434. Studies in Polymorphism. Part III. The Linear Velocity of the Transformation of α- into β-o-Nitroaniline.

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In Part I (J., 1930, 727), preliminary observations on the rate of transformation of the " unstable " into the " stable " form of *o*-nitroaniline in thin films of the substance were described. [In Part II (J., 1931, 2583), these two forms were designated the α- and the β-form respectively, owing to the discovery of a third form (γ) of higher stability.] The present paper describes a further study of the linear velocity of the process and its dependence upon the temperature and other factors.

The kinetics of reactions in the solid state have recently attracted considerable attention. Most of the reactions studied have been of the type $\text{solid}_1 = \text{solid}_2 + \text{gas}$, *e.g.*, the decomposition of permanganates and dichromates (Hinshelwood and Bowen, *Phil. Mag.*, 1920, **40**, 569; *Proc. Roy. Soc.*, 1921, *A*, **99**, 203), of hydrates, notably copper sulphate pentahydrate (Garner and Tanner, J., 1930, 47; Hume and Colvin, *Proc. Roy. Soc.*, 1931, *A*, **132**, 548; Smith and Topley, *ibid.*, **134**, 224; Bright and Garner, J., 1934, 1872), and of azides (Garner and Gomm, J., 1931, 2123; Harvey, *Trans. Faraday Soc.*, 1933, **29**, 653).

The theoretical approach to the subject would be facilitated if more data were available regarding the simplest type of reaction in the solid state, *viz.*, the type $\text{solid}_1 = \text{solid}_2$, important examples of which are the transformations of polymorphic solids. Unfortunately, comparatively few kinetic studies have been made on such reactions, owing no doubt to the difficulty of finding examples susceptible of easy measurement.

In determining the rates of reactions in the solid state, most authors have determined the mass rate from the loss of weight (in decomposition reactions) or the change in volume accompanying the reaction; the linear rate of advance of the interface between the reacting and the resulting solid, or the rate of reaction per unit area of interface, is then deduced from the mass rate and the dimensions of the crystals, account being taken of the degree of nucleation of the latter. Few determinations of the linear velocity have been based on direct observations of the movement of the interface, as in the work of Bright and Garner (*loc. cit.*) on the growth of dehydration centres on crystals of copper sulphate pentahydrate.

As has already been shown, an interface between the α- and the β-form of *o*-nitroaniline is readily established by melting a little of the substance between a microscope slide and a cover slip, and then allowing the resulting film to crystallise. The interface can be clearly observed by transmitted light, owing to the difference in colour between the two forms (see Figs. 2, 3, and 4; Part I, *loc. cit.*), and its rate of movement is convenient to measure between 0° and 40°. The transformation thus affords an opportunity of measuring directly the linear velocity of a reaction of the simple type $\text{solid}_1 = \text{solid}_2$, at different temperatures.

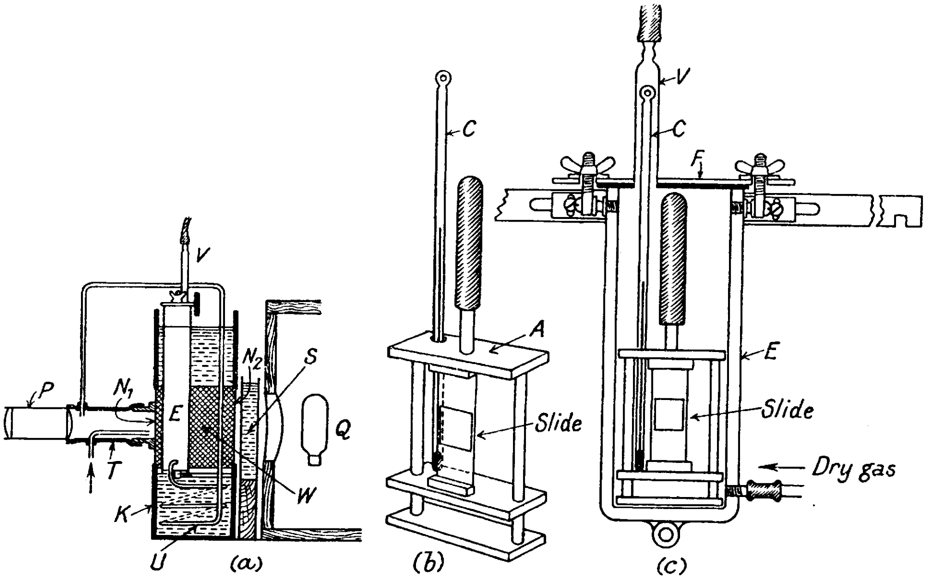
The reaction was followed by projecting a magnified image of a film, prepared as above, on a screen by means of a suitable optical apparatus, the slide being maintained at a constant temperature. The position of the interface was traced on the screen with a pencil or pen at equal intervals of time, and the linear velocity subsequently computed from the "average distances" between successive lines thus obtained. These "average distances" were the averages of measurements made at points equally and closely spaced along the interface. It was hoped that by making a sufficient number of such measurements, variations in velocity, due to differences in the relative orientations of the α- and β-crystals at different parts of the interface, or to other causes, would be averaged out. However, these variations proved to be so large, owing partly, no doubt, to the low symmetry of the substance, that this hope was only partially fulfilled, despite the fact that over 20,000 measurements were made in studying three specimens at four temperatures each. Nevertheless, the results suffice for the evaluation of the critical increment to within a few thousand calories.

It is of great interest that the velocity is not constant at constant temperature, but falls as the reaction proceeds. Schaum and Unger (*Z. anorg. Chem.*, **1924**, **132**, 90) observed a similar phenomenon in the polymorphic transformations of *p*-chloro-, *p*-iodo-, and *p*-hydroxy-benzophenone in thin films, but they did not comment upon it. A theory and a semi-empirical equation which account for this fall of velocity are advanced.

EXPERIMENTAL.

