 0·023 *mm.)*

A and E was that, when heated, A and E underwent transformation at the transition point (presumably because they consisted of a mass of small crystals, the large specific surface of which favoured the formation of nuclei) and melted at the stable m. p., whereas the former did not do so and melted some 5° lower. Why this should have led to such a profound difference in the mode of transformation of the monoclinic films prepared from these melts is not clear and further investigation is required. Possibly the reason is to be sought in a difference in the mosaic structure, or other type of crystal imperfection (see p. 1113). A less likely explanation is that the " abnormal " films contained some γ-sulphur (one of the monotropic monoclinic modifications, commonly called " nacreous " sulphur). This sometimes appears when a thin film between a slide and a cover slip is allowed to crystallise spontaneously, though usually only when the supercooling is great, and we have observed that, when it is inoculated with rhombic sulphur, the interface advances much more rapidly than in ordinary monoclinic (β) sulphur. We have also noticed, however, that γ- changes very rapidly into β-sulphur at about 80° when the two are present in the same film, and it therefore seems very unlikely that, if the former had appeared in the films prepared for the rate measurements, it would have survived the period in the thermostat before inoculation.

Microscopic Study of the Advance of the Interface.—It must be said at once that the details of the manner in which the rhombic phase advances as revealed by high-power microscopy are very complex and varied, and merit a much closer study than has been made so far. New information is being sought by application of the cinephotomicrographic technique. The main results of microscopic study obtained up to the present are as follows. Except where otherwise stated, they refer to observations made on very much thinner films than those used for the rate measurements. The reasons for using thinner films have already been given (p. 1101).

(1) The interface advances, not as a plane wall normal to the plane of the film, but as a wedge which penetrates the monoclinic phase. Between crossed Nicols and with the stage turned so that the monoclinic phase is in extinction, this wedge is clearly revealed by bands of polarisation colours running parallel to the interface and rising in Newton's scale from the leading edge to the body of the rhombic phase. In monochrome, these bands of colours may be seen in the photomicrographs in Figs. 8, *a*, *b*, and *c*. Very considerable variations in the width of this wedge-shaped fringe were observed at different parts of the interface in the same film, and at temperatures below 40° it was often much wider than the examples shown in the photomicrographs. In general, however, the fringe was narrower the higher the temperature.

The observed widths of the fringe in relation to the order of thickness of the films are not inconsistent with the supposition that the wedge surfaces correspond to crystal faces of low indices (though very imperfect ones at the lower temperatures), except perhaps in the case of the greatest widths (about 0·05 mm.; order of film thickness, 0·01 mm.). Owing to the relatively large *c* spacing of rhombic sulphur ($a = 10{\cdot}34$, $b = 12{\cdot}92$, $c = 24{\cdot}55$ A.; Warren and Burwell, *J. Chem. Physics*, 1935, **3**, 6), very acute-angled forms commonly occur. Thus the internal angle between opposite $\{111\}$ faces on the same pyramid is only about 37°, and a growth front bounded by these faces would show a very pronouncedly wedge-shaped contour. Above the temperature of maximum velocity, the surfaces of the narrow wedges seen on the borders of the well-developed crystals that are formed in this range are more certainly recognisable as definite crystal faces. Thus the width of the narrow wedge running along the top edge of the spearhead in Fig. 8, *d* (80°) is about 0·003 mm. Assuming that the film is 0·01 mm. thick, and that the leading edge of the wedge lies on the lower glass surface, we have that $\tan^{-1} 0{\cdot}01/0{\cdot}003 = 73°$, which is the wedge angle and also the polar angle between the upper surface of the wedge and the plane of the spearhead. This is equal to the angle $(111):(1\bar{1}1)$ (Groth, " Chemische Kristallographie," Vol. I), and the measured profile angle of the spearhead, 36°, agrees almost exactly with that calculated from Groth's data for a (111) face on an unmodified pyramid. Although the close agreement between the estimate of the wedge angle and the angle $(111):(1\bar{1}1)$ must to some extent be fortuitous in view of the approximate nature of the values for the wedge width and film thickness, it does suggest strongly that the wedge surface is a (111) face, and this is supported by the cleavage cracks seen in the figure to be running parallel to the wedge (with others parallel to the concealed face along the lower edge of the spearhead), for rhombic sulphur is known to have a (111) cleavage.

