310. *Studies in Polymorphism. Part IV. The Linear Velocity of Polymorphic Transformation of Mercuric Iodide.*

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The paper describes the results of direct measurements of the linear rate of movement of the interface between red and yellow mercuric iodide in thin polycrystalline films. From 0° to 40° (yellow ⟶ red), where the transformation is directed towards the denser form, the interface starts preferentially at the edges of the film and the rate shows a decline with time at constant temperature, given very nearly by the equation $t = k_1 s^2 + k_2 s$, where s is the linear distance moved by the interface in time t, and k_1 and k_2 are constants. The apparent energy of activation between 0° and 30° is of the order of 10,000—11,000 cals., which is very much less than the internal latent heats of sublimation of the two forms, which are of the orders 22,000 (red) and 19,000 (yellow) cals. The rate when $s = 0$ is about 1000 times greater than that calculated on the assumption that it is governed by the difference between the rates of evaporation of the two forms into a vacuum.

At 130° (red → yellow) the reaction occurs mainly by the growth of nuclei of the yellow form in the interior of the film. In unannealed films, the linear rate shows a strong decline, owing presumably to the presence of cracks and possibly also to the loss of material from these cracks by evaporation. In annealed films, sealed to prevent evaporation, the rate is roughly constant in the early stages, but when the process is followed for a sufficient distance, the s–t curve is sigmoid in shape. The rate varies considerably from film to film.

Damiens (*Compt. rend.*, 1923, **177**, 816) studied qualitatively the dependence of the mass rate of transformation of yellow into red mercuric iodide on the previous thermal history of the specimen, and also (*ibid.*, 1924, **178**, 326) the rate of nucleation of large pseudomorphs of the yellow form. Kohlschütter (*Kolloid-Beih.*, 1927, **24**, 319) made qualitative observations on the rate of transformation of single crystals of the red, yellow, and orange forms, and Benton and Cool (*J. Physical Chem.*, 1931, **35**, 1762) measured the mass rates of interconversion of the red and the yellow form dilatometrically. Coppock (*Nature*, 1934, **133**, 570) measured the mean linear rate of advance of the interface between the red and the yellow form in single crystals at 20°.

The present paper describes direct measurements of the linear rate of advance of the interface between the red and the yellow form in thin polycrystalline films. The measurements were made over the range 0—40° (yellow ⟶ red) and at 130° (red ⟶ yellow). The method of measurement was similar in principle to that used in the case of *o*-nitroaniline (Part III, J., 1935, 1860) but certain improvements in technique were made.

Experimental.

Purification of Materials.—Finely divided mercuric iodide, precipitated by adding potassium iodide solution to mercuric chloride solution, and dried over calcium chloride for several days, was fractionally sublimed 6—9 times in a vacuum as follows.

The pump and dry gas train were the same as those used in Part III (*loc. cit.*, Fig. 3), and the sublimation tube was of the same type, but was longer and narrower (5—6 ft. × $\frac{1}{2}$ in., narrowing to $\frac{1}{4}$ in. for 1 ft. at the end attached to the pump) and was made of soda glass, since mercuric iodide attacks Pyrex glass at higher temperatures (Miller, *J. Physical Chem.*, 1931, **35**, 2955). A water-cooled trap was interposed between the sublimation tube and the pump. The tube was cleaned and baked, and the substance introduced through the side tube, all as described in Part III. After the side tube had been sealed off and the apparatus evacuated, about nine-tenths of the substance was sublimed a short distance up the tube by means of a small electric oven working at about 170°. The place at which it was desired to form the sublimate was kept cool by a cloth continuously moistened by water dripping from a funnel. After the apparatus had cooled, dry air was admitted and the tube sealed off between the sublimate and " tail " fraction. The sublimate was then fractionated into main and " tail " portions as before, and so on ; after about the third sublimation, the " tail " fraction left no residue when completely sublimed.

After the last fraction had been deposited (in the last few inches of the wider part of the sublimation tube) and sealed off from its " tail," the tube was evacuated and sealed off at a point on the narrow part, several inches from where this joined the wider part. It was then placed in a vertical electric furnace, and the specimen melted so as to run down and occupy the narrow part of the tube. After cooling, the tube was opened in dry air by breaking it off at a file mark inside a rubber tube attached to a drying train. The part containing the specimen was crushed by means of pliers tipped with platinum foil, and the compact lumps of solid picked out with forceps. These lumps were used for preparing the films (see below). The m. p. of all specimens obtained as above was 255·5° : it is not easy to determine, since the substance appears to soften and becomes orange before yielding the dark red liquid. The point taken in this case was that at which all the iodide appeared to have become dark red, this change occurring fairly suddenly. The m. p.'s given in the literature vary from 250° to 259°, but most of the later values are near to 255°.

