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that a kinetic mechanism effects the major part of the separation.

It is apparent that before any proper explanation of the mechanism of the electrolytic separation process can be forthcoming, there must be a much greater extension of the experimental material. The writer has work in progress at present on the electrolytic separation of nitrogen isotopes which is based on the discharge of the ammonium ion at a mercury cathode. The experimental curve of Fig. 1 predicts the α-value for

nitrogen to be near that of oxygen. It will be of interest to check this prediction. Because of the much more rapid method of mass spectrometer analysis employed in this nitrogen work instead of the long and tedious crystal suspension method employed in previous work, much greater variation in experimental conditions of the electrolyses are made available. It is hoped that the results of the nitrogen work will furnish experimental data that can serve as a more adequate basis for interpreting the mechanism of the separation.

An X-Ray Diffraction Investigation of the Thermal Decomposition of Silver Oxalate[*][†]

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A single crystal of silver oxalate was studied by x-ray diffraction during the process of thermal decomposition. The diffraction patterns indicated that some fragmentation of the single crystal occurred early in the reaction. Except for distortion, the monoclinic structure was maintained until all trace of silver oxalate disappeared. The gradual appearance of polycrystalline silver was apparent. The diffraction patterns showed that a portion of the silver assumed preferred orientations, the ratio of oriented to unoriented silver remaining constant throughout the reaction. Four different preferred orientations were found and were defined relative to the silver oxalate lattice.

SILVER oxalate, when heated, undergoes thermal decomposition, the products being metallic silver and carbon dioxide.[1,2] The crystal structures of silver oxalate[3] and metallic silver[4] are known. It seemed quite probable, therefore, that information regarding the behavior of the silver oxalate structure during decomposition, the growth of silver, and its crystalline form and orientation with respect to the silver oxalate structure could be obtained by means of x-ray diffraction studies during the process of thermal decomposition. Such information is useful in connection with the development of photo-

thermographic processes[5] and also in connection with the theory of photographic development.

A thick plate-like crystal of silver oxalate, prepared by slow evaporation of a concentrated ammoniacal solution,[2] was mounted on the goniometer head of a Weissenberg x-ray diffraction camera and so oriented as to rotate about its a axis. The crystal was then reduced to a cylindrical form having a diameter of approximately 0.4 mm, by rotating it against a small piece of sponge soaked in ammonium hydroxide. The goniometer head could be removed from the camera without disturbing the attached crystal.

The experimental procedure consisted in heating the crystal, still attached to the goniometer head, for a period of time in an oven at a controlled temperature ranging from 100° to 140°C for the various periods of heating. After each interval of heating, the crystal was returned to

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† Communication No. 1068 from the Kodak Research Laboratories.
[1] J. Y. Macdonald and C. N. Hinshelwood, J. Chem. Soc. 127, 2764 (1925).
[2] J. Y. Macdonald, J. Chem. Soc. 832, 839 (1936).
[3] R. L. Griffith, J. Chem. Phys. 11, 499 (1943).
[4] R. W. G. Wyckoff, *The Structure of Crystals* (Chemical Catalog Company, New York, 1931), second edition, p. 204.

[5] U. S. Patent, 1,976,302, S. E. Sheppard and W. Vanselow (assigned to Eastman Kodak Company).

TABLE I. Diffraction patterns of silver oxalate during thermal decomposition.