The marked variations in the width of the wedge observed in different parts of the same film at lower temperatures could, on the above basis, be due to the differing orientations of the rhombic phase along the interface. Unfortunately, it has not yet proved possible to trace any such relation, owing to the difficulty of obtaining clear interference figures from the rhombic phase in this region (see below). The very wide wedges referred to above may possibly arise through the interface advancing preferentially along cleavage cracks in the monoclinic phase that are parallel to the *plane of the film.* Some support for this possibility comes from one of our cinephotomicrographic records, which at one stage shows two apparently independent interfaces advancing at different levels in the film. This kind of transformation is already known to occur in (001) tablets of yellow mercuric iodide (Kohlschütter, *Kolloid-Beih.*, 1927, **24**, 319) and splits them into leaflets parallel to the (001) cleavage.

The wedge-shaped fringe appears just as prominently in films from which the cover slip has been stripped, and also in flakes which have been completely detached from the slide by gentle scratching with a needle. It is not therefore due in any way to the presence of the glass surfaces between which the films are normally confined.

(2) As seen in fine detail, the advance of the interface over any small element of its length exhibits continual and spasmodic fluctuations of rate arising from (*a*) local small-scale surges of growth, and (*b*) the formation of cracks due to the shrinkage attending the transformation, which hinder the advance to a greater or less degree. The surges are of three kinds : (i) the sudden protrusion of small promontories at the leading edge of the wedge; (ii) the rapid spreading of layers along this edge; (iii) the rapid spreading of layers over the surface of the wedge. These layers recall those described by Bunn and Emmett (*Discuss. Faraday Soc.*, No. 5, *loc. cit.*, p. 119), which are seen on crystals of certain substances growing from strongly supersaturated solutions. The size of the promontories is variable, but their diameter is commonly of the order of 10^{-4} cm. or less (approaching the limit of resolution of the microscope), and at lower temperatures they appear to be very rounded. The finer serrations on the interface in Fig. 8, *a* are typical of the appearance of the larger ones. The layers spreading along the edge of the wedge are about 10^{-3} to 10^{-4} cm. thick.

It should be explained that these rapid movements are superimposed on what appears to be a steady advance of the leading edge of the wedge; *i.e.*, between two successive surges at the same part of the interface, movement does not stop but proceeds smoothly (or appears to do so within the limits imposed by the resolution of the microscope) at a lower rate.

It is very difficult to compare accurately the relative contributions of the three kinds of surge at different temperatures by visual observation alone, because of the differences in the average rates of advance of the interface as a whole. At the lower temperatures events succeed one another so slowly that they are apt to be missed; at higher temperatures everything happens so quickly that the eye cannot take it all in. The further application of the cinephotomicrographic technique will, it is hoped, resolve this difficulty, and also enable the local rates of the advance to be measured. The results of visual observation and of the study of the few cinephotomicrographic records made so far are as follows. At room temperature, the leading edge of the interface advances in the main steadily, but very small rounded promontories push ahead continually at frequent intervals along the length (see Fig. 8, *a*). Sharp re-entrants between two closely neighbouring promontories soon fill up by lateral growth. Occasionally, a thick layer spreads across the surface of the wedge. As the temperature rises, the promontories become progressively more " crystalline " in contour, and an increasing proportion of the interface consists of straight lengths (see, *e.g.*, that at the middle of Fig. 8, *b*). Along these straight sections layers are seen to travel, these layers originating from promontories formed at one end or the other. At 60—70°, where the average rate is a maximum, the interface has lost almost completely the finely serrated contour characteristic of the lower temperatures, and consists of straight or nearly straight sections, along which layers spread in rapid sequence both along the leading edge of the wedge and over its surface, the latter moving from the body of the rhombic phase towards the leading edge, but not possessing the regular and parallel contours of those observed by Bunn and Emmett (*loc. cit.*) on crystals growing from solution. A close study of the mode of advance of the interface at still higher temperatures has not yet been made, but from preliminary observations the well-formed crystals (Fig. 8, *d*) appear to grow by a combination of a steady forward movement and the spreading of layers along the leading edge.

The cracks which form as a result of the shrinkage attending the transformation (referred to hereafter as " growth cracks ") may be classified into (*a*) short cracks along the leading edge of the interface, (*b*) short cracks parallel to the interface and just behind it, and (*c*) cracks which start in the rhombic phase and then penetrate through the interface a little way into the monoclinic phase. At lower temperatures all these cracks are irregular and often strongly curved, and it is not possible to trace any relation between their directions and the extinction directions of the rhombic phase, as would be the case if they formed along definite cleavage planes.

