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The Formation and Constitution of Crystals of Lead Salts Containing Water-Soluble Colloid

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V—The Formation and Constitution of Crystals of Lead Salts Containing Water-Soluble Colloid

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1—INTRODUCTION

The influence of small amounts of dissolved foreign substances on the growth of crystals from saturated solutions has been the subject of much investigation. Usually the added substances have been electrolytes. Dyestuffs have not been neglected, but with some few exceptions comparatively little attention has been given to the effect of non-ionized water-soluble electrolytes such as gelatine or dextrine.

As a rule, the presence of the foreign substances is found to cause the crystals to assume a different habit. Whenever this occurs the absorption must have occurred on certain crystal-faces in preference to others, but, although the added material is active by virtue of its close attachment to such faces, it is rarely found to be incorporated into the solid to any great extent. The growing crystals appear to reject the impurity—thrusting it outwards as the growth advances.

The action of water-soluble colloids on the halides and certain other salts of lead is exceptional in several ways. Although when such colloids are present in small concentrations one can generally observe a modification of habit, at higher concentrations there may be little selective adsorption, and the result may be a rounded crystal on which no plane faces at all can be distinguished, as if the forces by which atoms are attracted to the structure had been equalized in every direction. In his examination of the action of dyes on certain crystals, BUCKLEY* has distinguished between the selective action of a dye on particular crystal faces and a "colloidal effect" which is exerted more generally and often results in the repeated growth of smaller crystal units. The lyophilic colloids used for this work show both effects, the second in an eminent degree. Throughout the mass of an apparently homogeneous crystal the colloid may be present to the extent of about 4% and if the crystal growth has been allowed to become complex there may be 10% or even more. Previous work has not as a rule dealt very fully with the amount of absorption into the crystal, and in fact the amount seems in all but a few cases to have been very small.

These peculiarities are exhibited by the slightly soluble salts of lead, such as the chloride and bromide. Lead azide displays more especially a variety of changes in crystalline habit. It is well known that if a salt is dimorphous, or can be accompanied by a hydrated form, a substance added to the solution may affect the stability of one or other form very considerably. The colloids used will be seen to show this power very definitely with the bromide and the azide of lead.

The first part of this paper will be mainly descriptive, and will give an account of the changes in crystal shape and habit, and of the alterations in stability of various physical forms, which are induced by the presence of dextrine or gum-arabic in the solution. The absorption of colloid from solution during crystallization, or by crystals already formed, will be treated exhaustively in Part II. In Part III the methods and results of an X-ray examination of the complexes of lead salt and colloid will be given, and finally, in Part IV the whole of the available evidence bearing on the constitution of these complexes will be discussed.

PART I—THE EFFECT OF COLLOIDS ON THE STABILITY AND HABIT OF CRYSTALS OF THE HALIDES AND AZIDE OF LEAD

2—METHODS AND MATERIALS

The rapid crystallizations were all carried out in a special apparatus consisting essentially of a jacketed crystallization vessel in the form of a glass tube $1\frac{1}{2}$ inches in diameter, with arrangements such that the contents could be cooled at any given rate and transferred very rapidly to a filter without any further change of temperature. In the tube a helical glass stirrer, $\frac{3}{4}$ inch wide and 2 inches long, was rotated at 750 r.p.m. When a saturated solution was to be used it was heated to well above its saturation temperature and filtered into the tube through oil-free cotton wool. In addition, numerous slower crystallizations were made. Flasks containing 250 cc of

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* 'Z. Kristallog,' vol. 85, p. 58 (1933).

the solution to be cooled were immersed in a tank of hot water and allowed to cool down from about 80° to 30° in about 18 hours. In all cases the solid was separated and made as dry as possible on the plate of a suction-filter. It was then shaken up with about $1\frac{1}{2}$ times its weight of water (heated to 35°–40° for a precipitate made at a temperature of 50° or more), and refiltered as rapidly as possible. Finally it was dried to constant weight *in vacuo* over calcium chloride.

All the precipitates were examined with the petrological microscope. Mounting of the specimens in very viscous media in which individual crystals could be turned over in any direction facilitated the determination of the optical characteristics so much that the crystallographic orientation could always be discovered.

All the lead salts were recrystallized twice from water. The same dextrine was used for nearly all the work. It was a perfectly white powder, which gave, when dried, the following analytical figures :—

Optical rotation $[\alpha]_{20^\circ}^{5461}$	224°
Solubility in cold water	44·8%
Acid by titration equivalent to HCl	0·16%
Reducing sugars, as maltose	4·8%
Ash	0·30%

No purification of this and other colloids was attempted for the greater part of the work. Solutions were made by heating slowly to 80° with stirring, and when cool were made neutral to phenolphthalein.

3—Lead Chloride

Rapid deposition

A preliminary study was made of the rapid crystallization of lead chloride. In each experiment a solution saturated at 80° was cooled to 20° at a constant rate.

Even when the rate of cooling was reduced to 0·4°/min no single crystals could be grown. The product was always in clusters of prisms joined to each other at various angles, often by penetration twinning. There was ample evidence that a crystal could grow a new branch more readily from a surface on which it had been chipped or broken by the stirrer than from any normal crystal face. Dendritic parallel growth did not begin to appear until the rate of cooling was very rapid—about 6°/min. The introduction of seed crystals at the beginning of the crystallization made little difference ; as in many other crystallizations which proceed more slowly, growth takes place on fresh nuclei rather than on completed crystal faces.

When a saturated solution containing even 0·025% of dextrine is slowly cooled, the formation of new crystals is far less common and many of the nuclei (even when they consist of broken fragments) grow into complete unaggregated prisms with the characteristic extension on the [100] axis and (001) planes. With a higher rate of cooling (2°/min or more) the most notable phenomenon is the deposition in the range 60°–80° of well-defined sphenoidal crystals. The obvious hemihedry must have arisen from the selective effect of the optically active dextrine on the two sets of holohedral faces which are related by planes of symmetry. By varying the concentration of dextrine from 0·10% to 0·05% the sphenoidal faces can be given very different degrees of prominence with regard to those of the prisms. Lead bromide gives similar results. The phenomenon has been illustrated and discussed in detail elsewhere.*

The influence of colloid is shown in the same way when the lead chloride is precipitated by double decomposition. Such experiments show clearly the dependence of the colloid action on the temperature. In one set a solution of lead nitrate (20 gm/100 cc) was run into twice its volume of an equivalent solution of potassium chloride, in 10–12 minutes. Each solution contained 0·25% of dextrine. The characteristics of the products at three different temperatures are given in Table I.

TABLE I

Temperature ° C	Type of crystal	Optical properties	%$PbCl_2$ in precipitate
60	Sphenoidal	Sharp extinction . . .	99·6
25	Long, rounded, “ boat-shaped ” crystals	Fairly sharp extinction .	98·3
0	As at 25°, but more rounded and with warty accretions	Very confused extinction	96·9

Taking the defect of the percentage figure from 100 to represent adsorbed dextrine, the decrease in the amount of adsorption with rising temperature is very marked. Fig. 8, Plate 21, is a photomicrograph of the product obtained at 25°.

Slow Crystallization with Colloid

The effect of colloids on the shape of crystals is most evident in solutions which are very slowly cooled and are not stirred. Gum arabic and dextrine give very similar results. If sufficient dextrine is present, say 0·10% of the solution, the edges of the crystals are all curved, although the internal structure, as revealed by polarized light, remains very much the same. In presence of still more dextrine or gum arabic the internal structure becomes confused, and no longer gives uniform extinction between crossed Nicols. Later, a spherulitic structure tends to develop. A series of experiments was carried out by the method of slow cooling. The percentages of dextrine in the solutions, and of lead chloride in the final precipitates, are shown on the graph of fig. 1. As the concentration of colloid in solution is increased that of the colloid absorbed tends to a saturation value of about 3·5%. Fig. 9, Plate 21, is a photograph of the crystals deposited in the first experiment of the series and containing 0·85%

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* Miles, ‘Proc. Roy. Soc.,’ A, vol. 132, p. 266 (1931).

of colloid. This material was optically almost uniform. Fig. 10, Plate 21, represents the precipitate of the fourth experiment, which contained 2·6 %of colloid, and had a complex spherulitic structure. Such growths as the last mentioned show a great variety of shape and aggregation, and resemble the " Somatoid " forms of calcium carbonate and other salts which have been discussed in detail by KOHLSCHÜTTER.*

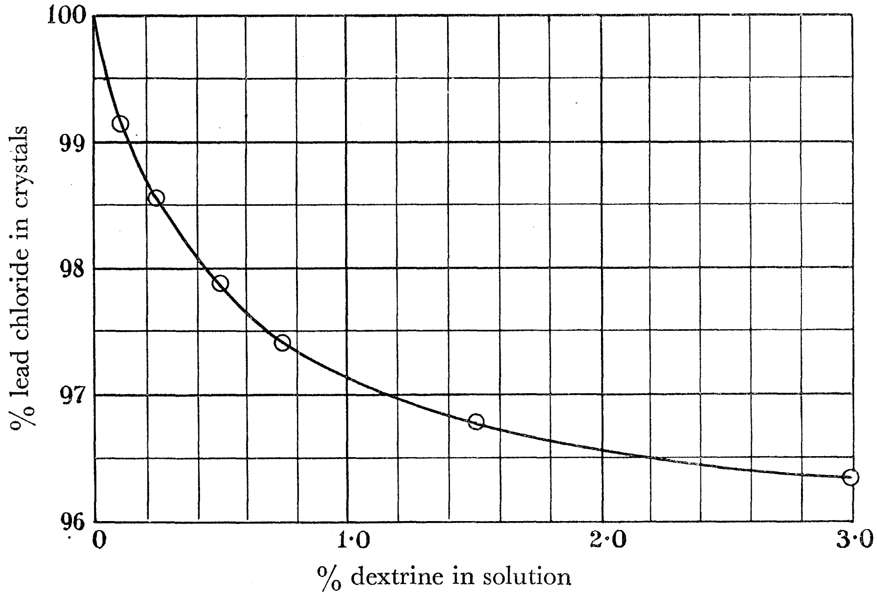

FIG. 1.—Absorption of dextrine by lead chloride.

4—LEAD BROMIDE

Like the chloride, lead bromide is holohedral orthorhombic, and can be precipitated from hot solution in prisms extended on [100] and on (001). The action of water is to form insoluble basic bromide. In a solution containing 2·70% of bromide it was found that hydrobromic acid equivalent to a normality of 0·0014 must be present at 80°–90° if the solution is to remain clear.

The Hydrated Form

The anhydrous prisms were always precipitated when potassium bromide solution was run at 80° into a stirred solution of lead nitrate containing this amount of hydrobromic acid, but if the temperature was lower, or if a clear solution saturated at 80° were cooled down, long silky needles were formed which on standing in a desiccator lost water and disintegrated. This hydrated modification was accompanied by more or less of the anhydrous form and to obtain it alone it is advisable to crystallize from a 2% solution below 40°. The principal optical axes lie in the same direction as for the

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* 'Helv. Chim. Acta,' vol. 8, pp. 457, 470 (1925.)

anhydrous form, the γ axis being parallel with the elongation, and the α axis perpendicular to the principal face.

The only reference to a hydrate in the literature is that of DITTE*, who stated that if hydrobromic acid were added " in considerable excess " to a 0·5% solution of the bromide, a hydrate $PbBr_2 3H_2O$ crystallized out in silky needles on cooling. The composition of this material proved to be quite different. The analysis gave some trouble because the dehydration of the hydrate caused a slow hydrolysis even in vacuum, with consequent loss of hydrobromic acid. After drying in the air crystals were found to contain Pb=55·0, 55·15% ; H_2O (estimated by heating in a closed crucible at 130°)=2·42, 2·29%. These figures indicate the composition of the salt to be $2PbBr_2H_2O$, for which the calculated values are Pb=55·10%, H_2O=2·39%. The anhydrous bromide formed at 80° was found to contain Pb=56·45, 56·42% (calculated for $PbBr_2$–56·46%).

Slow Deposition

When clear solutions of lead bromide which had been saturated at 70° were cooled down slowly in the same way as those of lead chloride, the crystals deposited were nearly always in the form of branched aggregates of stout prisms. The modification due to the colloid was found to be much less than for the chloride ; even with 1% of dextrine in solution the internal structure of the crystals did not appear confused in polarized light. In the experiments with dextrine the adsorbed colloid was far less, as the figures in Table II show.

TABLE II

%Dextrine in solution	Analysis of Precipitate		
	%Pb (*a*)	%Br	$\%PbBr_2$ from (*a*).
0·25	56·49	43·50	99·9
—	56·49	43·48	99·9
—	56·44	—	99·8
0·50	56·08	—	99·3
1·00	55·82	—	98·9

Fig. 11, Plate 21, illustrates the fourth preparation of this series, made with 0·5 % of dextrine in the solution. The rounding of the crystal surfaces is very evident, but the effect is as a whole much smaller than for a lead chloride deposited under similar conditions. In no case were there any spherulitic or other complex growths.

All these precipitates were dried in the air and then analysed. All of them evidently consisted of anhydrous bromide. This is remarkable, because in every case the greater part of the salt was deposited below 40°, and it has been seen that similar solutions containing no colloid gave only hydrated bromide in this range of temperature. Gum arabic gave the same result. Either of these colloids, therefore, can inhibit the deposition of the hydrate. Further work with dextrines other than the

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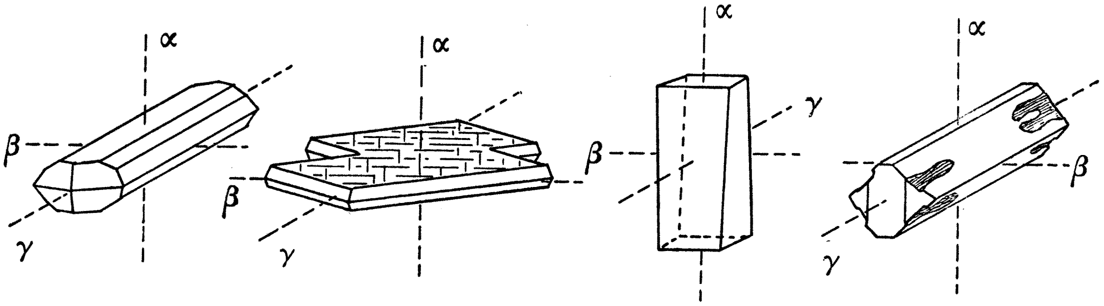
* 'C. R. Acad. Sci., Paris,' vol. 92, p. 78 (1881).

standard showed that all did not behave in the same way. One in particular showed no power of inhibition at all, and others showed it in varying degrees, giving rise to mixtures of hydrated and anhydrous salt. These results recall those obtained by KOHLSCHÜTTER*, who found that congo-red tended to suppress the deposition of aragonite from a calcium bicarbonate solution in the temperature range (above 30°) in which aragonite was the main product when no dye was present. Other dyes were less active, and some had no action at all.

In addition to the usual aggregates of prisms of anhydrous salt and to the needles of the hydrated form, two more types of crystal were found. In an experiment in which 0·25% of gum arabic had been used, parallel growths of flat plates, of rhomboidal outline, were deposited with the extinction directions bisecting the angles between the edges. The principal faces—(001) as before—are deeply etched parallel to their edges. This variety, " *a* ", is shown in fig. 12, Plate 21. Estimation of lead gave $Pb=56·49\%$ (Pb in $PbBr_2=56·46\%$). When attempts were made to repeat this preparation, the " *a* " variety was never the sole product, but another modification, " *b*," was obtained, which could be regarded as " *a* " elongated on the [001] axis. The etch markings on the basal planes appeared as before. The crystallographic relation between " *a* ", " *b* " and the ordinary crystals made by rapid precipitation at 80° in the absence of colloid will be made clear by fig. 2. X-ray powder diagrams were made for all three types and showed them to be identical in structure.



(1) (*a*) (*b*) (*c*)

FIG. 2.—*Various Forms of Lead Bromide Crystal*—(1) Ordinary form, free from colloid; (*a*) from gum arabic solution, slow cooling; (*b*) from gum arabic solution, more rapid cooling; (*c*) from dextrine solution, rapidly by double decomposition.