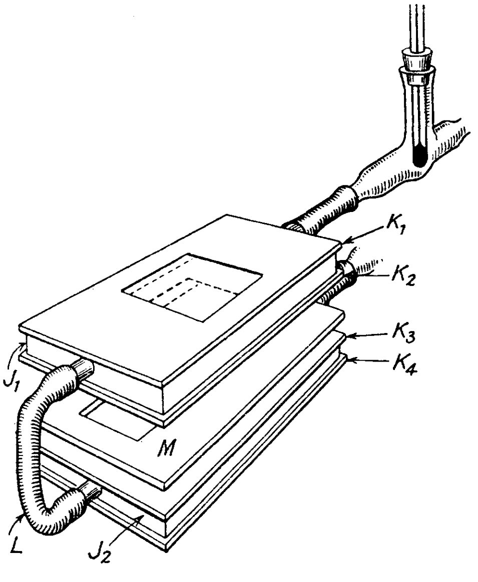
Projection Apparatus.—The reaction was studied at 0°, 20°, 30°, and 40°. For the first three temperatures, the apparatus shown in Figs. 1*a*, *b*, and *c* was used (Apparatus I). The slide was held in the holder *A* (Fig. 1*b*) by small leaf springs (not shown), and *A* was placed in the cell *E* (Fig. 1*c*), the back and front of which were made of plate glass. The top of *E* was closed by a well-fitting cover *F*, held in place by means of thumb-screws. *E* was rigidly fixed in the thermostat *K* (Fig. 1*a*, in which *E* is viewed from the side), provided with windows N_1, N_2. By means of the optical lantern *Q* and the projection lens *P*, an enlarged image of the film on the slide was projected on to a sheet of paper pinned to a vertical board placed 14 feet from the apparatus. A dry atmosphere was maintained inside *E* by passing a stream of dry oxygen or nitrogen through the wide rubber tube *T* (Fig. 1*a*), connecting *P* and N_1 (in work at 0°, this prevented the formation of dew on N_1), thence through the copper tube *U*, in which the gas acquired the temperature of the thermostat, into *E*. The gas escaped through *V*, which was connected to a calcium chloride guard-tube. In work at 0°, lumps of ice were prevented from being stirred into the field of view by the gauze screens *W*. A dilute solution of copper sulphate, *S*, absorbed heat rays from the lantern. The magnification obtained with this apparatus was 21·7.

FIG. 1.



As the reaction proceeded, small patches of the β-form appeared and grew in the α-areas. The interface gradually joined up with these patches, and so with the passage of time the length available for measurement decreased. It was necessary to distinguish " peninsulas " on the interface formed in this way from those due simply to more rapid growth at places of favourable crystal orientation. Using Apparatus I, it was fairly easy to do this at 0°, 20°, and 30°, because, although the definition on the screen was not very critical, the relatively low linear velocities at these temperatures gave the observer time to take note of the course of events at all parts of the interface. At 40°, however, the velocity was much higher, and it became very difficult to estimate with this apparatus the part played by the small patches in the stabilisation process. Accordingly, for work at this temperature, a polarising projection microscope (Apparatus II) was used. With this, the film could be observed either in polarised light or between crossed Nicols, whereby all boundaries between the α- and β-forms were very sharply defined and their movement was easy to follow despite the higher velocity. The image was projected upwards on to a screen consisting of tracing paper stretched over a horizontal glass plate. The hot stage used with this apparatus consisted of two cells, J_1 and J_2 (Fig. 2), made of sheet brass with openings $1\frac{1}{4}''$ square at the top and bottom. These openings were covered with glass plates, K_1, K_2, etc., sealed to the brass with De Khotinsky cement. The cells had outlet and inlet tubes for the passage of a stream of water, and were connected together by the rubber tube *L*, inside which was a coil of wire to prevent kinking. The slide was placed between the cells inside the thick rubber washer *M*, and the whole assembly was held together by rubber bands. To minimise conduction of heat to the microscope stage, four discs of cork were cemented to the under side of the lower cell at the corners.

FIG. 2.

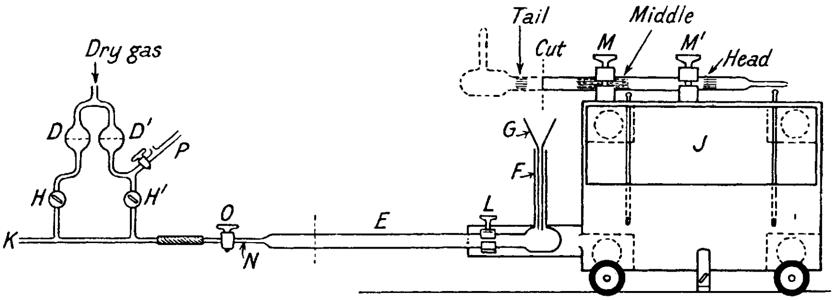


The stream of water was previously freed from dissolved air, which would have collected in the cells and obscured the field of view, by heating and passage through a bubble trap. It was led at a constant head through a copper coil in a thermostat and then through the cells. Two thermometers (one of which is shown in Fig. 2) registered the temperature of the water on entering and on leaving the cells. Their readings differed by 1° ± 0·1°, and the mean value was taken as the temperature of the slide. The magnification obtained with this apparatus was 28·5.

Purification of Material.—(i) *By recrystallisation* (with W. O. M. Williams). The first measurements were made on material purified as follows. Schuchardt's " pure " *o*-nitroaniline was recrystallised 12 times from aqueous alcohol (1 : 1 by vol.). Ordinary absolute alcohol and distilled water were used for the earlier fractions, but absolute alcohol, freed from traces of aldehyde by Winkler's method (*Ber.*, 1905, **38**, 3612), and conductivity water were used for the later ones. The solutions, saturated at about 70°, were allowed to cool in a large beaker wrapped in felt, and were meanwhile stirred with a rotating stirrer passing through a copper lid, which covered the top of the beaker and prevented ingress of dust. The stirring resulted in the deposition of small separate crystals unlikely to contain occluded mother-liquor. They consisted of the γ-form, as shown by their m. p. and their optical properties, determined under the polarising microscope.

Specimens of each fraction were retained, and after drying, their m. p.'s were determined by means of the apparatus described in Part I (*loc. cit.*). The m. p. became constant at 71·25—71·3° after the first three or four recrystallisations.