Fig. 8, *a* illustrates their varying shapes and directions. As the temperature rises and the crystallinity of the rhombic phase increases, the cracks become straighter and obviously tend to form more and more along definite cleavage planes. Thus the cracks parallel to the edges of the spearhead in Fig. 8, *d* may be identified as the traces of (111) cleavages (see above).

Growth cracks of type (*a*) halt the advance of the interface temporarily where they form. The advance is resumed either as the result of growth spreading around the ends of the crack, as is seen happening at the large crack in the upper part of Fig. 8, *d*, or because there is a " bridge " somewhere along the crack (*i.e.*, the crack is incomplete at some point) over which growth can continue. Cracks of type (*b*) have no apparent effect on the rate of advance, and those of type (*c*) only hinder the advance if they are inclined to the advancing front, or curve round so as to run approximately parallel to it. Such cracks often continue to open up ahead of the interface as it advances, for some considerable distance.

In addition to these growth cracks there are also present in the films a considerable number of what will be called " thermal cracks," which form when the monoclinic crystals are cooling after the film has been prepared, owing to the unequal coefficients of expansion of sulphur and glass. In thin films as used for the microscopic work, these thermal cracks can be seen to pass right through the film and they form complete barriers to the advance of the interface where they are parallel to it. The interface at the ends of such a crack, however, spreads inwards and joins up as in the case of growth cracks (*a*) and thus advance ahead of the crack is resumed.

These thermal cracks were also present, of course, in the thicker films used for the rate measurements, and it might be thought that they had an important effect on the average rate. Microscopic examination of a number of slides undergoing transformation showed, however, that this was not so. In the first place only those cracks which were parallel or nearly parallel to the film edge were potential barriers of any importance. A crack which is normal or much inclined to the edge offers little or no hindrance to the advance; the interface travels along each side of it. Secondly, many of the cracks in these thicker films appeared not to pass right through, for the interface crossed them without hesitation. Thirdly, the cracks were all short in relation to the length of interface studied, and were usually spaced in the direction of growth at intervals greater than their length. Thus when a barrier crack parallel to the film edge was encountered, the advance continued on either side and spread inwards to fill the area in front of the crack. Calculation shows that, this inward spreading being assumed to proceed with the same velocity in all directions (*i.e.*, the spreading fronts are arcs of circles—a reasonable assumption for the average behaviour in a large number of crystals), 95·7% of the area in front of the crack * will have been filled up by the time the interface on either side has advanced a distance equal to the length of the crack. The microscopic examination also showed that, at any time, less than 20% of the length of the interface was held up by barrier cracks, so their effect on the time taken to reach a given grid line would be proportionally reduced. Still less would be the effect on the *difference* between the times to reach two successive grid lines, *i.e.*, on the Δt values. In any case, the hindrance due to these thermal cracks would not be expected to vary appreciably with temperature, so the effect on the temperature coefficient should be negligible.

(3) The interference figures presented by the monoclinic crystals in the thin films show that the orientations relative to the plane of the films (and presumably this applies also to the thicker films used for the rate measurements) are much more varied than was thought when Part V was written. The frequent occurrence of extinction angles near to the maximum value of 44° led at the time to the conclusion that $b(010)$ was the favoured orientation. In monoclinic sulphur, however, the optic axial plane is parallel to $b(010)$, and $2V$ is fairly large (*ca.* 58°). This combination of optical properties results in an initially very slow decline in the extinction angle relative to c as the section changes from (010) towards (100). Thus the extinction angle for (110) which is inclined at about 45° (polar) to (010) is 38°, and even for (210) [64° to (010)] it is as high as 29°. Moreover, (001) sections with edges defined by (110) faces show an extinction angle of about 45°.

In addition to (010), which is often seen but is by no means the most frequent orientation, we now find that (100), (001), (110), and (210) are commonly present, as was found by Gaubert (*Bull. Soc. franç. Min.*, 1905, **28**, 157). In addition, (101) has been observed, and also another ($h0l$) section, the indices of which have not been identified, but which is recognisable by its nearly centred optic axial figure. Moreover, elongations along all three crystallographic axes occur.

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* *I.e.*, the area which would have been transformed if the crack had not been present.