Rapid Deposition

The experiments on the rapid precipitation of lead bromide by double decomposition at various temperatures discovered very little colloid effect. The amount of absorption was smaller than for lead chloride, and the crystal surfaces were rarely rounded. One variety of face development, " *c* ", proved to be of some interest, and its relation to the others is indicated in the diagram, fig. 2. The principal faces

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* 'Helv. Chim. Acta,' Vol 8, p, 697 (1925).

are the form {011}. It has previously been pointed out* that this and the "*b*" modification have features which are incompatible with holohedral symmetry, and that in these cases, as in that of the sphenoids of lead chloride, the optical activity of the colloid has exerted a characteristic effect.

5—Lead Iodide

Lead iodide is hexagonal. The retarding effect of gelatine on its crystallization has been studied extensively by Bolam and others, but the influence of this colloid or of dextrine or gum arabic on the crystal habit is comparatively small. It is easy to obtain crystals so fine that many of them are in vigorous Brownian movement even when 5–6% of dextrine is present, but they are still thin basal plates, often with recognizable hexagonal outlines.

6—Lead Azide

Lead azide is a powerful and sensitive explosive which should not be made or used in the laboratory without special and constant precaution. The stable modification is orthorhombic,† and the most general habit of microscopic crystals is the same as that of the chloride or bromide, prismatic and elongated on [100] (the β axis) but flattened on (013). The azide is much less soluble in water than either of the other two—0·023 gm at 18° and 0·090 gm in 100 cc at 70°— and partly on this account it is much more difficult to obtain in single crystals ; parallel growths of prisms in the plane (001) or (010) are far more common.

The Unstable Variety

The monoclinic β variety, which can be formed from solution,‡ is stable when dry, but in presence of water is dissolved and redeposited in the α form. When a very small proportion of gum arabic or dextrine is present the formation of β crystals is greatly retarded and if the solution contains 0·01% of a sufficiently active dextrine it is inhibited. It would appear that the adsorption of colloid on the nuclei of β material is more pronounced than on the α nuclei, but it must be very considerable in both cases for if 1% of either colloid is added to a 10% solution of lead nitrate or acetate, in contact with which the lath-like β crystals are normally quickly converted into α prisms (fig. 13, plate 21 shows this conversion taking place), the change is not complete after several days.

Certain dyes, eosin, erythrosin, and neutral red, were found to have an effect contrary to that of the colloids. When solutions of lead nitrate (20%), and of an azide were run continuously into water at 20°, only α crystals appeared, but if 0·02% of any of these dyes were present in the reaction liquid a precipitate of

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* Miles, 'Proc. Roy. Soc.,' *loc. cit.*

† Miles, 'J. Chem. Soc.,' p. 2532 (1931).

‡ Wöhler and Krupko, 'Ber. deuts. chem. Ges.,' vol. 46, p. 2056 (1913).

the β material was formed. Eosin was particularly effective and caused β crystals to be produced, and to remain without change in contact with water (containing the dye) even at 50°. The curiously specific nature of these relations may be illustrated by another fact. Mercuric azide also exists in both a stable orthorhombic α form and in an unstable one of lower symmetry,* but the presence of dextrine is quite without influence on the formation of the β modification or on its stability when formed.

Rapid Deposition

The effect of dextrine or gelatine on the crystallization of the α azide was first noticed by Lowndes†. In whatever way the precipitation may be carried out in the absence of colloid there is always a marked tendency for some or all of the crystals to appear either in one or other of the two types of parallel aggregation which have been mentioned, or in twinned combinations. An unusually perfect aggregation in the (001) plane is shown in fig. 14, Plate 22.‡ In the presence of small amounts of any of the colloids this tendency is more or less repressed, and often it is possible to produce single crystals exclusively.

The changes of habit which are induced by colloid are most clearly seen if the precipitation is carried out by running the solution of azide into that of the lead salt. The presence of lead nitrate, for instance, increases the rather low solubility of lead azide, and as a consequence twins and parallel growths are much less common than if another method of mixing is used. Just as with the chloride the influence of the colloid, and (as will be seen later) the amount of its absorption become less as the temperature is raised. Precipitations were made at 20°, 50°, and 80° with various concentrations of dextrine up to 0·5%. The results showed an interesting gradation. When no colloid was present comparatively large crystals flattened on (013) were formed. Fig. 15, plate 22, shows the product of an experiment at 50°. At 20° parallel aggregations were the usual result. The first effect of dextrine on the solution was to produce single crystals, with hardly any aggregations. These crystals were developed mainly on the (011) faces, so that in each an optic axis, which is nearly normal to such a face, was easily visible. Fig. 16, plate 22, shows an example of this type, made at 80°, with 0·25% of dextrine in solution, and containing 1·8% of absorbed colloid. A slight curvature of some of the prism edges could be seen. If the temperature of this precipitation was changed to 50°, with 0·5% dextrine, the prisms became rounded into ellipsoids slightly flattened on the (001) faces, and still showing optic axes in the normal positions (fig. 17, plate 22—absorbed colloid 2·9%). Finally, if 0·5% of dextrine were used at 20° the precipitate consisted of minute spheroids which gave straight extinction and often could be made to show an optic axis just as before. This last stage is illustrated by fig. 18, plate 22 (absorbed dextrine 6·68°). Here the spheroids are even slightly flattened on (100).

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* Miles, 'J. Chem. Soc.,' p. 2532 (1931).

† 'Trans. Faraday Soc.,' vol. 16, Appendix, p. 128 (1921).

‡ I am indebted for this photograph to Mr. W. O. Littlebury.

It is therefore possible by adjusting the amount of absorption to prepare a series of crystals which show a gradual rounding until no faces or other evidence of a preferred direction of growth can be seen, and yet they remain single individuals exhibiting at least the more important optical signs characteristic of the structure free from colloid.

These effects were found to be dependent on the acidity of the solution from which the azide was precipitated. By adding increasing amounts of hydrazoic acid the modifying action of the dextrine could be gradually suppressed. Special tests showed that the dextrine had suffered no direct change from the action of the acid. The same effects were obtained with lead chloride, but they were not so marked. It is clear that the hydrolytic dissociation in the saturated solution of the precipitated salt must have a very considerable influence on the action of the dextrine. The hydrogen ion concentration due to this hydrolysis is much greater for a saturated solution of the chloride than for one of the azide. The comparatively small amount of absorption of dextrine or gum arabic by the bromide appears in the same way to be due to the inevitably high acidity of a solution of this salt. Nevertheless, as will be seen more clearly in the next section, the hydrolysis cannot be the sole factor which controls the amount of absorption.

Finally, the action of dyestuffs of many types was examined. The majority favoured the growth of the (001) planes, and rendered the crystals extremely thin. Others gave rise to new forms of aggregation of such crystals, or to aggregations of needles, but none showed the " colloid " effect which has just been described.

7—COMPLEX CRYSTALLIZATION

The general rounding of individual crystals, which was seen to occur with lead azide and lead chloride, happened when the solubility of the crystal in the medium was comparatively high, the rate of precipitation low, and the stirring vigorous. If these conditions are departed from the growth very readily becomes complex. Often it is fibrous or spherulitic, *i.e.*, in aggregates of needles which form bundles or radiate from a common point, but have otherwise no regular orientation. In such conditions the presence of colloid does not seem to make invalid the rule that the crystallographic direction in which the needles are elongated is the same as that of fastest growth in the normal single crystal*. The prisms of lead azide shown in fig. 19, plate 22, provide an example of this. They show incipient spherulitic formation, and are fibrous at the ends, but the direction of this growth is still [100]. Nevertheless, very high concentrations of colloid in the solution seem to paralyse the normal processes of crystallization to such an extent that any regular organization is uncommon. When much colloid has been absorbed splinters of the crystals often show under the microscope an irregular and wavering extinction as the Nicols are steadily rotated. There is little of the regularity which is to be expected from simple fibrous or spherulitic growth.

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* Jansen, 'Z. Kristallog.,' vol. 85, p. 239 (1933).

PART II—THE ABSORPTION OF COLLOID FROM SOLUTION BY CRYSTALS OF LEAD AZIDE AND OTHER LEAD SALTS

For quantitative study of the absorption lead sulphate was added to the salts used previously. First of all precipitations in presence of various amounts of dextrine or gelatine were made under standard conditions, so that the relation between the amount of absorbed colloid and the concentration in solution might be traced. The microscopic examination of the precipitates is briefly described. The study of the adsorption of dextrine on preformed crystals of pure salts is then taken up, and an account is given of the results obtained with lead chloride and lead azide, and of the experimental technique which was necessary. Finally, the question whether the union between colloid and crystalloid precedes the precipitation is discussed.

8—The Absorption of Colloid during Growth

General Method

All the precipitations were made by the simultaneous addition of the reacting solutions. To ensure that the rates of addition were equal throughout the experiment, an apparatus was employed in which the two solutions were confined over mercury in two vertical tubes of the same bore, each communicating with one of the delivery jets. The mercury was caused to rise at the same rate in each tube, and thus to displace equal volumes of liquid. The reaction vessel and stirrer were the same as used in the work of Part I. The stirrer was run at 1,000 r.p.m. throughout.

A solution of pure recrystallized dry lead nitrate containing 40·0 gm in 100 cc was made. The other solution of whatever salt was required was made exactly equivalent to this. The solution of colloid was made of just twice the concentration required in the reaction liquid. For each experiment six parts by volume of water were placed in the reaction tube with an equal measure of colloid solution, and each tube of the dropping apparatus was filled with one part of a reagent and one of the colloid solution. In this way the variations in the composition of the reaction-liquid were made as small as was practicable. The time of the precipitation was 10 minutes. At the end the precipitate was at once filtered and treated in the same way as in the earlier work (Part I, §2), except that centrifuging was substituted for filtration in some cases, and that when more than 4% of colloid had been present in the reaction liquid the washing was repeated. The effect of this washing on the absorbed colloid cannot completely be defined, and it is possible that, on this account, the absolute values of the amounts of absorption are slightly in error. Later experiments show that the adsorption on the external surface is generally small in comparison with the total absorption. Washing might remove some of this outer layer, or might extract colloid from the interior of the crystal. A series of tests showed that such an error could not be great. The washing process described was repeated for a number of the precipitations, and the dextrine extracted was found polarimetrically. The loss of colloid was never more than 4% of that absorbed, and usually much less.

The solution of dextrine was usually made neutral to phenolphthalein with sodium hydroxide.

Lead Azide and Dextrine

Since lead azide is nearly always slightly basic, lead and azide ions were determined separately in the precipitates, lead, by weighing as sulphate (after repeated evaporation with nitric acid to destroy organic matter), and the azide ion by oxidation with cerium ammonium nitrate and measurement of the nitrogen evolved. The results were calculated in terms of PbN_6 and PbO, and the deficit from 100% was taken to be colloid. The relation between the concentration of colloid in the solutions and in the precipitate is shown in fig. 3 for two temperatures of precipitation.

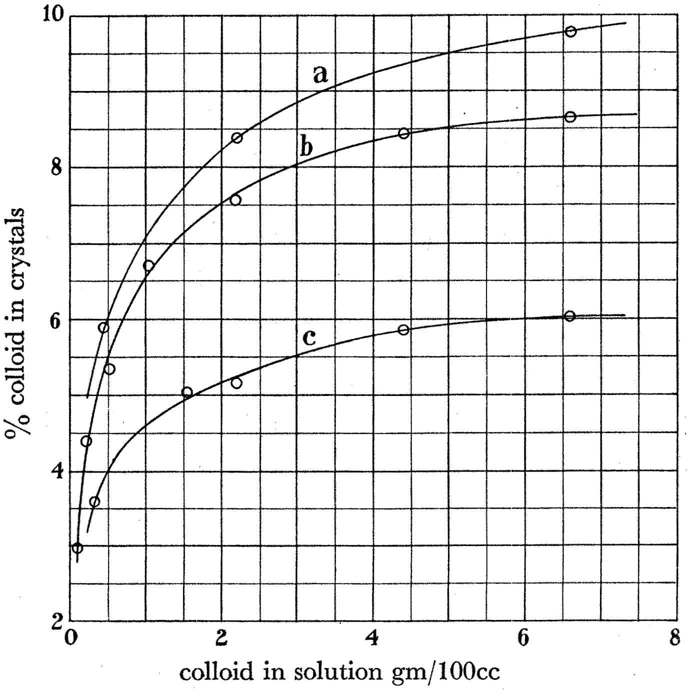

FIG. 3.—*Absorption of Dextrine by Crystals of Lead Azide*—(*a*) Neutralized dextrine at 20° ; (*b*) ordinary dextrine at 20° ; (*c*) neutralized dextrine at 60°.

It is evident that the absorption of colloid increases at first rapidly with the concentration in the reacting solution, but less and less rapidly as the concentration rises. It would be very difficult to carry out these preparations with more than 7% of colloid in solution, but the indication in each case is that a limit to the absorption would be approached at concentrations higher than this. The curve for 60° becomes almost level more rapidly than the others, and tends to a much lower limiting absorption. The data for 20° show that when the acidity of the dextrine was not neutralized the limiting absorption was more readily reached. At 60° the influence of this acidity was found to be very small, probably because the hydrolytic dissociation of the lead salt is so much more important. These differences between the several series of results are in accordance with the observation previously made that the change in crystal form which results from the absorption is partly controlled by the acidity of the reaction-solution, which in its turn must be largely dependent on the degree of hydrolysis of the salt itself.

Lead Sulphate—Dextrine and Gelatine

Lead nitrate and ammonium sulphate were used. The gelatine was Coignet's "gold label" brand. Precipitations with this colloid could not be made at 20°.

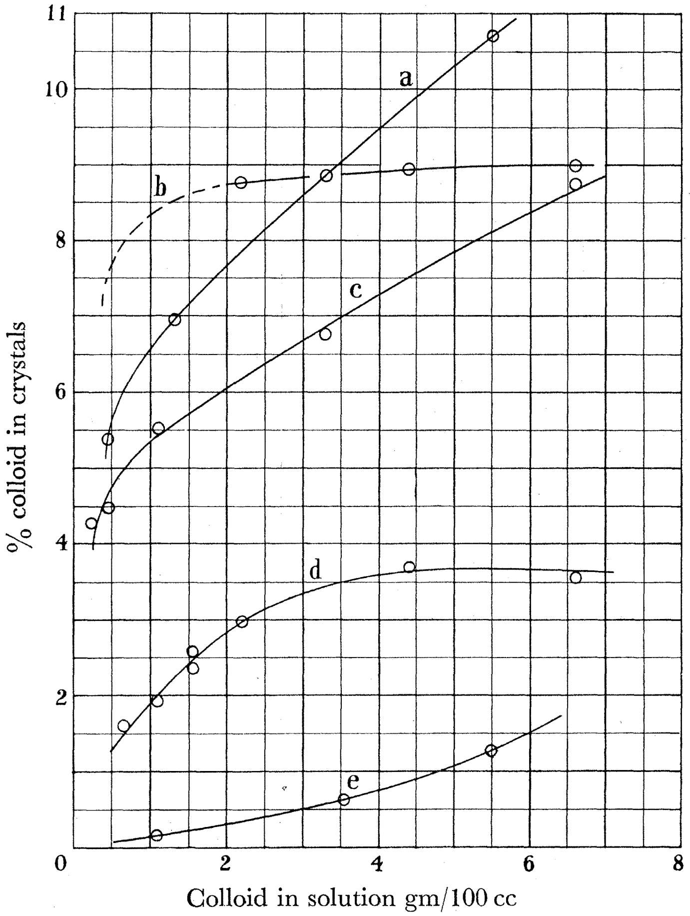

Fig. 4—*Absorption of Colloid by Crystals of Various Lead Salts*—(*a*) Lead Sulphate—neutralized dextrine at 20°; (*b*) Lead Sulphate—ordinary dextrine at 20°; (*c*) Lead Sulphate—gelatine at 60°; (*d*) Lead Chloride—neutralized dextrine at 20°; (*e*) Lead Iodide—neutralized dextrine at 20°.