Photograph No.	Type	Heat treatment Time (Hr.)	Temp. °C	Silver oxalate pattern	Silver pattern
3	R	1½	100	Normal single crystal.	None.
4	R	3	100	Normal pattern plus ten weak spots just off 0 and ±1 layer lines.	None.
5	R	5½	100	Normal pattern. Extra spots slightly stronger.	Three weak powder lines.
6	R	4	100	Normal pattern slightly diffuse at large angles. About 50 extra spots.	Six silver lines. Maxima on lines.
7	R	5	100	Normal pattern same as in No. 6. Extra spots stronger.	Pattern considerably stronger.
8	W	None		Normal pattern. Spots at large angles slightly diffuse.	One line visible. Maxima on line.
9	R	6	100	Normal pattern becoming more diffuse. No additional extra spots.	Same as No. 7.
10	W	None		Same as No. 8.	Two silver lines with distinct maxima.
11	R	15	100	About same as No. 9.	Lines much stronger.
12	W	None		Spots diffuse.	Four lines present. All have maxima.
13	R	21	100	Normal pattern and extra spots becoming weaker and more diffuse.	Intensity greater.
14	W	None		Same as No. 12.	Intensity greater than No. 12.
15	R	17½	110	Same as No. 13.	Same as No. 13.
16	R	17	125	Normal pattern and extra spots are weaker.	Stronger. Eight lines. Maxima at same points on lines.
17	W	None		Same as No. 14.	Six lines visible. Same maxima present.
18	W	43	125	Pattern considerably weaker.	Seven lines visible. Maxima on all.
19	R	None		Much weaker. All extra spots present.	Pattern stronger.
20	R	39	130	Weaker. Spots quite diffuse.	Same as No. 19.
21	W	None		Spots quite diffuse.	Same as No. 18.
22	W	42	140	No evidence of pattern.	Eight lines. Maxima not as sharp as on No. 18.
23	R	None		No evidence of pattern.	Maxima not as sharp as on No. 20.

the camera where rotation and usually zero-layer Weissenberg photographs were obtained, using filtered copper K radiation. By this procedure the effect of thermal decomposition on the silver oxalate diffraction pattern and the appearance and growth of the diffraction pattern of the thermally produced silver could be observed.

The photographs obtained and the observations concerning these photographs are summarized in Table I. Column 1 gives the number of the photograph; Column 2 indicates the type of photograph, W, indicating Weissenberg and R, rotation photograph. Columns 3 and 4 give the thermal treatment received since the previous photograph. Notes concerning the silver oxalate and silver patterns are in Columns 5 and 6. Typical photographs are shown in Figs. 1–7, these figures representing the photographs listed in Table I as 3, 7, 20, 23, 8, 18, and 22, respectively.