Preparation of the Films.—The films were prepared by melting the substance between 3″ × 1″ slides and 5/8″ or 7/8″ cover-slips, previously cleaned as described in earlier parts of this series. Powdered material gave films full of bubbles, but this was avoided by using lumps of material prepared by melting in a vacuum as described above.

The yellow form crystallised from the melt on the slides largely as plates parallel to (001), and the transformation of these below the transition point (127°) took the form of a sudden appearance of red bands parallel to {110}, as described by Kohlschütter (*loc. cit.*). These bands form a trellis-like structure over the film, and the growth of such a complicated interface could not readily be followed. It was found, however, that if, after transformation into the red form was complete, the slide was reheated to about 200°, a granular film of the yellow form was obtained, and on cooling this by placing the slide on a water-cooled iron plate, and turning it over and over until quite cold to the touch, the transformation began at the edges and proceeded inwards with a comparatively regular interface. The work below the transition point was mainly concerned with interfaces established in this way. In addition to this " edge growth," some isolated nuclei of the red form appear in the interior of the film, but not in sufficient numbers to hamper the study of edge growth, provided the film is not thicker than 0·01 mm.

In work above the transition point, which, as will appear later, involved prolonged annealing of the films, evaporation of the substance was prevented by placing a 1″ square cover-slip over the smaller one confining the film, and sealing it round the edges to the slide with a phenol–formaldehyde cement kindly supplied by the British Scientific Instruments Research Association. This cement sets on baking for 3 hours at 140°.

The thickness of the films was measured in arbitrary units by comparing the average depth of colour in transmitted light, when entirely in the red form, with a standard solution of methyl-orange in a colorimeter. Extremely thin films showed an abnormally low rate, and thus behaved oppositely to similar films of *o*-nitroaniline (Part III, *loc. cit.*). Care was taken to select films that were outside this range of abnormal behaviour. The order of thickness of those used was 0·01 mm.

The rate was much faster than in the case of *o*-nitroaniline at the same temperature (about 400 times at 20°), and this necessitated recording the positions of the interface photographically, and arranging that the slides acquired the temperature of the thermostat rapidly, so that the first photograph could be taken with as little delay as possible.

Apparatus.—Apparatus I (Part III, *loc. cit.*), modified as follows, was used.

The projection lens and screen were replaced by a bellows camera fitted with a wooden extension, which enabled photographs of the films magnified by about 3 diameters to be taken on quarter plates. A new slide holder was made, which did not have to be removed from the cell in the thermostat for the purpose of inserting a slide. It consisted essentially of a flat metal tube fixed vertically to the under side of the cover of the cell, and having openings in the broader walls, which were at right angles to the optical axis of the apparatus, to permit the passage of the light beam. The slide, with the cover-slip towards the camera, was dropped down this tube through a slot in the cover, and came to rest in the path of the light. The slot was then closed with a screw-down lid. The slide was next pressed lightly against the wall facing the camera by two horizontal leaf springs operated by turning a vertical rod to which they were attached. The camera had previously been focused on the plane now occupied by the film. The rod was clamped in position by means of a locking collar. This modification of the apparatus reduced the time needed for the slide to acquire the temperature of the thermostat to a minimum, since it was brought at once into contact with the somewhat massive metal holder which was already at the thermostat temperature. This time was determined by separate experiments at each temperature in which one junction of a thermocouple was pressed against the centre of a slide by the rod and spring device mentioned above, and the other hung free in the cell. Equilibrium was shown by the thermal *E.M.F.* becoming zero. The period was found to be about 2 mins., depending on the temperature of the thermostat, and in practice a slightly longer time than this was given. In order to keep the front window of the thermostat dry in work at 0°, the stream of dry nitrogen passing through the cell was first passed through a glass-fronted box affixed to this window, before entering the coil in the thermostat.

For work above the transition point, the thermostat cell and slide holder were replaced by a small electrically heated and controlled air-thermostat consisting of a brass box 5″ × 4″ × 1·4″, made of thick brass plates bolted to a brass casting forming the top, bottom, and sides. The front and back walls (formed by the plates) were each heated by an element of nichrome ribbon wound on and insulated by mica, and contained a zig-zag channel through which a preheated stream of dry gas could be led through the interior if necessary. The box was lagged with uralite, and there were circular double glass windows for the passage of the light in the back and front. The slide was introduced through a slot in the top, covered by a brass lid, and slid down guides to its proper position. It was then brought to the position of focus by means of a rod and spring device similar to that described above. An Anschütz thermometer and a small mercury thermoregulator were placed one on each side on the slide. The temperature at the place occupied by the film was compared with that recorded by the thermometer by means of a thermocouple in a separate experiment, and the necessary correction applied to the reading of the thermometer. At 130° this correction amounted to − 4°.