The results are set out in fig. 4. The behaviour of the sulphate is as remarkable as that of the azide. As before, the effect of acidity of the dextrine is to flatten the curve and lower the absorption limit. In neutral solution the limit of absorption must be much higher.

Lead Chloride and Dextrine

Precipitations were made with lead nitrate and potassium chloride. The saturation limit in this case is more clearly marked. It is about 3·7% of the weight of the crystals. The whole curve is, in fact, almost coincident with that representing a previous set of experiments in which the lead chloride was allowed to crystallize out slowly from a saturated hot solution as it cooled (fig. 1), and the saturation value is practically the same as that given by the other very different method (3·6%).

Lead Iodide

The absorption of dextrine by lead iodide during its growth is much less than for any of the other salts, and the curve—fig. 4—is nearly straight. It has already been noticed that dextrine, as well as other colloids, has little power to affect the crystallization of this compound.

The Absorptive Power of Crystals of Lead Salts

The data of this section show that the absorptive powers of crystals of lead salts may be very high, but that there are remarkable differences between them. The acidity of the reaction-solution influences the absorption during growth, but that it is insufficient entirely to account for the differences can readily be seen. The p_H values of the saturated solutions of the several salts were estimated by means of mixed indicators and the buffer solutions of McIlvaine*, standardized against the hydrogen electrode. Writing down the salts in the order of their absorptive powers we have the following: lead azide and sulphate (the absorptions of which at 20° are almost equal)—p_H 3·6 and 5·75 respectively; lead chloride—p_H 3·85 (calculation from the hydrolysis data of Wood† gives about 4·0); lead iodide—p_H 3·5.

It will be seen later that there is little chance of finding the explanation of these differences in any property which is manifest in solution. The reasons are more likely to lie in special features of the crystalline structures. The structure of the sulphate resembles, on the whole, the normal co-ordinated type in which each lead atom is surrounded by a number of opposite ions, each of which is evenly surrounded by lead atoms in the same way. The iodide is of the quite different layer lattice type ‡ having the lead and iodine atoms arranged so that the whole crystal could be divided into electrically neutral sheets containing the two elements in equivalent proportions. The other halides of lead have also been investigated, and their structures have been compared by Bijvoet and Verweel§, who have shown that the chloride and bromide structures are intermediate in type between that of the iodide and the purely co-ordinated structure of the fluoride.

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* 'J. Biol. Chem.,' vol. 49, p. 183 (1921).
† 'J. Chem. Soc.,' p. 888 (1910).
‡ Van Arkel, 'Rec. trav. chim.,' Neerland, 45, 437 (1926).
§ 'Rec. trav. chim.,' Neerland, 51, 605 (1932).

Since the iodide ion is strongly polarized by the lead ion, the result is to decrease the field external to the crystal and reduce the absorptive power. The bromide and chloride, as has been seen, are intermediate instances. In lead sulphate the structure necessitates little polarization, and the external field is stronger. These four compounds can be arranged in the same order with respect to the absorption data of this section. The inference may therefore be made that the absorptive power for colloid is depressed as the polarization of the ions increases. The structure of lead azide is not known in detail, but from its optical properties and lack of a definite cleavage, it can be seen not to belong to the simple layer-lattice type.

Microscopic Features of the Preparations

Beginning with the series of azides made at 20°, it was found that with 3% of adsorbed dextrine almost all the crystals were single, tending to be fibrous at the ends. The optic axes were easily found in their normal positions, and the extinction of each crystal was fairly complete. Average length, 0·014 mm. With 4·4% they were still nearly all individuals, although extinguishing less clearly than before. Their outline was rounded and tended to be oval. After increase to 5·35% the majority were still individuals, many of them with quite straight extinction, but crystals of elliptical outline showing complex extinction effects had become more common. Average length 0·007 mm. At 6·7% there were spherical and lenticular outlines, and although the formation was not spherulitic, it was certainly composite. If even more dextrine was incorporated the confusion of structure was increased. The series prepared at 60° showed very nearly the same degree of complexity for the same dextrine percentages.

From these observations the conclusion may be drawn that an amount of dextrine varying, according to the conditions, between 4% and 5% of the weight of azide can be taken up before the crystal ceases to be single and continuous—the word "continuous" meaning that it has grown without any interruption of the structure which can be detected polariscopically, and has preserved the original directions of its axes.

With lead sulphate (20°) the limiting concentration of dextrine seemed to be about the same. The crystals were very much smaller, but the great majority were nevertheless rectangular single prisms. Gelatine gave a different effect, for with only 4·2% the tough, horny, dried preparation consisted entirely of spherical particles of about 0·001 mm in diameter and quite devoid of any sign of structure. The maximum absorption by lead chloride had been found to be lower than in the others, and it is interesting to observe that the tolerance of colloid by the single crystals appeared to be lower also. It is about 3%. Above this complete spherulites appear.

As TRAUBE and BEHREN* have shown with mercuric chloride and some other substances, certain crystals when dissolved rapidly may give off numerous smaller particles which are often ultra-microscopic. By observing the extent of disintegration it should be possible to form an idea of the relative homogeneity of various types of

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* 'Z. phys. Chem.,' vol. 138, p. 85 (1928).

crystal. A Leitz dark-ground condenser and a 100 c.p. Pointolite lamp were used. The slides and cover clips were carefully cleaned with acid bichromate and kept under water. Well-formed small single crystals of the pure azide dissolved in 1% nitric acid with no sign of fission, but any containing more than about 1½% of dextrine gave off numerous small fragments as it dissolved. When 3% of dextrine was present these pieces were very numerous. With 5% they were more so ; the whole crystal was surrounded for a short time during the action of the acid by a cloud of rapidly dissolving crystallites, most of them clearly acicular and all in violent Brownian motion, brilliant against the darkness of the background. Since the crystals containing 3% of dextrine were continuous in the sense mentioned above, these observations provide ground for the belief that even in an apparently individual crystal containing dextrine, the discontinuities which are known nearly always to be present must be greater in extent than when no colloid is embodied.

9—Adsorption of Dextrine by Preformed Crystals

Methods of estimating Adsorption of Dextrine

Lead azide and lead chloride were selected for these experiments, the second because it can be obtained in crystals of easily measurable size.

To be able to estimate a slight amount of adsorption from solution some accurate method of determining the concentration of the adsorbed substance must be found. For colourless colloid substances most of the usual methods of analysis are of little use and the most practicable means is the interferometer. Even this cannot be used when the adsorbent is appreciably soluble. It is fortunate that dextrine, the most important colloid for our purpose, has a very high optical rotation, and can therefore be determined accurately by means of this property.

The polarimeter was a Hilger instrument (M5) and the illuminant a mercury arc placed close to the end of the polarimeter without any intermediate apparatus other than a piece of plate glass. Readings could be taken for the green line (5461 A.) to 0·005°. The rotation of a 1% solution of the standard dextrine in a 2 dm tube was 4·48°, so that, for this concentration, the precision was about 1 in 800. Certain preliminary tests were first made. Between 18° and 27° C the rotation of a 1% solution was found to increase by only 0·057% for 1° C. Variations of a few degrees could safely be neglected. Dissolved lead salts were proved to have no effect, for a solution containing 1 gm of dextrine and 1·5 gm lead nitrate in 100 cc, or one containing 0·5 gm dextrine and 20 gm of lead acetate, had the rotation to be expected if no lead salt were present.

Preliminary trials had shown that crystalline lead azide or chloride could, in fact, adsorb optically active material from a dextrine solution, but ordinary dextrine is a complex mixture, and there was no certainty that the small fraction adsorbed in this way was of the same nature as the much larger quantity taken up when the crystals are formed and grow in a dextrine solution. Two precipitations were therefore made by a method very similar to that of §8, and the absorption from the solution found polarimetrically was compared with the absorption into the crystal found by analysis. The effective concentrations of dextrine in the reaction-liquid in the two cases were 2·30% and 044·%. In the first case the loss of rotation in the solution was found to be 80%, in the second 73% of what might be expected from the analysis. It may be said that what is absorbed during growth has, for the most part, but not entirely, the same rotation as the average of what is in solution.

Experimental

Lead azide was prepared by the method of simultaneous addition as usual, the colloid being omitted. The precipitate was always slightly basic, and to make it less so, the reaction liquid was made 0·01 N with hydrazoic acid. More basic material is formed at higher temperatures, but even at 20° with acid present some is produced, as the following analyses show :—

No. 1. . . . Temp. 50° $P_bN_6 = 99{\cdot}37$ $PbO = 0{\cdot}73$
$= 99{\cdot}33$ $PbO = 0{\cdot}82$
No. 2. . . Temp. 20° $P_bN_6 = 99{\cdot}55$ $PbO = 0{\cdot}50$
$= 99{\cdot}43$ $PbO = 0{\cdot}51$

The lead chloride and iodide had been twice recrystallized from water. The method of determining the adsorption was usually the following : a weighed quantity of the pure dry salt, from 5 to 7·5 gm of the azide or about 25 gm of the chloride, was placed in a glass tube sealed at one end. Dextrine solution just sufficient in volume to allow the required test to be made was then added. The tube was closed with a specially cleaned rubber stopper, and was packed with corks and rubber bands into a wider tube which in turn was closed with a rubber cork. The outer tube was placed in a wheel thermostat, usually at 30°, and rotated for 24 hours. The solution was then filtered from the precipitate with precautions against evaporation, and its rotation was taken, the rotation of some of the solution originally poured into the tube being taken at the same time. Sometimes it was of advantage to remove on the centrifugal a little very finely divided salt which failed to settle.

Adsorption on Lead Azide

The adsorption took place very rapidly. In several experiments both the azide and chloride were shaken with 1% dextrine solution, and the liquid filtered off within one minute. By this time the adsorption was complete, for no change in the rotation greater than the experimental error took place as the tubes revolved in the wheel thermostat. Even after three weeks, the concentration of dextrine had not changed. What is usually known as the " internal surface " cannot therefore take part. That the system was in a state of real equilibrium between the surface and at least the greater part of the optically active matter in solution was seen to be very probable from the results of certain tests in which, after 24 hours or more, the solution was poured off and replaced by another of the same (final) rotation. There was no considerable change in the rotation of this second solution after shaking with the solid as there should have been if the adsorbed substance were some small but very active fraction of the dextrine.

Duplicate results with the same preparation agreed to 10% or less, but there were much greater differences, evidently dependent mainly on grain size, between one sample and another. For all the preparations in Table III the initial dextrine concentration was about 0·9% of the solution. No. 1 showed under the microscope a coarser grain than the others.

Table III

Preparation No.	Azide gm	Dextrine solution cc	Fall in rotation (1 dm tube)	Equilm. concn. of dextrine, from rotation	Adsorption % wt. of azide
1	4	20	0·030/2·030	0·89	0·067
2	6·25	25	0·075/2·030	0·87	0·134
2*a*	6·25	25	0·080/2·030	0·87	0·142
3	5·0	15	0·103/1·905	0·81	0·141

The effect of variation on the dextrine concentration was examined. As a rule it was advisable to make, in one batch, no more azide than sufficed for two or three experiments, so that a complete series of results cannot be given for the same sample.

Table IV

Preparation No.	Azide gm	Dextrine solution cc	Fall in rotation (1 dm tube)	Equilm. concn. of dextrine, from rotation	Adsorption % wt. of azide
3*a*	4·5	55	0·0275/0·4625	0·20	0·151
2	5	35	0·035/0·9775	0·42	0·110
2	6·25	25	0·075/2·030	0·87	0·134
3*a*	4·5	17·5	0·100/4·950	2·17	0·174

Evidently the adsorption rises only slowly as the concentration of colloid is increased, in the range throughout which the polarimetric estimation is sufficiently exact. It shows therefore the principal characteristic of a surface phenomenon.

When the crystals were single and fairly regular in shape it was possible to make very rough estimates of the external surface by measuring a large number under a microscope fitted with a net micrometer eye-piece. Two measurements at right angles were made for each crystal, and the average values were used to calculate the volume on the assumption that the crystal was a cylinder. The three preparations used for the experiments and another (No. 6) which had the unusually low adsorption of 0·035% in 2·5% solution, were found to have surface areas of 1·6, 2·6, 0·9 and 0·72 $\times 10^3$ cm^2 per gram (Nos. 1, 2, 3*a* and 6, respectively). Dividing these figures in each case by the observed adsorption per gram, the areas accommodating 1 gram of dextrine appear to be 2·5, 2·0, 0·51 and 2·1 $\times 10^6$ cm^2 for the four in the same order.

The low value for No. 3*a* should, perhaps, be rejected because the crystals of this preparation were by no means quite uniform or all single, so that the measurement was very uncertain.

When the temperature of investigation was raised from 30° to 60°, efficient precautions against evaporation being taken, there was still a measurable adsorption, but the results were discordant ; on the average, the figures were about one half of those obtained at 30°.

Adsorption on Lead Chloride

The work with lead chloride was carried out in just the same way as that with the azide, except that as there was no danger more solid could be used, and a more favourable ratio of solid to liquid was therefore possible.

A correction of 0·33% was added to the final rotation of the dextrine solution at 20°, the temperature of measurement, to compensate for its increase of volume due to solution of the lead chloride. Two preparations of the salt were used, differing strangely in habit. The first was nodular and rounded, the second was quite tabular and larger in average size.

Preliminary trials which were carried out as with the azide, proved that the adsorption was complete in one minute, and had not increased after several days at 30°. Replacing the dextrine solution by a fresh one of the equilibrium concentration, made, as before, no appreciable difference.

Comparison of the behaviour of the two varieties of chloride in solutions containing about 0·9 gm of dextrine per 100 cc gave the figures shown in Table V

Table V

Preparation	Chloride gm	Dextrine solution cc	Fall in rotation (corrected) (1 dm tube)	Equilm. concn. of dextrine, from rotation	Adsorption % wt. of chloride
Nodular	50	75	0·059/1·980	0·86	0·039
Tabular	50	50	0·033/2·030	0·89	0·015

For the nodular variety the adsorption was found in three different concentrations :—

Table VI

Chloride gm	Dextrine solution. cc	Fall in rotation (corrected) (1 dm tube)	Equilm. concn. of dextrine, from rotation	Adsorption % wt. of chloride
50	50	0·136/1·955	0·44	0·031
50	75	0·059/2·030	0·88	0·039
50	50	0·105/4·740	2·07	0·045

The increase with rising concentration is again very slow.

At the higher temperature of 60° lead chloride differed from the azide in showing no measurable adsorption. This observation is in accordance with the fact already known that crystals of the chloride formed at higher temperatures take up very little dextrine from the solution during growth.

Advantage was taken of the tabular form of the second preparation to make a direct estimation of area more precisely than had previously been possible. The preparation consisted of flat oblong plates of varying lengths up to 1·3 mm, generally with square ends. About 1 mg was weighed out on an assay balance, and the basal area of each crystal was measured with a net micrometer. From the sum of these areas, the weight and the density, the area of the sides could be found, assuming the shape to be that of a flat prism on a square base. Three estimations of the total superficial area, each carried out with from 100 to 200 crystals, agreed within 30%. In all 375 crystals were measured, weighing 2·85 mg. The average area per gram was 162 cm². From this figure and that of 0·014% adsorption in 1% solution, unit weight of adsorbed dextrine is seen to take up $1 \cdot 15 \times 10^5$ cm², an area rather less than on lead azide, but of the same order. No adsorption of dextrine on lead iodide could be detected.

Dialysed Dextrine

Azide.—The dextrine used up to this point contained about 0·10% of hydrochloric acid, sugars, and small amounts of other impurities. The latter had been made neutral to phenolphthalein but were not necessarily without effect on the adsorption. Some control experiments with dextrine from which these impurities had been removed by dialysis were thought to be desirable. The dialysis was carried out at 80° by a modification of the method of NEIDLE.[*] A sac formed by wrapping a disc of cellophane sheet round one end of a short glass tube, 2 inches in diameter, was immersed in a 2·5% solution of the standard dextrine, and distilled water was run into and removed from the inside of the sac by means of an automatic flush arrangement and a siphon.