The orientations of the rhombic crystals could not in general be determined with certainty. At lower temperatures, areas of the rhombic phase 0·2—0·3 mm. or more in diameter extinguished as a whole between crossed Nicols, and it was possible to determine their " fast " and " slow " directions, but they were extremely " fuzzy " in appearance (probably each such area was a crudely oriented aggregate of very small crystals), and they mostly gave poor interference figures. At higher temperatures where the crystallinity was better, it was possible to recognise (111) pyramids by their profile angles and (111) cleavage (*e.g.*, Fig. 8, *d*), but even here the interference figures were frequently obscure, and so the attempt to make a systematic study was abandoned.

Fraenkel and Goez's statement (*Z. anorg. Chem.*, 1925, **144**, 45) that one crystal direction of the monoclinic system is preserved in rhombic crystals resulting from transformation has not been substantiated by our observations. Indeed, no definite relation between the orientations of the two phases on either side of the interface was found to exist, and the reason for this is apparent from (4) below. In 50 cases studied to investigate this point, however, evidence was found that the relative orientations were not completely random. In these cases the mean angle between the " slow " directions of the two forms was 32°, whereas for random, orientation it should be 45°. A statistical test shows that the chance that this difference was a random sampling error is less than 0·1%.

(4) The most important result so far obtained from the microscopic study of the transformation is that *when the interface crosses a boundary between two differently oriented monoclinic crystals there is no change in the orientation of the rhombic phase.* This is illustrated by the example shown in Figs. 9, *a*, *b*, and *c*, photographed between crossed Nicols. In *a*, the interface with the rhombic phase in extinction is seen advancing towards the boundary between two monoclinic crystals, the different orientations of which are apparent from the fact that the upper one is nearly in extinction, and the lower one is not. In *b*, the interface has gained a bridgehead at a place where the two monoclinic crystals are in contact, and in *c* it is well across. There is, however, no departure from extinction after crossing, and therefore no change in orientation.

This result shows that the transformation process is essentially one of crystal growth in a solid medium. Molecules from the unstable phase are added to a pattern already laid down, *i.e.*, the stable crystal, as in the growth of crystals from fluid isotropic media. The orientation of the unstable phase does not influence that of the growing crystal once this is established, though it may influence the rate of growth. This latter point remains to be investigated.

The orientation of the unstable phase may, however, govern the orientation of a nucleus that starts spontaneously within it, and it may have been an observation of this kind which led Fraenkel and Goez to make the statement referred to above. An attempt has been made to investigate this possibility by a study of the nuclei which form spontaneously in films that have been remelted (see Part V, p. 591), but so far without success. The difficulty has been that very few of these nuclei appear in thin films, and by the time one has been noticed it has been found to have grown over several monoclinic crystals, so that it is impossible to say in which one it was generated. On general grounds it seems very probable that such an initial orientational relationship does exist, but if so, the indications of it to be found in a polycrystalline film will decline with the number of crystal boundaries crossed by the interface. The significant departure from random orientation in the 50 cases mentioned above (in all of which the interface had travelled some distance into the film) may perhaps be taken as evidence that there was a definite relationship at least in some crystals at the film edge where nucleation was effected. (In artificial nucleation by the methods used in this work, it is to be expected that some of the monoclinic crystals will be " touched off " by mechanical shock with a result similar to that of spontaneous nucleation, and not by contact with the particles of rhombic dust scattered by the inoculating device.)

The Temperature-independent Factor.—In the Faraday Society Discussion (*loc. cit.*) the suggestion was made by the senior author that the large temperature-independent factor of the transformation (*ca.* 10^7 times the product of the vibration frequency and the lattice spacing) could be explained by a " trigger " mechanism analogous to that proposed independently by Burgers and Mott (*Proc. K. Ned. Akad. Wet.*, 1947, **50**, 719) to account for a similar discrepancy in the rate of recrystallisation of metals. The fact that there is no change of orientation of the rhombic phase on crossing a crystal boundary which was not then known, is, however, strongly opposed to this idea. It means that molecules in the course of their transfer from the monoclinic to the rhombic lattice must be free to adopt whatever orientations are demanded for a continued build-up of the latter. The trigger mechanism on the other hand implies that the removal of one molecule from a mosaic block by thermal activation enables a rearrangement to the stable pattern to sweep through the block, as though the one molecule has been acting as a sort of keystone propping up the unstable edifice. If this were so, it would surely mean that there would be a definite spatial relationship between the new and the old patterns, so that when the interface passed from one crystal to another which was differently oriented, there would be a sharp change in the orientation of the rhombic phase, and this does not occur.

