Studies in Polymorphism. Part VII. The Linear Rate of Polymorphic Transformation of Cubic to Monoclinic Carbon Tetrabromide.*

By N. H. HARTSHORNE and P. McL. SWIFT.

[Reprint Order No. 6075.]

Measurements of the linear rate of transformation of cubic to monoclinic carbon tetrabromide have been made in thin polycrystalline films at temperatures just below the transition point. Previous annealing of the films appears to increase the tendency for the rate to decline at constant temperature. Unannealed films mostly show a constant rate. The rate is much greater than that of the β- to α-transformation of sulphur at the same supersaturation.

The change in the rate with temperature does not follow either the linear law (rate proportional to the supersaturation) or Dunning's equation based on the theory of two-dimensional nucleation. On the basis of the best available value of the transition temperature, the rate very near to this temperature is proportional to the square of the calculated supersaturation, or very nearly so, and on the assumption, by analogy with the sulphur transformation, that the activation energy is of the same order as the sublimation energy, the absolute value of the rate in this region is not inconsistent with the requirements of the dislocation theory of crystal growth at low supersaturations.

Some new optical crystallographic data for monoclinic carbon tetrabromide have been obtained.

IT has long been known that carbon tetrabromide undergoes an enantiotropic transformation between a lower-temperature monoclinic phase and a higher-temperature cubic phase (Lehmann, " Molekularphysik," Vol. I, 1888, p. 178). Values given for the transition point (referred to subsequently as T_0) are 46·1° (Schwarz, Preisschrift, Göttingen, 1892, p. 47), 46·2° (Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1915, **51**, 55), 46·9° (Frederick and Hildebrand, *J. Amer. Chem. Soc.*, 1939, **61**, 1555), and 46·91° (Rothmund, *Z. phys. Chem.*, 1897, **24**, 705), of which the last two seem to be the preferred ones (International Critical Tables give 46·9° $\pm <1°$) and are consistent with our own determinations (see below). The m. p. reported by Wahl (*Phil. Trans.*, 1913, **212**, *A*, 117) and by Frederick and Hildebrand (*loc. cit.*) is 92°. Our observations indicate a somewhat higher value than this but we did not determine it accurately.

The main object of this investigation was to determine the linear rate of transformation of the cubic form into the monoclinic form in thin polycrystalline films as a continuation of similar studies described in earlier parts of this series. It was thought possible that, since the parent phase is isotropic, the rate of advance of the interface might show less variance than in the other cases studied (*e.g.*, sulphur, Part VI, *J.*, 1951, 1097). This hope has not been fulfilled, for the variance in the rate has proved to be considerable. Also, the isotropism of the parent phase has prevented observation of its grain size and crystal orientation by optical means, and this has imposed some limitations on the study of the transformation. Further, the rate increases so rapidly as the temperature is lowered from T_0, that it has only been found possible to make determinations corresponding to interface temperatures which are known or can be estimated, over a range of less than 2°. Many attempts were made to " rush " the cubic phase through the temperature range of high velocities to the expected low-velocity region at low temperatures by intense chilling, *e.g.*, by plunging the films into alcohol–solid carbon dioxide, but they were defeated by the very high tendency of the cubic phase to nucleate spontaneously. We have thus been unable to obtain any direct evidence regarding the activation energy of the transformation.

The conclusion reached in the cases of sulphur (*loc. cit.*) and *o*-nitroaniline (Part III, *J.*, 1935, 1860) was that the activation energy involved in the passage of a molecule from

---

* Part VI, *J.*, 1951, 1097.

the unstable crystal to the transitional layer was of the same order as the heat of sublimation. Later work on sulphur at low temperatures (Hartshorne and Thackray, unpublished work) has confirmed this, and the same conclusion has been reached by Hodkin and Taylor (*J.*, 1955, 489) in a recent study of the II $\longrightarrow$ I transformation of azoxybenzene. If this is generally the case for transformations in molecular solids, then a high rate with carbon tetrabromide is to be expected, since the internal heat of sublimation of the cubic form at the mean temperature of our experiments can be calculated to be only 11,535 cal./mole, as compared with 22,500 cal./mole for sulphur (*loc. cit.*) and *ca.* 19,000 cal./mole for *o*-nitroaniline (Part III, *loc. cit.*). Comparison of the rates for carbon tetrabromide and sulphur at the same supersaturation (made possible by new data obtained by Hartshorne and Thackray, see above) show, however, that the difference between them is not nearly so great as would be expected if this were the only factor involved, and the matter is discussed later in this paper. Thus at a supersaturation of 0·0042 which exists at 319·4 °K for carbon tetrabromide and 367·2 °K for sulphur, the ratio $\{d_1 \exp(-11{,}535/\boldsymbol{R} \times 319{\cdot}4)\}/\{d_2 \exp(-22{,}500/\boldsymbol{R} \times 367{\cdot}2)\} \approx 10^5$, whilst the ratio of the observed rates ≈ 60 (d_1 and d_2 are the mean lattice spacings).

The above value for the heat of sublimation of the cubic form is derived from the vapour pressures of the liquid determined by Bolas and Groves (*J.*, 1871, **24**, 780) and the heat of fusion determined by Frederick and Hildebrand (*loc. cit.*). The latter authors also found the heat of transition to be 1420 cal./mole, from which the internal heat of sublimation of the monoclinic form is 12,955 cal./mole. Other values reported for the heat of transition are 1590 cal./mole (Marshall, Hart, and Staveley, *Nature*, 1951, **168**, 519) and 1670 cal./mole (Bridgman, *loc. cit.*). The use of either of these, and the correspondingly increased value of the heat of sublimation of the monoclinic form, makes no difference to the order of the results of our later calculations, and for consistency we shall use Frederick and Hildebrand's value.

Despite the narrow temperature range within which study of the rate was possible, the results are of interest as being the first to be obtained in this series so near to a transition point. From the temperature dependence of the rate in this region, some conclusions, admittedly mainly negative, regarding the mechanism of the transformation have been drawn. Some interesting facts about the way in which the monoclinic crystals grow in the cubic phase have been collected. An attempt to determine T_0 as the temperature at which the interface between the two phases is stationary has shown that, within a narrow temperature range, movements of the interface in *both* directions at one and the same temperature occur. Finally, some new optical crystallographic data for the monoclinic form have been obtained.

EXPERIMENTAL

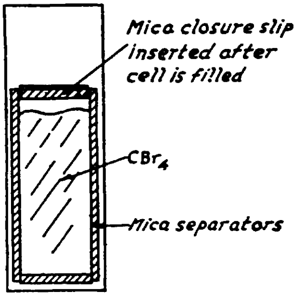
Purification of Material.—The carbon tetrabromide was purified by recrystallisation from alcohol followed by two, or in some cases three, sublimations at low pressure. The sublimation apparatus consisted of a horizontal tube 18 × 1¼ in., closed at one end and connected at the other to a water-pump through a guard tube containing calcium chloride, manometer, and trap cooled by alcohol–solid carbon dioxide. The closed end of the sublimation tube containing the carbon tetrabromide to be purified was heated by an electric coil to 70°. The other end was cooled by allowing cold water to drip on to a cloth wrapped around it, and contained a loosely fitting glass sleeve about 5 in. long to collect the sublimate and facilitate its subsequent removal. The product of this process was colourless and showed no sign of decomposition when heated to prepare the films for the rate measurements, or subsequently.

Preparation of Slides and Films.—Films confined in glass–mica–glass cells as used for the work with sulphur were first tried but did not give reproducible results, probably because the cells were too thick to allow the film to come to thermal equilibrium with the thermostat sufficiently quickly, so that a large amount of rapid lower-temperature growth occurred before this was achieved. Eventually the type of cell shown in Fig. 1 was adopted. This was built up of a 3 × 1 in. slide and a 2 × ⅞ in. cover-slip with mica separators, the whole assembly being sealed together with phenol–formaldehyde cement as used in the cells for sulphur. The separators and closure slip (see above) were all cut from the same sheet of mica (0·05 mm.

thick, and subsequent measurements on a number of the filled cells gave values for the film thicknesses ranging from 0·07 to 0·9 mm.

To fill the cells they were placed on an inclined hot plate kept at 100°, so that the bottom of the cell as shown in Fig. 1 was the lower end. The substance was melted in at the open end little by little, the amount being adjusted so that the cell was nearly full. The mica closure slip was then inserted. This slip prevented excessive loss of the substance by evaporation in subsequent operations. The film was allowed to solidify and when required for the rate measurements was converted into the cubic form under controlled conditions as described below.