The growth studied above the transition point was that of nuclei of the yellow form, which appeared in the interior of the film. In order to detect the formation of these nuclei at the earliest possible moment, the film was kept under observation by a low-power microscope, placed at right angles to the optical axis of the main projection apparatus, light being reflected into the microscope by a mirror placed between the camera and the thermostat. This mirror could be quickly swung out of the way when it was required to photograph the film. (To avoid raising the temperature of the film, the projection lamp was only switched on at full power for the short time needed to take a photograph. For the same reason, when the formation of nuclei was being watched for with the microscope as just described, only sufficient current was passed through the lamp to make the film clearly visible, and even in this case, it was not kept on for more than a few seconds at a time.)

Method of Measurement.—(i) *Below the transition point.* The sharp difference in colour between the two forms made it possible to record the successive positions of the interface on the same plate, by giving an exposure of about t/n sec., where t is the " correct " exposure in the photographer's sense, and n is the number of positions recorded (4—7). The positions appeared on the negative as boundaries between bands of different shades of grey. A positive transparency was then made, as this was found to increase the contrast, and this was magnified by being projected on to a paper screen by an optical lantern. The positions of the interface and the edge of the film were then traced on the screen with a pen, the different positions being distinguished by different coloured inks. The total magnification thus obtained was 23·5 diameters.

Those sections of the tracing which did not show marked irregularities or prominences on the interface, indicating possible interference by nuclei, were marked off by lines at right angles to the film edge, and the average linear distances between the successive positions of the interface

determined by finding the areas enclosed between these and the film edge by means of a planimeter, and dividing these areas by the length of the interface found by means of a rotameter. This method is much more satisfactory than that of making direct linear measurements, used in the case of o-nitroaniline, since it makes use of the whole length of the interface covered by the measurements, but it cannot be applied where the interface shows marked small-scale convolutions since the planimeter is not then trustworthy.

The average linear distance between the edge of the film and the first recorded position of the interface was different for different sections of the same film, and for different films studied at the same temperature, because the time elapsing between the starting of growth from the edge and the taking of the first photograph was not the same from case to case, owing to growth not starting at the same instant at all parts of the edge, and to differences in the thermal history of the films prior to their being placed in the thermostat. The results had therefore to be averaged in the following way. The distance (s)–time (t) curves for the different sections were plotted on the same axes, s being reckoned from the film edge. Equally spaced parallel lines were drawn at right angles to the s axis, thus dividing the diagram into a series of equal s intervals. The time taken for the interface to travel over a given s interval was then read off for each curve, and the average time calculated, each figure being "weighted" according to the length of interface to which it referred. From these results the average s–t curve was constructed, and this was extrapolated back to s = 0, thus enabling the times from the true zero of the reaction to be calculated.

(ii) *Above the transition point.* As stated above, the growth of yellow nuclei appearing in the interior of the film was measured, edge growth being practically absent. These nuclei did not appear until the film had been at the thermostat temperature for some time, so that the necessity for extrapolation to zero time did not arise. The interface was too irregular for the planimeter to be used with accuracy, and the method of direct linear measurement at points spaced 0·5 cm. apart was used.

RESULTS AND DISCUSSION.

Experiments below the Transition Point.—The results are given in Table I and are plotted in Fig. 1. It will be seen that smooth curves may be drawn through the points with only occasional minor deviations. The interface lengths on which the values of t are based were greatest in the middle part of each curve, because more measurements were available at medium values of s than at low and high values. In extrapolating the curves to s = 0, the data marked with an asterisk were ignored or duly weighted, wherever their inclusion in the curve would have involved an abrupt change of curvature. These low values being excluded, the lengths of interface covered the following ranges (all in cm. × 23·5) : 0°, 65—233; 10°, 25—52; 17·5°, 22—49; 25°, 37—49; 30°, 23—50; 35°, 30—57; 40°, 27—68.

TABLE I.

s = linear distance from true zero (film edge) × 23·5, in cm.; t = time from true zero, in mins.
Values based on an interface length of less than 20/23·5 cm. are marked with an asterisk, and are considered to be less trustworthy.

s.	t, at 0°.	10°.	17·5°.	25°.	30°.	35°.	s.	t, at 0°.	10°.	17·5°.	25°.	30°.	35°.
0	0	0	0	0	0	0	1·38	15·33	8·09	7·00	3·77	2·86	1·20
0·20	1·35	—	0·65*	—	—	—	1·57	18·78	9·65	8·49	4·54	3·65	1·49
0·39	2·87	—	1·45	0·74*	0·56*	—	1·77	22·78	11·38	10·08	5·39	4·38	1·83
0·59	4·66	2·60	2·50	1·21	0·84	—	1·97	27·06	13·36	11·66*	6·36	5·12	2·23
0·79	6·76	3·76	3·42	1·73	1·25	—	2·16	—	15·55	13·47*	7·25*	5·90	2·67
0·98	9·43	5·12	4·47	2·33	1·79	0·77*	2·36	—	17·60	—	—	—	3·12
1·18	12·23	6·69	5·68	3·00	2·38	0·97	2·56	—	—	—	—	—	3·54