To remove all dialysable material from 500 cc of solution about 36 hours' extraction at 80° C were necessary. None of the hydrochloric acid present in the original material could be detected in the dialysed product. The specific rotation of the original material, dried at 90°—$[\alpha]^{5461}_{20^\circ}$—was 224°, in 1% solution. During the dialysis this rose to 229·0°, and could not be increased further. The purified dextrine left 0·10% of ash on ignition. The p_H of a 1% solution was 5·9. The electrical conductivity of the solution (given later) was found to be very low.

For the estimation of adsorption an azide preparation (No. 4), having the same apparent grain-size as No. 2, was taken. The estimations were carried out by the methods already described. The adsorptions were found to be 0·10%, 0·13%, and 0·115% in equilibrium dextrine concentrations of 0·24, 0·96, and 2·47% respectively, so that the previous adsorption results obtained with undialysed material are generally confirmed.

Since an estimate of the molecular weight of the standard dextrine was very desirable, the osmotic pressure of a dilute solution of the dialysed material was

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[*] 'J. Amer. Chem. Soc.,' vol. 38, p. 1270 (1916).

measured. The method used was mainly that described by ROBINSON and MILLS,[*] omitting the special precautions which these authors took to guard against carbon dioxide. The sacs were made of nitro-cotton, and were filled with a solution of 0·5% of dextrine in boiled-out water. The capillary tubes, with the sacs depending from them, were immersed in distilled water in glass cylinders, surrounded with water in a thermostat at 20°. The rise of the solution in the tubes had ended in 48 hours and was (after correction for capillary ascent) in two experiments: (*a*) 4·13 cm and (*b*) 4·18 cm. Taking 4·16 as the mean rise and 0·0821 for the value of R in litre-atmospheres, we have $M = (5 \cdot 0 \times 0 \cdot 0821 \times 293 \times 76 \times 13 \cdot 55)/4 \cdot 16 = 29{,}800$.

In order to give a reliable value of the molecular weight, the osmotic pressure of colloids of this type should be measured at very great dilution. As the concentration increases the pressure rises increasingly fast. BILTZ[†] determined the molecular weight of many samples of dextrine by the osmotic pressure method. Only two of his samples had a molecular weight approaching that of this one, but from his figures it appears that the estimate of 29,800 is not likely to be more than 2000 greater than the value which would result by extrapolation to infinite dilution.

Dialysed Maltose

Although it had been found previously that glucose and cane sugar had no appreciable effect on the habit of crystals of lead azide or chloride, there was nevertheless no certain evidence that a sugar, in particular the maltose which is always present in crude dextrine, could not be adsorbed. The determinations described in this section might therefore be in error. A 10% solution of Merck's ordinary maltose was placed inside the cellophane cell of the dialysis apparatus so that the sugar diffused outwards, the dextrine and brown colouring matter being retained. Maltose was obtained in yield equal to 60% of the crude starting material in about 24 hours. The specific rotation of the pure material for green light (5461) was found to be 162·0°. The value given by BROWN and MORRIS (LANDOLT and BÖRNSTEIN) for pure maltose is 138·0° for sodium light (5893), corresponding to 160·7° for light of wave-length 5461.

This pure maltose was tested as the dextrine had been. It showed no measurable adsorption.

10—THE CONSTITUTION OF SOLUTIONS OF LEAD SALTS AND DEXTRINE

When such a colloid as dextrine is present in a saturated solution of one of the lead salts chosen for this work, the intrinsic velocity of crystallization at every face is reduced, and the super-saturation of the solution is raised far more than is possible in the absence of colloid. But it is natural to ask whether a super-saturated solution

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[*] 'Proc. Roy. Soc.,' A., vol. 131, p. 596 (1931).

[†] 'Zeit. phys. Chem.,' vol. 83, p. 683 (1913).

of lead azide, for instance, has been entirely prevented from depositing solid or whether there could be found in the solution minute invisible crystallites, the further growth of which has been inhibited. There is also the possibility that the salt and the colloid are already associated in the solution, so that when crystallization occurs a preformed complex of the two is at least part of what is thrown down. If this were so, the activity of the lead ion, or perhaps that of its partner, should be changed when colloid is added to the solution. Both these points were taken up.

Ultramicroscopic Examination

It was found by trial that if 0·5% of dextrine were present no lead chloride was deposited for many hours from an equivalent mixture of lead nitrate and potassium chloride solutions when the super-saturation was 100% of the normal solubility (1·0 gm/100 cc at 20°). With 2% of dextrine a super-saturation of 150% could be maintained. Both solutions were examined in the slit ultra-microscope, and were compared with others containing only the same proportion of dextrine. The first appeared to contain no more visible particles than the dextrine solution and the second was distinguishable from it only by a slight increase in the bluish background which can never be resolved into separate points of illumination.

This result was not surprising for Bolam and Donaldson[*] have shown that gelatine, which greatly delays the precipitation of silver chromate, has the effect of preventing the formation of nuclei. At least the larger part of the chromate is present in the super-saturated solution as silver and chromate ion of greatly increased activity. The case of lead iodide and agar-agar has been investigated by Bolam.[†] Here also he came to the conclusion that no colloidal solid salt is present. The super-saturation in this instance may be 300%.

The Conductivities of Solutions of Lead Salts and Dextrine

The conductivities of certain unsaturated solutions of lead nitrate, lead chloride, and dextrine were measured at 25° ± ·01 in a pipette cell made of Pyrex glass. A calibrated metre bridge was used. The lead compounds had been subjected to two recrystallizations additional to those already given. The dialysed dextrine referred to above was made into 2% solution and pipetted off as required. The results (corrected for the conductivity of the water—$3 \cdot 0 \times 10^{-6}$ r.o.—) are given in Table VII.

The equivalent conductivities of the pure salts given in the last column agree to less than 1% with published values. The last column but one records the sum of the conductivities which would have been found if the salt and the dextrine had each been present alone. The conductivity of the mixture is always lower than this sum, but

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[*] 'Trans. Faraday Soc.,' vol. 29, p. 864 (1933).

[†] 'Trans. Faraday Soc.,' vol. 26, p. 133 (1930).

only by 1% when 0·4% of dextrine was present, and by 2% in the single case when 0·8% was used. Potassium chloride also shows a depression of 1%. The conductivity of the dextrine is remarkably low for an organic colloid—an indication of the effectiveness of the dialysis. There can be no question, therefore, of any significant change in the activity of either the lead or the negative ion, and any hypothesis of association in solution between the lead salt and the colloid must be excluded.

TABLE VII—SPECIFIC CONDUCTIVITIES OF LEAD NITRATE AND OTHER SOLUTIONS WITH AND WITHOUT DEXTRINE

Solution		κ solution × 10³	κ salt solution + κ dextrine solution × 10³	Equivalent conductivity K/η
Dextrine	0·44%	0·007	—	—
„	0·80%	0·014	—	—
Lead nitrate 0·01 N		1·211	—	121·1
„ „ + dextrine	0·40%	1·205	1·218	—
„ 0·02 N		2·268	—	113·4
„ „ + dextrine	0·40%	2·252	2·275	—
„ 0·05 N		5·087	—	101·7
„ „ + dextrine	0·40%	5·049	5·094	—
„ „ + dextrine	0·80%	4·998	5·101	—
Lead chloride 0·0217 N		2·310	—	106·5
„ „ + dextrine	0·40%	2·281	2·317	—
Potassium chloride 0·02 N		2·768	—	—
„ „ + dextrine	0·40%	2·754	2·775	—

In his studies of the delayed precipitation of silver chromate and lead iodide, BOLAM has obtained numerous data in relation to the activity of the ions both by conductivity and electrometric methods. Although in a super-saturated solution of one of these salts the excess is, for the most part, present as free ions, it cannot all be accounted for in this way, and he has inferred that the gelatine combines with both the chromate and the silver ion, because there is a considerable depression of the conductivity when gelatine is added to either reagent solution. BOLAM* and BOLAM and MACKENZIE† found that the conductivities of lead nitrate (0·0126N), potassium chromate (0·01N), and potassium iodide (0·010N) were depressed by 17·2%, 11·2%, and 5·5% respectively when the solutions contained about 1% of agar-agar or gelatine. It is to be remembered, however, that the gelatine and agar used by BOLAM had a far higher conductivity than the dialysed dextrine, and impurity may have been responsible for some of the depression of the activity, without necessarily playing an essential role in the delay of the crystallization.

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* 'Trans. Faraday Soc.,' vol. 24, p. 467 (1928).

† 'Trans. Faraday Soc.,' vol. 22, p. 173 (1926).

PART III—THE X-RAY EXAMINATION OF THE CRYSTALLINE COMPLEXES OF LEAD AZIDE AND SULPHATE WITH COLLOID

Since the proportion of amorphous material can be so high—10% or more by weight—and because the crystalline structure in the earlier stages is not greatly affected, it is essential to try to form an idea of the influence of the introduction of colloid on the subdivision of the crystal or, as it may be expressed, to estimate the particle-size. In spite of the many difficulties both of theory and experiment which such work still involves, X-ray methods remain the only means of doing this. The determination depends on the broadening of the diffraction lines which occurs when the dimensions of the individual crystals of the substance fall below a limit which is generally taken to be about 1×10^{-5} cm. Since lead azide and lead sulphate show the highest degree of absorption, the complexes of these two salts with dextrine, and also of the latter with gelatine, were chosen for investigation.

There is one important point which must be borne in mind. The proper subjects for particle size-measurement by X-rays are powders in which each grain is a separate crystal. This is assumed in the derivation of the formulae in use, but the crystals of the complexes to be examined are by no means all random aggregates of smaller grains ; some of them seem to be individual crystals of microscopic size. In such cases the particle sizes based on the X-ray results must be accepted with reserve, for sometimes the correspondence of each crystallite with its neighbour may be so exact as to make the line-broadening less than it would be for a quite random arrangement of the same crystalline elements. The line-broadening is thus to be regarded as a general expression of the degree in which the crystal is heterogeneous, and the particle width calculated from it as the superior limit of the real width. This difficulty will be referred to later ; for the present it will be convenient to express the results formally in terms of particle-size in the usual way as for a powder.

For orthorhombic substances, especially for one with so large a unit cell as that of lead azide, the determination requires specialized methods, which will be discussed first.

11—The X-Ray Estimation of Particle-Size

Methods

Apart from the well-known equation of Scherrer, which is valid only for cubic substances of negligible absorption, the only basis for the determination of particle-size from the breadth of diffraction lines is the more complete mathematical work of von Laue.* He assumed that the particles were uniform in size and oriented entirely at random, and that there was no lattice distortion.† As in the method of

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* 'Z. Kristallog.,' vol. 64, p. 115 (1926).

† The possibilities of lattice irregularity are not well known, but cannot be excluded altogether. Broadly speaking, size-determination should be more affected by variation of lattice constant from one particle to another than by random *distortion*. There seems no reason to expect such variation in these ionic crystals, particularly for the larger crystalline units.

Scherrer, the substance is made into a pillar which is set up coaxial with the cylindrical camera, but the radiation is supposed to come from a point-source on the cylindrical surface, *i.e.*, to be completely divergent, instead of parallel as Scherrer assumed it to be. The equations derived by von Laue involve a quantity η which for an orthorhombic crystal has the value

$$\frac{\lambda}{4\pi}\sqrt{\frac{\left(\frac{h}{m_1a^2}\right)^2+\left(\frac{k}{m_2b^2}\right)^2+\left(\frac{l}{m_3c^2}\right)^2}{\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2}}, \tag{1}$$

m_1, m_2, and m_3 being the three dimensions of the average particle, in terms of the three cell dimensions, a, b, and c. Since η depends on these numbers it is possible, by comparing different planes, to form an idea of the shape as well as the size of the particles. If two indices are zero (k and l for instance) η has the value

$$\frac{\lambda}{4\pi m_1 a}. \tag{2}$$

On the basis of von Laue's investigation, Brill and Pelzer have made several calculations. For the present purpose, one of their papers is particularly important,* since in it is described a method for substances of medium or of high absorption. The substance is coated on the outside of a pillar of lead glass, or, if its absorption is high, is itself made into a pillar. Diffraction is assumed to take place only from a thin surface layer. The linear breadth of the line (B) is connected with the quantity η by a very complicated equation, which involves the angle 2θ between the primary and the diffracted ray (θ is the glancing angle in the Bragg equation $\lambda = 2d \sin \theta$), the radius R of the cylindrical camera, and the radius r of the cylindrical pillar of substance under examination (*see* fig. 6A). Some calculations, to be referred to later, were made with this equation, but usually when the line-broadening is moderately great there is little need to use it, since Brill has given a set of curves connecting 2θ and B/r for various values of η R/r (*loc. cit.*, p. 149). His method has been followed, since it is best adapted to deal with very highly absorbent material.

The Photometric Measurement of Line-Breadth

A careful calibration of Agfa-Laue film for long exposures to very weak monochromatic radiation showed that the intensity of the radiation (time of exposure being constant) might be taken without serious error as proportional to the density of blackening indicated by the Moll photometer, from a density of 1·0 to the lowest measurable value.† The density D is equal to $\log_{10} I_0/I$, I_0 and I being the intensities of light from a constant source which passes through unexposed and exposed film respectively, and, since the deflection of the galvanometer of the Moll instrument can

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* Brill and Pelzer, 'Z. Kristallog.,' vol. 74, p. 147 (1930).

† Miles, 'Trans. Faraday Soc.' vol. 31, p. 1452 (1935).

be made accurately proportional to the light falling on the thermopile, it is also equal to $\log_{10} d_0/d$, d_0 and d being the deflections under the same conditions as before.

In the mathematical derivation of particle-size formulae, the line-breadth is nearly always defined as the quotient of the integrated X-ray intensity by the maximum intensity. The linear breadth may therefore be written—

$$B = \frac{1}{D_{\max}} \int D\,dx, \tag{3}$$

D being the density (above that of the background) and x the lateral distance, reckoned in the scale of the film. This definition has rarely been accepted in practice, because it involves the troublesome conversion of the photometer record of each separate line into a density curve, the ordinates of which are the values of $\log_{10} d_0/d$ instead of the original deflections, and then integrating each curve, but it avoids some uncertain corrections and gives breadths more independent of the shapes of the intensity curves than those obtained by the more usual method of measuring the "half intensity width," which are generally smaller. The breadth defined by (3) has therefore been adopted.

The integration can be carried out on the photometer record, without replotting the photometer traces to represent density, by a simple method which is accurate enough for the purpose. The principle is that the area between the traces of a diffraction line and of the background can be integrated directly in terms of density if it is divided into narrow horizontal strips, the heights of which are different, but all correspond to the same increment of density. A rectangular piece of celluloid is ruled with horizontal lines spaced to an antilogarithmic scale and such that the reading y cm from the lower edge is $\log_{10} y$. This sheet is placed over the photometer chart with its lower edge against a straight-edge marking the line of no galvanometer deflection, which is taken as zero line. By means of a stylus it can be made to traverse in succession all the strips into which the horizontal lines divide the area to be integrated. Some slight direct estimation of area which is necessary where the summit of a trace does not coincide with a line on the sheet is made easy by vertical lines ruled on the sheet 1 mm apart. The total distance of traverse, multiplied by the density value of the scale interval and divided by the magnification of the photometer, gives the integrated density A in terms of D × mm of film. The breadth is then $A/(D_{\text{peak}} - D_{\text{background}})$.

Effect of Size of the Aperture

In VON LAUE's calculation, and in those made by BRILL, it has been assumed that the pinhole is very small. VON LAUE (*loc. cit.*, p. 314) worked out the condition that the distribution of intensity in the line should not be affected by the size of the hole, but, as CAMERON* has pointed out, with a camera of 10 cm diameter and the smallest practicable pinhole of 0·25 mm diameter, the particles to be measured must

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* 'Physics,' vol. 3, p. 57 (1932).

not be wider than 60A, if the degree of error which VON LAUE allowed for is not to be exceeded. This difficulty is a very serious limitation of the whole method, and has been given little consideration, possibly because at large angles, when cos θ is small, the limit of measurable size is greatly extended. In this work, only lines at small angles could be used, and there was urgent need for some method, even a rough one, of estimating from the measured breadth of the line the breadth which it would have had if the pinhole had been very small.

