407. *Studies in Polymorphism. Part VIII.* The Linear Rate of Transformation of β- into α-Sulphur at Low Temperatures and at Temperatures just below the Transition Point.*

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Extension of the measurements of the linear rate to $-15°$ has afforded further evidence that the activation energy for the transfer of molecules from the β- to the α-phase corresponds closely to the heat of sublimation of the former. At the lowest temperatures of the investigation the observed rate is about 10^3 times that calculated for a simple evaporation–condensation mechanism on the assumption that the rate of impact of molecules on the advancing α-surface is given by the Langmuir evaporation equation; but between 90° and the transition point (95·5°) the observed rate agrees with that calculated on this basis to within a power of 10.

Treatment of the results by Dunning's equation based on the theory of two-dimensional nucleation shows that above 80° the observed rate is far higher than that predicted from the application of the equation at lower temperatures.

IN Part VI [1] of this series, the linear rates of transformation of the enantiotropic monoclinic (β-)form of sulphur into rhombic (α-)sulphur over the range 0—80° were reported. With falling temperature the temperature coefficient of the rate appeared to tend towards a limiting value corresponding closely to the latent heat of sublimation of the β-form, suggesting that the activation energy of the transformation is the same as, or near to, that required for molecules to evaporate from the unstable form, or, in other words, that molecules in the transitional layer at the interface are energetically equivalent to molecules in the vapour state. This conclusion was in harmony with the results of an earlier study (Part III [2]), and if correct appeared to be of such fundamental importance for the theory of the transformation kinetics of molecular solids that it seemed desirable to test it further by extending the work to lower temperatures. New measurements, at

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* Part VII, Hartshorne and Swift, *J.*, 1955, 3705.

[1] Hartshorne and Roberts, *J.*, 1951, 1097.

[2] Hartshorne, Walters, and Williams, *J.*, 1935, 1860.

temperatures down to **-15",** have therefore been made, with samples **of** sulphur purified by different methods, and these are described in the first part **of** this paper. The results accord well with the previous conclusion. The paper also reports measurements of the rate between **80"** and the transition point, and these show a similar dependence **of** the rate on temperature to that found for carbon tetrabromide near its transition point (Part VII [3]).

<center>EXPERIMENTAL</center>

Puvification **of** SuZphuv,-Four specimens of sulphur, **as** follows, were used : (i) the residue of Specimen E used in the previous study (ref. **1,** p. **1108)**; (ii) a similarly purified Specimen F **(z.e.,** recrystallised from carbon disulphide, and then melted and degassed), derived from the same batch of recrystallised sulphur **as** E; (iii) Specimen G, purified by the method of Bacon and Fanelli,' *i.e.,* by boiling it with magnesium oxide until a filtered sample gave no black **spots** on being boiled for a few minutes in a clean dust-free Pyrex test-tube, the starting material being B.D.H. ·· crystalline ·· sulphur **as** used for E and F; (iv) Specimen H, supplied by the British Rubber Producers' Research Association by the kindness of its then Director, Dr. **G.** Gee, F.R.S., and purified by Bacon and Fanelli's method and then vacuum-distilled, the starting material being flowers of sulphur. Before use, Specimens G and H were annealed at **100"** for **2** days in order to convert the insoluble sulphur (resulting from the heating of the liquid to the boiling point in the purification process) into the soluble form. The amount of this insoluble sulphur, determined by extraction with carbon disulphide, was **-3%.**

Bacon and Fanelli's method removes traces of organic impurity, which, according to these authors, the more conventional methods fail to do. The presence of such impurity is shown by the black-spot test (above), which they claim is sensitive to **1** part per million. The recrystallised sulphur from which Specimens E and F were prepared gave a slight black spot reaction.

The source material from which E, F, and G were prepared gave **a** negative reaction for selenium when tested by Hughes and Wilson's method.[6] Mr. **C.** H. Manley, the City Analyst of Leeds, very kindly tested F, G, and H for the presence of arsenic, using the method given in the British Pharmacopoeia, **1948,** and found: in F, **0.0004%;** in G, **0.0002%;** in H, nil. Insufficient of E was left for any to be spared for this test, but it is unlikely that it would have differed appreciably from F. Specimen G was also tested for the presence of sulphur dioxide and hydrogen sulphide by allowing **a** finely ground sample to remain in contact with dilute permanganate solution for two days, but no decolorisation was observed. (These gases would be formed in the Bacon-Fanelli process as results, respectively, of the Iong period of boiling and the destruction of hydrocarbon impurity, and some might have been retained in the solid sulphur.)