Figure 1, which is photograph No. 3 of Table I, is the diffraction pattern obtained by rotating a single crystal of silver oxalate about its a axis. The pattern consists of sharp spots, all distributed along straight lines across the pattern, the so-called layer-lines. There is no evidence of the silver diffraction pattern on this photograph. That silver was undoubtedly present was indicated by the darkening of the crystal, but the amount was too small to give a detectable diffraction pattern. Figure 2, photograph No. 7, contains, in addition to the pattern for rotation of a single crystal of silver oxalate, spots which are not on layer-lines. These spots can be accounted for by assuming that the crystal has undergone fragmentation in which small portions
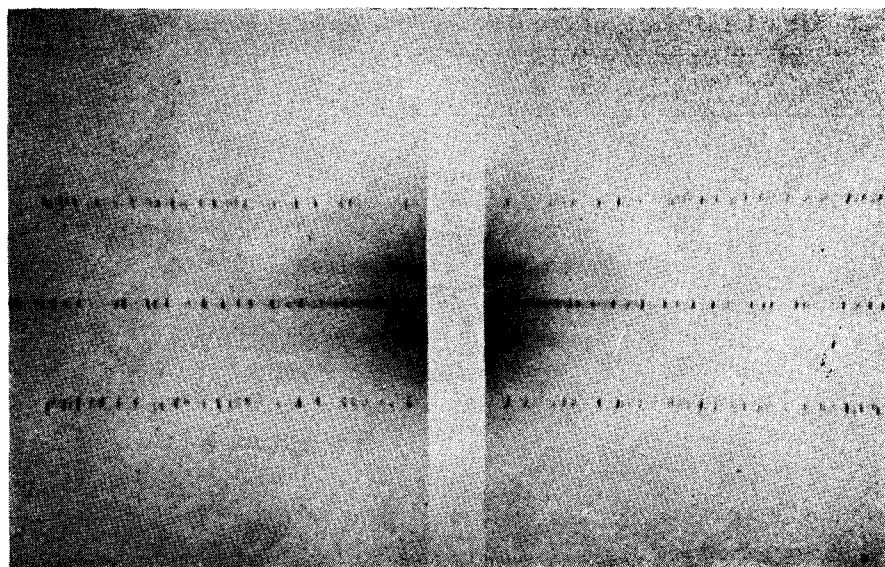
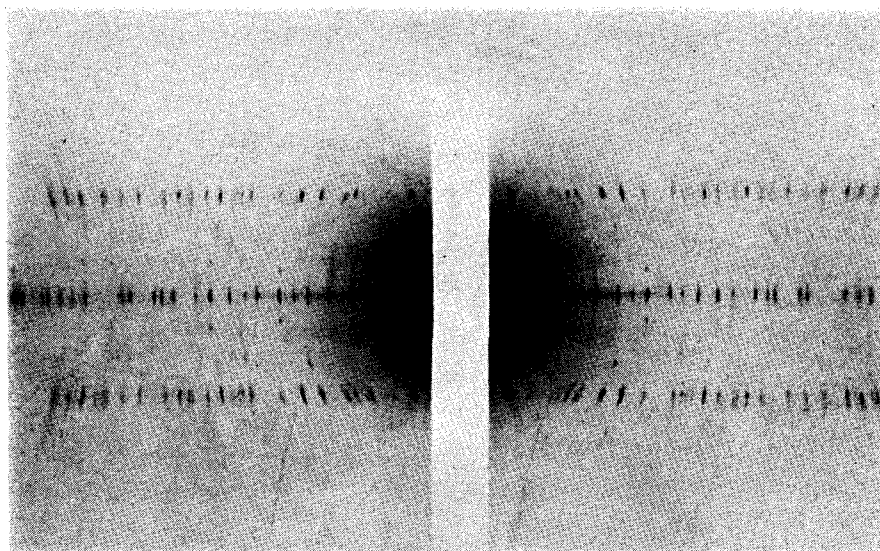FIG. 1. Rotation photograph. Heat treatment: 1½ hr. at 100°C.

FIG. 2. Rotation photograph. Heat treatment: 19 hr. at 100°C.