FIG. 1.



In what follows the prepared cells with their carbon tetrabromide films will be referred to simply as " slides."

Conversion of Films into Cubic Form before Rate Measurements.—For this a modified form of the apparatus described in Part I (*J.*, 1930, 727) for determining the m. p.s of the different polymorphs of *o*-nitroaniline was used. The object of using the apparatus in the present work was to find out for each slide the temperature at which the cubic phase first crystallised and to control its rate of crystallisation as far as possible, in case these conditions should have any influence on the rate of transformation into the monoclinic form. The temperature of the outer bath was first set to 94° ± 0·5°, and the slide was inserted in the inner tube. After melting was complete (usually in 5—15 min.), the temperature was lowered at about 0·1° per min. Crystallisation of the cubic phase always began before the bath temperature had fallen to 93° and was usually complete in 5—10 min. Supercooling thus appears to be very small and it may be deduced that all the films were grown within the same narrow range of conditions of time and temperature.

When crystallisation was complete the slide was either transferred direct to the projection apparatus by means of which the rate was measured or, if it was to undergo a preliminary period of annealing, to a stoppered bottle in an air-oven at 50° ± 1°.

Apparatus for Rate Measurements.—This was the same as that used for sulphur at temperatures above 0°, but owing to the different characteristics of the transformation the procedure for making the measurements had to be modified. In the first place it was necessary to bring the slide to the temperature of the thermostat as rapidly as possible, otherwise it was likely that a considerable area of the film would have been transformed before equilibrium was achieved. The lower part of the inner glass cell of the apparatus was therefore filled to a depth of about 2 in. with clean dry mercury, and on insertion of the slide holder and slide in the cell they were immediately lowered so that the film was immersed in the mercury, and were left there for 1 min. before being raised to the position for projection of the film. This quickly brought the slide to thermostat temperature.

At 45·7°, at which the majority of the measurements were made, the advance of the interface was too rapid to be recorded by tracing on the screen. Since the transformation started by spontaneous nucleation at one or more randomly situated points, and not as in the case of sulphur as the result of deliberate inoculation along a straight start line, it could not be followed by projection on to a grid. Nucleation usually occurred almost as soon as the slide had been placed in the thermostat, or within 20 min. of this, though in one case two hours elapsed before nucleation. The position of the interface was recorded photographically at 5-min. intervals by means of the same camera as was used in the work on sulphur at 0° (*loc. cit.*, p. 1110) except that, in order to take in the whole width of the carbon tetrabromide film on the plate, the opening at the back of the camera had to be widened, and only four records instead of eight could be obtained on one quarter-plate. Since the position of the interface was not sufficiently defined in ordinary light, two polaroid screens were fixed in the path of the light, one in front of, and one behind the thermostat, and were adjusted to be 15—30° from the crossed position. This setting was found to give the best compromise between definition and illumination. Crossed polaroids made the interface invisible at places where the monoclinic crystals were in extinction. Plate I shows an example of the records obtained. These records were subsequently projected on to a screen as in the sulphur work, but the successive positions of the interface were traced, different colours being used to distinguish the different positions. The measurements made on these tracings were the distances advanced by the growing points of the dendritic crystals (see below).

At temperatures nearer to the transition point the transformation was very much slower and it was then possible to make direct tracings of the positions of the interface on the screen. Spontaneous nucleation did not occur, so that after the slide had acquired the thermostat temperature it was momentarily raised to the top of the cell and the top of the film inoculated by pressing a piece of cold metal against the cover slip. The slide was then at once returned to its proper position. At these temperatures growth was not dendritic and a sufficiently good estimate of the rate could be made by taking measurements on the tracing along a number of equally spaced parallel lines running from top to bottom of the slide, *i.e.*, in the general direction of the interface advance.

Cinephotomicrographic Records of the Transformation.—A number of 16-mm. cinephotomicrographic records of the transformation were taken between crossed Nicols at different magnifications and in both black-and-white and colour. These have proved most valuable for subsequent detailed studies of particular features of the transformation, notably the characteristics of the interesting phenomenon of secondary growth, which is described below. We have come to regard the taking of such films as almost essential in the investigation of transformations between crystalline phases. A particular event, or sequence of events which might never be observed again or be difficult to repeat, is captured once for all and can be studied again and again at leisure. Approximate measurements of the rate can also be made by means of the films in certain cases where the camera speed is known. The projector is focused on a small gridded screen and turned over by hand, the position of the interface being noted, say, every 20 frames. In this way some comparisons between the rates of primary and secondary growth (see later) were made. Under these conditions of use of the projector, the film is protected by a heat filter and so does not suffer.

RESULTS AND DISCUSSION

Crystallography of Carbon Tetrabromide and Determination of the Optical Crystallographic Properties of the Monoclinic Form.—The crystal structures of both forms were studied by Finbak and Hassel (*Z. phys. Chem.*, 1937, *B*, **36**, 301). They found 32 and 4 molecules respectively in the unit cells of the monoclinic and the cubic form. The monoclinic cell is pseudo-cubic and may be regarded as derived from 8 of the cubic cells by a very slight distortion. This means that the centres of gravity of the molecules are in nearly the same positions in both forms, and they suggested that the molecules rotate in the cubic form, since it gives very weak *X*-ray reflections. Marshall, Hart, and Staveley (*loc. cit.*) conclude, however, from consideration of their own heat-capacity data for the compound, that the molecules undergo torsional oscillations only in both forms.

The following morphological and optical data for the monoclinic form were obtained by Zirngiebl and are given in Groth's " Chemische Kristallographie," Vol. I, p. 230 : $a : b : c = 1{\cdot}7414 : 1 : 1{\cdot}9617$ (which agree reasonably well with the *X*-ray cell dimensions) and $\beta = 125° 3'$. Crystals from acetone are tabular on *c*{001}, and have also *r*{10$\bar{1}$} and *m*{110}. Crystals from alcohol are much elongated along *b* but are still tabular on *c*{001}. Cleavages are *c*{001} (perfect) and *b*{010} (pronounced). The optic axial plane is parallel to 010 and an inclined optic axial interference figure is presented by 001.

This information was inadequate to enable us to identify the orientations of the monoclinic crystals in our films under the microscope and we therefore decided to make as complete an optical examination of the compound as possible. Three difficulties at once arose: (1) carbon tetrabromide is readily soluble in the usual immersion media used for determining refractive indices; (2) the usual alternative media for such cases, namely, aqueous-glycerol solutions of potassium mercuric iodide, have a maximum index of about 1·71 and this is lower than both γ and β for the compound; (3) well-formed crystals persistently present the 001 section when mounted in the ordinary way between a slide and cover slip, and examination of other sections is therefore difficult. These difficulties were eventually overcome by using solutions of barium mercuric iodide as immersion liquids and by the use of a single-axis rotation apparatus by means of which a single crystal could be rotated about a given axis while immersed in the liquid.. The apparatus together with an auxiliary apparatus for mounting the crystal is described elsewhere (*J. Roy. Microscop. Soc.*, in the press).

The barium mercuric iodide solutions ($BaHgI_4$) were prepared by mixing stoicheiometric quantities of mercuric iodide and iodine with an excess of barium oxide. Water was added with warming and the residue of barium iodate and barium oxide was filtered off through asbestos. The filtrate was then concentrated under reduced pressure and the most concentrated solution thus obtained had a refractive index of about 1·76, which is considerably higher than γ for carbon tetrabromide. Unfortunately, on exposure to the atmosphere such concentrated solutions take up water vapour and the refractive index falls—rather rapidly if the specific surface of the solution is large. For example, on one occasion when the index of a drop of solution was being measured on a Leitz–Jelley refractometer, the index fell from 1·74 to 1·73 in 2 min. However, by adopting the following procedure and working quickly, values of the principal refractive indices were obtained which are probably accurate to within $\pm 0{\cdot}001$. A crystal from alcohol was mounted on the rotation apparatus so that its long axis (= b and β, see data above) was the axis of rotation; α and γ were then determined indirectly by Wood and Ayliffe's method (*Phil. Mag.*, 1936, **21**, 324), which depends on the linear relation between $1/n^2$, where n is the refractive index of the liquid in the cell of the rotation apparatus, and $\cos^2\theta$, where θ is the angle (measured from the position in which the α vibration direction is normal to the axis of the microscope) through which the crystal must be rotated to achieve equality between its index for light vibrating normally to the axis of rotation (the " cross " index) and that of the liquid. This method is at its best when the birefrigence of the crystal is high so that the matching position is sharply defined. In the present case the birefringence is less than 0·02 and it was found that when the ordinary Becke line test was used there was considerable uncertainty about the exact position at which the cross index equalled that of the liquid. However, reasonably reproducible readings were obtained by illuminating the crystal with a narrow pencil of oblique rays produced by two off-centre stops 1/16 in. in diameter, one in the back focal plane of the objective and the other in the conjugate focal plane of the condenser. This arrangement gave a rapid variation in contrast around the matching position and enabled it to be fixed to the nearest 0·5°, which was about the lower limit to which the two-inch drum of the rotation apparatus could be read.