Fig. 3.



The final fraction was filtered off on a sintered-glass Büchner funnel, the top of which was then connected to a drying train (concentrated sulphuric acid and phosphoric oxide) and a cotton-wool dust filter. Air was drawn through the whole system for several days, after which the specimen was transferred to a vacuum desiccator containing phosphoric oxide. This specimen is referred to in the sequel as the " recrystallised specimen."

(ii) *By sublimation in a vacuum.* The experiments on material purified as above revealed a marked fall in the linear velocity as the reaction proceeded at constant temperature. It was thought that this might be due to the presence of traces of accelerative impurities at and near the interface at the beginning of the reaction, these impurities being left behind as the interface advanced. This explanation was suggested by the method of preparing the films, which almost certainly results in concentration of any impurity at the boundaries between the spherulites, for it is at these places that the last of the melt solidifies. To test this point, a method of intensive purification of the material was sought. It did not seem likely that anything would be gained by further recrystallisation, for during the operations it is impossible completely to protect the crystals from dust, and, as pointed out by Richards (*J. Amer. Chem. Soc.*, 1932, **54**, 493), beyond a certain point the process merely introduces more impurity. It was therefore decided to purify the material by fractional sublimation in a vacuum, after it had been recrystallised a few times from aqueous alcohol. The sublimation apparatus (Fig. 3) was so designed as to minimise the possibility of contamination of the crystals by dust or other atmospheric impurities.

Dry oxygen filtered through cotton-wool was passed through the sintered-glass diaphragms *D*, *D'*, which removed the last traces of dust, and then through the sublimation tube *E*, which had previously been cleaned with benzene, followed by chromic–nitric acid mixture, washed, and steamed. *E* was thoroughly baked in the oxygen stream by heating every part to dull redness with a Bunsen flame. The side tube *F*, through which the oxygen escaped, was covered with a loosely fitting glass cap during this operation, in place of the funnel shown in the figure. The sublimation tube was then allowed to cool in the stream of oxygen, after which *o*-nitroaniline (recrystallised five times from aqueous alcohol and dried in the manner previously described) was introduced by means of the funnel *G*; *G* was removed, and *F* sealed off a few inches from the top, the oxygen stream being stopped when *F* was nearly sealed. The air thermostat *J* was then moved so as to envelop *E* up to about the dotted line in the figure, and *E* was evacuated by means of a Töpler pump connected to *K*; *J* was a thick wooden box with a glass window, and was heated by four 220-volt gas-filled lamps, two at each end, which were covered with asbestos paper to stop direct radiation. An ordinary mercury regulator and a standard type of relay were used, and two thermometers situated at different places in the box showed agreement to 0·1° and a constancy to less than 1°. The thermostat was mounted on flanged wheels running on rails and so could easily be moved to enclose any length of the sublimation tube *E*. The left-hand end (in the figure) of the thermostat had an opening sufficiently large to allow the side tube *F* and the bulb of the sublimation tube *E* to pass through. Once these parts were inside, the opening was covered with two pieces of thick cardboard meeting at a vertical junction and cut so as to fit the main part of *E* closely. The cardboard was fixed to the thermostat by means of thumb-screws.

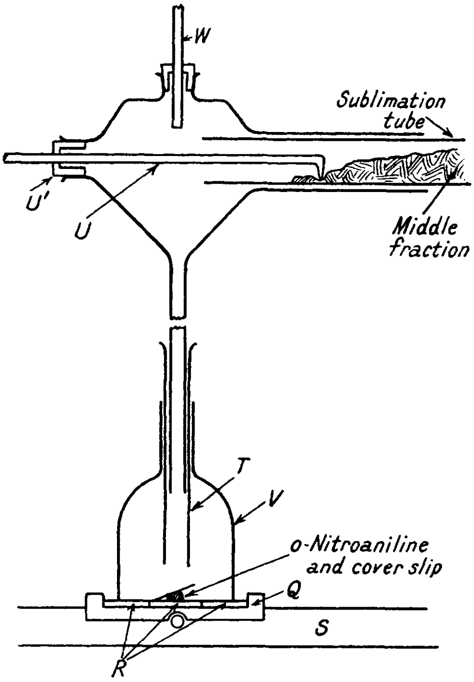
The thermostat was set at 60°, *i.e.*, some 10° below the m. p. of *o*-nitroaniline. After a small " head " fraction had sublimed to the left-hand end of *E*, the thermostat was moved to the right and the major part of the material was allowed to sublime to the middle portion of the tube, the thermostat being moved farther to the right from time to time so as to cause the sublimate to deposit over a large area. This last procedure was necessary to prevent the tube becoming blocked, and to facilitate the subsequent removal of the material. Finally, the thermostat was moved still farther to the right so as to enclose only the bulb and side tube of *E*, and the remainder of the nitroaniline was allowed to sublime completely to form a " tail " fraction. The whole process was very slow, several days being required for its completion, but this probably assisted in affording a pure product.

On completion of the sublimation process, the thermostat was moved to the position shown in the figure, and *E* allowed to cool completely. Dry dust-free oxygen was admitted slowly from the gas train, and the tube was then sealed off at *N* and placed in the clamps *M*, *M'* on the top of the thermostat, pointing in the same direction as before, and not as shown in the figure, which as regards this part refers to later experiments. Another sublimation tube which had been cleaned, washed, and steamed, was now placed in the clamp *L*, attached to the gas train, and baked as previously described. By means of a glass knife, a deep scratch was made on the first tube at the clear space between the head and the middle fraction. Glass dust was removed from the scratch with a camel-hair brush, and the portion of the tube containing the head fraction was broken off by the usual method of applying a piece of hot glass to the scratch. The funnel *G* was placed in the side tube of the second sublimation tube, and the now open end of the first tube was arranged so as to be immediately above *G*. By means of a nickel scraper, portions of the middle fraction were transferred directly to microscope slides, which were at once " prepared," *i.e.*, the material on each slide was melted and covered with a cover slip, and the prepared slides were then placed in a desiccator. The remainder of the middle fraction, except a small sample, which was retained for making further slides if necessary, was scraped into the second sublimation tube, large lumps being broken up and pushed down the funnel with a glass rod. This tube was sealed and evacuated, and the nitroaniline sublimed into a small head, a middle, and a small tail fraction exactly as in the previous case. The tube was then mounted on the top of the thermostat as shown in Fig. 3, and cut between the middle and the tail fraction (the space between the middle and head fractions, where the previous tube was cut, not being entirely free from crystals in this case). Some of the middle fraction was retained for slides, and the rest transferred to a third sublimation tube as before, and so on. The middle fractions from the first, second, etc., sublimation tubes are referred to in the sequel as the " once-sublimed," " twice-sublimed," etc., specimens respectively.