At 40°.

s′ = linear distance × 23·5, in cm.; t′ = time, in mins., reckoned from an arbitrary zero 1·77/23·5 cm. from the film edge.

s′	0·30	0·59	0·79	0·90	1·10	1·39
t′	0·37	0·68	1·10	1·55	2·03	2·56

It will be noted that a much greater length of interface was studied at 0° than at other temperatures. One reason for this was that the work was begun at this temperature and considerable experience was necessary before the technique became familiar. Another was that two specimens of material were studied in order to see whether there was any difference in their behaviour. The ranges of interface lengths were : Specimen 1, 43—161 ; Specimen 2, 38—75 ; and the two *s–t* curves agreed throughout their whole length to within a few units %. This result showed that the method used to purify the material was satisfactory, and the different specimens obtained by this method were hereafter used indiscriminately. It also indicated that the length of interface studied in each case was sufficient to ensure a reasonably good value for the average linear velocity. The average interface lengths studied at other temperatures were somewhat lower than that of Specimen 2, but they were of the same order, and it may be assumed that in these instances also the average velocity was given approximately. In any case, in view of the comparatively large number of temperatures at which the reaction was studied, and the fact that at any temperature the observed velocity was just as likely to be too high as too low, it may be concluded that the results suffice for the approximate evaluation of the temperature coefficient. Further, since failure to study a sufficient length of interface merely means that the result is not truly representative of all possible crystallographic orientations, it should not interfere with the search for the form of the equation followed by the *s–t* curve, since only the values of the constants in this equation would presumably be affected.

At 35° and 40°, the linear rate was too great for data to be obtained at low values of *s*, for the interface had advanced a considerable distance before the slide had acquired the thermostat temperature. At 35° the first reliable value was at $s = 1\cdot18$ (see Table I). Consequently, the extrapolation to $s = 0$, which was in no case entirely free from doubt, was here very uncertain, and the values of *t* for this temperature cannot be regarded as *absolute* values. It is also possible that the film edge in this case was not the zero position, for the first interface position recorded may have been partly derived from nuclei forming some distance from the film edge and then joining up. Any such nuclei would not have been noticed. At 40°, the first reliable value was at $s = 1\cdot77$ and extrapolation was out of the question. Accordingly, the data for this temperature are given in the table as from $s = 1\cdot77$ as the arbitrary zero. There is little doubt, however, that the linear velocity at 40° was higher than that at 35°.

The direction of transformation below the transition point is towards the denser red form, and all the curves show a fall of velocity with time, as was observed with *o*-nitro-aniline (Part III, *loc. cit.*). In that work it was suggested that the fall is due to the development of a gap at the interface, and we have since found that a similar suggestion was made by Lehmann (" Molekularphysik," 1888, Vol. I, 168) in connexion with his study of the transformations of mercuric iodide and other polymorphic substances.

The curves were tested for conformity to the equation $t = k_1 s^3 + k_2 s$ by the method of calculating k_1 and k_2 from two points on the curve (see Part III), but the rate falls less rapidly than this equation demands. On the trial assumption that the correct relation is nevertheless of the form

$$t = k_1 s^n + k_2 s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the curves were then tested graphically as follows.* Equation (1) may be rewritten as $t/s - k_2 = k_1 s^{n-1}$, whence

$$\log(t/s - k_2) = \log k_1 + (n - 1)\log s \quad . \quad . \quad . \quad . \quad (2)$$

Hence, if $\log(t/s - k_2)$ is plotted against $\log s$, a straight line is obtained, with a slope of $n - 1$, and an intercept on the $\log(t/s - k_2)$ axis of $\log k_1$. Now, k_2 is the reciprocal of the velocity at $s = 0$, for differentiation of (1) gives $dt/ds = nk_1 s^{n-1} + k_2$, and when $s = 0$, $dt/ds = k_2$. The result of applying this test to the curves for 0—30° in Fig. 1 is shown

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* We are indebted to Mr. F. James, Research Department, Woolwich Arsenal, for suggesting this test.

in Fig. 2; k_2 was determined by means of a mirror tangent drawer, and the values are given in the col. 3 of Table II.

TABLE II.

	True zero.			Experimental zero.		
Temp.	k_1.	k_2.	n.	k_1.	k'_2.	n.
0°	3·2	6·3	2·24	3·6	7·4	2·20
10	1·5	3·8	1·95	1·7	5·3	1·97
17·5	1·0	3·5	2·18	1·3	3·8	2·05
25	0·7	1·67	2·20	0·9	2·13	2·15
30	0·7	1·11	2·20	0·9	1·53	2·03
35	—	—	—	0·5	1·01	2·13
40	—	—	—	0·8	1·01	2·05

All the plots approximate closely to straight lines with a slope of nearly 1, *i.e.*, the value of n to the nearest whole number is 2 (col. 4, Table II). The data for 35° were also plotted, but did not give a straight line. The reason for this may be that the extrapolation of the curve and therefore the value of k_2 were incorrect. The uncertainties attached to this extrapolation have already been pointed out.