The method of conducting the experiment was to start with a solution in the cell of the apparatus having an index greater than γ for the crystal. The index of the liquid gradually fell by absorption of water vapour from the atmosphere, and as soon it was below γ, readings of θ were begun. Immediately after each reading was taken a drop of the liquid was transferred to the Leitz–Jelley refractometer, and the index measured as rapidly as possible. Throughout the measurements, the composition of the liquid in the cell was kept uniform by frequently partly withdrawing it into a capillary tube and then expelling it back into the cell. Two crystals were studied in this way, and the plot of $\cos^2\theta$ against $1/n^2$ is shown in Fig. 2, which also gives the two best straight lines obtained by the method of least squares, one taking the values of $\cos^2\theta$ as exact and the other the values of $1/n^2$. Both give the same values of α and γ to the third decimal place. The diagram also shows the values of $1/n^2$ corresponding to other near values of n, from which the accuracy of the determination can be judged. The scatter of the points is probably mainly due to the fact that the refractive index of the liquid could not be determined at the same instant as the matching angle was read, rather than to errors in reading this angle.

From a direct measurement of $2V$ (optic axial angle) on the rotation apparatus, the value of β was calculated.* Also the 100 and $10\bar{1}$ faces were identified from Groth's description (*op. cit.*) and the optic orientation in relation to them determined. The refractive indices were determined in sodium light. The optical data are summarised below and the optic orientation in Fig. 3.

$$\alpha_D\ 1{\cdot}710,\ \beta_D\ 1{\cdot}713,\ \gamma_D\ 1{\cdot}726;\ 2V = 53^\circ \pm 0{\cdot}25^\circ.\ \text{Sign positive.}$$

A useful confirmation that the indices are of the right order is that the mean index $\sqrt[3]{\alpha\beta\gamma} = 1{\cdot}716$, whereas that calculated from the Lorenz–Lorentz equation by use of

---

* A direct measurement of $2V$ strictly requires that the liquid used in the cell should have $n = \beta$, *i.e.*, that β be known in advance. In our experiments the measured angle varied inappreciably over the short range of refractive indices of the liquids used.

Eisenlohr's refraction equivalents and a density of 3·45 (determined by Marshall, Hart, and Staveley, *loc. cit.*) is 1·718.

Rate Measurements at 45·7°.—The transformation was more extensively studied at this temperature than at any other, and many measurements were made with the object of finding out whether the linear rate was constant and whether it was influenced by previous annealing of the films. The monoclinic phase grows at this temperature in a most interesting way and two distinct processes are involved. The main, or *primary* growth as we shall term it, is dendritic. In our cells it nearly always originated at points on the surfaces of the mica separators. The dendrite branches are large clear crystals which often attain a length of between 10 and 20 mm. and a width of about 1 mm. Following on the heels of this primary growth is a *secondary* growth of small grains which fill the spaces between the primary crystals and also isolated pockets between these and the glass surfaces.

FIG. 2.

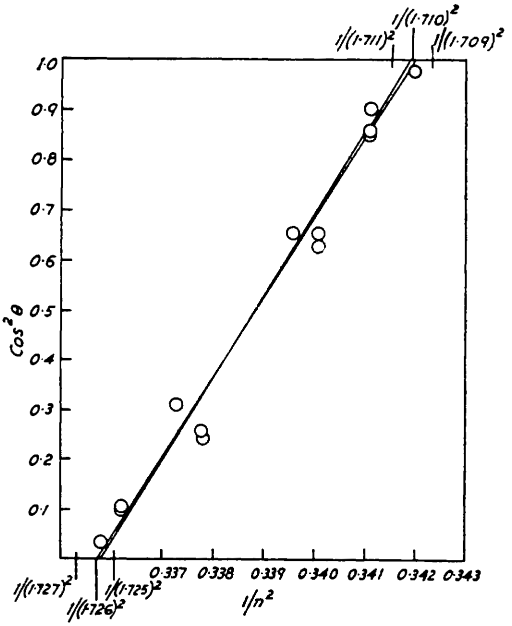
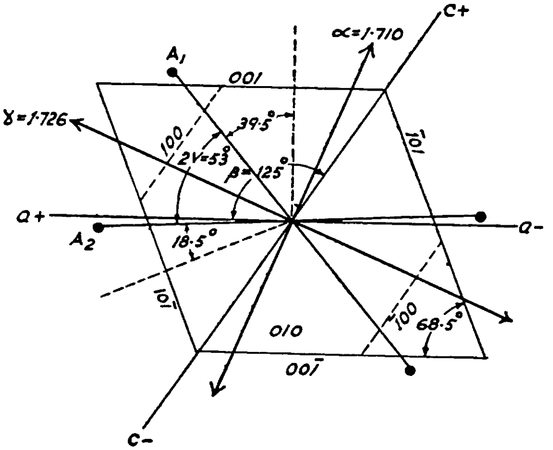


FIG. 3. *Optic orientation of monoclinic carbon tetrabromide on* 010.

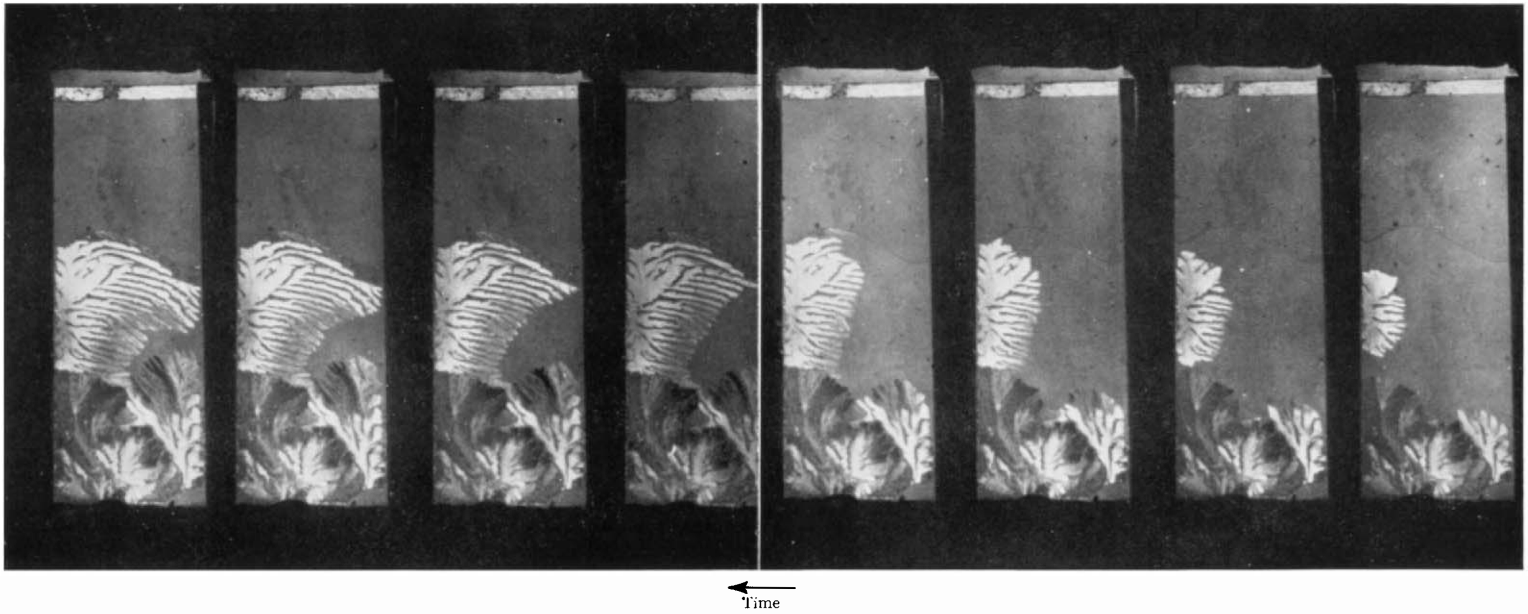


Plates II and III are photomicrographs of a fully transformed film and show clearly the results of the two modes of growth.