On examining the bulb of the first sublimation tube under the microscope when sublimation had finished, an appreciable amount of dust was seen, together with a few tiny globules of a yellow liquid, similar in appearance to that formed when *o*-nitroaniline is heated to charring in air and the vapours are condensed (see Part I, *loc. cit.*, p. 728). A similar residue was left when an old specimen, which had been recrystallised twelve times from aqueous alcohol and stored for a year over phosphoric oxide, was completely sublimed in a vacuum. These observations confirmed the suspicion that a high degree of purity could not be obtained by the recrystallisation method. After the second sublimation operation, however, no residue whatever could be detected, showing that the method had resulted in a definite advance in purity.

As will appear later, the once- and twice-sublimed specimens did not behave differently from the recrystallised specimen as regards the fall in velocity at constant temperature. Before abandoning the idea that the fall was due to the presence of impurity, however, a final effort was made to improve the conditions of purification of the material and preparation of the slides as follows. After the fourth sublimation tube had been baked, nitrogen instead of oxygen was passed through the gas train and used for the subsequent operations, *i.e.*, during the introduction of the substance, and for filling the tube after the sublimation. The substance was removed from the tube, and slides were prepared from it, entirely in an atmosphere of nitrogen. These modifications were devised to eliminate any possibility of oxidation of the substance, and to protect it further from contamination by dust. The details of the procedure after the sublimation was finished and the tube filled with nitrogen were as follows. The tap *O* (Fig. 3) was turned off, and the whole tube was disconnected from the gas train and fixed in the clamps *M*, *M'*, with *O* on the right. The nitrogen supply was reconnected to *O* by a rubber tube leading from the side arm *P*, and *O* was then reopened, the nitrogen being allowed to escape through a safety valve on the gas train. The sublimation tube was cut as previously described between the middle and the tail fraction, the stream of nitrogen thus released preventing the entry of air. The apparatus shown in Fig. 4 was then quickly fitted over the open end of the tube as indicated. The lower parts of this apparatus, *T*, *V*, *R*, and *Q*, though free to move independently, fitted each other closely, as did the upper part the sublimation tube, so that an atmosphere of nitrogen could be maintained inside provided that the stream of gas was fairly rapid.

Fig. 4.



After time had been allowed for all the air to be expelled, the brass frame *Q*, carrying the three slides *R* (shown in end-section) and the cover *V*, was raised some inches above the hot plate *S*, and clamped in that position. The tube *T* was allowed to rest on the middle slide. By means of the scraper *U*, working in a rubber cap *U'*, a few crystals were scraped out of the sublimation tube and fell down *T* on to the middle slide. (Large crystals tending to stick in transit could be pushed down by the rod *W*.) *T* was then fixed at a higher level, and a cover slip was placed over the crystals with the aid of forceps, the cover *V* being momentarily lifted for this purpose. After a few minutes to allow any air thus introduced to be expelled, *Q*, *R*, and *V* were lowered on to the hot plate. When the substance had melted, *Q*, etc., were raised again to allow the film to crystallise. Several slides were thus prepared, and their contents also remelted and allowed to crystallise in the apparatus prior to measurements being made. When not in use they were stored in dry nitrogen. When measurements were made with these slides, nitrogen instead of oxygen was used for maintaining a dry atmosphere inside the cell *E* of Apparatus I (Fig. 1).

General Procedure.—The glass slides and cover slips were cleaned and dried before use as described in Part I. In the experiments with the sublimed specimens, they were also baked in a stream of dry oxygen at 300° and then allowed to cool in the stream. This was done just before they were to be used for preparing the films, with the object of removing traces of organic dust.

The maximum temperature of the hot plate used for preparing and remelting the films was about 90°, and the slides were removed from the plate as soon as melting was complete. This ensured that no decomposition of the nitroaniline occurred, as shown by the fact that no drift in the linear velocity of stabilisation accompanied successive remeltings of the same film. (As previously mentioned, the substance chars somewhat when heated in air, but this does not seem to occur below about 150°.) Films about to be measured were allowed to crystallise in a small air-oven set at 30—35° (radiation to this temperature gave the most suitable interface), and were then immediately placed in the projection apparatus. When using Apparatus I at 20° and 30°, 15 minutes were allowed for the slide to reach the temperature of the thermostat before the "zero" position of the interface was marked on the screen. This time was based on observations of the thermometer *C* (Fig. 1, *b* and *c*) and on experience with the m. p. apparatus described in Part I (*loc. cit.*, p. 730). At 0°, however, about 40 minutes were necessary to bring the slide to this temperature, because, owing to the danger of the formation of dew on the slide, it was not possible to add the ice to the thermostat until the cell *E* (Fig. 1) had been closed and swept out with dry gas. When using Apparatus II (measurements at 40°), since the film was very close to both water cells, 5 minutes were considered ample for the slide to acquire the cell temperature.

The position of the interface on the screen was marked at the end of 8 hours at 0°, every hour (in some cases, every half hour) at 20° and 30°, and every 5 minutes at 40°. Only the one reading was made at 0° because the displacement of the interface at times under 8 hours was too small to be accurately measured, and it was not convenient to keep the thermostat at 0° for a longer period than this. 3—4 Minutes were needed to mark the position of the interface on the screen of Apparatus I, and about 45 seconds on that of Apparatus II, the length of interface in the latter case being much smaller. These times were appreciable fractions of the time intervals between readings, but the resulting error was reduced by always beginning to work at the same place and following round in the same way at as nearly as possible the same speed. A sharp pencil was used for Apparatus I (cartridge-paper screen) and a mapping pen for Apparatus II (tracing-paper screen). In both cases the projection lamp was only switched on when marking was in progress. The distances between the lines were measured directly with a 0·5-mm. scale etched on a glass slip. The measurements were made every 0·5 cm. along the lines, and the averages calculated with the aid of an adding machine.