The absorption spectra of alcoholic solutions of F, G, and H showed no differences in either the visible or the ultraviolet region. The arc spectra of these specimens, obtained with pure carbon electrodes and a copper spark for calibration, showed only the occasional presence of silicon as an impurity, and this might have been due to small particles of glass which were liable to be present in all specimens, since in all cases the final stage in the purification leaves the sulphur **as** an intractable block in *a* glass tube from which it is extracted by gently breaking up the glass in a mortar (see, *e.g.,* Part **V,** [6] p. **689).**

The m. p.s of the specimens were compared in pairs on a hot stage under the microscope, the temperature being raised very slowly. No differences were detected, other than that due to some particles' escaping transformation after passing the transition point and melting **as** a-sulphur.

From the above tests and observations it may be concluded that all the specimens were chemically pure by ordinary standards.

Preparation **of** Slides.—As in earlier work on sulphur in this series, the transformation was studied in polycrystalline films confined in glass−mica−glass cells (these with their sulphur films being referred to in the sequel simply **as** ·· slides "), and mostly covering the same range of thicknesses **(0-OS-0.10** mm.). In the hope of reducing the variance in the rate between slides,

[3] **Hartshorne and Swift,** *J.,* **1966, 3706.**
[4] **Bacon and Fanelli,** *I d . Eng. Chem.,* **1942,** *84,* **1043.**
[5] **Hughes and** Wilson, *J. SOCChem. Ind.,* **1936, 55. 359.**
[6] **Elias, Hartshorne, and James,** *J.,* **1940, 588.**

the temperature at which the β-form was crystallised was controlled more closely than before by adopting the following procedure. The hot plate, made of aluminium, was recessed on top to take the slide, and the recess was normally covered with a thin glass plate to protect the slide from draughts. When the sulphur was completely melted (at a temperature not exceeding 123° as before), the apparatus was allowed to cool until the temperature reached $108° \pm 1°$, and the β-form was then caused to crystallise by running a platinum point along the edge of the film. This temperature was chosen as giving most nearly the same texture of β-film as did the previous method (ref. 6, p. 589). Since the slide was protected during cooling by the glass plate, and the cooling was quite slow, about 6 min. being usually required before the temperature reached 108°, it is probable that the temperature of the slide closely followed that of the plate.

The slides used in some runs at the lower temperatures were annealed by heating them in a closed vessel at 100° for two days after the β-form had been brought out from the melt, in order to convert into soluble sulphur, the small amount of the insoluble form (about 0·1% as determined on separate samples by extraction as before) resulting from the melting of the sulphur in preparing the films, and, for Specimens E and F, in the final stage of the purification. A statistical comparison between the rates given by annealed and unannealed slides made with the same specimen showed, however, no significant difference.

Methods of Measuring the Interface Advance.—In the low-temperature work, measurements were made at −15° and 0°. For work at − 15° a cold room with thermostatic control to $\pm 0·1°$ was used, and the 0° thermostat was a large, well-lagged, Dewar vessel containing melting ice, and stationed between the double doors leading to the cold room. The top of the Dewar vessel was closed with a thick cork cover, and the slide boxes (see below) were placed in a central container made of copper sheet.
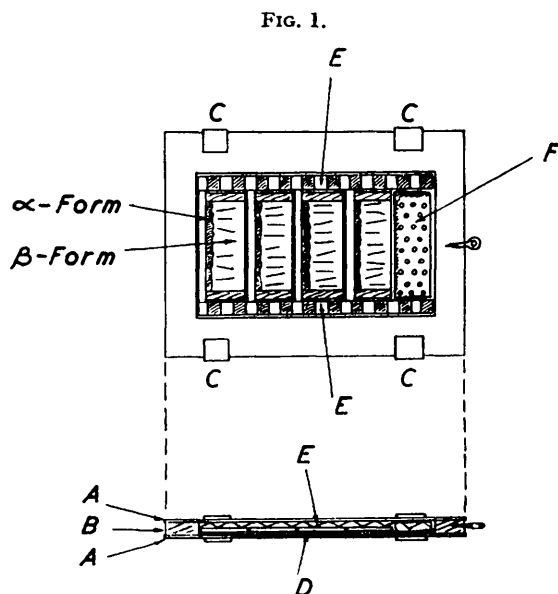
FIG. 1.