of the original single crystal break away and assume orientations in which their a axes are not parallel to that of the parent crystal. These extra spots first appear on photograph No. 4 and increase in number and intensity on going from No. 4 to No. 7. All rotation photographs following No. 7 up to and including No. 20, Fig. 3, show the same extra spots at about the same intensity relative to that of the normal silver oxalate pattern. Beyond photograph No. 20, as is shown in Fig. 4, there is no evidence of the silver oxalate pattern nor of the extra spots. Examination of the series of photographs shows that as the reaction progresses, the silver oxalate pattern and the extra spots become gradually weaker and more diffuse. This is caused by disappearance of silver oxalate and the distortion of the structure of the remaining silver oxalate.
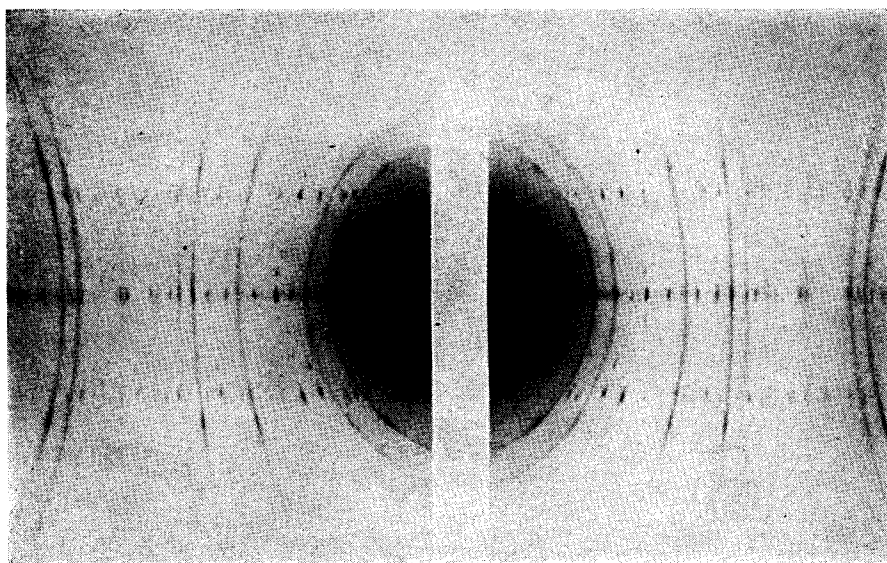
FIG. 3. Rotation photograph. Heat treatment:
61 hr. at 100°C   60 hr. at 125°C
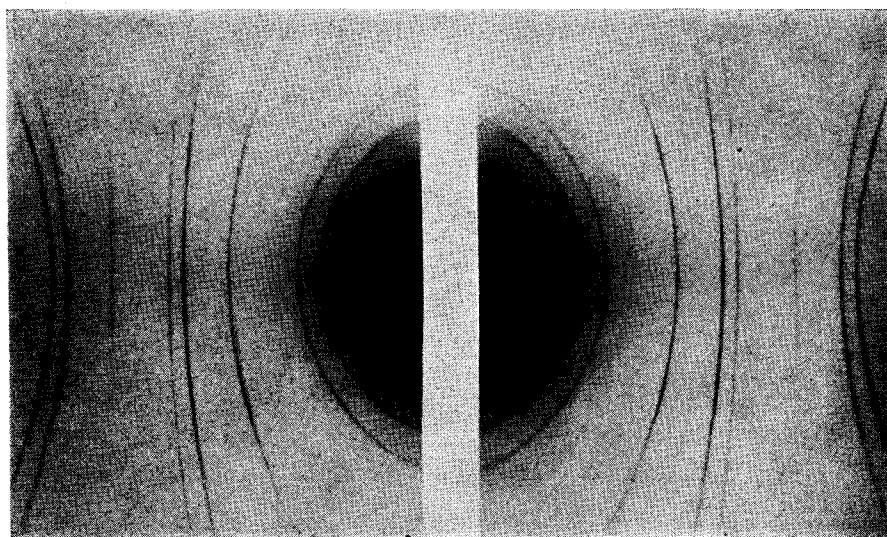17½ hr. at 110°C   39 hr. at 130°C

FIG. 4. Rotation photograph. Heat treatment:
61 hr. at 100°C   39 hr. at 130°C
17½ hr. at 110°C   42 hr. at 140°C
60 hr. at 125°C

Apparently, the time required for the decomposition to occur in the parent crystal and in the fragments which split off is about the same. The increase in number and intensity of the extra spots between photograph No. 4 and No. 7 may be caused by the growth and increased perfection of the fragments which split off from the parent silver oxalate crystal. The extra spots do not appear on the Weissenberg photographs because of the presence of the layer-line screen in the camera when the photographs were taken.