At the same Discussion, Garner (*loc. cit.*, p. 194) put forward an alternative explanation of the large temperature-independent factor, based on studies of the linear rate of growth of dehydration nuclei on chrome alum crystals, which shows a similar anomaly, and this explanation has been further developed in private correspondence with the senior author. Briefly, it is to the effect that the reaction can proceed with a small activation energy and therefore rapidly over small homogeneous elements of volume such as mosaic blocks, but that periodically the interface encounters obstacles which may be either cracks at mosaic block boundaries or growth cracks resulting from shrinkage. The passage of such an obstacle requires the formation of a bridge across it, and this will necessitate a large activation energy, which, if the bridge is formed by the condensation of vapour molecules in the crack, will be of the same order as the heat of sublimation. This large activation energy will determine the temperature coefficient of the reaction. This picture avoids the difficulty associated with the trigger theory discussed above, for the bridge would be a continuation of the pattern of the rhombic phase.

Let the width of the homogeneous blocks in the direction of advance of the interface be w cm., the width of the intervening cracks being assumed to be negligible in comparison. Further, let the rate of advance within a block be $\nu d \mathrm{e}^{-a/RT}$, where ν is the vibration frequency of the molecules in the monoclinic lattice, d is the average spacing in this lattice, and a is the activation energy, which is a small quantity, or at least considerably smaller than the heat of sublimation, since it is supposed that within the block the molecules can take up their positions on the rhombic lattice without having to escape completely from the attractive field of the monoclinic lattice (*e.g.*, by executing small rotational movements). If E is the activation energy for bridge formation (of the same order as the heat of sublimation; see above), then the time taken to form a bridge may be put equal to $K\mathrm{e}^{E/RT}$ secs., where K is a constant. The number of block-crack pairs in 1 cm. is $1/w$, and therefore the time taken to advance 1 cm. is

$$\frac{1}{w}\left(\frac{w\mathrm{e}^{a/RT}}{\nu d} + K\mathrm{e}^{E/RT}\right) = \frac{\mathrm{e}^{a/RT} + (\nu d/w)K\mathrm{e}^{E/RT}}{\nu d} \text{ secs.}$$

or the rate is

$$\frac{\nu d}{\mathrm{e}^{a/RT} + (\nu d/w)K\mathrm{e}^{E/RT}} \text{ cm./sec.}$$

If a is sufficiently small compared with E, the first term in the denominator is negligible in comparison with the second, and the expression for the rate simplifies to $(w/K)\mathrm{e}^{-E/RT}$. If we take w as the order of the width of a mosaic block, 10^{-5} cm., and E as 22,500 cals., K at 0° (rate = 0·029 mm./hr.; see Table II) works out to 10^{-17} sec. This seems to suggest that the vibration frequency of the molecules in the lattice from which the bridge is formed is at least as great as 10^{17}, whereas the usual estimate is 10^{12}—10^{13} for the mean frequency. A discrepancy of about this order, 10^4, has however been found by R. S. Bradley (personal communication; paper in the press) between the observed rate of evaporation of crystals of rhombic sulphur, and the rate calculated from the equation $\nu d\mathrm{e}^{-L/RT}$, where L is the heat of sublimation, so the above value of K probably does not constitute an important objection to the theory. Of course, if the homogeneous blocks are larger than has been assumed above, *e.g.*, if they are the regions between the visible growth cracks, K will be proportionally increased.

Calculation shows that if E = 22,500 cals., a can be as great as 10,000 cals. without affecting the validity of the approximation that the rate $= (w/K)\mathrm{e}^{-E/RT}$. Thus the theory allows for quite a large amount of energy for the transformation within the homogeneous blocks.

In the above treatment, no account has been taken of the reverse reaction, and the expressions as they stand are therefore only applicable to temperatures far below the transition point. They may be made general by multiplying by $(1 - \phi\mathrm{e}^{q(1/T_0 - 1/T)/R})$, if eqn. (i) is taken as the theoretical basis, or by $\mathrm{e}^{-A''/RT}$, where A'' is the activation energy for two-dimensional nucleation, if Dunning's nucleation theory be accepted. On the latter theory, the two-dimensional nucleus would itself constitute the bridge across the crack, if the width of the latter were of the order of a single lattice spacing.

The general idea that the reaction proceeds by a series of rapid sweeps over small elements of volume is supported by the spasmodic character of the advance of the interface which is revealed by microscopic examination as described above. A closer test of the theory must however, await the more detailed measurements of the local rates of advance, which it is hoped to carry out by means of the cinephotomicrographic technique.

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