FIG. 1.
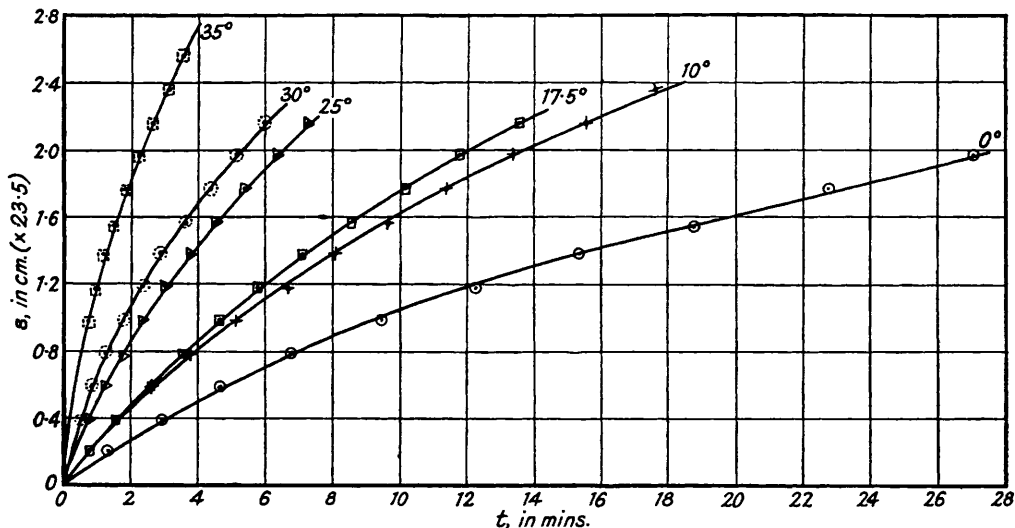
This result is of interest because the corresponding equation, *viz.*, $t = k_1 s^2 + k_2 s$ may be deduced theoretically on the assumption that molecules, or presumably ion-associations in the present case, are transferred from one lattice to the other, either (i) as vapour diffusing across the gap according to Fick's law or (ii) as a mobile layer diffusing along the glass surfaces confining the film. These deductions are somewhat lengthy and it would be premature to publish them without further experimental support.

If $n = 2$, then it may be shown as follows that the equation is valid no matter what point on the curve is taken as the zero. Let t' and s' represent the time and distance, respectively, measured from the point $t = t_0$ and $s = s_0$, where s and t are the time and distance measured from the true zero. Then

$$t = t' + t_0 = k_1(s' + s_0)^2 + k_2(s' + s_0) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$t_0 = k_1 s_0^2 + k_2 s_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Subtracting (4) from (3), we obtain

$$t' = k_1 s'^2 + (k_2 + 2k_1 s_0)s' \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

But for any particular case, s_0 is a constant, and the equation may therefore be written as

$$t' = k_1 s'^2 + k'_2 s' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $k'_2 = (k_2 + 2k_1s_0)$, and is the reciprocal of the linear velocity at the arbitrary zero s_0, t_0, as may be readily shown by differentiating (6) and equating s' to zero. Thus, the relation between s' and t' is of the same form as that between s and t. The curves can therefore be tested for conformity to the equation $t = k_1s^2 + k_2s$ by taking the first reliable point on the experimental curve as the zero, and the test is uninfluenced by the uncertainties attaching to the extrapolated portion. Fig. 3 shows the result of applying this test to