After being inoculated the slides were placed in groups of four in flat transparent boxes (Fig. 1), built up from two sheets of thin glass A, held against a Perspex frame B by four strong phosphor-bronze clips C. The Perspex–glass junctions were sealed with silicone vacuum grease. The four slides, which were of the type used at 0° in the earlier work (ref. 1, p. 1099), were supported film downwards with their two free ends resting on brass strips D, and were held in that position by crimped strips of copper foil E as shown. Calcium chloride in a perforated zinc container F maintained a dry atmosphere in the box.

While in the cold room at −15°, these boxes were kept under a cover made of thick corrugated cardboard to prevent their being affected by any temporary rise of temperature which might occur when the room was entered. Observations of a thermometer fixed in the cardboard cover showed no appreciable change in its inside temperature on these occasions, which in any case were infrequent.

Records of the position of the interface were made by laying the box with the sulphur films downwards on a photographic plate, and exposing it to the light from a 48-w compact-filament microscope lamp, masked by a stop of *ca.* 3/16 in. diameter, and fixed a few feet above the cell. This was done in the cold room, which was illuminated by a red safe-light during the operation. Calculations showed that under these conditions the lamp should behave effectively as a point source and that the image, or rather shadowgraph, of the films cast on the plate would not be appreciably magnified. In fact extremely sharp records were obtained, which showed the position of the interface with great clarity. Ilford Ortho Halftone plates developed for maximum contrast were used. Measurements of the rate of advance of the interface were

made by projecting the negatives in sequence on to a gridded screen as in the earlier work at 0° (ref. 1, p. 1100).

In order to extend the range over which comparison with previous work could be made, the boxes were placed in a constant-temperature room at 22° ± 0·5° after the runs at −15° and 0° were finished, and the films photographed at the beginning and end of a known interval of time by the method described above. The measurements obtained from these records were of a lower order of accuracy than the rest, since by this time the contour of the interface had usually become very ragged, and because of the rather poor temperature-control, but they served as a check on the behaviour of the different specimens in this temperature region.

For work at temperatures near the transition point (T_0), the projection apparatus of Hartshorne and Roberts [1] was used, the slides being studied singly. Since in general only two records of the position of the interface were now required at each temperature (see below), the tedious and exacting method of following the advance visually was abandoned and the following substituted. A grid very similar to that used on the screen in the visual method, but corresponding to a much smaller magnification ($\times$ 11·4) was scribed on a sheet of Perspex by means of a milling machine, and the lines well blacked by rubbing with Indian ink. This Perspex sheet was hinged vertically to the adjustable screen of the projection apparatus, and could be folded flat against it and held in that position by a catch. The distance between the projector and the screen having been adjusted to give the same magnification as that of the grid, and the screen adjusted to make the image of the film edge coincident with the zero vertical line on the grid, the room was darkened except for a red safe-light, a strip of bromide paper was placed between the grid and the screen, and the catch secured. By switching on the projector lamp (exposure 2—3 sec.) a record of the film showing the position of the interface superimposed on the grid was obtained. From a series of such records, the advance of the interface in each section of the grid could be quickly read off.

The type of inoculating brush used in the earlier work would not withstand the higher temperature of 90° to which the work was now extended, and a fine steel point was used instead. Although the action of this was purely mechanical, it was almost invariably effective in initiating transformation along the whole of the edge of the film in this temperature region.
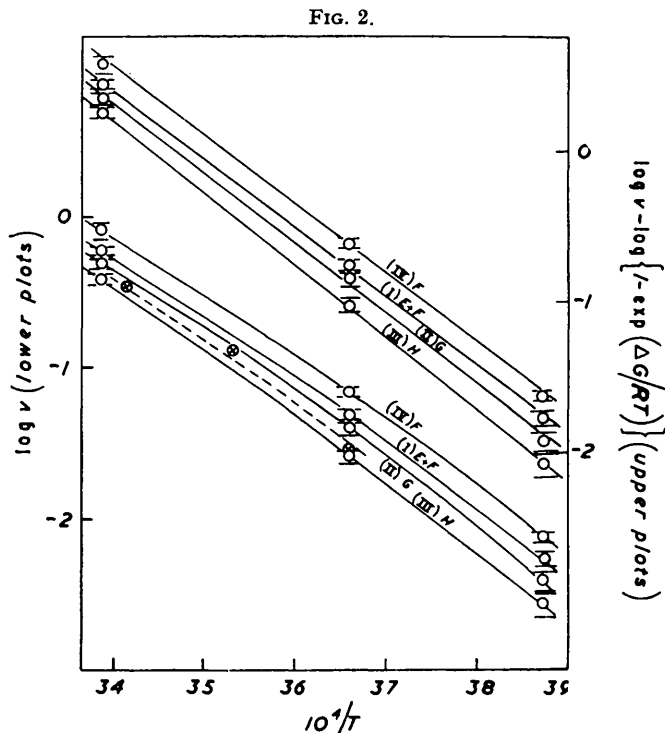
RESULTS