Density Determinations (with W. O. M. Williams).—The value for the density of β-*o*-nitroaniline (used later) was obtained with a modified form of Garner and Ryder's volumenometer (J., 1925, **125**, 726). The modification consisted in substituting for the single manometer partly inside and partly outside the thermostat, a mercury U-gauge inside the thermostat attached through an air column to the manometer proper outside the thermostat. This avoided the somewhat uncertain correction for temperature differences in the same column of mercury, and enabled the apparatus to be readily removed from the thermostat. (In the present work, however, the temperature correction was negligible in comparison with the errors of the determinations.) Provided that the air column was screened from draughts and sunlight, no difficulty was experienced in keeping the mercury meniscuses steady while the cathetometer readings were being taken.

Jaeger (*Z. Krist.*, 1905, **40**, 114) gave the density of *o*-nitroaniline (presumably the γ-form) as 1·442 at 15°, but did not state his method. Working with a finely powdered recrystallised sample, we obtained the values 1·449, 1·445, 1·444 (mean 1·446) for this form at 20°, and since these variations almost corresponded to the calculated error of the determination (about 1 in 300) the apparatus was considered to be in order.

The density of the β-form could not be determined very accurately owing to its slow transformation into the γ-form. After some preliminary experiments which indicated a value near 1·3, two determinations were carried out as follows. Molten *o*-nitroaniline was chilled, thereby producing a mixture of the α- and the β-form. This was at once powdered, transferred to the volumenometer, and pumped out for 20 hours, this period having been found to be necessary to remove all air from the powdered γ-form in the previous determinations. (Previous observations on slides had shown that all the α- would be converted into the β-form within this period, and that very little of the latter would be changed into the γ-form.) The final readings were then taken. The results were 1·272, 1·283 (20°), and the rough mean, 1·28, suffices for the present purpose.

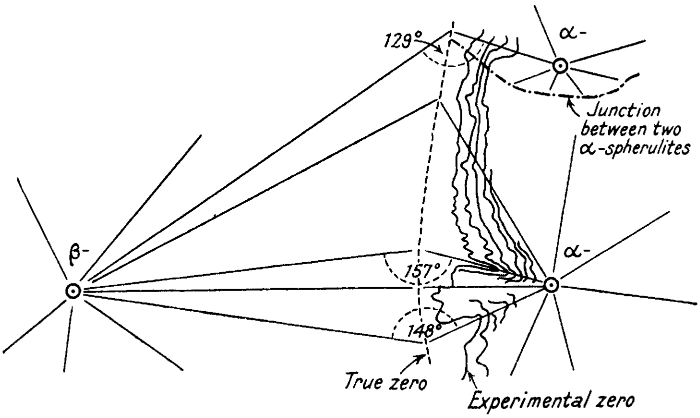
Owing to the extremely labile nature of the α-form, no absolute determination of its density was possible, but a qualitative comparison of the densities of the α- and the β-form was made by means of a dilatometer using mercury as the recording fluid. The bulb of the apparatus, in which the substance was confined above the mercury, consisted of a wide horizontal tube, and this was sealed at one end to a U-tube, the open limb of which was a capillary. The nitroaniline was melted and chilled under the tap. Since it occupied the long flat space at the top of the bulb, it responded quickly to changes of temperature, and from previous observations on the rapid cooling of thin films of the substance it was known that the chilling would produce a mixture of the α- and the β-form containing a considerable proportion of the former. The apparatus was immediately placed in a thermostat at 20°, and after it had acquired this temperature, the mercury meniscus was observed for a few hours. A marked contraction showed that the α-form is the less dense.

Results.

Fig. 5 is a reproduction of a part of the screen at the end of a typical experiment. Despite the irregularity of the interface movement, the fall in the average velocity with the time is evident.

The results are collected in Table I. Cols. 2 and 3 give the times and linear movements (× 21·7—the magnification of Apparatus I) measured from the "experimental zero," *i.e.*, from the line drawn on the screen when the slide had taken the thermostat temperature (Fig. 5). The figures in parentheses in col. 3 give the number of linear measurements on which each result is based. It will be noted that this number decreases rapidly with the time, corresponding to the decrease in the length of interface available for measurement due to the development of small β-patches mentioned previously. We endeavoured to make at least 400 measurements at the beginning of the reaction with each specimen at each temperature (this number was arbitrarily chosen as the minimum likely to give a good average), but the development of β-patches was excessive in the sublimed specimens, and in certain cases so much so that this number could not have been attained without an unreasonable expenditure of time, and the attempt was abandoned.

FIG. 5.



Twice-sublimed specimen at 40°. *Interface traced at* 5 *minute intervals. Centres of spherulites marked by ringed dots.*

On plotting the movement against the time, smooth curves were obtained from which very few of the points deviated. The deviations were both positive and negative and did not exceed 0·4 on the movement axis. Where they occurred, values interpolated from the curves have been substituted for the experimental values and are marked with an asterisk in col. 3.

The experimental zero differed considerably from the true zero, *i.e.*, the original position of the interface, because considerable movement occurred while the slide was cooling and while it was acquiring the temperature of the thermostat. The true zero position could be clearly seen on the screen, since the beginning of the stabilisation process is always marked by a sharp change in the texture of the β-crystals. A recent study of the results has made evident the importance of measuring the interface movement from the true zero, but at the time the measurements were made, this was not realised, and the records of the position of the true zero are incomplete. However, except at 0°, this position was marked on the screen in most cases (see, *e.g.*, Fig. 5), and it has been possible to arrive at a fairly close estimate of the linear distance between this and the experimental zero. By extrapolating the movement–time curves back to the true zero, the times which it would have taken the interface to move from the true to the experimental zero, *if this movement had occurred wholly at the temperature of the thermostat*, have been obtained. The times and movements thus computed as from the true zero are given in cols. 4 and 6 of Table I, and are plotted in Fig. 6.