The first photograph exhibiting any evidence of the diffraction pattern of silver is No. 5, on which three weak powder lines are visible. These
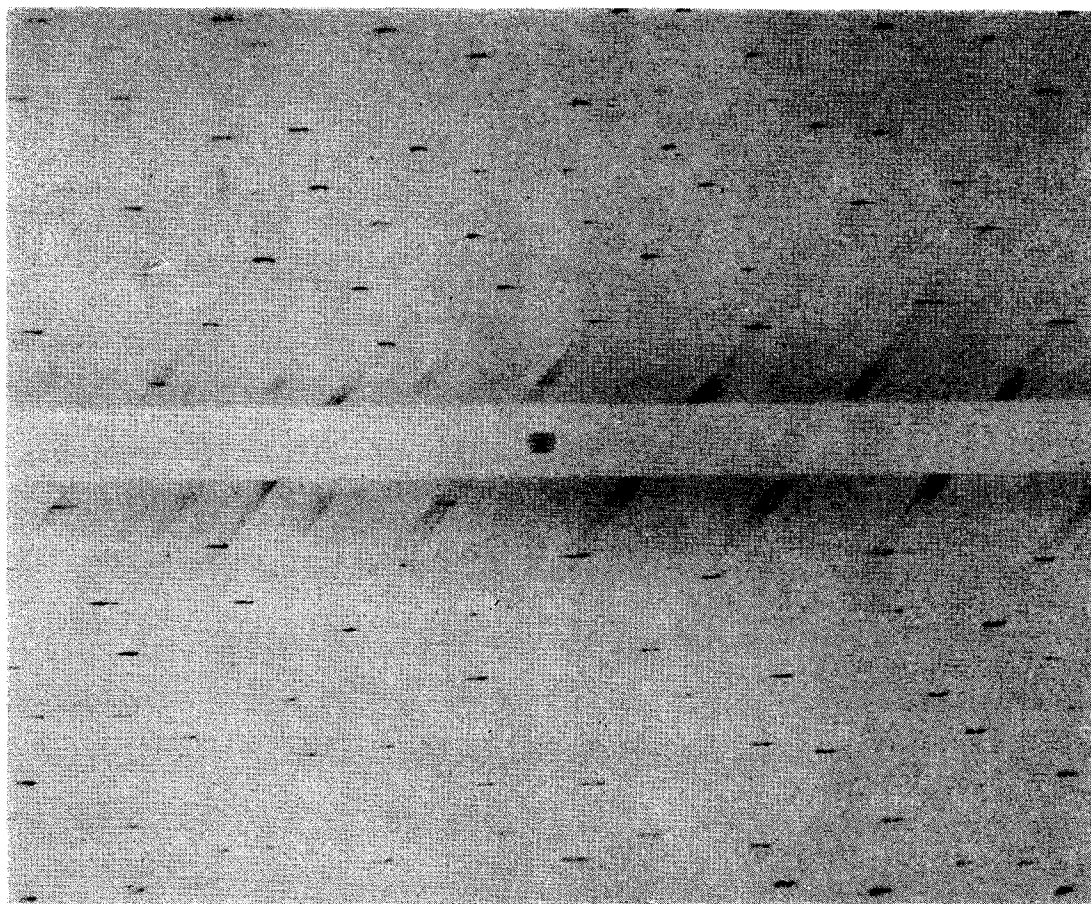
FIG. 5. Weissenberg photographs. Heat treatment: 19 hr. at 100°C.

lines and those on succeeding photographs are caused by face-centered cubic, polycrystalline silver. On photograph No. 6, the silver pattern is considerably stronger and close examination shows that the powder lines are not of uniform density over their length but exhibit definite density maxima. This can be seen in Fig. 2, which is photograph No. 7. Fig. 5, photograph No. 8, a Weissenberg photograph, shows one powder line for silver. This line exhibits density maxima. As the decomposition progresses, the lines on the diffraction pattern increase in intensity and number. Density maxima are present on the lines at the same points in all photographs. Comparison of Figs. 3 and 4 shows that the density maxima are less pronounced on Fig. 4—the photograph taken after all the silver oxalate pattern had disappeared—than on Fig. 3, which was taken before the disappearance of the

oxalate pattern. This may be caused by the orienting influence exerted on the silver crystallites by the residual silver oxalate lattice. Continued heating at 130°C after the silver oxalate pattern disappeared did not diminish the maxima any further.

The fact that the lines due to silver are of about the same breadth on all patterns, allowance being made for differences in exposure, is consistent with the view that when the growth of a small crystal is initiated it rapidly grows to final size, the over-all process taking place by the initiation and growth of new crystals rather than by the simultaneous growth to a large size of a small number of crystals. The mass of polycrystalline silver left at the completion of the reaction was a pseudomorph of the original crystal.