A careful microscopic study of the orientations presented by the primary crystals has been made on a large number of the fully transformed films. These orientations have proved to be very varied and appear not to be closely defined by principal lattice planes. Moreover, crystals having a given orientation may have different directions of elongation, and in short, there seems to be no preferred axis of growth. The results of this study are being analysed statistically in order, for example, to ascertain whether the significant differences in mean rate between slides (see below) is traceable to differences in the growth directions of the primary crystals, though there is no obvious sign that any such correlation exists.

The characteristics of the secondary growth have been studied by means of our ciné films and also directly on the hot stage under the microscope. The primary branches as they advance in the direction of elongation also spread laterally, but when the growing tip has passed on, this lateral growth soon comes to a halt, leaving long narrow " inlets " between the branches. Shortly after the lateral growth has ceased, the secondary grains begin to appear. The growth of the grains is spasmodic. Each one grows rather rapidly at first, then slows down and may even stop for a time. It then accelerates or resumes its advance unless in the meantime the surrounding cubic phase has been transformed by

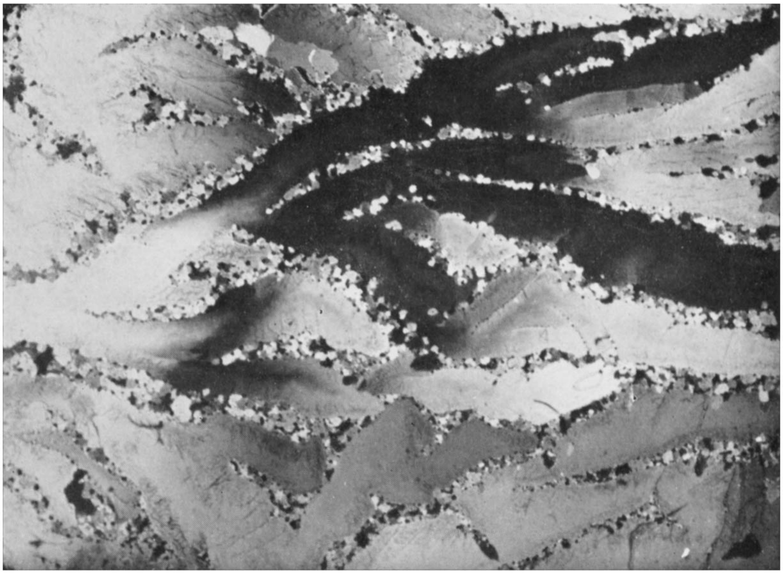
PLATE I.



Two quarter-plate records of the same slide at 45·7°. Exposures were made at 5-min. intervals.

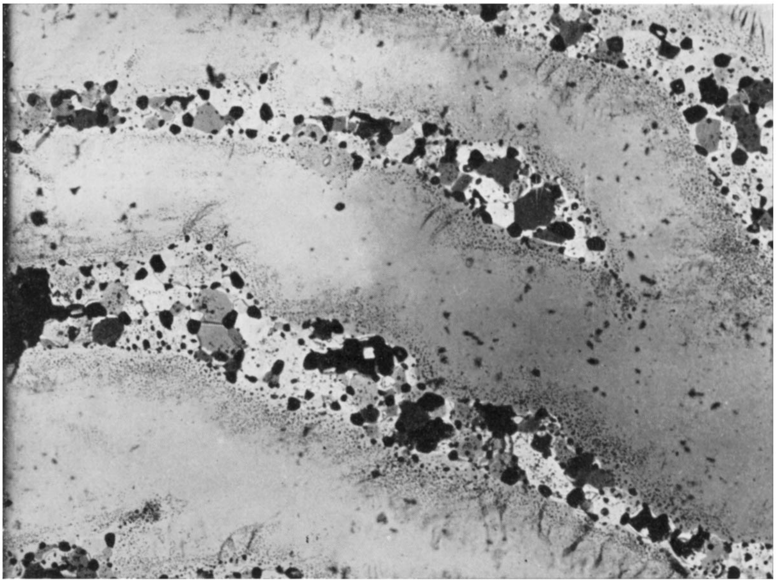
[*To face p.* 3710.

PLATE II.



Primary and secondary growth. Between crossed Nicols. (×10.)

PLATE III.



Primary and secondary growth. Between crossed Nicols. (×27—28.)

the growth of neighbouring grains. The grains always seem to originate from the surfaces of the primary crystals but usually to have quite different orientations from them. The filling up of the inlets by this process nearly always occurs some distance behind the growing tips of the primary crystals. The appearance of secondary crystals between the primary crystals and the glass surfaces as seen between crossed Nicols is accompanied in many cases by a fall in the polarisation colour, or even complete compensation, over the area which they cover, thus demonstrating very beautifully that they are differently orientated from the substrate.

The cause of the secondary growth is not obvious. The formation of the inlets in which it occurs is probably a temperature effect. The heat of transformation is fairly high for a polymorphic change, and the rate of transformation as expressed by the rate of advance of the tips of the dendrite branches is of the order of 15 mm./hour, *i.e.*, about three times the maximum rate observed for sulphur (Part VI, *loc. cit.*). Moreover, this high rate occurs at a temperature which is only 1·2° below the transition point, so that the temperature coefficient is very large. Calculations by means of Davidson's equation (Part VI, *loc. cit.*) show that the rise of temperature at the interface under these conditions could amount to about 0·06° for an infinite linear interface, and it is therefore not unlikely that the lateral growth of neighbouring branches would be very much slowed down or even temporarily stopped by the development of heat which could not flow away fast enough. But as the advancing tips of the branches push further ahead these retarded or halted parts left behind must cool again to thermostat temperature, and one would expect that the growth of the original crystal would then simply be resumed. Instead, a crop of quite differently oriented crystals (the secondary grains) appears although, within the limits of microscopic resolution, they appear to originate at the surfaces of the primary crystals. Very careful attempts were made to ascertain whether there was any sign of strain birefringence in the inlets before secondary growth occurred. The isotropism of the cubic phase here offered an advantage. Intense illumination and carefully crossed Nicol prisms were used, and the field was examined after insertion of a first-order red selenite plate, but the results were negative. We are therefore forced to the conclusion that, when lateral growth of the primary branches ceases, some actual discontinuity in the structure arises at the interface and that the secondary growth, though appearing to originate from the halted surface of the primary crystals, actually represents the result of three-dimensional nucleation of the opposite side of the discontinuity. Any suggestion that the secondary grains are another modification of carbon tetrabromide may be dismissed, since films having the structures shown in Plates II and III have been preserved for over four years without apparent change.

Some rough comparisons of the rates of primary and secondary growth were made by slow projection of the ciné films as mentioned on p. 3708. The mean linear rate for the secondary granules was of the same order as the rate of advance of the growing tips of the primary branches, but the initial rate of growth of the granules was considerably greater than this.

The measurements of primary growth made on the tracings were the rates of advance of the growing tips of the primary branches, as already stated. These were the only measurements which could conveniently be made. The results of the studies of orientation and directions of elongation referred to above, indicate, however, that these directions of growth probably covered a wide range of lattice directions. Moreover, since the growing tips had an " open sea " of the cubic form ahead of, and partly around, them, the heat of transformation must have been much more rapidly dissipated from them than from the inlets between the branches. It seems likely, therefore, that their temperature was not appreciably different from that of the thermostat, or at least that the result of applying Davidson's equation represents an upper limit to the temperature rise.

Three series of slides were studied as follows : (1) unannealed slides, *i.e.*, slides transferred direct from the crystallisation apparatus to the projection apparatus, (2) annealed slides, which after being removed from the crystallisation apparatus were transferred to a stoppered bottle in an air oven at 50° ± 1°, and left there for either (*a*) 1 day or (*b*) 3 days before being transferred to the projection apparatus.