At Low Temperatures.—An analysis of the variance of some of the results obtained previously [1] showed that the groups of measurements obtained on individual slides, *i.e.*, the " Δ values " (times to advance over small sections of the films), cannot be regarded as random samples of the whole population of measurements (cf. results with carbon tetrabromide [3]). Thus at 10° the ratio of the variance between slides to that within slides was 40, whilst the corresponding ratio at 0° was 23. For a probability of 5% and the very large number of degrees of freedom within slides (228 and 1148 respectively), these values correspond to a very highly significant difference between the slide mean rates, which must therefore be regarded as the individual measurements from the standpoint of statistical analysis. The meaning of this is of course that despite the care taken to prepare the films under closely similar conditions, not all the factors determining the mean rate of advance of the interface in a slide are in fact under complete control. Included among these factors may be variations in the orientations of the β-crystals and in their secondary structure, and in the distribution of dislocations or other growth-assisting imperfections in the α-phase.

In view of this, and of the constancy of the rate which had been found at the lower temperatures (see, *e.g.*, ref. 1, plots for 0° and 20° in Fig. 3) and was confirmed at −15° by a preliminary experiment in the present work, there seemed to be no point in continuing with the earlier method of making a large number of measurements at successive short distances of advance. At each temperature therefore only two positions of the interface were now recorded to obtain the slide mean rate.

In another analysis of the previous results, plots of log v against $1/T$ were found to give practically the same slopes at corresponding temperatures, irrespectively of whether v was based on the upper 10% of the Δ values, or on the lower 10%, or on all these values. This showed that the variance in the rate was due mainly, if not wholly, to variance in the non-exponential factors determining the rate, and not much, if at all, to variance in the activation energy. In the present work, a " split-run " procedure was followed, measurements being

made at $-15°$, $0°$, and $22°$ on every slide studied (half the slides being done at $-15°$ first, and half at $0°$ first), with the object of keeping the non-exponential factors constant as far as possible, and this procedure yielded values of the logarithm of the temperature coefficient lying within narrow limits of probability, as will appear below.

Fig. 2 shows the plots (lower group of curves) of the logarithms of the mean slide mean rates against $10^4/T$ for different sets of slides. 95% fiducial limits are indicated by short strokes above and below each point. The three lower full-line curves are for sets differing in respect of the source and method of purification of the sulphur used, thus : set (I) 17 slides prepared with Specimens E and F (3 with E, 14 with F) ; set (II) 12 slides prepared with Specimen G ; set (III) 14 slides prepared with Specimen H. In all these slides the film thicknesses were within the range 0·6—0·10 mm. as in the earlier work. The differences in rate shown by these 3 sets are

FIG. 2.

The uppermost plots (IV) in each group have been shifted upwards to avoid overlap with (I).
⊗ Earlier results.
Plots (IV) are for thicker films.

significant, and the rates for set (I) are 50—100% greater than those for set (III). The uppermost curve in the group, (IV), is for a set of 7 slides prepared with Specimen F, which had films 0·11—0·15 mm. thick. These gave mean rates 10—20% greater than the thinner ones prepared with this specimen, in qualitative agreement with earlier observations of the effect of film thickness (ref. 6, p. 595). In plotting this last curve the vertical scale has been shifted upwards a little in order to avoid overlap with the point circles of set (I). The group also contains the smoothed curve (broken line) * drawn through the earlier results [1,6] obtained at $0°$, $10°$, and $20°$. It will be noted that there are no marked differences in the slopes of these five curves.