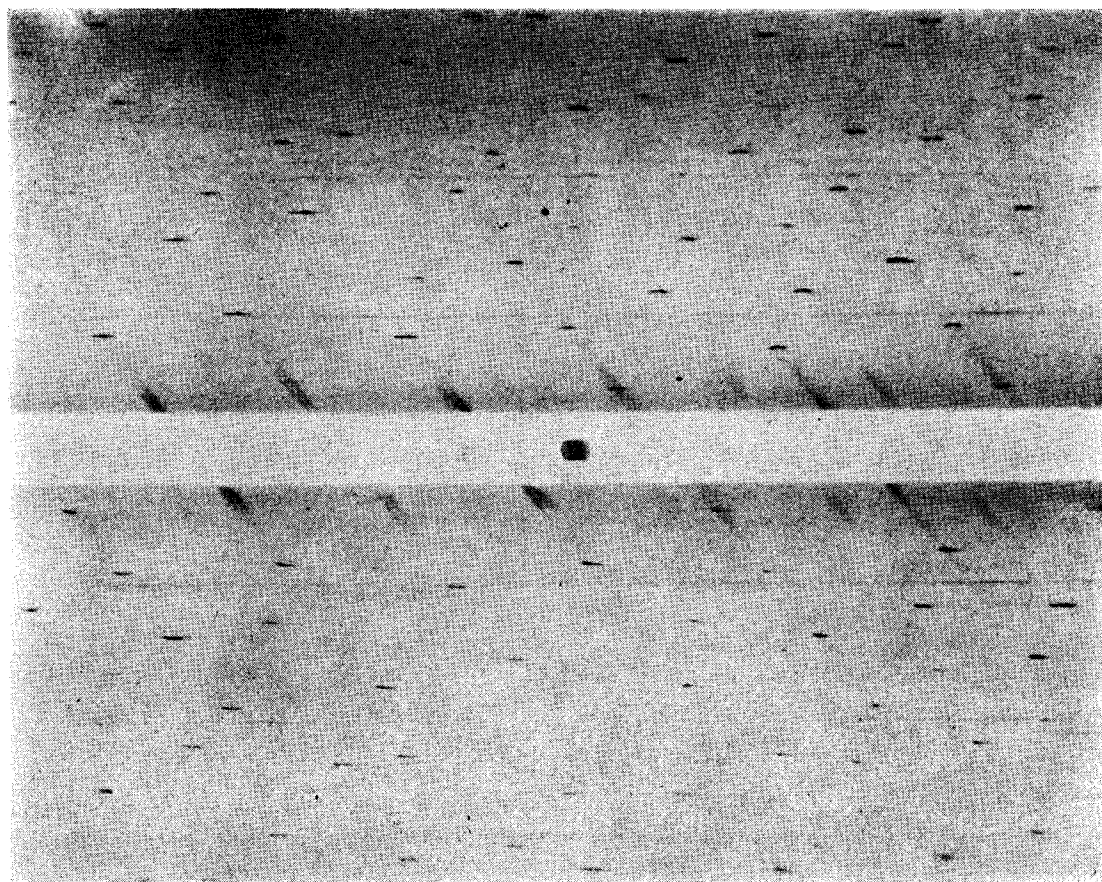All the maxima on the diffraction lines of the

FIG. 6. Weissenberg photograph. Heat treatment:
61 hr. at 100°C   60 hr. at 125°C
17½ hr. at 110°C

silver pattern on the rotation photographs can be accounted for both as to position and relative intensity by assuming that a portion of the polycrystalline silver which is formed assumes a preferred orientation with respect to the silver oxalate lattice such that the [011] direction of the silver structure is parallel to the a axis of silver oxalate. The fact that the intensity maxima are arcs rather than spots indicates a range of orientations. From the lengths of these arcs one may conclude that the orientation of nearly all of those crystallites which are oriented lies within ±4° of that described here.