Figs. 4, 5, and 6 give the t–s plots for individual slides in the three series, where t is the time (the time of insertion of the slide in the thermostat being taken as zero) and s is the " average distance " advanced. The latter was obtained by progressive addition of the mean advances (Δs) for successive intervals of 5 min. (see p. 3707). The s scale thus set up is to some extent fictitious since on many slides crystals grew from two or more centres and these started at different times. Thus crystals originating from the later centres would have high t values and low true s values, but their results would be pooled with those of crystals from earlier centres which by this time would have achieved higher s values. (New crystals resulting from branching can be regarded as having the same origin as the

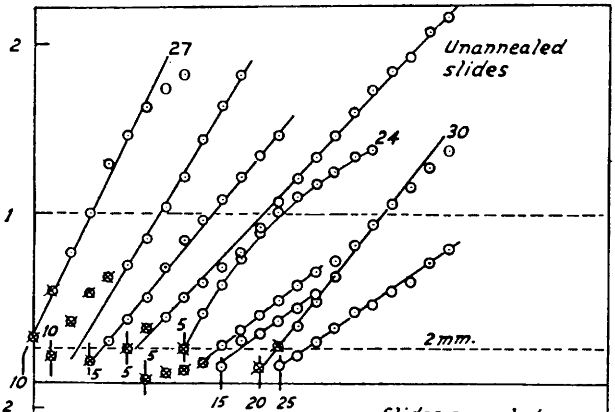


FIG. 4.

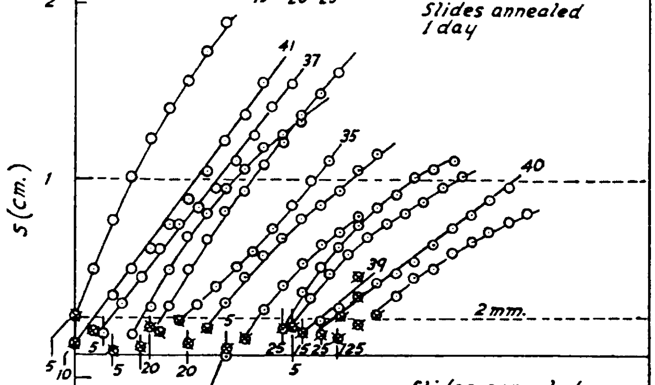


FIG. 5.

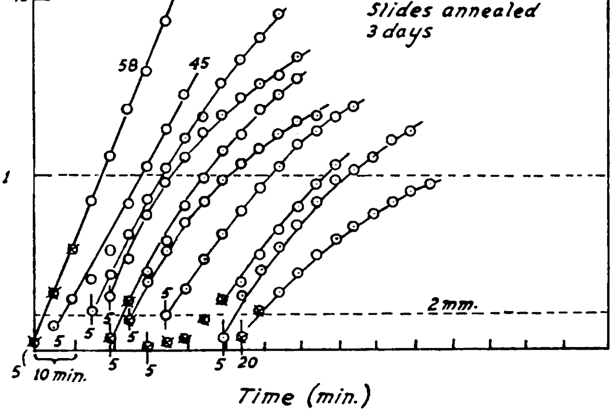


FIG. 6.

parent stem.) The *t–s* plots afford, however, a convenient means of showing whether there was any trend in the rate with time.

The number of measurements on which the majority of the individual Δs values were based varied between 1 and 25. Points in Figs. 4—6 based on less than 5 measurements are distinguished by a superposed cross, and little or no weight has been given to these points in drawing the smoothed plots.

The origins of the plots have been distributed along the time axis in order to avoid superposition and confusion. The figure at the foot of each plot gives the *t* value (to the nearest 5 min.) for the first point. Thus for a slide which nucleated at once on insertion in the thermostat the first point is marked " 5," whilst for one which did not nucleate until 10 min. after insertion it is marked " 15 " and so on.

In the unannealed series (Fig. 4) all the plots are good or reasonably good straight lines (27 and 30 shows a slight decline at high *t* values) except that for slide 24, which shows a continuous decline of rate with *t*. In the 1-day series, slides 41, 37, 40, and probably 39 give straight lines and the others show declines, with the exception of 35 which shows a slight rise of rate with *t*. In the 3-day series, 58 and 45 give straight lines and the remainder show a decline. There is thus an increasing proportion of cases in which the rate declines with time in the direction : unannealed, annealed one day, annealed three days.

This decline could (1) be a real effect, meaning that *individual crystals* show a progressive decline in rate owing, say, to shrinkage resulting from the difference in density between the two forms (as suggested for *o*-nitroaniline, Part III, *J.*, 1935, 1860, and mercuric iodide, Part IV, *J.*, 1938, 1636) or could (2) result from the way in which the results are grouped. Thus even if individual crystals grow at a constant rate but those which start late are slower than the earlier ones, the *s–t* plot must necessarily show a decline. Measurements of the rate of advance of a number of single crystals made on the tracings (those crystals being selected which could be followed for the longest possible time so that any trend would not be obscured by local variances) and a qualitative examination of the tracings for evidence of the effect of grouping have shown that in fact both this and real declines in the average rate of some crystals do occur. It has not, however, proved possible to disentangle the two effects completely. Thus in a number of slides which nucleated near the upper solid–vapour interface of the film the monoclinic phase spread preferentially along this interface and developed a progressively increasing number of crystals growing inwards which were slower than those in the body of the film. In no such case, however, was it possible to say that the decline was due to this cause alone, because either the single crystals measured on the slide themselves showed a decline or else no acceptable single-crystal measurements covering a large *t* range could be made.

It should be noted that the range of *s* values covered by most of the slides, namely, 10—20 mm., far exceeds that in previous studies in this series. In the cases of *o*-nitroaniline and mercuric iodide (Parts III and IV, *locc. cit.*), which showed a marked decline of rate, the maximum *s* range was of the order of 1 mm. In the sulphur transformation (Parts V and VI, *J.*, 1940, 588; 1951, 1097), in which the rate was constant, it was about 2 mm. It may well be that if it had been possible to confine the measurements on carbon tetrabromide to such narrow *s* ranges no decline would have been detected, for the rate of decline was much smaller than was found in the earlier studies. For example, in slide 24 (Fig. 4) the average rate fell to half its initial value after an advance of about 10 mm., whilst with mercuric iodide a similar relative decline occurred for an advance of only about 0·5 mm. The initial 2-mm. interval is indicated by horizontal lines on Figs. 4—6, and rough extrapolation of the smoothed plots to $s = 0$ shows how small a change of rate would have occurred over this interval.

A possible explanation of the constant rates shown by almost all the unannealed slides and of the increase in the incidence of cases of decline of rate with annealing is as follows. In the unannealed slides, the fairly rapid descent from the temperature of the crystallisation apparatus to that of the thermostat may have resulted in the formation of a granular cubic film in which the transformation started afresh, as it were, at each grain boundary, so that whatever the tendency of the rate to decline while the interface was traversing a single grain, it was on the average constant. It may then be supposed that the annealing process applied to the other slides would result in grain growth of the granular film leading to the formation of much larger homogeneous domains, in traversing which the interface would suffer a decline in its rate of advance owing to the shrinkage resulting from the density change accompanying the transformation. (The densities are: cubic 3·21, monoclinic 3·45; Marshall, Hart, and Staveley, *loc. cit.*) If the sizes of these domains were comparable with the total advance measured, this decline would be reflected in the average rate of advance.

The rise in rate shown by the plot of slide 35 (Fig. 5) is difficult to account for. Examination of the tracing showed that it was not due to any grouping effect but to a rise in the rate of advance of some of the single crystals. Other crystals on the slide showed a constant rate.

It seemed to be very difficult to make any quantitative use of the results obtained on slides which showed a non-constant rate, and we therefore decided to take the constant or near-constant results obtained with the unannealed slides (except No. 24) as the " normal " case, and to make all subsequent measurements at other temperatures on unannealed slides. The mean rates of these eight slides ranged from 9·4 to 22·4 mm./hr. Analysis of variance of the single Δs measurements showed that the ratio of the variance between slides to that within slides was 96·6, which is very highly significant, showing that the sets of measurements representing the individual slides cannot be regarded as random samples from the same population. We must therefore treat the slide means as single measurements in assessing the probable limits within which the true mean lies. The slide means being taken as of equal weight, which is justified since each is based on a large number of Δs measurements (minimum 61, maximum 185), this leads to a grand mean of 14·8 mm./hr. with 95% fiducial limits of ±4·2. The coefficient of variation of the slide means was 0·35.

The limits of the thermostat temperature during these measurements were about ±0·025°. Allowing for the possibility that the interface temperature might be up to 0·06° higher than that of the thermostat (see above), this makes the limits of uncertainty 45·675—45·785°.