The upper plots in Fig. 2 show the result of applying Hartshorne's equation, i.e., the linear law (see ref. 3, p. 3717), to the new results, by plotting $\log v - \log\{1 - \exp[q(1/T_0 - 1/T)/R]\} = \log v - \log\{1 - \exp(\Delta G/RT)\}$ against $10^4/T$, ΔG, the free-energy increase attending the reverse

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* Lest this smoothing should appear rather arbitrary in the present figure, it should be explained that it depends also on the points obtained for higher temperatures (see, e.g., Fig. 1, ref. 9).

transformation, being calculated from Lewis and Randall's equation.[7] [Values of ΔG based on more recent heat-capacity data (Eastman and McGavock [8]) are nearly the same, and do not affect the plots appreciably.] This should give a straight line if the equation is obeyed, and it is evident that this condition is nearly fulfilled, in fact straight lines are drawn in the Figure and these lie inside the 95% limits in all cases. Since, however, the earlier results indicated a closer conformity with the equation the lower the temperature (Hartshorne [9]), and the results at 22° are less trustworthy than the others, as explained above, we have used only the results at 0° and −15° to estimate the activation energy. Between these two temperatures there was no significant difference between the temperature coefficients for set (II) (G) and set (III) (H), so a mean value for these two sets has been calculated. This is a little, but significantly, higher than the mean value for sets (I) (E + F) and (IV) (F, thicker films) which gave almost identical coefficients. The split-run procedure led to a high degree of correlation between v_0 and v_{-15} for these two main groups of slides, the correlation coefficients (by ranks) being 0·83 for the former group (G + H), and 0·82 for the latter (E + F). The activation energies and their 95% limits corresponding to these results are 23·1 ± 0·6 kcal./mole for G and H, *i.e.*, those specimens purified by the Bacon and Fanelli process, and 21·9 ± 0·4 kcal./mole for E and F, *i.e.*, those specimens purified by recrystallisation and degassing. These values accord well with 22·6 kcal./mole, the mean internal latent heat of sublimation of β-sulphur between T_0 and −15° derived from the vapour-pressure data of Neumann [10] and Bradley [11] (which are very closely consistent), and Lewis and Randall's equation for the heat of transformation,[7] and support our previous conclusion regarding the activation energy.

From the differences between the rates of the different " pure " specimens (Fig. 2), it is clear that the rather good degree of reproducibility obtained in the earlier work [6, 1] cannot be depended on when the range of specimens and methods of purification are extended. The differences are probably due to varying minute amounts of impurities (possibly also to physical contamination by broken S_8 rings in some cases), and it is perhaps not surprising that these should have a significant effect on the rate. We may distinguish two possibilities : (i) that the impurities affect the secondary structure of the β-phase and that this influences the rate (see later) ; (ii) that in the case of impurities which have a solvent action on sulphur, they may reduce the activation energy by establishing a solution layer in place of a vapour layer at the interface, though perhaps only locally.

The reproducibility of the temperature coefficient, particularly for groups of slides in which the same or similarly purified specimens of sulphur were used, may be regarded as very good, and this is much more important than a close reproducibility of the rate. Thus set (I) may be broken down into three groups as follows : (*a*) 3 unannealed slides prepared with Specimen E ; (*b*) 6 unannealed slides prepared with Specimen F ; (*c*) 8 annealed slides prepared with Specimen F. These three groups together with set (IV) (F, thicker films) gave temperature coefficients between 0° and −15° the logarithms of which agreed to within just over 1%. The logarithms of the temperature coefficients for sets (II) and (III) (G and H) agreed to within just over 3%.

The reason for the somewhat lower temperature coefficient given by E and F, than by G and H, may be that the method of purification used for the former specimens did not completely remove all solvent impurities, *e.g.*, the carbon disulphide used in the recrystallisation.

At Temperatures near the Transition Point (T_0).—Measurements were made at 80°, 85°, and 90° on each slide. Specimens G and H were used since the chemical tests and the low-temperature measurements had indicated that they were likely to be the purest.

In the previous work, the rate at the higher temperatures was not strictly constant over the range 0—2 mm., but showed a rather marked initial increase (ref. 1, Table I). A detailed analysis of the results obtained at 60°, 70°, and 80° in this work has shown that for the large majority of slides the rate became sensibly constant after an initial advance of 0·5—1·0 mm., provided that the slide had then been in the thermostat for at least 80—90 min., *i.e.*, that both a distance effect and a time, or annealing, effect were involved.

The result of this analysis formed the basis of the method of starting an experiment in the

[7] Lewis and Randall, *J. Amer. Chem. Soc.*, 1914, **36**, 2468.
[8] Eastman and McGavock, *J. Amer. Chem. Soc.*, 1937, **59**, 145.
[9] Hartshorne, *Discuss. Faraday Soc.*, 1949, **5**, 149.
[10] Neumann, *Z. phys. Chem.*, 1934, **171**, 416.
[11] Bradley, *Proc. Roy. Soc.*, 1951, *A*, **205**, 553.

present work. After the slide had been in the thermostat for about 30 min., it was inoculated and the interface allowed to advance to an estimated mean distance of 0·75 mm. from the film edge. The first photographic record was then made. This stage should have been reached about 80 min. after the slide was inserted in the thermostat if the initial rate had been the same as in the earlier work, but most of the present slides proved to have greater rates than this, and measurements on them were in fact started before the full annealing time had elapsed. However, a statistical comparison between the mean rates for these slides and for those fully annealed showed a difference, in the expected direction to be sure, but of only doubtful significance. (This only concerns measurements at 80°. By the time that measurements at 85° and 90° were made, the full annealing time had been exceeded in all cases.)