To do this, it is necessary to adopt some equation which will express the form of the intensity curve of the line due to an infinitely fine pinhole, and then to calculate the effect of giving the pinhole a finite diameter. To represent the form of the elementary line, there are, besides the very unsatisfactory approximation by two straight lines, two types of expression—the error function and an equation of the inverse parabolic type. The equation $I = I_{max}/(1 + b^2x^2)$ reproduces quite well the observed shapes of lines from fine apertures, and is much more manageable than the error function. I_{max} is the height of the peak above the background. The total area under the curve is $\pi\ I_{max}/b$, and the breadth in linear measure, according to the definition of equation (3) is π/b. b is a measure of the rate of falling off from the peak value.

Radiation passes through the pinhole and falls on a vertical cylindrical pillar of the substance, coaxial with the camera. If we consider a thin vertical strip of the area of the pinhole, it is evident that the Debye circles produced by each small element of this strip will, for the most part, reinforce each other near to the equatorial plane in which the measurement is made, producing a more intense line but not appreciably increasing its breadth. Since the aperture is at the same distance from the specimen as is the film, each strip, distant x from the pinhole centre, will give rise to a line on the film at the same distance x from the centre of the whole composite line. We require the height of the intensity curve of the composite line.

Let α be the radiation transmitted by unit area of cross-section of aperture. The central vertical strip of width dx will transmit intensity equal to $2\alpha\ s\ dx$, s being the radius of the pinhole. If the intensity curve of the line produced by this slit has the assumed form, and b is the parameter of the curve, the width is π/b by definition, and the height must therefore be

$$2\frac{b}{\pi}\alpha s dx.$$

To find the height of the composite curve, the contributions from every other strip at any distance x from the centre of the aperture must be added. The sum of all these will be, as may be seen from fig. 5, the same as may be obtained by integrating over the intensity curve of the line formed by the central strip from $x = -s$ to $x = +s$, if for every element, distant x from the centre, $\sqrt{s^2 - x^2}$ is written instead of s. The total height will then be

$$H = 4\alpha\frac{b}{\pi}\int_0^s \frac{\sqrt{s^2 - x^2}}{1 + b^2x^2}\,dx,$$

which gives on reduction

$$H = \frac{2\alpha\sqrt{b^2s^2+1}-1}{b},$$

but the total intensity passing the aperture is $\pi\alpha s^2$, so that dividing by H, the width of the composite line is by definition.

$$B = \frac{\pi s^2 b}{2\sqrt{b^2s^2+1}-1} \qquad (4)$$

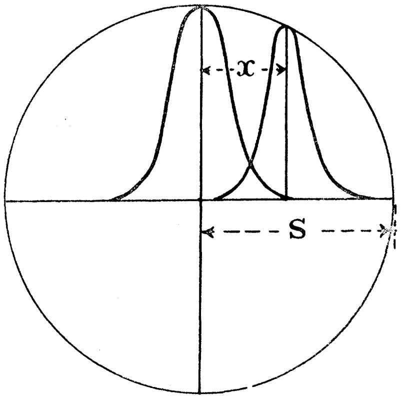

FIG. 5.

Since the width of the line, if the aperture were a point, would be $\beta = \pi/b$, equation (4) enables us to connect the ideal width β with the determined breadth B. A graph connecting B and β was therefore drawn, s having the value of the radius of the pinhole used (0·1315 mm).

The corrections worked out by BRILL* for the slope of the background and for the superposition of the α_1 and α_2 elements of radiation were not applied, because the definition of breadth and the absence of asymmetry from the photometer traces of lines made them unnecessary.

12—ESTIMATION OF THE CRYSTALLITE SIZE OF LEAD AZIDE AND SULPHATE, PURE AND CONTAINING COLLOID

Materials and Method

The complexes which were examined were those described in Part II, Section 8. Pure azide and sulphate were obtained for comparison in crystals about one millimetre in length, by slow crystallization of the first from sodium acetate solution† and of the second from sulphuric acid.

The essential features of the apparatus are shown in fig. 6. A camera (radius = 2·98 cm) was arranged to comply with the Laue conditions. The aperture was formed by two conical holes made from both sides of a lead plate, so that the narrow ends of the holes met exactly on the inside surface of the camera in a circle of 0·263 mm diameter. Copper α radiation was produced in a gas-tube of special design, of which the earthed anticathode head, turned from a solid block of stainless steel, is shown in the figure. The tube was operated at a constant voltage of 50 kV., RMS, by automatic control of the gas-pressure. The radiation was freed from the beta constituent on passing through the window of nickel foil (0·009 mm).

The materials were finely ground in an agate mortar (the azides under oil). The powder was made into a very stiff paste with a 2% solution of nitro-cellulose in a

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* 'Z. Kristallog.,' vol. 68, p. 387 (1928).

† MILES, 'J. Chem. Soc.,' p. 2532 (1931).

solvent of medium volatility, and was then formed into rods about 6 mm long with a small screw-press. The diameter of the rods, measured when they had dried, was 0·526 mm.

The background-density of the diagrams obtained for all the lead compounds was very high. It was found of advantage to make the front of the film envelope of thin metal foil (0·009 mm). Even then the background of a line, for which θ was less than about 15°, was too high for photometry.

The lines on the film were identified with the aid of the published data for lead azide* and sulphate†, and of a set of oscillation diagrams made for the former crystal for another purpose, the observed separation distance of each line being reduced by the proper correction ($4r \cos^2\theta$) for an impervious pillar of radius r. In such cases as this the number of lines is very great, and there is a risk that even at moderate angles adjacent lines given by one of the complexes may overlap. To avoid this difficulty, and to use that part of the film where the background was least, it was found necessary to sacrifice the advantage of working at larger angles and to consider only those lines for which θ lay between 15° and 25°. A careful examination of the lines between these limits and of their photometer curves showed that there was no

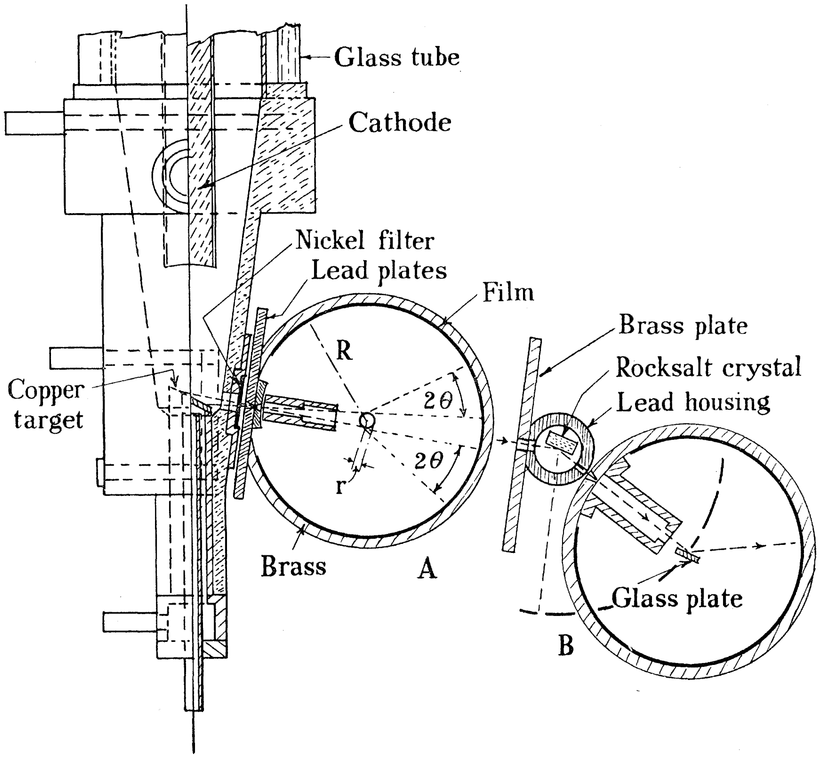

FIG. 6.—X-ray apparatus.

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* MILES, 'J. Chem. Soc.,' p. 2532 (1931).

† JAMES and WOOD, 'Proc. Roy. Soc.,' A., vol. 109, p. 611 (1925).

overlapping, and that for the first two-thirds at least of this angular range the position of the background line was in no doubt.

A photometer of the Moll type was used. The width of the image of the slit-opening formed in the plane of the film by the lens was from 0·005 to 0·0075 mm. Calculation showed that the results could be in error on account of this width by 3% at the most. The distance between the vertical marks on the record (*see* fig. 7) corresponding to 1 mm of film was 25 mm. The densities of the peak and of the background were measured directly with an antilogarithmic scale, and the integrated net density (A) and then the breadth (B) were found for each line by the method already given.

Lattice Dimensions Unaffected by the Presence of Colloid

Direct comparison of the diagram of the complex, and of that of the pure salt, always showed exact coincidence of corresponding lines at any angle, although the relative intensities were by no means the same. This identity of spacing is a proof that the structure of the individual constituent crystals must be essentially identical with that of the normal salt, and that the unit cell has not been changed by the entrance of any foreign material into them.

Results of Measurements

In the upper section of Table VIII are given the percentages of colloid in the complexes of both azide and sulphate used for the X-ray work (D = dextrine; G = gelatine) and the temperatures (T) at which they were made. The middle section gives the indices* and breadths (B) of all the measurable lines. Reproductions of parts of two photometer records of lead azide are given in fig. 7. Each includes the angular range from (033) ($\theta = 14·9°$) to (126) ($\theta = 20·2°$). The upper record is that of pure lead azide, the lower that of the complex containing most dextrine. (8·55%).

Considering, first of all, the pure azide and sulphate, it is remarkable that whereas the azide shows for any line a measured breadth which is near to or even slightly below that which should be given by very large particles ($\pi s/2 = 0·205$ mm) all the lines of the sulphate are broader. This was hardly to be expected, since the crystals of the sulphate were larger and seemed the more perfect of the two. Passing to the complexes containing colloid, we observe an increase in the line-breadths which in regard to all the lines of any one preparation is quite definite, but is nevertheless very irregular for corresponding lines of various materials. In addition, certain lines showed marked differences of intensity from one preparation to another, indeed several lines were sometimes missing altogether. These differences in intensity, of which the photometer records of fig. 7 give an illustration, were shown to be due, in all probability, to slight differences in the shape of the ground particles, which affected their packing in the pillars.

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* Axes: $a=6·64$, $b=11·34$, $c=16·25$. The c axis should be doubled as Sutton claims ('Nature,' vol. 133, p. 463 (1934)), but the two halves of the enlarged cell must be very similar.

With such data, and in view of the limited choice of lines, there is no hope of defining crystallite dimensions in different directions by using equation (1) for each line separately as BRILL has done in the very much simpler case of the cubic nickel oxide*, but since the angular range is not wide it is possible to obtain an idea of the relative degrees of disorganization by taking the mean value of B for each preparation and finding the ideal breadth β from it by the graph derived from equation (4). The corresponding values of $\eta R/r$ were found from those of β/r by reading from a large-scale graph† drawn through points calculated from BRILL and PELZER's equation (*loc. cit.*, p. 154) for $\theta = 19°$. Finally, the mean particle width was obtained from equation (2), *i.e.*, $ma = \lambda/4\pi\eta$ or $= 13{\cdot}90/(\eta R/r)$ in the present instance. There is little error in its determination, for the graph from equation (4) as well as that drawn from BRILL's equation in very nearly a straight line, and the effect of a few degrees' variation in θ is by no means serious.

TABLE VIII—MEASURED WIDTHS (B) AND OTHER DATA FOR LINES GIVEN BY LEAD AZIDE AND SULPHATE, PURE AND CONTAINING COLLOID ($\theta = 14{\cdot}5° - 23°$)

	Lead azide						Lead sulphate			
No.	1	2	3	4	5	No.	1	2	3	4
% coll.	Nil	2·96 D	5·35 D	8·55 D	5·15 D	—	Nil	5·4 D	10·2 D	8·7 G
T°	20°	20°	20°	20°	60°	—	20°	20°	20°	60°
(033)	0·18	0·20	0·25	0·23	0·25	(211)	0·22	0·21	0·33	0·315
(124)	—	—	—	—	—	(112)	0·255	0·31	0·31	0·335
(132)	0·185	0·205	—	0·22	—	(020)	0·285	0·33	0·295	0·315
(040)	0·195	0·235	0·26	0·24	0·25	(212)	0·245	—	0·32	0·39
(006)	0·170	0·19	0·25	0·185	0·215	(220)	0·235	—	0·28	0·265
(125)	0·19	0·215	—	—	—	(221)	0·250	—	—	—
(134)	0·19	0·21	0·22	—	0·28	(113) (122)	0·260	0·25	0·41	0·40
(230) (126)	—	0·175	0·185	0·26	0·25	(401) (203)	0·260	0·255	0·35	0·345
(135)	0·205	0·28	0·28	0·25	—	(410)	0·215	0·27	0·33	—
(217)	0·19	0·325	—	—	—	(303)	0·210	0·21	0·325	0·355
(243)	0·225	0·31	0·29	0·35	0·27	(004)	0·280	—	0·305	—
(226)	0·175	0·225	0·29	0·23	0·20	(313)	0·270	0·225	0·355	0·39
B (av)	0·190	0·234	0·253	0·246	0·245	Av.	0·249	0·257	0·328	0·346
β	0	0·051	0·084	0·072	0·070	—	0·079	0·091	0·198	0·222
β/r	—	0·194	0·319	0·274	0·266	—	0·301	0·346	0·753	0·845
$\eta R/r$	—	0·105	·0215	·0175	·0165	—	·0195	·0235	·0600	·0680
ma.A°	$\propto$	1325	645	795	845	—	713	592	232	205

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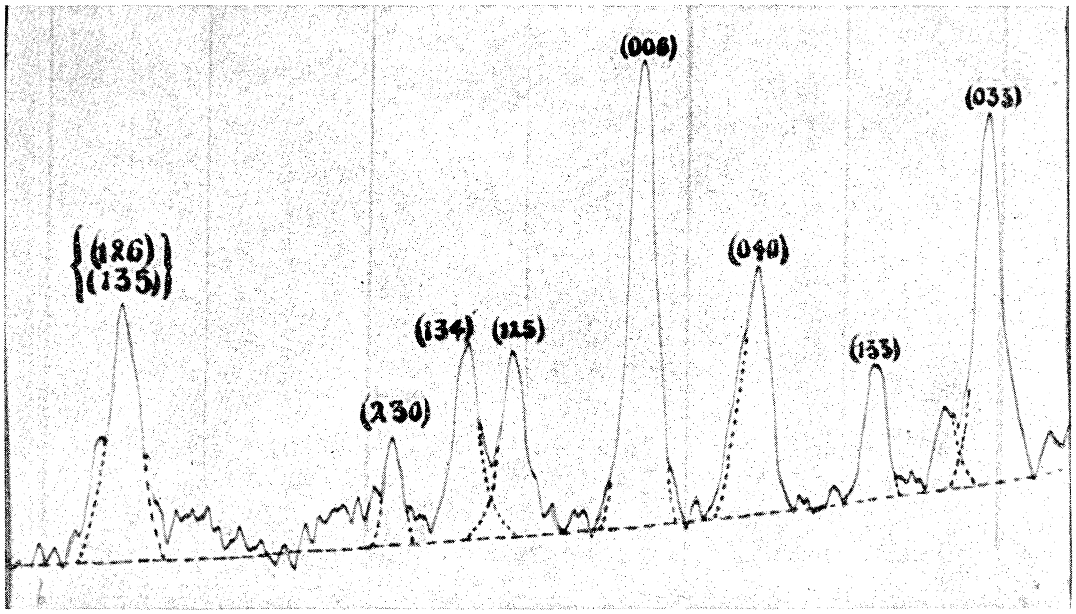
* 'Z. Kristallog.,' vol. 75, p. 217 (1930).

† From $\beta/r = 0{\cdot}20$ to $\beta/r = 1{\cdot}00$ this graph is practically coincident with the straight line $\eta R/r = 0{\cdot}0883\ \beta/r - 0{\cdot}0067$.