All the curves show a marked fall in the velocity with the time. There are considerable variations between different specimens at the same temperature, but there is no overlapping between the results for different temperatures. Also, no relation can be traced between the velocity and the degree of purity of the specimens. There is fairly close agreement between the recrystallised and the twice-sublimed specimens at all temperatures, but the once- and four-

TABLE I.

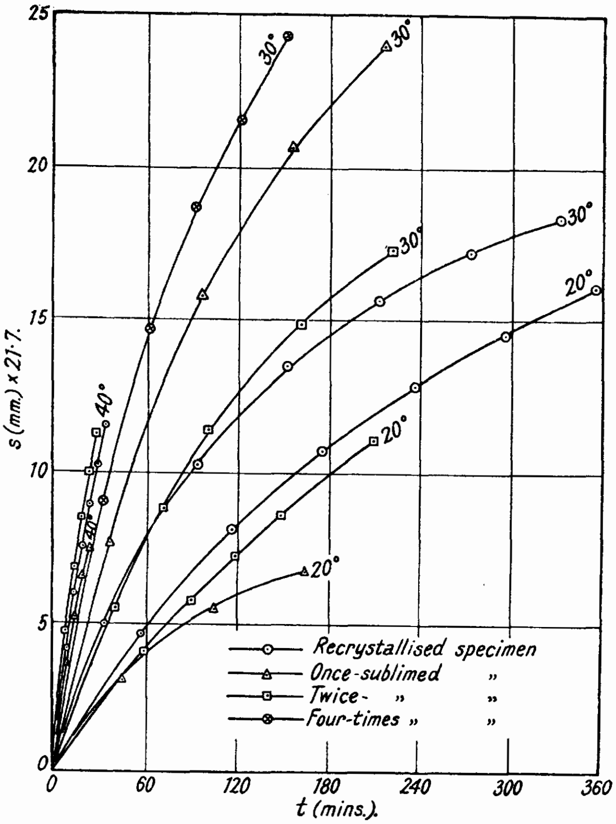
Temp.	Time from exptl. zero (mins.).	Linear movement (mm.) × 21·7 measured from exptl. zero.	Time from true zero (mins.).	*t*, calc.†	Linear movement (mm.) × 21·7 measured from true zero.
Recrystallised specimen.					
0°	480	1·25 (425)			
20	0	0	56	59	4·6
	60	3·41 (1938)	116	—	8·01
	120	6·07 (1813)	176	—	10·67
	180	8·14 (1540)	236	234	12·74
	240	9·87 (1047)	296	294	14·47
	300	11·43 (415)	356	355	16·03
30	0	0	33	33	4·9
	60	5·26 (2381)	93	—	10·16
	120	8·51 (1855)	153	—	13·41
	180	10·70* (1469)	213	210	15·60
	240	12·28* (930)	273	257	17·18
	300	13·45* (86)	333	298	18·35
40	0	0	8·5	8·7	4·1
	5	1·81 (482)	13·5	—	5·91
	10	3·84 (391)	18·5	—	7·44
	15	4·77 (318)	23·5	24	8·87
	20	6·10* (166)	28·5	30	10·20
	25	7·38* (103)	33·5	38	11·48
Once-sublimed specimen.					
0	480	1·63 (682)			
20	0	0	44	39	3·1
	60	2·31 (886)	104	—	5·41
	120	3·56 (240)	164	—	6·66
30	0	0	36	34	7·6
	60	8·18 (298)	96	—	15·78
	120	13·08 (125)	156	—	20·68
	180	16·38 (63)	216	220	23·98
40	0	0	9	9	3·6
	5	1·58 (263)	14	—	5·18
	10	2·90* (116)	19	—	6·50
	15	3·82 (71)	24	23	7·42
Twice-sublimed specimen.					
0	480	2·35 (192)			
20	0	0	59	60	4·1
	30	1·66 (1006)	89	—	5·76
	60	3·08 (604)	119	—	7·18
	90	4·43 (152)	149	153	8·53
	150	6·99 (118)	209	233	11·09
30	0	0	41	41	5·5
	30	3·24 (755)	71	—	8·74
	60	5·85 (365)	101	—	11·35
	120	9·37 (121)	161	154	14·87
	180	11·78 (51)	221	198	17·28
40	0	0	8	8·1	4·7
	5	2·07 (422)	13	—	6·77
	10	3·77* (251)	18	—	8·47
	15	5·28* (94)	23	24	9·98
	20	6·57 (25)	28	29	11·27
Four-times sublimed specimen.					
30	0	0	32	32	9·0
	30	5·58 (217)	62	—	14·58
	60	9·66 (113)	92	—	18·66
	90	12·50* (18)	122	119	21·50
	120	15·36 (9)	152	151	24·30

† See equation (i), p. 1870.

times-sublimed specimens differ from them considerably, having higher velocities at 30°, and the former having lower velocities at 20° and 40°. Some of the curves suggest that the velocity is approaching a constant value, but on two slides (once- and twice-sublimed specimens respectively), which were exceptionally free from β-patches in one part, it was possible to follow the reaction for about 45 hours, and in each case the velocity was still falling at the end of this period.

Effect of Film Thickness.—The normal thickness of the films studied was 0·01—0·02 mm.* After repeated remeltings, however, the films often became much thinner in parts, owing to loss of the substance by evaporation and to the slides and cover slips not being absolutely plane. These very thin parts, which could always be recognised by their giving interference colours when viewed obliquely, and by the order of their polarisation colours between crossed Nicols, were characterised by abnormally high linear velocities, often 2—3 times that in the rest of the film. Measurements made in these parts were ignored in calculating the average movements given in Table I (except possibly in a few early slides studied before the effect had been detected), because the higher velocity was thought to be a phenomenon allied to the abnormally low m. p.'s possessed by very thin films.

FIG. 6.