On the majority of the 11 slides studied (4 made with Specimen G and 7 with H), the interface advanced in a comparatively regular manner over all its length, but in a few slides one or two promontories developed, usually in the later stages of the experiment, which could fairly be described as representing an " abnormal " rate of advance (ref. 1, p. 1108). The advance of these promontories was not included in the measurements on which the slide means were based. (Abnormality in this temperature range in the earlier work was associated with those specimens which melted as α-sulphur. Observations on powdered G and H on the microscope hot stage showed that a considerable proportion of the particles melted as α-sulphur.)

There was no significant difference between the mean rates shown by the two specimens at any of the higher temperatures, and their results have therefore been pooled. This contrasts with what was found at low temperatures (see Fig. 2), and may have been partly due to the greater variance in the rates (95% limits ranging from ± 21—44%, in contrast to ± 8—19% at low temperatures). This in turn may have been partly due to the smaller number of slides of each specimen studied, though an increase in the variance near T_0 is to be expected, since quite small changes in the conditions at the interface, such as local temperature fluctuations, will have a relatively large effect on the supersaturation.

The results are plotted in Fig. 3 (curve A), the 95% limits being indicated as in Fig. 2. The curve is asymptotic to the temperature axis as was found for carbon tetrabromide.[3] The rates (in mm./hr.) and 95% limits are : 80°, 2·58 ± 0·54; 85°, 0·72 ± 0·18; 90°, 0·131 ± 0·057. The value at 80° is higher than the figure of 1·62 ± 0·14 obtained by Hartshorne and Roberts[1] at this temperature with " normal " sulphur purified by recrystallisation and degassing. (This figure refers to the advance beyond 0·75 mm. from the film edge, so that it can be compared directly with the present results. The figure 1·60 previously published was the mean rate of advance beyond 0·25 mm. from the film edge.) This discrepancy can, however, be reasonably attributed to the fact that G and H showed a slightly higher temperature coefficient, *i.e.*, a steeper mean-rate curve, at lower temperatures than the specimens purified by recrystallisation and degassing, as were all the earlier ones. They might therefore be expected to show a higher rate than the latter specimens at higher temperatures.

In any case it seems justifiable to take the present results at 80°, 85°, and 90° as consistent among themselves since the split-run procedure was followed. There was in fact a high degree of correlation between v_{85} and v_{90}, namely, 0·74 (by ranks), though no significant correlation between v_{80} and v_{90}.

DISCUSSION

It has been shown in earlier papers [9, 1] that the rate in the lower temperature range is considerably greater than that calculated from the linear law, assuming a simple evaporation–condensation mechanism. The value of the factor (B) by which the observed and calculated rates differ, depends on the expression used for the rate of evaporation of molecules from the β-phase, which will be equal to the rate of impact of molecules on the growing α-phase for an interface region of the order of one or a few molecular diameters in thickness (see ref. 3, p. 3717). If this rate be expressed (in terms of molecules per lattice site) as $v \exp(-L_{II}/RT)$, where v is the vibration frequency of the surface molecules, taken as 10^{12}—10^{13}, and L_{II} is the internal latent heat of sublimation of β-sulphur, B works out to $\sim 10^7$ (see ref. 9, p. 156 *). Now :

$$v \exp(-L_{II}/RT) = (p_{II}/p_I) v \exp(-L_I/RT) = (x + 1) v \exp(-L_I/RT)$$

* In the calculation referred to here a modified form of the linear law equation was actually used, but this makes no difference to the order of the value of B.