The lower section of Table VIII gives these data. The two salts give rather different results. Lead azide in the pure form consists of crystallites so large (or so well co-ordinated) that they escape measurement. If only 3% of dextrine is absorbed



Pure lead azide

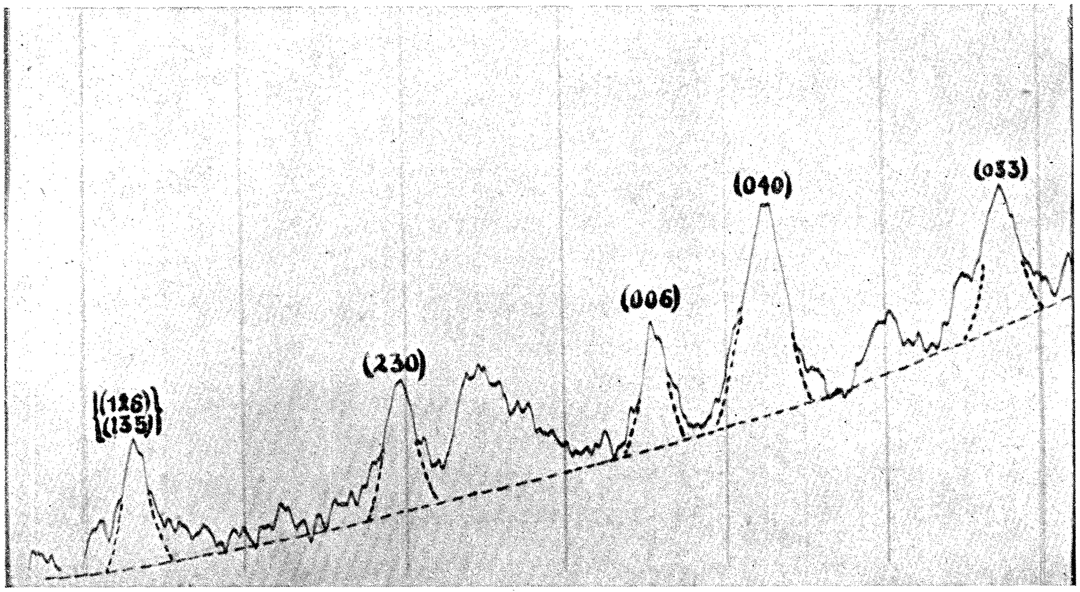


FIG. 7—Photometer curves of lead azide—pure, and with 8·6% dextrine.

—an amount which does not prevent all the salt appearing in individual crystals 0·14 mm long—there is an immediate decrease of apparent width, to an apparent average of about 1300 A ($1\cdot3 = 10^{-4}$ mm). Further increase of the dextrine absorbed at 20° causes a further decrease, but beyond 5·35% of absorption there seems to be little effect.

Carefully prepared pure lead sulphate, on the other hand, appears to be only about $0\cdot7 = 10^{-4}$ mm in average width, and the incorporation of dextrine causes this width to become progressively smaller until, when over 10% of dextrine has been added, it has fallen to $0\cdot2 = 10^{-4}$ mm. Gelatine (8·71) at 60° has about the same effect.

13—EXAMINATION FOR THE PRESENCE OF COLLOIDAL LEAD COMPOUNDS

On the X-ray diagram of any azide containing much colloid, the lines were always seen to stand out less well from the background than on that of the pure substance. It seemed possible that some of the azide, or of a complex of lead salt and colloid, might be present in crystals which were very much smaller (or much more disorganized) than the rest. A possible test of this is to find whether, as colloid is introduced, there is a decrease in the coherent radiation scattered in definite, although broadened, lines, relative to that which is scattered indiscriminately.

Since the relative intensity of any line may vary very much from one preparation to another of the same salt, the comparison had to be made over the greatest possible angular range. The dextrine or gelatine is unlikely to be crystalline and will itself cause scattering, but to a negligible extent. From the known F values of the amplitudes of scattered radiation at various angles*, it is easy to show that in the range $\theta = 15°$ to 25°, the copper radiation scattered by one part of dextrine will be only 1/65 of that scattered in one way or another, by 10 parts of lead azide or sulphate.

Use of the Ordinary Diagrams

The first method used was to compare for each substance the sum of the integrated net densities of all the lines (ΣA) with the sum of the integrated densities of the sections of background on which the lines stand ($\Sigma(\mathrm{BD}_b)$). Table I gives one set of such data. The resulting figures, to which the ratio of coherent to scattered radiation should be proportional, are given below in Table IX.

TABLE IX—FIGURES PROPORTIONAL TO RATIOS OF COHERENT TO SCATTERED RADIATION IN THE RANGE 14–23° (θ)

$$\frac{\Sigma \mathrm{A}}{\Sigma\ (\mathrm{BD}_b)} \text{ for azide and sulphate}$$

	Pure	No. 2	3	4	5
Lead azide	0·81	0·47	0·35	0·32	0·27
		Pure	No. 1	2	3
Lead sulphate		0·64	0·72	0·54	0·46

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* BRAGG, 'The Crystalline State,' vol. I, p. 329 (1933).

It is evident that the continued introduction of dextrine into lead azide causes a marked progressive decrease in the proportion of coherent radiation. The preparations of sulphate showed no difference on which any stress can be laid.

Confirmation with Monochromatized Radiation

Measurements made with the ordinary filtered radiation are not very reliable because of the large amount of scatter from the continuous spectrum, and to check them experiments were carried out with copper rays first filtered through a nickel window as usual and then made more strictly monochromatic by reflection from the face of a rock-salt crystal. On account of the low primary intensity a modified method of exposure was used. A camera of 3 cm radius was used here also, but with a slit 2 mm high and 0·5 mm wide instead of a pinhole. The powder was spread in a coherent layer on a small piece of ground glass, and was oscillated through the angular distance 20°±2·5° for three hours. The rocksalt crystal was mounted in a housing clipped to the face of the tube, and the spectrometer was conveniently arranged to rotate about a vertical axis passing through the crystal. Fig. 6B is a diagram of this arrangement.

The integrated densities above and below the background line of the photometer records were found as before, except that a planimeter was used, the chart being divided into narrow horizontal zones of approximately the same density value. In regard to lead sulphate, the pure crystal and No. 3, containing 10% of dextrine, both gave so low a background that no useful comparison could be made. The fraction of colloidal lead compound in the second preparation must have been very small. Pure lead azide and No. 4, containing 8·6% of dextrine, proved to be quite different. The ratio of density above to that below the background line was 3·55 in the first case and 1·63 in the second. There can be little doubt that the results of the first method of estimation were not vitiated by the continuous radiation and that the introduction of dextrine must therefore be accompanied by the deposition of colloidal lead compound. It is interesting that only the azide seems to contain this less organized material, and that the sulphate, which is free from it, shows a considerably greater degree of subdivision of the normal crystal.

PART IV—THE CONSTITUTION OF THE COMPLEXES OF LEAD SALT AND COLLOID

The absorption of substances from solution into growing crystals has long been a subject of interest. The older ideas of double salt formation between the substance of the crystal and that taken up from solution have given place to the conception of adsorption at what is called the inner surface. It is now known that a crystal is rarely homogeneous, and is nearly always a composite structure of small blocks or other elements laid down in not quite parallel alignment. When the discontinuities are regarded as definite fissures they are often referred to as Smekal cracks, and the inner surface is the area of the additional surface they expose. Perhaps the investigation of the highest general interest among those dealing with the precipitation of difficultly soluble salts was that carried out for fifteen years by BALAREV[*] on barium sulphate. BALAREV showed that the almost inevitable contamination of this precipitate by any salt in solution could be explained only as inner absorption.

The absorption of colloid dealt with here is of even greater interest, for the proportion which can exist in intimate union with the crystals is high and its relative volume is higher; the mechanism of ion-interchange by which the adsorption of salts from solution may be effected cannot be operative. Nevertheless, the only case of a crystal-colloid complex which has been investigated in detail is that of copper deposited electrolytically in presence of gelatine. As much as 6% of gelatine may be present. The absorption is dependent on the acidity; at p_H 3·2 it is a maximum. The X-ray evidence shows that crystals of copper are present, but so much reduced in size as to be comparable with those in the catalytically active metal made by reducing the nitrate at 200°.[†]

The only other well-known example, that of the photographic emulsions of the silver halides in gelatine solution, is of the greatest importance on account of the striking phenomena with which the absorption is connected. REINDERS[‡] showed that gelatine and other colloids were absorbed during crystallization and was the first to prove by his work on the light-sensitiveness and the coloration of the crystals, that the colloid must be uniformly distributed through them. He found that silver bromide precipitated from ammoniacal solution containing 2% of gelatine took up about 0·1%. But the available quantitative data are very sparse. SHEPPARD, LAMBERT, and KEENAN[§] stated in 1932 that beyond this observation of REINDERS and a single earlier one by EDER, they had been unable to glean anything from the literature.

They have themselves given the most recent figures (*loc. cit.*). Silver bromide was prepared " in gelatine solution " and was washed at 50° and centrifuged. After two washings the absorption had become constant at 0·34%. Acidity of the medium had no effect. Only one-half of the absorbed gelatine could be removed by long treatment with boiling water. This fact seems to indicate clearly that most of the gelatine had been taken up during growth and had become embedded in the crystal. When precipitates of bromide free from colloid were placed in contact with gelatine solutions of stated concentrations, much higher adsorptions were found, tending to a limit of, roughly, 3% in a solution containing about 10% of gelatine. This high adsorption by the preformed crystals is difficult to understand when compared with the results given here, but may be explained according to SHEPPARD by the much finer grain of the colloid-free bromide.

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[*] 'Kolloid Chem. Beih.,' vol. 30, p. 249 (1930).

[†] MARIE and CLAUDEL, 'C.R. Acad. Sci., Paris,' vol. 187, p. 170 (1928); MARIE and JACQUET, *ibid.*, vol. 187, p. 41; TRILLAT, 'Brit. Chem. Abs.,' A, p. 41 (1928).

[‡] 'Z. phys. Chem.,' vol. 77, p. 686 (1911).

[§] 'J. Phys. Chem.,' vol. 36, p. 174 (1932).

It was shown in Part II that the absorption tends to reach a maximum in the cases of the azide and the chloride. Since the highest percentage absorption (8·55%) actually obtained for azide was clearly below the possible maximum, and since 10% was actually reached in the case of the sulphate, we may select an absorption of 10% of the weight of either complex as the first phenomenon to be explained. The conclusion which follows from 8 also stands out; we have to explain how from 4% to 5% of dextrine may be taken up by the crystal in such a way that the continuity as shown by the microscope is not destroyed. Since the spacings as revealed by X-rays remain the same, the colloid must be external to the elements of crystalline structure.

It is generally accepted that starch, and therefore dextrine, has a chain structure and that the links of the chain are gluco-pyranose residues. Since the molecular weight of the dextrine investigated has been seen to be about 28,000 there must be an average of about 170 links to each molecule. It is, perhaps, more probable that the molecule consists of shorter chains attached to each other or to some central nucleus than that it is made up of a single continuous chain; but at present no very definite statement on such a point seems possible. Haworth has shown that the residues are of the α type, differing only in stereochemical arrangement from the β units which make up the cellulose molecule. The peculiarity of the α form of junction is that a model made of several chains cannot be made to lie flat in one plane like that of cellulose. There is some doubt, therefore, whether in any case each ring of the adsorbed dextrine molecule can occupy the full area usually assigned to the glucose residue, but we may assume for the sake of argument that it may.

The estimate of area which Adam found to be correct for films of cellulose spread on water* was 55–60 sq. A for one glucose ring, the weight of which is $162 \times 1 \cdot 66 \times 10^{-24}$ gm. The gram of dextrine will therefore occupy an area of

$$\frac{60 \times 10^{-16}}{162 \times 1 \cdot 66 \times 10^{-24}} \text{cm}^2 = 2 \cdot 23 \times 10^7 \text{ cm}^2.$$

Now the area of lead azide on which unit weight was taken up (§9) was about $2 \cdot 0 \times 10^6$ cm². These measurements were very rough. Those made for the tabular variety of lead chloride were more accurate and gave the figure $1 \cdot 15 \times 10^3$ cm². The fact that in both cases the adsorption was very rapidly accomplished, proves that there cannot have been any slow creep of the colloid into the interior of the crystal such as is found with iodine on charcoal. Further, it was shown by Paneth† that with the exception of certain crystals, which probably were of unusual perfection, the microscopic measurements of area agreed well with those made by his radioactive method. On the whole, therefore, it appears probable that the dextrine on lead azide and chloride occupies only about one-tenth of the adsorption area required by a single layer of rings lying flat on the surface.

It has been seen that a 10% absorption of dextrine by either salt is quite possible; let us now calculate the size of the constituent element in a crystal which has retained

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* 'Trans. Faraday Soc.,' vol. 29, p. 100 (1933).

† 'Z. phys. Chem.,' vol. 101, p. 445 (1922).

this amount of dextrine by the adsorption of a monomolecular layer between two adjacent crystallites. If a cube of 1 cm edge is divided into smaller equal cubes by three sets of parallel planes, N in each set, the total interfacial area will be 3N cm^2 ; N, of course, being large. Since one gram of dextrine requires $2 \cdot 23 \times 10^7$ cm^2, the amount in 1 cc of azide (the density of which is about 4·4) will require $0 \cdot 10 \times 4 \cdot 4 \times 2 \cdot 23 \times 10^7 \text{ cm}^2 = 9 \cdot 8 \times 10^6 \text{ cm}^2$, and since 3N must be equal to this, $N = 3 \cdot 27 \times 10^6$. The edge of the cube is $1/N = 0 \cdot 3 \times 10^{-6}$ or 30 A. This is only a little more than twice the intermediate axial dimension of the unit cell of lead azide and is not even as great as the length of the longest edge. (*See* note on p. 155.) Hence, particles small enough to take up 10% of dextrine in this way would show a much greater broadening of the X-ray lines than is ever observed.

One further simple calculation is significant. It is quite possible that a single long dextrine molecule might remain anchored in the crystal by one end while the advancing crystallization built up the crystal all round the chain. If all the dextrine molecules were built up in this way, how much clear crystalline matter would lie between them? Imagine all the dextrine chains arranged at equal intervals in straight lines parallel to each other and to one side of a unit cube. In 1 cc of complex ($d = 4 \cdot 4$) there is 0·44 gm dextrine, and the number of residues is $0 \cdot 44/(1 \cdot 66 \times 162 \times 10^{-24}) = 1 \cdot 64 \times 10^{21}$. Each residue is 5·15 A in length if we take the value obtained for the straight chain in cellulose. Hence the number of single-chain filaments 1 cm long is $1 \cdot 64 \times 10^{21} \times 5 \cdot 15 \times 10^{-8} = 8 \cdot 42 \times 10^{13}$, and the average distance between two adjacent ones is $1/\sqrt{8 \cdot 42 \times 10^{13}} = 0 \cdot 11 \times 10^{-6} \text{ cm} = 11$ A. The thickness of the glucose residue itself cannot be, as X-ray data show, less than 4 A. Only 7 A would be left for the azide—a space insufficient for more than the short axis of one unit cell at the most.

The dextrine cannot therefore all be packed either in monomolecular layers or single isolated chains ; much of it must be present in thicker layers between the crystallites. Recollecting that the limit of tolerance of dextrine by the single undistorted crystal is about 5%, and that there is imperfect continuity at even higher percentages, we may finally draw the following picture of the origin and structure of these complexes.

During the crystallization, the colloid is adsorbed on the crystal blocks as they are formed, preventing them from growing to the size they would attain if colloid were absent and separating them partly from each other by layers of adsorbed material. But in spite of this the continuity of the crystallites with each other is not lost. They must still be connected, and the result is a continuous skeletal array of crystallites, all in nearly the same crystallographic orientation, with layers of colloid in between.* In view of the tenacity with which the dextrine is held, it seems quite likely that any molecule which has adhered to the crystal will not be displaced by the crystallization,

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* BUERGER has maintained, in an interesting paper which did not come to hand until this had been written ('Z. Krystallog,.' vol. 89, p. 195 (1934)), that a skeletal "lineage" arrangement is a common feature of crystal structure.

so that the layers may be supposed to consist of irregular bundles of long dextrine molecules anchored to the crystal by some of their hydroxyls, but having the rest free As the amount of colloid taken up is increased beyond 5%, the extinction of the crystal as a whole in polarized light becomes complex, because the skeletal structure can no longer maintain the same orientation throughout its growth.