FIG. 2.
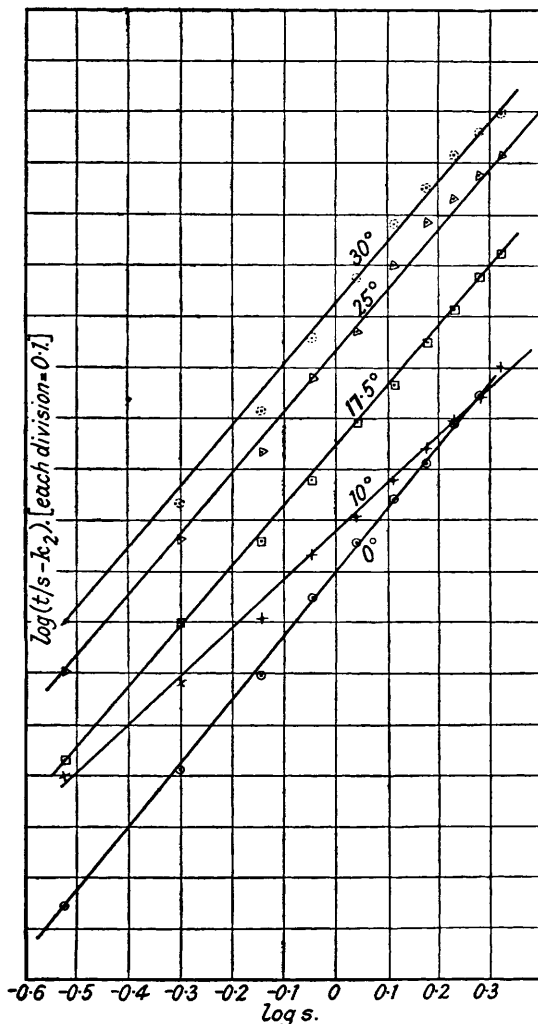
FIG. 3.
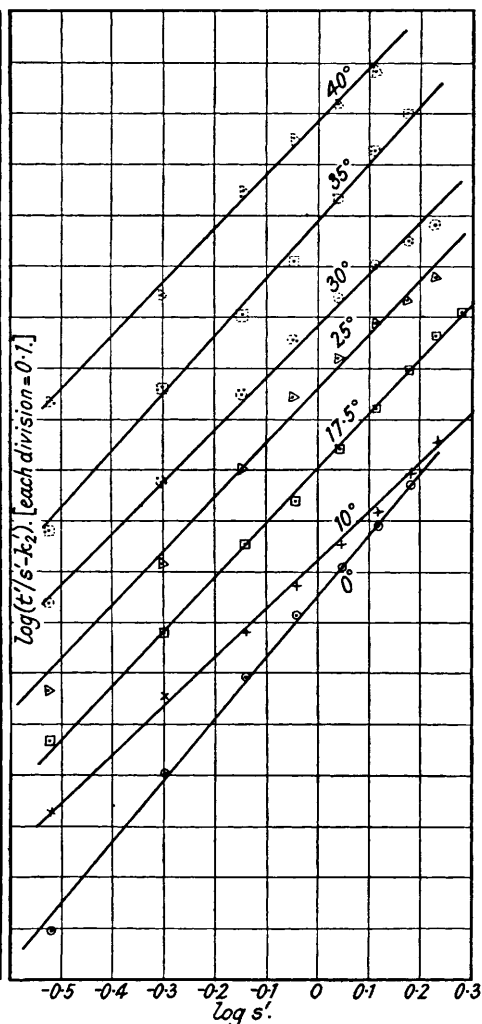
the data at all temperatures. Good straight lines are obtained in practically every case, and the slopes are all near to unity. The corresponding values of n are tabulated in the last column of Table II.

Table II also gives the values of k_1 obtained by the two methods of testing. For a perfect curve with $n = 2$, equation (6) shows that these should be the same : rough agreement is obtained.

The above method appears to be superior to, and is certainly less tedious than, that used in Part III, for it depends almost entirely on the accuracy of k_2, *i.e.*, the accuracy of the curve near the origin, small errors in other parts of the curve merely causing small deviations from the main straight-line plot. The latter method depends, not only on the

extrapolation, which determines the *t* values, but also on the individual accuracies of the two points from which the constants are calculated.

The graphical method has been applied to the curves for *o*-nitroaniline, *t* and *s* being reckoned both from the true zero and from the experimental zero, and the results cast considerable doubt on our previous conclusion that the equation $t = k_1 s^3 + k_2 s$ is in general accord with the curves, though they do correspond on the whole to a decidedly more rapid fall of velocity than in the present case. Comparatively few of the plots are really good straight lines, but from the mean slopes, the values of *n* are as follows : true zero, 2·32—2·85, with one of 1·96 ; experimental zero, 2·1—3·03, with two of 1·96 and 1·85. These irregularities are probably to be attributed to errors in the extrapolation, which had to be done over greater distances than in the present work, and to the less satisfactory method of measurement used.

TABLE III.

Absolute velocities.

Temp.	ds/dt at s = 0.		ds/dt at s = 1·4 cm./23·5.	
	Cm./min.	Mm./hour.	Cm./min.	Mm./hour.
0°	0·00677	41	0·00268	16
10	0·0112	67	0·00575	34
17·5	0·0122	73	0·00604	36
25	0·0255	153	0·0110	66
30	0·0333	200	0·0123	74
35	(0·0777)	(466)	(0·0325)	(195)

Table III gives the absolute values of the linear velocities in cm./min. and, for the sake of comparison with the results for *o*-nitroaniline, in mm./hour, at both *s* = 0 and *s* = 1·4. The latter value of *s* was chosen because it is within the experimental part of all the *s–t* curves from 0° to 35°. For reasons already given, the values at 35° are not very trustworthy and are therefore bracketed. Fig. 4 gives the logarithms of the velocities plotted against the reciprocal of the absolute temperature, and if the results at 35° (left-hand points) be ignored, the plots both correspond to an apparent activation energy of 10,000—11,000 cals.