Having established that the [011] direction of the oriented silver structure is parallel to the a axis of the silver oxalate structure, we can define completely the relative orientation in space of the two structures by determining the angle between some direction in the silver oxalate lattice which is normal to its a axis, for example, the b axis, and a direction in the lattice of the oriented silver which is normal to its [011] direction, for example, the [01$\bar{1}$] direction. The angle between these directions can be determined by well-established methods[6] from the zero-layer Weissenberg photographs shown in Figs. 6 and 7. From these patterns it was determined that there are at least four different preferred orientations of silver with respect to the silver oxalate structure. In all four cases the [011] direction of silver is parallel to the a axis of silver oxalate. The four orientations are then completely defined by the angles between the [01$\bar{1}$] directions and the b axis of the silver oxalate structure. These

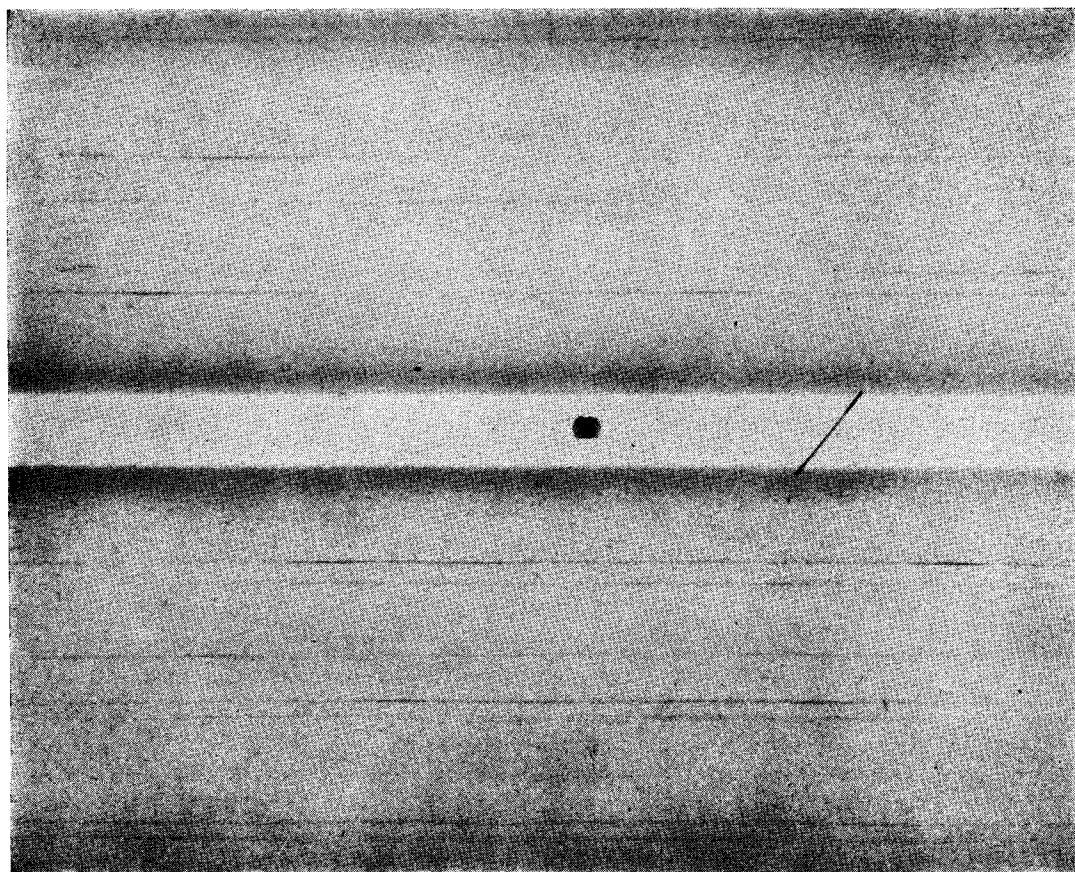[6] M. J. Buerger, *X-Ray Crystallography* (John Wiley and Sons, New York, 1942).

FIG. 7. Weissenberg photograph. Heat treatment:
61 hr. at 100°C   39 hr. at 130°C
17½ hr. at 110°C   42 hr. at 140°C
60 hr. at 125°C

angles are −30°, 35°, 75°, and 100°, with a range of ±5°. These four preferred orientations of silver account for all the density maxima which appear on the diffraction lines of silver in the photographs shown in Figs. 6 and 7.