In order to test whether the unevenness of the slides and cover slips contributed to the irregularity of the interface movement in films of normal thickness, some films were prepared between optically true cover slips. No improvement on the ordinary slides was observed.

Effect of Crystal Orientation.—As indicated in Parts I and II, the needles comprising the β-spherulites have the *b* axis as their axis of elongation, but for the α-needles this axis is *c*. The relative orientation of the α- and β-needles meeting at the interface appeared to have a marked effect on the linear velocity at the beginning of the reaction. Thus, when the two kinds of needles were in line, the movement was generally small; when they were at an angle of 120—160° to one another (this angle could only be roughly measured) the velocity was high, and fell again as the angle approached 90°. These effects are clearly shown in Fig. 5. With regard to the

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* We take this opportunity of correcting some values of film thicknesses given in Part I, p. 731. The figures should have been 0·02 to 0·025 mm.

high value at 120—160°, it is perhaps significant that when the angle between a β- and an α-needle showing the maximum extinction angle (a very common orientation on the slides) is 154°, the *ac* plane of the former is parallel to a prominent cleavage plane of the latter.

On one occasion an α- and a β-needle were found lying side by side with good contact. Both crystals were fairly large, and the β- was better developed than usual. No linear movement of the β- into the α-crystal could be detected, although stabilisation began later from a number of nuclei on the α-crystal. This particular relative orientation appears, therefore, to be associated with a very low linear velocity, although it is not impossible that the large size of both crystals and the good development of the β-crystal may have been connected with the effect, for small, imperfectly developed crystals have more surface energy, which might lead to a more rapid transference of molecules from one lattice to the other.

DISCUSSION.

The Fall of Velocity at Constant Temperature.—The experiments with progressively purified specimens showed that the main cause of the fall in the linear velocity at constant temperature was not the presence of traces of impurity, although these may have had a minor effect. This is made particularly clear by the values of the quotient (s in second hour)/(s in first hour) at 30°—where s is the linear distance moved by the interface from the true zero. These are: recrystallised, 0·53; once sublimed, 0·57; twice sublimed, 0·62; four times sublimed, 0·51.

Instead, it is suggested that the fall is due to the fact that the α- is less dense than the β-form, so that, as the reaction proceeds, an ever-widening gap develops at the interface, rendering the transfer of molecules from one lattice to the other increasingly difficult. If this is the case, we may suppose that the time required to form a layer of molecules on the β-lattice is the sum of (*a*) a constant term, K_2, and (*b*) a term depending on the width of the gap, w, at that stage. Now, from the way in which the interface is established, it may be assumed that the two forms are in contact * at the beginning of the reaction, so that w is directly proportional to s, and term (*b*) is a function of s. It has been found empirically that if the term (*b*) is taken as Ks^2, where K is a constant, the resulting equation connecting the time, t, and s is mainly in harmony with the experimental results. Regarding the formation of a single layer of molecules as an infinitesimal step in the transformation process, we have then

$$dt/ds = Ks^2 + K_2.$$

Integrating ($t = 0$ when $s = 0$), we obtain

$$t = Ks^3/3 + K_2s,$$

or, replacing $K/3$ by K_1,

$$t = K_1s^3 + K_2s \quad \text{(i)}$$

The values of t calculated by means of equation (i) are given in col. 5 of Table I, and may be compared with the experimental values in the preceding column. [K_1 and K_2 were calculated in each case by inserting the second and the third experimental values of t and s (selected as being the most reliable) in equation (i). Consequently, no calculated values of t appear opposite these figures in the table.] It will be seen that satisfactory agreement with the equation is given at low values of t in practically every case. At higher values of t, good agreement is given by the recrystallised specimen at 20°, the once-sublimed specimen at 30° and 40°, the twice-sublimed specimen at 40°, and the four-times-sublimed specimen; whilst the recrystallised and twice-sublimed specimens at 30° show positive deviations, and the recrystallised specimen at 40° and the twice-sublimed specimen at 20° negative deviations. The once-sublimed specimen at 20° did not yield values beyond the third. Table II gives the values of K_1 and K_2.

* By this is not meant that the two forms are in perfect contact—there is almost certainly a layer of permanent gas molecules between them—but they may be thought of as being so close that a molecule which leaves one lattice condenses on the other immediately.

TABLE II.

Constants in the equation $t = K_1s^3 + K_2s$.

[t in mins., s (× 21·7) in mm.]

Specimen.	K_1. 20°.	K_1. 30°.	K_1. 40°.	K_2. 20°.	K_2. 30°.	K_2. 40°.
Recrystallised	0·040	0·030	0·0099	11·9	6·08	1·95
Once sublimed	0·36	0·0082	0·014	8·7	4·03	2·33
Twice sublimed	0·061	0·0151	0·0080	13·5	6·97	1·55
Four times sublimed	—	0·00505	—	—	3·18	—

The Critical Increment of the Reaction.—By drawing tangents to the curves in Fig. **6** at the origin, the velocities at the true zero ($s = 0$) have been obtained and are given in Table III. The corresponding critical increments obtained from graphs of log velocity against $1/T$ (Fig. 7) are given in the last column. The velocities have also been calculated by means of the differential form of equation (i), both at $s = 0$ and s (× 21·7) = 20 mm., and they yield almost the same critical increments as those given in Table III. From these

FIG. 7.

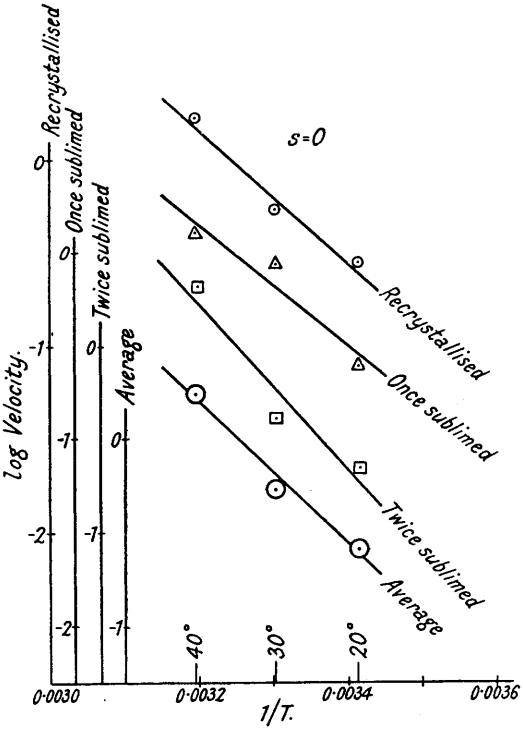

TABLE III.