The X-ray results are quite in accordance with such a conception. Their chief value is that of *relative* measures of the average dimensions of the constituent crystallites. For both azide and sulphate there is an undoubted decrease when colloid is introduced, but the decrease is usually less than might be expected from the large proportion of absorbed material. For instance, the average dimension of the particle of lead sulphate falls only from about 700 A for the pure crystal to 200 A for the complex containing 10% of dextrine by weight. In view of what has already been said, this must mean that the intercalations of dextrine are many times thicker than a single glycopyranose chain.

There is, however, another factor which may modify this result, but it is difficult to say how far it is effective. It has already been pointed out that since the complex crystals are not random aggregates the elementary crystallites may to some extent reinforce each other's diffractions, so that the line broadening is less than if they were altogether at random. The values given must be taken as superior limits to the actual particle-size. Now, although an exact discussion is not possible, it is to be expected that this effect will become less as more colloid is introduced. When 10% is present, and the microscope in fact shows only irregular masses with fluctuating extinction, the phase relation of adjacent crystallites is probably too inexact to reduce the broadening seriously. If we accept the result for the complex of azide containing 10% of dextrine as an approximate measure of the actual size, we find the average width of the crystallite is more than 20 times that required for all the dextrine to be present between the surfaces in a single layer. On the other hand, if the crystallites are smaller than this, and are exactly reinforcing each other's diffractions, such a degree of co-ordination can result only from their being parts of larger, branched, parallel aggregates.

Between the results for the azide and for the sulphate there is an interesting difference. In the former case there is, of course, a decrease when dextrine is introduced, but beyond 5% of the weight of the complex further addition has very little influence. With the sulphate, on the other hand, the decrease in size of the crystallites is more continuous, and when 10% of dextrine is present they are smaller than in any of the azides for the same amount of colloid. The investigation also showed that in the latter case azide was deposited in a form so fine that it gave only a general scattering of the radiation. This colloidal salt must be in the separating layers with the colloid. Since it has been shown to be fairly certain that there can be no association of salt and dextrine previous to the crystallization, we must conclude that the colloidal material consists of very minute crystals which have formed in and become enmeshed by the bundles of dextrine molecules, and are in all probability attached to them by hydroxyl groups not already appropriated by the main structure.

I am indebted to Messrs. Imperial Chemical Industries, Limited, for permission to publish this paper, and am glad to acknowledge the helpful interest which my colleague, Mr. W. O. Littlebury, has always taken in these investigations.

14—Summary

The work is a study of the absorption of dextrine, gum arabic or gelatine in growing crystals of lead chloride, bromide, iodide, azide and sulphate. More than 10% may be firmly bound and 5% may be present in a crystal without confusing its structure.

An account is given of the changes in crystal habit, and of alterations in stability of various physical forms and hydrates, which are induced by absorption of colloid during both slow and rapid precipitation.

The relation between amount of absorption and colloid solution-concentration was followed. Differences shown by the salts are discussed. Microscopic observations of the precipitates were made. The adsorption of dextrine on preformed crystals of chloride and azide was measured and compared with the estimated available surface. Results were checked with dextrine purified by dialysis, the osmotic pressure of which was determined. Maltose was not absorbed. Solutions containing chloride and dialysed dextrine were examined in the ultra-microscope and their conductivities were measured. There was no evidence for the association of lead ion and dextrine in solution.

X-ray examination showed that the lattice spacings of the pure salts are unaffected by the introduction of colloid. The difficulties in applying the known methods of estimating particle-size are mentioned. An approximate correction for finite size of the aperture is worked out. The results show that as colloid is taken up the average particle-width is decreased, but the two salts examined—azide and sulphate—behave differently. Measurements were also made of the ratio of coherent to incoherent radiation, with the conclusion that in the complexes of azide (but not sulphate) extremely fine (colloidal) lead compound must be present.

The whole of the evidence is discussed, and it is concluded that the constitution of the complexes is that of a connected skeletal growth of crystallites, all in nearly the same crystallographic orientation, with layers of colloid in between. These layers consist of irregular bundles of long dextrine molecules anchored in the crystallites by some of their hydroxyls, but having the rest free.

Fig. 8—Lead chloride, rapid crystallization at 25° from 0·25% dextrine solution × 100

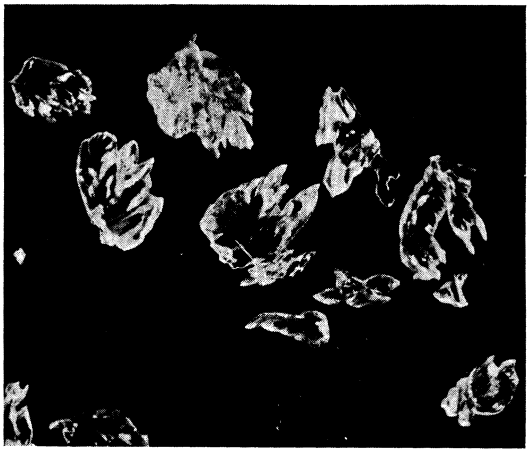


Fig. 9—Lead chloride, slow crystallization from 0·10% dextrine solution × 10

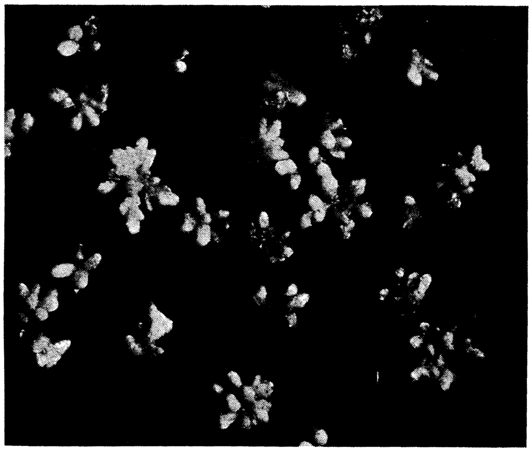


Fig. 10—Lead chloride, slow crystallization from 0·75% dextrine solution ×10

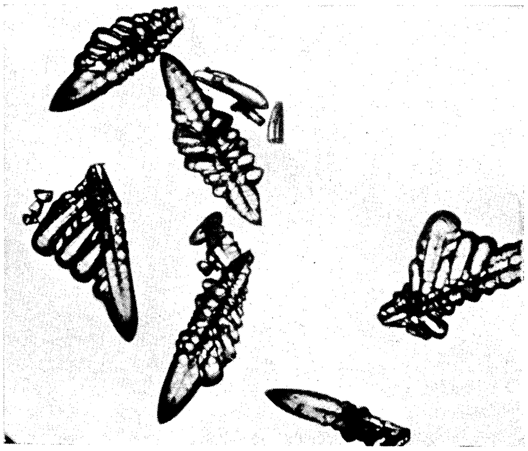


Fig. 11—Lead bromide, slow crystallization from 0·5% dextrine solution × 20

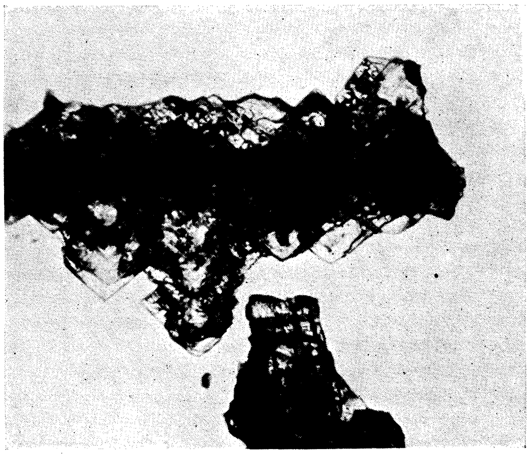


Fig. 12—Lead bromide, slow crystallization from 0·25% gum-arabic solution ×35

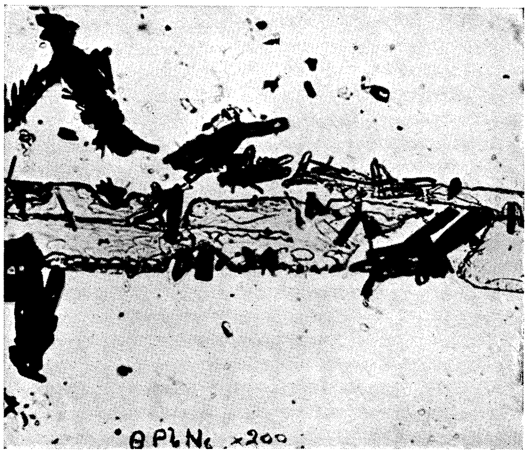


Fig. 13—Lead azide, showing β → α change × 200

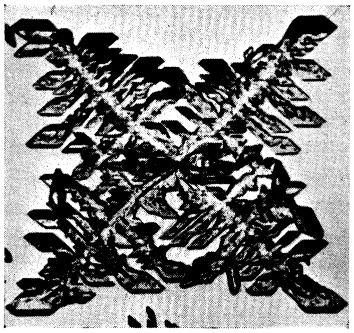


Fig. 14—Aggregation on (001) × 75

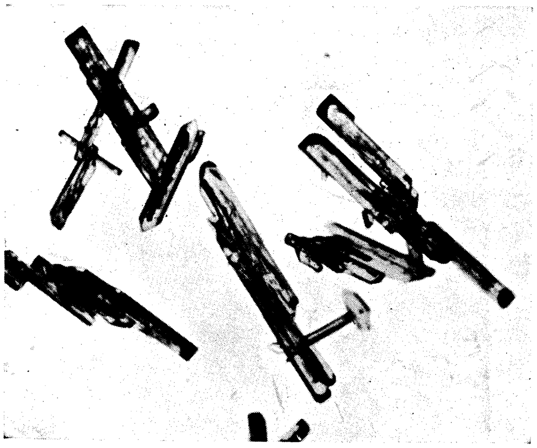


Fig. 15—Rapid crystallization, no colloid, 50° × 150

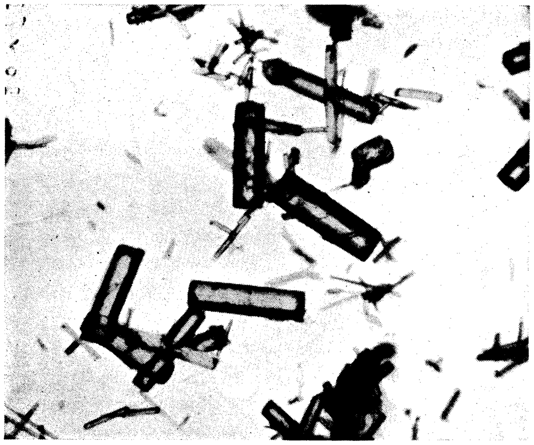


Fig. 16—Rapid crystallization from 0·25% dextrine solution at 80° × 200

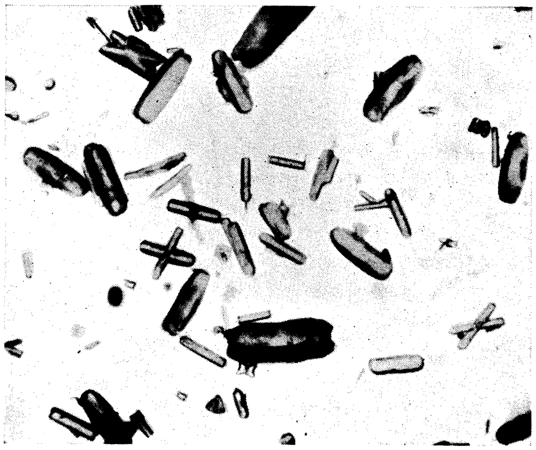


Fig. 17—Rapid crystallization from 0·5% dextrine solution at 50° × 200

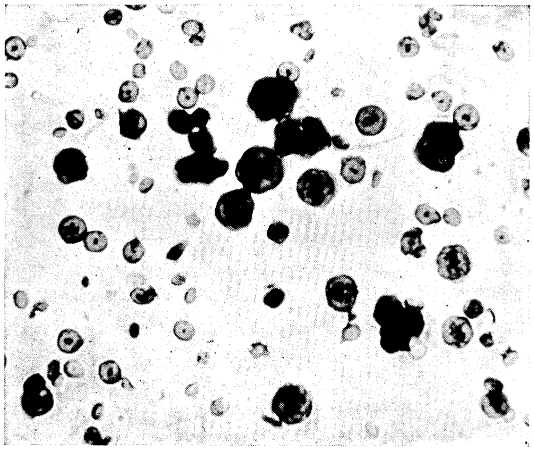
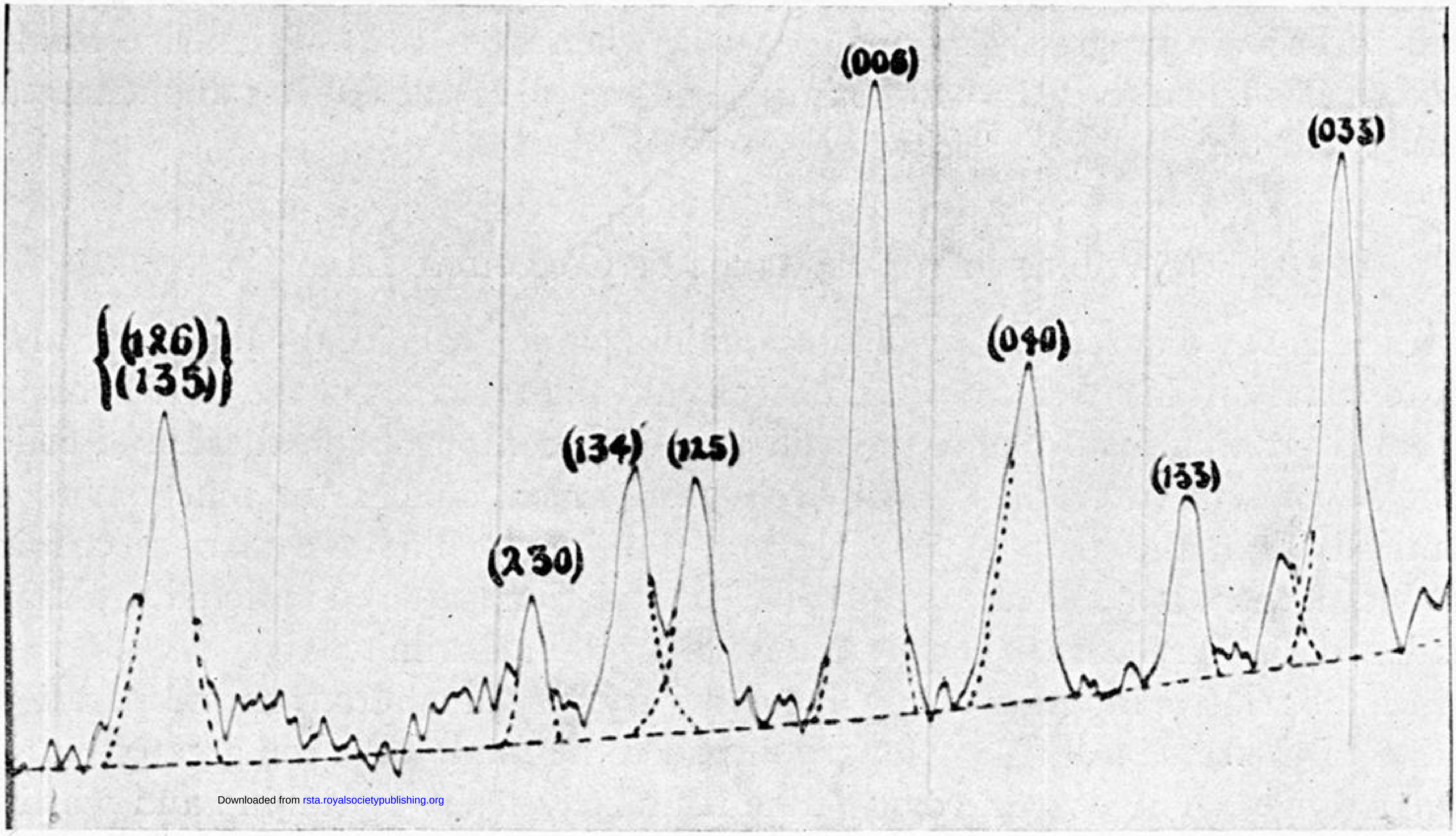