where p_{II}, p_I are the vapour pressures of β- and α-sulphur respectively, x is the supersaturation, and L_I is the internal latent heat of sublimation of the α-sulphur. In this treatment, $\nu \exp(-L_I/RT)$ expresses the rate of impact of molecules on α-sulphur from the vapour at its equilibrium pressure, and this will be equal to the rate of evaporation of α-sulphur if the condensation coefficient is unity. Since, however, Bradley [11] found that the actual rate of evaporation is $\sim 10^4$ times that given by this expression, but that it agrees with that given by the Langmuir evaporation equation with a condensation coefficient of approximately unity, it seems clear that a more realistic calculation of the rate of transformation to be expected for a simple evaporation–condensation mechanism will be made if the Langmuir equation is substituted for the expression given above. This follows a similar procedure suggested by Bradley in the work on carbon tetrabromide (see ref. 3, p. 3720.) Starting with the convenient form of the linear law given by the dislocation theory of crystal growth from the vapour, namely, $v = \nu d \exp(-L_I/RT) x$, where v is the linear rate, and d the mean lattice spacing, and substituting for $\nu \exp(-L_I/RT)$ the expression $Nd^2 p_I/(2\pi MRT)^{\frac{1}{2}}$,

FIG. 3.
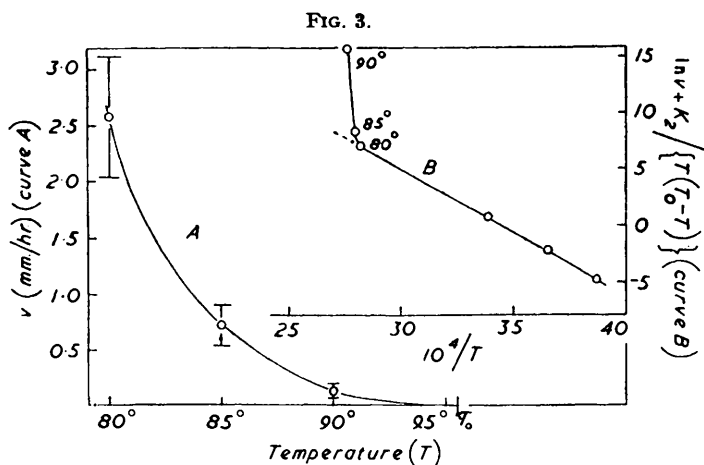
the rate of impact of molecules on α-sulphur from the equilibrium vapour as given by the Langmuir equation (N is the Avogadro number) we obtain for the linear rate

$$v = Nd^3 p_I x/(2\pi MRT)^{\frac{1}{2}} \qquad \text{. . . . . (i)}$$

By taking the pooled results for Specimens G and H, and calculating p_1 from Bradley's [11] and Neumann's [10] data, and x from the expression $[\exp(-\Delta G/RT) - 1]$, this equation gives B = constant at $2 \cdot 1 \times 10^8$ at $-15°$ and $0°$, falling to $1 \cdot 5 \times 10^8$ at $22°$, followed by a more rapid fall to *ca.* 10^2 at $80°$, and $3 \cdot 6$ at $90°$. Interpolation of curve A, Fig. 3, between $90°$ and T_0, which can be done with rather good reproducibility up to $94°$ by using a steel-strip curve-tracer, shows that the further application of eqn. (i) gives $B = 1$ at *ca.* $94°$. This interpolation, however, suggests another interpretation of the results near T_0, since between $90°$ and $94°$ the interpolated values are very nearly proportional to the square of the supersaturation, *i.e.*, they obey approximately the parabolic law in dislocation theory, as was found in the case of carbon tetrabromide.[3] This would be consistent with the asymptotic approach of the rate curve to T_0, which on the above interpretation in terms of eqn. (i) arises from the progressive decrease in B as T_0 is approached. (The unmodified linear law requires that dv/dT is finite at T_0.)

The equation for the parabolic law put into the same form as eqn. (i) would be :

$$v = Nd^3 p_I(x^2/x_1)/(2\pi MRT)^{\frac{1}{2}} \qquad \text{. . . . . . . (ii)}$$

4 A

where x_I, the critical supersaturation, is given by $(2\pi\gamma_M/RT)$ exp $\{ - (W_s' - U_s)/2RT\}$, where γ_M is the edge free energy of the growth step per mole, W_s' is the molar evaporation energy of surface-adsorbed molecules, and U_s is the molar activation energy for such molecules to migrate from one lattice site to an adjoining one (Burton *et al.*[12]). It is possible to set a lower limit to x_I, since it cannot be less than the value of x at 90°, namely, 0·018, if the square law holds down to this temperature. The upper limit is determined by (*a*) the maximum value assumed for γ_M, and (*b*) the minimum value assumed for $(W_s' - U_s)$. We have based (*a*) on a surface free energy of 100 ergs cm.$^{-2}$, *i.e.*, a value somewhat greater than that (60 ergs cm.$^{-2}$) of the liquid just above the melting point, and for (*b*), following Burton *et al.*,[12] we have taken a value somewhat less than $L_I/2$, namely, 11,000 cals. These considerations lead to $x_I = 0·0189$ at 91° and 0·0201 at 94°, and applying eqn. (ii) we obtain $B = ca.$ 3·6 at 91° and *ca.* 3·1 at 94°.