In the case of *o*-nitroaniline (Part III) the apparent activation energy and the internal latent heat of sublimation of the stable form were nearly the same, and to explain this it was suggested that the rate of transformation was determined by the difference between the rates of escape of molecules from the two lattices involving activation energies equal to their internal latent heats of sublimation, which were assumed to be nearly the same. On the assumption that the rate of escape was equal to that into a free vapour space (rate of evaporation into a vacuum, *v*), it was found that the observed linear velocity was

FIG. 4.

of the right order, though lack of data regarding the vapour pressures of the solid forms prevented a proper test of the theory being made.

In the present case more vapour-pressure data are available, and it is possible to calculate the linear velocity and apparent activation energy on the basis of the theory approximately as follows. Vapour pressures of mercuric iodide have been determined between 100° and 350° (Johnson, *J. Amer. Chem. Soc.*, 1911, **33**, 780 ; Wiedemann, Stelzner, and Niederschulte, *Ber.*, 1905, **38**, 161), and the latent heats of vaporisation of

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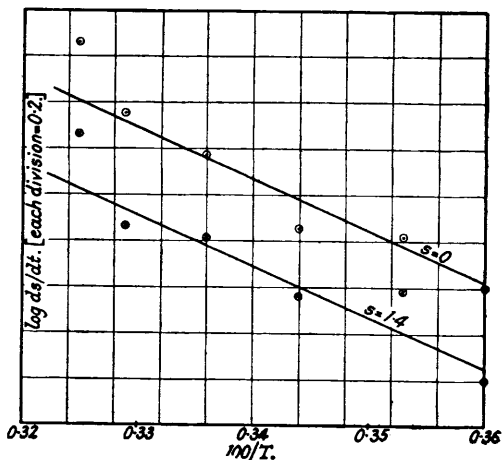
the liquid and the yellow form calculated from these are 15,260 and 19,800 cals., respectively. [The resulting latent heat of fusion, 4540 cals., agrees well with that determined independently by Guichant (*Compt. rend.*, 1907, **145**, 68, 320), *viz.*, 4450 cals.] The latent heat of transformation between the red and the yellow form is given as 3110 cals. (Berthelot, *Ann. Chim. Phys.*, 1883, **29**, 234; Varet, *ibid.*, 1896, **8**, 79; Bokhorst, Diss., Amsterdam, 1915), whence the latent heat of sublimation of the red form is $19,800 + 3,110 = 22,910$ cals. The mean internal latent heats between 0° and the transition point are, therefore, 19,000 cals. (yellow form) and 22,000 cals. (red form) to the nearest 1000 calories.

Two straight lines with slopes corresponding respectively to these values are now constructed on axes representing $\log v + $ const. and $1/T$, so as to intersect at the value of $1/T$ corresponding to the transition point. This makes the constant, which is unknown, the same for both lines, since $v_{yellow} = v_{red}$ at the transition point. The values of $v_{yellow} \times$ const. and $v_{red} \times$ const. may now be obtained from the graph for any temperature, and hence those of $\log (v_{yellow} - v_{red}) + $ const. These last values plotted against $1/T$ give the apparent activation energy of the reaction. Between 0° and 30°, the plot is practically a straight line with a slope corresponding to 18,000 cals. This is considerably greater than the experimental value (Fig. 4), and also than that which would be given if any weight were attached to the points for 35°, *viz.*, about 13,000 cals.

The linear velocity at $s = 0$ at 25° calculated from $v_{yellow} - v_{red}$ ($v = p\sqrt{M/2\pi RT}$, see Part III) is also not in agreement with that observed, being very much less. The values are : calc., 1.8×10^{-5} cm./min.; obs. (Table III), 2.55×10^{-2} cm./min. The calculation involves extrapolating the vapour-pressure results over a considerable range of temperature by means of the Clausius–Clapeyron equation, and the values of p used are therefore probably only approximate, but this could hardly account for the large discrepancy.

The fact that the activation energy is considerably less than that calculated from the heats of sublimation indicates that the process of transformation does not involve the removal of " molecules " of mercuric iodide from the lattice to a distance at which the attractive force becomes negligible. Whatever the process is, it would appear to be fundamentally the same at all stages of the reaction, because, as Fig. 4 shows, there is no evidence of any change in the activation energy as the reaction proceeds. The idea that transformation occurs through the medium of a mobile layer is attractive. It may be supposed that, at the beginning of the reaction, there is one mobile layer common to both lattices, but that, as the reaction proceeds and the gap develops, this layer separates into two, one on the surface of each lattice, and the transference from one to the other takes place by diffusion along the glass surfaces confining the film, or across bridges remaining at places where the gap has failed to form owing to some hindrance to reaction. The activation energy of the transformation process would be closely related to, and of the same order as, the energy needed to " mobilise " a molecule, which would be less than the heat of sublimation, as is actually found. The mobile units might also be single ions moving more or less independently.