The preferred orientation of silver with respect to the silver oxalate structure probably arises from the attempt of the silver crystals to grow in such a fashion that at the interface between silver and silver oxalate there will be as nearly as possible a correspondence in direction and magnitude of the silver-silver distances. There are no close silver-silver distances in these two structures which agree in magnitude. The closest distances in metallic silver are 2.88A and 4.08A. Those in silver oxalate are 3.34A, 3.35A, and 3.58A. The process of crystal growth must involve a considerable adjustment of silver-silver distances. The oriented silver probably grows in such a fashion as to produce a minimum of readjustment of distances. The probability that a silver crystal will be in a position of preferred orientation is about the same as the probability that it will have a random orientation, since, as is shown by the diffraction patterns, a considerable portion of the silver is randomly oriented. The ratio of oriented to unoriented silver remains about the same throughout the process of thermal decomposition. Continued heating of the mass of silver after decomposition is complete does not change the ratio of oriented to unoriented silver.

CONCLUSIONS

In the crystal of silver oxalate which was investigated, thermal decomposition is accom-

panied by fragmentation of the crystal, the fragments produced being slightly disoriented with respect to the original crystal. The undecomposed silver oxalate maintains its structure until the reaction is complete, except for distortion produced by removal of carbon dioxide from the lattice. The silver formed by the decomposition exists in the form of face-centered cubic crystals having a final size of approximately 10^{-5} cm. Some of the crystals of silver assume preferred orientations with respect to the silver oxalate lattice, the ratio of oriented to un-

oriented silver remaining approximately constant during and after the reaction. The explanation of the particular preferred orientations assumed is probably to be found in the structures of the two crystals but it is not immediately evident.

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The Behavior of Macromolecules in Inhomogeneous Flow

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Following up the ideas of W. Kuhn's skein theory, J. J. Hermans has recently elaborated a theory of the properties of dilute solutions of highly polymerized molecules. Hermans describes the behavior of linear molecules by the diffusion of their end points. He finds that the contribution of a single molecule to the viscosity coefficient as well as to the double refraction of the solution is proportional to the square of the degree of polymerization, in agreement with the experiments. In the present article we investigate the statistical behavior of the individual links of the solved molecules. In this way we arrive at results equivalent with those of Hermans. Our method, however, can also be applied to molecules which possess branching points and rings.

1. INTRODUCTION

IN connection with Kuhn's skein theory, Hermans[1] developed a simplified method to describe the influence of macromolecules on viscosity and double refraction. In this method the behavior of the molecule is characterized by the diffusion of the end points. This can be described as if two mass points which exert a fictive elastic force upon each other are diffusing in the liquid. The equilibrium distribution of the vector joining the end points, showing spherical symmetry in a liquid at rest, is deformed under the influence of the flow. It is assumed that this flow does not alter the elastic force. By means of a relatively simple calculation Hermans shows that the contributions of a molecule both to the viscosity and to the birefringence of flow are pro-

portional to the *square* of the number of elementary links, in conformity with experiment (Staudinger, Signer).

In the following we attempt to develop a more detailed theory. Our method also enables us to give a treatment of macromolecules which possess branching points and rings.

2. THE BEHAVIOR OF A SYSTEM OF MUTUALLY CONNECTED PARTICLES IN A FLOW DERIVED FROM A VELOCITY POTENTIAL

Let the systematic force which the liquid exerts on the ith particle be $-\zeta_i \mathbf{v}_i$, where $\mathbf{v}_i$ is the velocity of the particle with respect to the liquid. This velocity can be written $-\mathbf{v}_i' + \mathbf{v}_i''$, if $\mathbf{v}_i'$ represents the velocity of the liquid and $\mathbf{v}_i''$ that of the particle. If the streaming is irrotational and stationary and if its velocity potential is $\Psi(\mathbf{r})$, we have $\mathbf{v}_i' = -\nabla\Psi(\mathbf{r}_i)$. Consequently,

[1] J. J. Hermans, Physica 10, 777 (1943).