Determination of T_0.—Since the exact value of T_0 seemed to be in need of confirmation, and would be required for the accurate calculation of the supersaturation, we attempted to determine it with our apparatus by seeking the temperature at which the interface was stationary. This involved keeping the interface under observation at different temperatures for long periods, often of some days. The position of the interface was recorded either by tracing on the screen (magnification factor 21·5) or in later experiments by darkening the whole room and exposing a photographic plate carried in a dark slide affixed to the screen. In the latter method a transparent grid of 0·5 mm. squares was attached to the slide and appeared in the photographs as a reference net against which very small changes in the position of the interface were immediately obvious.

In preliminary experiments at bath temperatures ranging from 46·78—46·83° to 46·93—46·98° and lasting from 4 to 17 hours, it was found that, although the interface remained stationary over most of its length, it advanced (*i.e.*, cubic transformed to monoclinic) in some parts and retreated in others. Below this range only advances were observed, or advances with some parts stationary, while above it the interface was observed to retreat, or the monoclinic crystals showed interior regions of general conversion into the cubic form. [Spontaneous transformation to this form occurs without noticeable superheating, and as seen between crossed Nicols the process looks more as though the monoclinic crystals were melting than undergoing a solid–solid transformation. Wahl (*loc. cit.*) also reported this behaviour.] The temperature control was then improved to ±0·01° or better, but in an experiment at 46·88—46·89° lasting 3 days the same phenomenon of simultaneous advances and retreats of the interface was observed.

The specimen of carbon tetrabromide so far used had been sublimed twice. It was thought possible that the effect might be due to traces of impurity unequally distributed throughout the film, though phase-rule considerations show that a second component could only affect the value of T_0 if it formed solid solutions with the carbon tetrabromide. Further experiments were therefore done with a specimen which had been sublimed three times but the same effect was observed at 46·92—46·94° (4 days) and 46·96—46·98° (2 days), though the movements (which were of the order of 0·01—0·1 mm.) were not so marked as with the earlier specimen, and in two other experiments at 46·92—46·95° (3 days) and 46·92—46·94° (1 day) no movement either way was detected.

The only other difference between the behaviour of the two specimens was that the one sublimed three times showed advances only at 46·82—46·84° which lies within the range in which the twice-sublimed specimen showed both advances and retreats in the preliminary experiments, but this difference may have been due to the better temperature control in the later work. Observations on the hot stage of the microscope, in which closely adjacent edges of films of the two specimens were watched while the temperature was very slowly raised, failed to detect any difference in the point at which conversion into the cubic form began, and there seems little doubt that the specimens were very similar and of a high degree of purity.

A more likely explanation of the simultaneous advances and retreats is that the movements are caused by small free-energy differences arising from localised strains in the two structures, and they may possibly be a manifestation of the " indeterminacy " in phase transitions postulated by Ubbelohde (see, *e.g.*, *Nature*, 1952, **169**, 832). It is hoped to investigate the phenomenon more closely.

Even if these small movements be disregarded as being a purely local effect, it is evident that the method, at least with the present apparatus, is not capable of giving a precise value for T_0, since the range of temperature over which most of the interface showed no detectable movement was (taking all our experiments) about 0·2°. This is certainly due to the fact that, as will presently appear, the linear rate (v)–temperature (T) curve tends to $\mathrm{d}V/\mathrm{d}T = 0$ at T_0, so that the rate must be inappreciable over a finite range of temperature near this point. Indeed, if the advance of the stable phase is analogous to growth from a vapour (see below), it may actually be halted over a finite temperature range because the growth mechanism is " frozen." For example, the dislocation theory of crystal growth predicts that at extremely low supersaturations growth must cease because the critical nucleus is too large to pass between adjacent dislocations (see Frank, *Phil. Mag.*, *Suppl.*, 1952, **1**, No. 1, 91).

The values for T_0 given by Frederick and Hildebrand and by Rothmund (*locc. cit.*) are consistent with the above observations, and for the present we shall take the rounded value of 46·90°.

Linear Rate between 45·7° *and* T_0.—The Table summarises the results of all the measurements made on unannealed slides. At temperatures other than 45·7° the number of measurements made on each slide was not large (14—21 in most cases) and, as already stated (p. 3708), the method of measurement was different since the growth was not dendritic, but they were sufficient to give a good estimate of the slide mean rate. In the light of the results at 45·7° the slide means have been treated as single measurements and for temperatures at which more than one slide was studied the 95% limits are given. The assumption was made that the rate was constant and this was justified by the results obtained on a number of the slides on which the advance for more than one time interval was measured. In these, although the results for successive intervals showed considerable variance as was to be expected, there was, taking the slides as a whole, no trend of rate in either direction.

Linear rate measured on unannealed slides.

Thermostat temp.	Mean rate (mm./hr.)	No. of slides studied	95% Limits
45·7° ± 0·025°	14·8	8	10·6—19·0
46·23 ± 0·01	0·735	1	—
46·30 ± 0·01	0·71	1	—
46·33 ± 0·01	0·67	1	—
46·44 ± 0·01	0·37	3	0·29—0·46
46·53° ± 0·01°	0·12	1	—
46·64 ± 0·01	0·094	3	>0—0·283
46·74 ± 0·01	0·029	3	>0—0·067
46·83 ± 0·01	0·009	1	—

The results are plotted in Fig. 7. The frame drawn round the 45·7° point is defined by the 95% limits and the uncertainty regarding the interface temperature mentioned above.

The 95% limits at other temperatures, where these limits were calculated, are also indicated on the Figure. The uncertainty regarding the temperature co-ordinates of these and the neighbouring points is practically negligible on the scale of the Figure, since the thermostat temperature was controlled to ±0·01°, and the rates were so low that there was no question of a detectable self-heating effect.

The curve approaches T_0 (which we have taken in the figure as 46·90°) asymptotically, and, as shown below, this rules out the possibility that it follows any equation of the general form of those proposed by Akulov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **32**, 340; 1943, **39**, 268), Laurent (*Rev. Metall.*, 1945, **42**, 22), and by one of us (N. H. H.) [*Discuss. Faraday Soc.*, 1949, **5**, 149, equation (3)]. All these equations involve the assumption that every molecule which arrives at the surface of the growing phase contributes to its growth, and as shown in the last-mentioned paper, near T_0 they approximate to the form

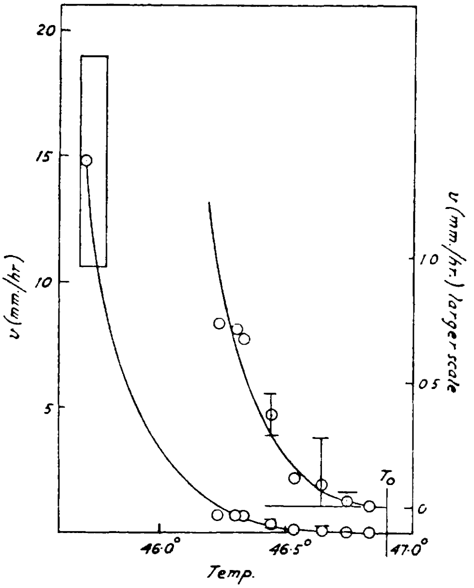


FIG. 7. *Right-hand curve shows results for temperatures above 46° plotted on a larger v scale.*

$$v = \text{const.}\ (-\Delta G/T)\ \exp\ (-E/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (\text{i})$$

(except that Akulov's equation contains no explicit reciprocal T factor), where v is the linear rate, $-\Delta G$ is the free-energy change attending the transformation, E is the potential barrier which the molecules must surmount in passing from the unstable to the stable structure, and the other symbols have their usual significance. Substituting $q(T_0 - T)/T_0$ for $-\Delta G$, where q is the heat of transformation, and differentiating, we find that, when $T = T_0$, $\mathrm{d}v/\mathrm{d}T$ is finite. Furthermore, in the very short temperature range just below T_0 which we are considering, by far the most important variable is $(T_0 - T)$, so that the plot of v against T should be very nearly a straight line. The experimental curve obviously does not fulfil these conditions.

In the Faraday Society Discussion (*loc. cit.*), it was shown that deviations in the rate of transformation of β- to α-sulphur from the requirements of Hartshorne's equation (3) (mentioned above) could be accounted for by the introduction of a semiempirical factor ϕ, which represented a supposed increase in the rate of escape of molecules from the α-form* owing to its fine state of division. This correction applied mainly to the region below the temperature of maximum velocity, in which the fine serrations on the front of the advancing rhombic phase were obvious, and it would be quite unrealistic to treat the present case

---

* In the derivation of the equation given in the Discussion section the symbols α and β denoted the unstable and stable forms respectively. In order to conform with the accepted designations of the forms of sulphur, they are used here in the reverse sense.

similarly, for just as has been observed in the case of sulphur near to the transition point, the growing crystals are large and exhibit few surface irregularities when viewed under the microscope.