Specimen.	Velocities at $s = 0$ (in mm./hour). 20°.	30°.	40°.	Critical increment, cals.	
Recrystallised	0·28	0·53	1·67	16,600	Mean 17,300
Once sublimed	0·25	0·85	1·30	14,900	
Twice sublimed	0·22	0·42	2·08	20,300	
Average	0·26	0·54	1·74	17,700	

[The four-times-sublimed specimen is omitted since it was only studied at 30°. In calculating the average velocities (last line), the number of measurements on which each individual result is based has been taken into account.]

figures it may be concluded that the critical increment of the reaction between 20° and 40° probably lies between 17,000 and 18,000 cals./mol., and is certainly of this order. Now, from determinations of the vapour pressures of liquid *o*-nitroaniline (Berliner and May, *J. Amer. Chem. Soc.*, 1925, **47**, 2350; Williams, unpublished) and of the latent heat of fusion (Andrews, Lynn, and Johnston, *ibid.*, 1926, **48**, 1274), it may be calculated that the internal latent heat of sublimation of the β-form is about 19,000 cals./mol. (The specimen used by the last workers melted at 69·3° and was therefore almost certainly mainly β-.) The close correspondence between this value and the critical increment is of considerable interest and the following explanation is suggested.

Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2221) gave the following equation for the effect of temperature on the rate of evaporation (v) of a solid into a vacuum,

$$v = A\sqrt{T} \, . \, e^{-\lambda/RT}$$

where A is a constant and λ is the internal latent heat of sublimation. Since the variation of $\sqrt{T}$ is very small in comparison with that of $e^{-\lambda/RT}$, we may write without serious error

$$v = Be^{-\lambda/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

where B is a constant. Thus λ is the critical increment of the evaporation process. Strictly, this equation relates to the evaporation of atoms from a simple atomic lattice, but, as Langmuir pointed out, the evaporation of molecules from the molecular lattice of an organic compound must be a similar process, and we may consider that the equation is at least substantially applicable to this case also, if v is taken as the average velocity of evaporation from the different crystal faces.

Consider the reaction at $s = 0$. If, as we have supposed, the two forms are then in contact at the interface, molecules which break away from one lattice will immediately condense upon the other, and the reaction may be likened to an exchange of shots at point-blank range. We may assume that the energy of activation of the breaking away process is equal to the internal latent heat of sublimation, and if the molecules acquire it at the same rate as if the solid surface were in contact with free vapour, then the rate of the reaction will be determined by $v_\alpha - v_\beta$, where these are the rates of evaporation into a vacuum of the α- and the β-form respectively. From equation (ii) we have

$$v_\alpha - v_\beta = B_\alpha e^{-\lambda_\alpha/RT} - B_\beta e^{-\lambda_\beta/RT},$$

and if λ_α and λ_β differ very little, as is likely since the heats of polymorphic transitions are usually small, we may write as a first approximation

$$v_\alpha - v_\beta = (B_\alpha - B_\beta)e^{-\lambda_\beta/RT},$$

and thus the critical increment of the reaction will be of the same order as λ_β. This conclusion would not be affected if, owing to the proximity of the lattices to one another, molecules acquired the latent heat of sublimation at rates different from v_α and v_β, for this would only alter the values of B_α and B_β. However, the following calculation shows that v_α may be quite large enough to account for the observed linear velocity.

By extrapolation of the vapour-pressure results mentioned above, it may be found that the vapour pressure of supercooled liquid *o*-nitroaniline at 30° is 0·0073 mm. That of the α-form must be less than this, but not necessarily very much so. The rate of evaporation corresponding to this pressure, calculated from the equation $v = p\sqrt{M/2\pi RT}$ (Langmuir, *loc. cit.*), is $12{\cdot}47 \times 10^{17}$ molecules/cm.^{2}/sec. The density of the β-form is 1·28 (see p. 1866), and from this the average spacing between layers of molecules in the crystal is $5{\cdot}62 \times 10^{-8}$ cm., and the average number of molecules in a layer 1 cm. square is $3{\cdot}17 \times 10^{14}$. Thus the number of layers of the β-form which would be completed in one second if the α-form had the above rate of evaporation and there were no passage of molecules from β- to α- would be $12{\cdot}47 \times 10^{17}/3{\cdot}17 \times 10^{14} = 3{\cdot}93 \times 10^3$. This corresponds to a linear rate of $3{\cdot}93 \times 10^3 \times 5{\cdot}62 \times 10^{-8}$ cm./sec. $= 2{\cdot}21 \times 10^{-3}$ mm./sec., or 7·95 mm./hour. The observed rate (Table III, last line) is 0·54 mm./hour.

The idea that the linear rate is governed by the difference between the rates of evaporation of the two forms is in harmony with the reversal in the sign of the temperature coefficient of the linear rate shown by enantiotropic substances below the transition point. In these cases the rate first increases with rise of temperature and then decreases as the transition point is approached. Now, if log v be plotted against $1/T$ for the two forms, two lines of, in general, slightly different slopes, corresponding to the small difference between $\lambda_{\text{unstable}}$ and λ_{stable} are obtained, and these lines intersect at the transition point. As this point is approached from below, $\log v_{\text{unstable}} - \log v_{\text{stable}}$ must, of course, decrease continuously, but $v_{\text{unstable}} - v_{\text{stable}}$ first increases and then decreases. At some distance from the transition point, the plot of $\log (v_{\text{unstable}} - v_{\text{stable}})$ against $1/T$ gives approximately the same slope as the log v, $1/T$ lines, and this will also happen in the case of a monotropic substance (transition point above the m. p.), which, in the absence of evidence of a transition point, we assume *o*-nitroaniline to be.

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