Experiments above the Transition Point.—In the first experiments made to measure the linear rate of transformation of the red into the less dense yellow form, the rate was found to fall with time at least as strongly as below the transition point, and this appeared to cast doubt on the gap theory of the fall. It was then realised that the films were probably permeated with cracks owing to the volume decrease attending the change yellow $\longrightarrow$ red, and to the thermal contraction, which necessarily occurred in the preparation of the films. Cracks might also have formed as a result of the volume decrease accompanying the crystallisation of the liquid, if pools of liquid became surrounded by crystals during the process. An interface advancing through such a film would encounter a succession of these cracks, and the process might, on the average, be represented by Fig. 5. *AB, CD*, etc., are blocks of the red form separated by the cracks *BC, DE*, etc. For simplicity it is assumed that the cracks are spaced at equal intervals. An interface starting at *A* proceeds with a constant velocity across *AB*, and on the assumption that the unchanged part of the block is free to move, it will be pushed forward owing to the increase in volume accompanying the reaction. When the block is completely transformed, it will have

expanded to B', BB' representing the difference in volume between the material of the block in the two forms. The interface will now encounter a gap $B'C$ representing the shrinkage, due to thermal contraction and causes other than the change yellow $\longrightarrow$ red, which occurred when the film was made. The linear rate will now fall, since material can only be transferred across the gap. The transformation of the second block will start at this reduced rate, but the rate will gradually increase, since, owing to volume increase, the gap will diminish in width. When the transformation of this block is complete, however, the interface will encounter the gap $D'E$, which is twice as wide as $B'C$, and a further and larger fall of rate will occur, and so on. If the cracks occur at very frequent intervals, these sudden changes of rate will be smoothed out into a continuous decline.
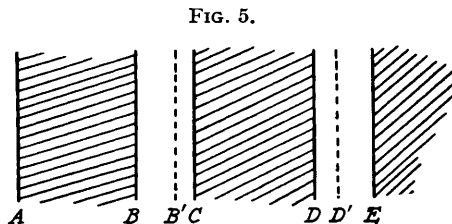
FIG. 5.

Cracks due to thermal contraction and to contraction attending the change liquid $\longrightarrow$ yellow form must also have been present in the yellow films studied below the transition point, but would merely have the effect of accentuating the decline of velocity due to the change yellow $\longrightarrow$ red; every time a crack was encountered, the gap would acquire an addition to its width, but on the average such additions would be smoothed out.

Above the transition point, the assumption made above that the first block can move is probably not justified in general, because it would be anchored to the glass at a number of points. The increase in volume would then be accommodated by the filling in of spaces between the block and the glass; in any actual film there must be many of these spaces. Also the transformation of subsequent blocks proceeds in such a way as to fill up these spaces, and the combined effect would be to shorten the linear distance advanced by the interface in the transformation of a block, and so to increase the gap width added at the end of each such transformation. Further, at the comparatively high temperature (130°) at which the reaction was studied, evaporation from an unprotected film is probably not negligible, and loss of material from the cracks owing to this cause would further accentuate the fall of velocity.

Accordingly, it was decided to attempt to close the cracks by prolonged annealing, and to stop evaporation as already described (p. 1637). The films were annealed for one week

FIG. 6.
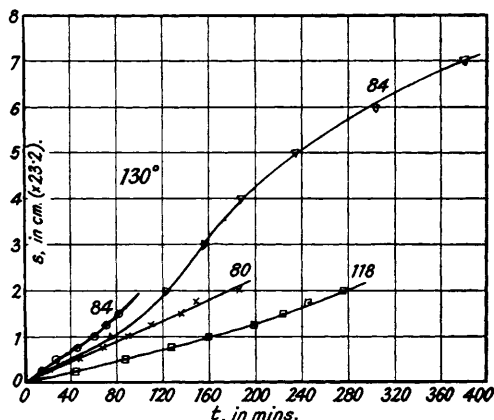
Each curve is marked with the average number of measurements per point on which it is based.

at 100°, then heated to 130°, and the growth of the yellow nuclei at this temperature recorded. Microscopic examination of the effect of annealing showed that a network of dark lines, presumably cracks, present at first disappeared after a few days, without apparently destroying the polycrystalline character of the film. Thus the annealing did

not result in the production of a few large crystals. The mechanism of this crack-healing process is not obvious.

The effect of this treatment was to stop completely the fall of velocity, but different films showed very different velocities. Curves for four films are shown in Fig. 6. In the early stages, up to $s = 1$, the rate is constant, but between $s = 1$ and $s = 2$, three of the curves show a slight increase, which, in one case where it could be followed up to $s = 7$, continues for some distance and is succeeded by a decline. At present we are unable to offer any explanation of this sigmoid shape, or of the differences between the rates of the different films.

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