If we assume, by analogy with the results obtained with sulphur (Part VI, *loc. cit.*) and the other molecular solids mentioned earlier, that the activation energy is the same as the heat of sublimation, we must suppose that the transitional layer at the interface is populated by molecules which are energetically equivalent to molecules in the vapour state. We may, in fact, treat the transformation process as being essentially one of growth of the stable phase from a vapour at a supersaturation determined by the vapour pressure of the unstable form. This picture does not require that the two solids be separated by a thick layer having the properties of a gas in bulk, so that the molecules suffer collisions in transit, though this state of affairs could arise at a late stage in the reaction owing to shrinkage resulting from the higher density of the stable form. If the solids are only one or a few molecular diameters apart, then molecules which leave the unstable form forthwith strike the surface of the stable form (as originally pictured in Part III, *loc. cit.*), and the rate at which they do this will be equal to the rate at which molecules would return to the unstable form if it were in contact with its saturated vapour in bulk. This rate is proportional to the vapour pressure multiplied by the condensation coefficient. If this coefficient is unity, and it is nearly so for many solids, it follows that (returning to the case under consideration) the rate of impact on the surface of the stable form will be the same as if it were in contact with free vapour at the vapour pressure of the unstable form.

We shall therefore now consider the results in terms of the modern dislocation theory of crystal growth from the vapour (Burton, Cabrera, and Frank, *Phil. Trans.*, 1950—51, **243**, *A*, 229). This theory predicts that when the mean migration distance of an adsorbed molecule on the surface of the growing crystal is greater than half the distance between successive turns of the spiral growth step, the rate of growth will be proportional to the first power of the supersaturation. This is the so-called "linear law" which may be stated as

$$v = Cx \exp(-L_{\text{I}}/\boldsymbol{R}T) \quad \ldots\ldots\ldots \quad \text{(ii)}$$

where C is a constant which in the simplest case is the product of the step height (d) and the vibration frequency (ν) of the surface adsorbed molecules in the crystal, L_{I} is the latent heat of sublimation of the crystals, and x is the supersaturation. Now

$$x = p_{\text{II}}/p_{\text{I}} - 1 = \exp(-\Delta G/\boldsymbol{R}T) - 1 = \exp[q(1/T - 1/T_0)/\boldsymbol{R}] - 1$$

where p_{II} is the pressure of the supersaturated vapour, and p_{I} the vapour pressure of the growing crystal, and the other symbols are as defined above. Applied to the present case, p_{II} is the vapour pressure of the unstable form, and substituting in (ii) we obtain :

$$\begin{aligned} v &= C \exp(-L_{\text{I}}/\boldsymbol{R}T)\{\exp[q(1/T - 1/T_0)/\boldsymbol{R}] - 1\} \\ &= C \exp(-L_{\text{II}}/\boldsymbol{R}T) \,.\, \exp(-q/\boldsymbol{R}T) \,.\, \{[\exp(q/\boldsymbol{R}T)/\exp(q/\boldsymbol{R}T_0)] - 1\} \\ &= C \exp(-L_{\text{II}}/\boldsymbol{R}T) \,.\, \{1 - \exp[q(1/T_0 - 1/T)/\boldsymbol{R}]\}/\exp(q/\boldsymbol{R}T_0) \quad . \ . \quad \text{(iii)} \end{aligned}$$

where L_{II} is the latent heat of sublimation of the unstable form. Now C has the same significance as the factor A_β in the derivation of Hartshorne's equation (3) (*loc. cit.*), and apart from the existence of an additional pre-exponential factor of $\frac{1}{2}$ in that equation,* it and the above equation (iii) are identical in form. Hartshorne's equation is, in fact, a general form of the linear law applied to a polymorphic transformation, and, as has been shown above, it cannot apply to the present results.

At very small supersaturations the dislocation theory shows that the turns of the spiral growth step will become greater than the mean migration distance of adsorbed molecules,

---

* For a vapour transitional layer this factor is only applicable if the layer is thick enough to behave as a gas in bulk (assuming that the condensation coefficients for the two forms are equal) (R. S. Bradley; unpublished work).

and predicts that the rate of growth will then be proportional to the *square* of the supersaturation (the so-called " parabolic law "). The equation may now be written as

$$v = (Cx^2/x_1) \exp(-L_{\mathrm{I}}/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

where C is the same as in (ii), and x_1 is a quantity called the critical supersaturation which at constant temperature has the significance that at supersaturations much below it the parabolic law is obeyed, whilst at supersaturations much above it growth follows the linear law (Burton *et al.*, *loc. cit.*). The other symbols have the same significance as before. x_1 is not temperature independent since it contains as factors $\exp[-(W'_s - U_s)/2\boldsymbol{k}T]$ and $1/T$, where W'_s is the evaporation energy of a surface-adsorbed molecule, and U_s is the activation energy required for such a molecule to migrate from one lattice site to an adjoining one, $\boldsymbol{k}$ being Boltzmann's constant. It also contains the edge free energy of the growth step as another factor. For a close-packed crystal, such as calculations based on Finback and Hassel's X-ray results (*loc. cit.*) show carbon tetrabromide to be, $(W'_s - U_s)/2$ is estimated by Burton *et al.* to be somewhat less than one-third to one-fourth of the total evaporation energy (per molecule), and so when the latter is not very large, as for carbon tetrabromide, the exponential factor will not change much over a small range of temperature. Its change is also partly compensated by that of $1/T$ though the effect of this is very small. Within the short range of temperature near T_0 which is now under consideration, calculations show that we can certainly ignore the variation in x_1 in comparison with that of x, so that (iv) reduces to

$$v = C'x^2 \exp(-L_{\mathrm{I}}/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

where C' is a constant. Furthermore since x is very small, we have that

$$x = \frac{p_{\mathrm{II}}}{p_{\mathrm{I}}} - 1 \approx \ln \frac{p_{\mathrm{II}}}{p_{\mathrm{I}}} = -\frac{\Delta G}{\boldsymbol{R}T} = \frac{q}{\boldsymbol{R}T_0}\left(\frac{T_0 - T}{T}\right)$$

and substituting in (v) we obtain

$$v = C'\left(\frac{q}{\boldsymbol{R}T_0}\right)^2 \left(\frac{T_0 - T}{T}\right)^2 \exp(-L_{\mathrm{I}}/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

or

$$\ln v + \frac{L_{\mathrm{I}}}{\boldsymbol{R}T} = 2 \ln\left(\frac{T_0 - T}{T}\right) + \ln C'' \quad . \quad . \quad . \quad . \quad . \quad \text{(vi}a\text{)}$$

where C'' is another constant which includes the factor $(q/\boldsymbol{R}T_0)^2$. By differentiating (vi) we find that when $T = T_0$, $\mathrm{d}v/\mathrm{d}T = 0$, and the same result is obtained if the full equation for the parabolic law is so treated, so that the result is not simply a consequence of the approximations which have been made. This condition is satisfied by the experimental curve (Fig. 7).

From (vi*a*) it follows that the plot of $\ln v + L_{\mathrm{I}}/\boldsymbol{R}T$ against $\ln[(T_0 - T)/T]$ should be a straight line with a slope of 2. This plot is shown in Fig. 8 (Curve A), from which it is seen that the points conform to this requirement reasonably closely, with the exception of the point for 45·7° (P), though it is possible, as shown, to pass a fairly well-fitting curve through all the points. The result near T_0 is naturally very sensitive to the value taken for T_0, and a change in this of ±0·05° gives quite a different slope to the lower end of the curve. An increase of 0·01°, however, which represents the difference between the rounded value of 46·90° here assumed, and Rothmund's value of 46·91° (*loc. cit.*), makes no essential difference to the slope.