Thus, whichever interpretation is correct, the rates near T_0 agree with those predicted for a simple evaporation–condensation mechanism to within a power of 10, provided that the Langmuir evaporation equation applies (as it is known to do for the evaporation of α-sulphur into a free vapour space), and that the critical supersaturation has not been grossly underestimated (which seems unlikely).

It should be noted that although for convenience we have made use of the equations of the dislocation theory of crystal growth, the above conclusions would be equally valid for any system of perpetual growth steps, no matter how perpetuated, if their spacing apart were related to the supersaturation as in dislocation theory. As far as the application of the linear law is concerned indeed, the only requirement would be that the spacing of the steps be less than twice the mean migration distance of surface adsorbed molecules.

The " mosaic block-crack " theory put forward in Part VI (ref. 1, p. 1113) to account for the discrepancy represented by the B factor does not seem capable of explaining its decrease with temperature, since it would be necessary to suppose that the block size decreases with rise in the temperature at which the rate is measured, whereas it is to be expected that the block size would be determined by the conditions under which the slides were prepared, and these conditions were the same throughout.

Cagle and Eyring [13] have proposed an equation for the rate of phase transformations in solids, which is based on transition state theory. Their paper is mainly concerned with the transformation between white and grey tin, which certainly does not proceed by way of an intermediate vapour-type phase, but mention is made of the sulphur transformation, including a reference to the earlier work in this series (Part V),[6] though not to the later work.[1] The equation is not applied in detail to this case because of lack of data, but the transformation is evidently regarded as amenable to this treatment in principle. It does not seem to us, however, that this approach can clarify the problem of the B factor, if, as we believe, the primary step in the transformation process involves the formation of an intermediate phase in which the molecules are energetically equivalent to molecules in the vapour state. Transition-state theory would interpret the existence of the B factor as due to an increased entropy of activation, and it is difficult to see how the transition state could possess greater disorder than if it were a vapour. This and other theories of solid–solid reaction kinetics have been recently discussed more fully by Bradley.[14]

We therefore seem to be forced back to the idea of a secondary step of low activation energy in the transformation process to account for the high rates (as was visualised in the mosaic block-crack theory), though as shown above it does not seem possible to relate this directly to mosaic-block dimensions. It is possible, however, that the secondary structure of the crystals enters into this mechanism in some way. A detailed study of the advance of the interface by high-power microscopy, which is now in progress, may possibly throw some light on this problem.

[12] Burton, Cabrera, and Frank, *Phil. Trans.*, 1950—51, **243**, *A*, 299.
[13] Cagle and Eyring, *J. Phys. Chem.*, 1953, **57**, 942.
[14] Bradley, *ibid.*, 1956, **60**, 1347.

Fig. 3, curve B, shows the application of Dunning's equation (ref. 9, p. 156) to the pooled results obtained with Specimens G and H, it being assumed for the purpose of calculating the second constant, that the equation is valid up to 80°. {The equation, $\ln v = \ln K_1 - E/RT - K_2/[T(T_0 - T)]$, is applied by first plotting $\ln v + E/RT$ against $1/[T(T_0 - T)]$, using an assumed value for E. From the slope of this plot, which should be a straight line if the correct value of E has been selected, K_2 is obtained. The plot of $\ln v + K_2/[T(T_0 - T)]$ against $1/T$ then gives a value for E. If this does not agree with that previously assumed, the value which fits both plots is determined by a process of successive approximation.} The four lower points, corresponding to the range $-15°$ to 80°, lie on quite a good straight line with a slope equivalent to an activation energy of 22·6 kcal./mole, but the results at 85° and 90° show a strong positive deviation from the requirements of the equation, as did those obtained with carbon tetrabromide near its transition point.[3] The result of applying the equation is striking, but the difficulties associated with this theory[9,1] do not seem to lose their importance after further consideration—namely the very low value of the edge free energy implied by the value of K_2, and the improbability that two-dimensional nucleation would be a necessary condition for sustained growth on such an obviously imperfect surface as is presented by the advancing front of the rhombic phase in the lower temperature range. The new finding that the observed rate above 80° deviates radically from the requirements of the equation is, however, of interest.

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