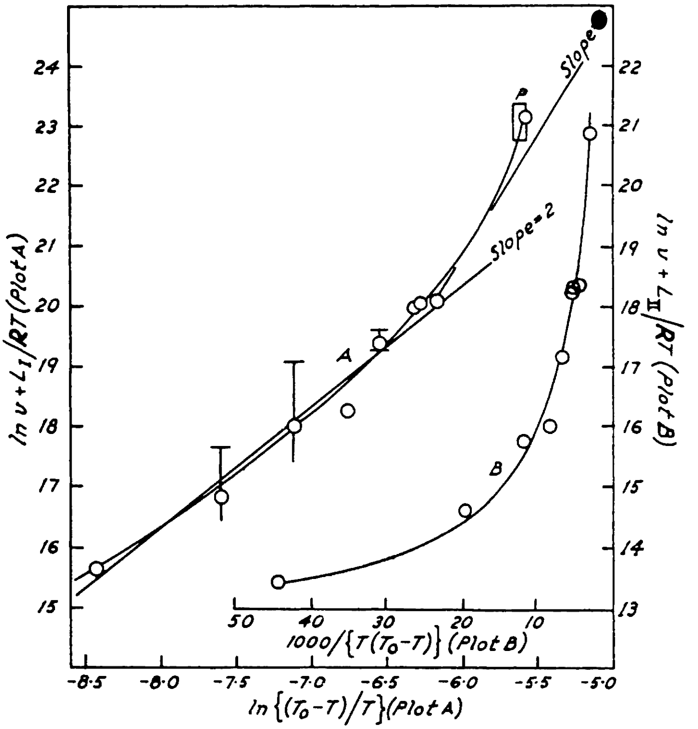
The two-dimensional nucleation mechanism proposed by Dunning (*Discuss. Faraday Soc.*, 1949, **5**, 194) does not account for the experimental curve, and it is hardly to be expected that it would apply at such very small supersaturations. Dunning's equation may be written as

$$\ln v = (\text{const.})_1 - \frac{L_{\mathrm{II}}}{\boldsymbol{R}T} - \frac{(\text{const.})_2}{T(T_0 - T)} \quad . \quad . \quad . \quad . \quad . \quad \text{(vii)}$$

Differentiation shows that when $T = T_0$, $\mathrm{d}v/\mathrm{d}T = 0$ as for equation (vi), but the equation also requires that the plot of $\ln v + L_{\mathrm{II}}/\boldsymbol{R}T$ against $1/\{T(T_0 - T)\}$ is a straight line. This plot is shown in Fig. 8 (*B*) and obviously does not fulfil this requirement irrespective of whether the point for 45·7° (the uppermost) is considered or not. The strong curvature of the plot is not appreciably affected if values ranging from 46·85° to 46·95° are assumed for T_0.

In these tests of equations (vi) and (vii), the values used for L_{I} and L_{II} are the internal latent heats of sublimation derived as explained on p. 3706, namely, 11,535 and 12,955 cal./mole, respectively. As far as the results of these tests are concerned, however, it makes practically no difference what values are taken for these quantities, provided that they are not considerably greater than those just stated. In the test of equation (vi) only 1% of the total change in $\ln v + L_{\mathrm{I}}/\boldsymbol{R}T$ is due to the change in the second term, and in the test of Dunning's equation the change in $L_{\mathrm{II}}/\boldsymbol{R}T$ represents less than 1% of the total change in $\ln v + L_{\mathrm{II}}/\boldsymbol{R}T$. The conclusions reached would therefore be equally valid for any mechanisms described by equations similar to these, but involving growth from a transitional layer which molecules could enter without acquiring the full sublimation energy. We will, however, continue to pursue the consequences of the assumption that the growth of the stable phase is a process analogous to that of growth from a vapour phase. On this basis the only mechanism of those mentioned above which might possibly account for the results at the lower supersaturations is that expressed in the parabolic law in dislocation theory. The difficulty here is that with increasing supersaturation the rate tends to a dependence on a higher power of the supersaturation than 2 (the upper part of the curve *A*, Fig. 8, has a mean slope of 4—5), whereas dislocation theory requires that the change should be in the opposite direction, *i.e.*, from the parabolic law to the linear law. The observed effect may be due to the fact already mentioned that in our experiments the growth at 45·7° (point *P*) was dendritic whilst that at the higher temperatures was not, so that the results for the latter may not be really comparable with those at 45·7°. Recent measurements of the rate of transformation of β- into α-sulphur near the transition point

FIG. 8.



(Hartshorne and Thackray, see above) indicate, however, a very similar dependence of the rate on supersaturation to that now described. Thus between 80° and 90° the mean rate is approximately proportional to the fourth power of the supersaturation, and between 90° and the transition point 95·5° ± 0·1°, a reasonable interpolation gives rates which are approximately proportional to the square of the supersaturation.

Although the change to a higher power in the dependence of the rate on supersaturation with increase in the latter does not conform to dislocation theory, and we can at present offer no satisfactory explanation of this change, the fact that at the the lowest supersaturations the rate appears to be proportional to the square of the supersaturation (as is required by this theory), or nearly so, justifies a closer examination of the application of equation (iv) to the results in this region.

Substituting $d\nu$ [see equation (ii)] for C in equation (iv), we obtain

$$v = (d\nu x^2/x_1) \exp(-L_I/\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

Taking for d the average spacing between the molecules in monoclinic carbon tetrabromide, namely, $5{\cdot}4 \times 10^{-8}$ cm., and for ν 10^{12}—10^{13}, say, 5×10^{12} sec.$^{-1}$, then we have at 46·3° (which is just inside the range in which the rate is approximately proportional to x^2) $x = 0{\cdot}0042$ and v works out to $2{\cdot}5/x_1 \times 10^{-1}$ mm./hr. Now Burton *et al.* (*loc. cit.*) estimate that a typical value for x_1 would be 10^{-1}, and calculations that we have made indicate that for carbon tetrabromide it would probably be between 10^{-1} and 10^{-2}. This would place v between *ca.* $2{\cdot}5 \times 10^{-3}$ and $2{\cdot}5 \times 10^{-2}$ mm./hr. The observed value (Fig. 7) is *ca.* 6×10^{-1} mm./hr., which is considerably greater.

The product $\nu \exp(-L_I/\boldsymbol{R}T)$ in equation (viii) represents the rate of arrival of vapour molecules at single lattice sites from the vapour at the *equilibrium* pressure (see Frank, *Phil. Mag. Suppl.*, 1952, **1**, No. 1, 91, for a treatment of the theory which emphasises the significance of this part of the equation), and if the condensation coefficient is unity, it must also be equal to the average rate of escape of molecules per lattice site from the surface into the vapour. R. S. Bradley has found, however, that in the case of rhombic sulphur, the rate of evaporation in a hard vacuum is *ca.* 10^4 times greater than that corresponding to the above product (*Proc. Roy. Soc.*, 1951, *A*, **205**, 553), but that the rate agrees with that calculated from the Langmuir expression $\alpha p(2\pi M\boldsymbol{R}T)^{\frac{1}{2}}$ (*J. Amer. Chem. Soc.*, 1916, **38**, 2221), where p is the vapour pressure, and M the molecular weight, if α, the condensation coefficient, is taken as 0·7, *i.e.*, near unity. Now an approximate value for the vapour pressure of monoclinic carbon tetrabromide at 46·3° can be obtained by extrapolation from the vapour-pressure data for the liquid (Bolas and Groves, *loc. cit.*) and the heats of fusion and transition (Frederick and Hildebrand, *loc. cit.*); it is 2·95 mm. of Hg. Calculating the rate of arrival of molecules at single lattice sites from this by means of the Langmuir expression (assuming $\alpha = 1$), and using this value in the calculation of v in place of that given by $\nu \exp(-L_I/\boldsymbol{R}T)$, we find that $v = 3{\cdot}3/x_1 \times 10^{-2}$ mm./hr., which is in much better agreement with the experimental value, if the same assumptions regarding x_1 are made as before. Calculation by the same method for the slightly higher temperature of 46·5° ($x = 0{\cdot}0028$) gives $v = 1{\cdot}5/x_1 \times 10^{-2}$ mm./hr. The observed value at this temperature is $\approx 2 \times 10^{-1}$ mm./hr. We are indebted to Dr. R. S. Bradley for having suggested this method of calculation.

The results at the lower supersaturations are thus not inconsistent with the requirements of dislocation theory, but in view of the marked deviation from these requirements shown by the experimental curve at the highest supersaturation studied (0·0084 at 45·7°) it is felt that the agreement shown by the above values should for the present be treated with considerable reserve.

One of us (N. H. H.) thanks the Council of the Chemical Society for a Research Grant. We are greatly indebted to Dr. B. L. Welch for assistance with the statistics of this problem, and to Dr. R. S. Bradley for many helpful suggestions and criticisms made during the course of the work.

Department of Inorganic and Structural Chemistry,
The University, Leeds.

[*Received, January 26th,* 1955.]