Fig. 18—Rapid crystallization from 0·5% dextrine solution at 20° × 200

Fig. 19—Showing incipient spherulitic growth × 250

Photomicrographs of Lead Azide



Pure lead azide

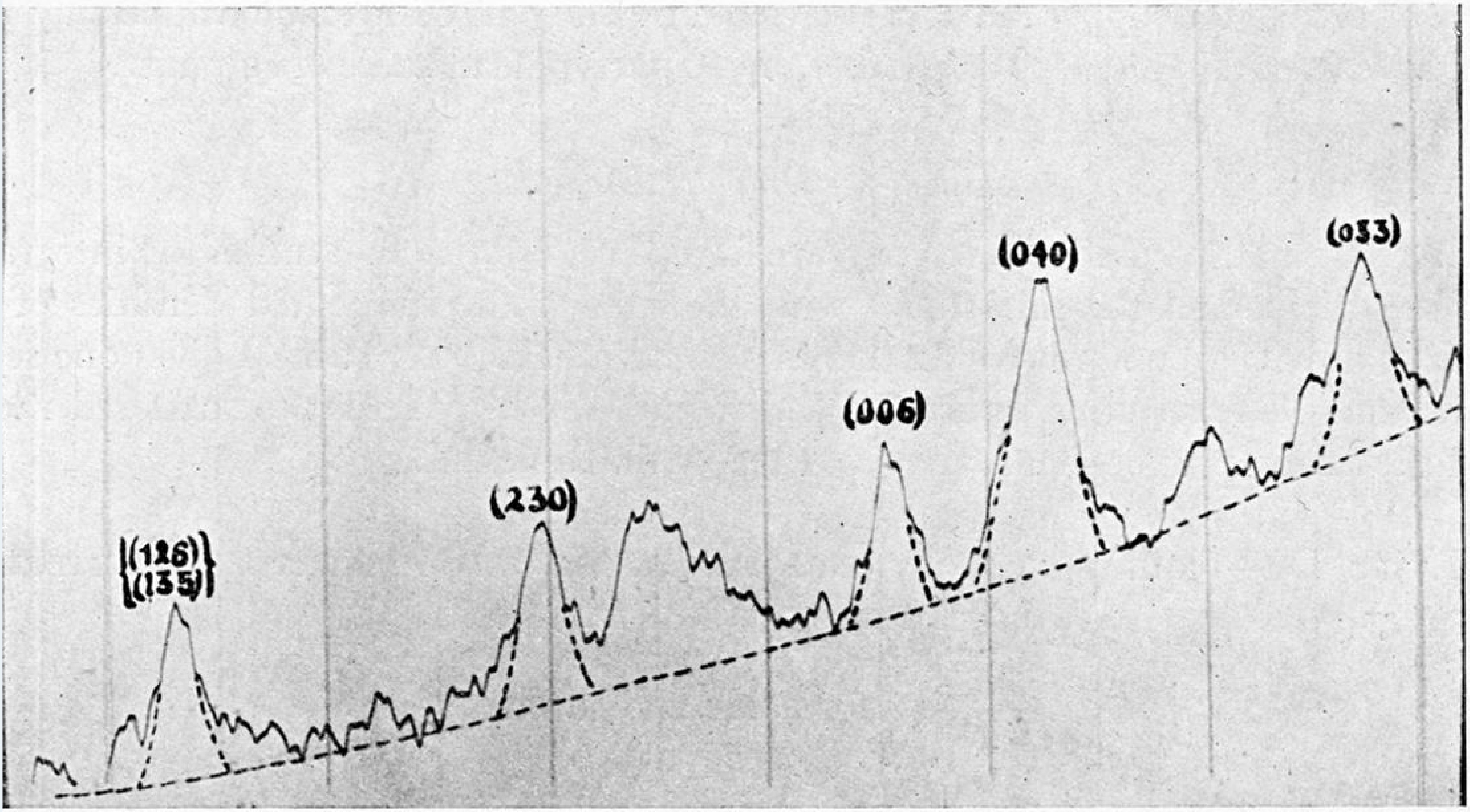
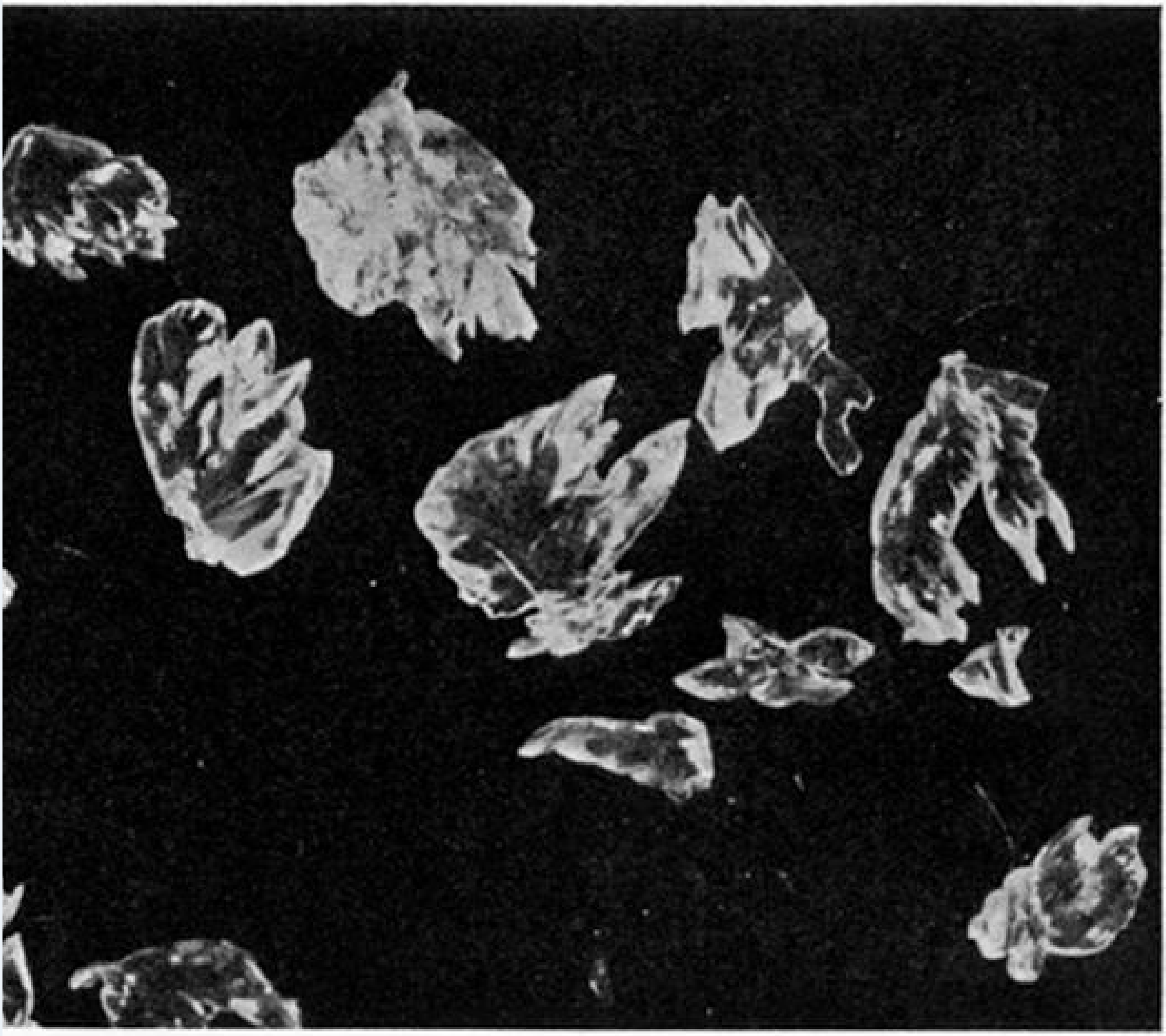
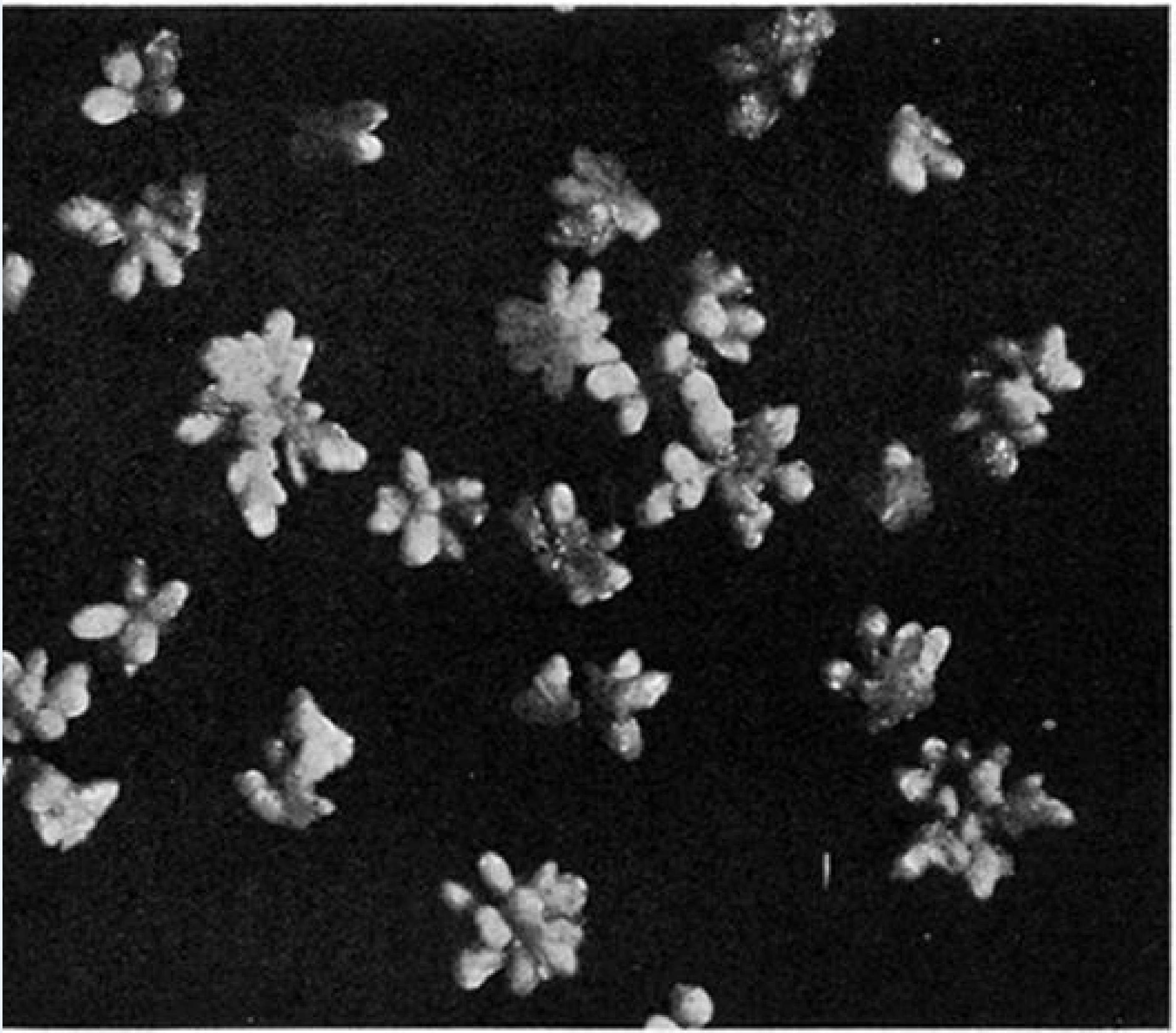


FIG. 7—Photometer curves of lead azide—pure, and with 8·6% dextrine.

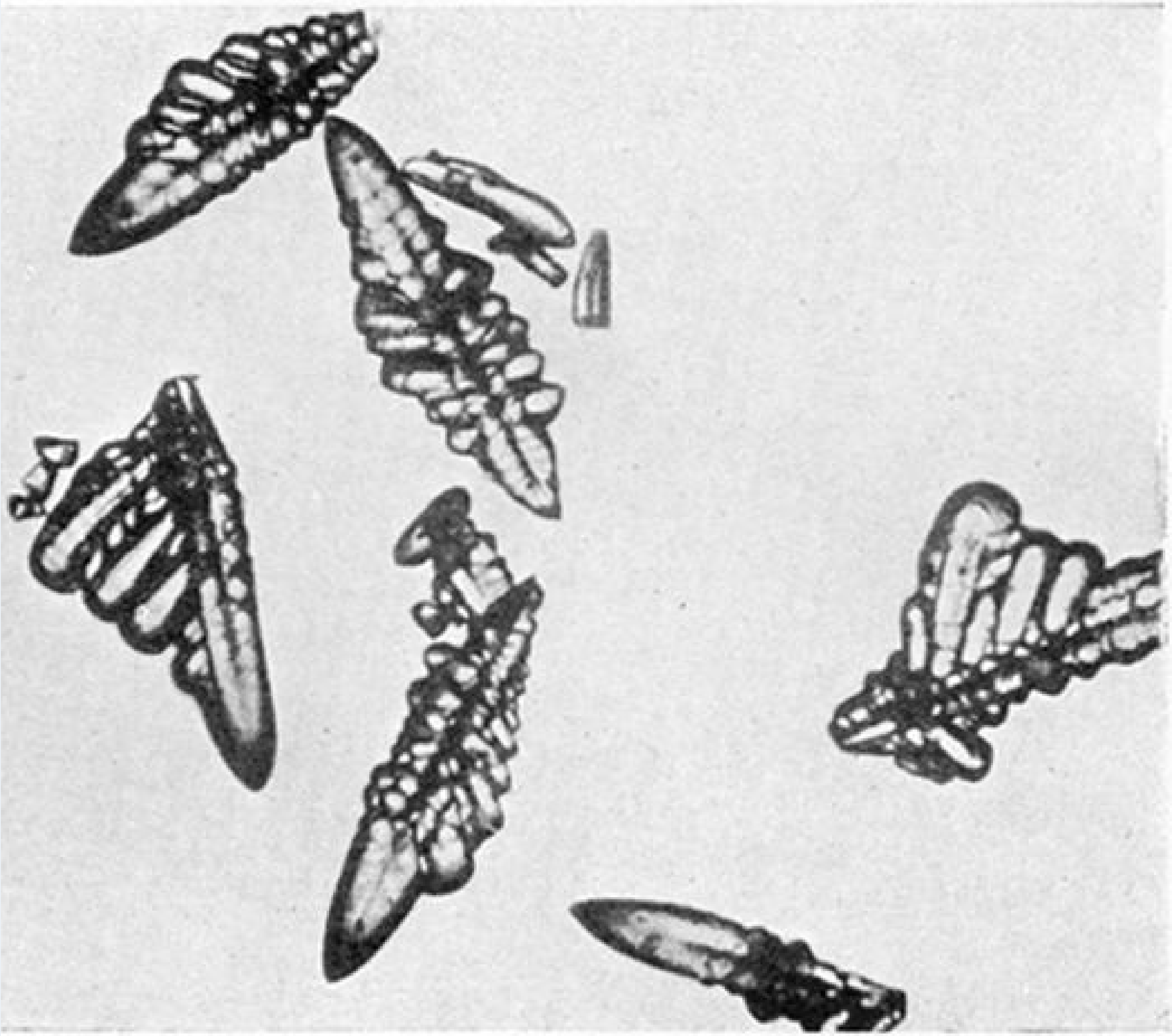
ig. 8—Lead chloride, rapid crystallization at 25° from 0·25% dextrine solution × 100



g. 9—Lead chloride, slow crystallization from 0·10% dextrine solution × 10



ig. 10—Lead chloride, slow crystallization from 0·75% dextrine solution ×10



ig. 11—Lead bromide, slow crystallization
from 0·5% dextrine solution × 20

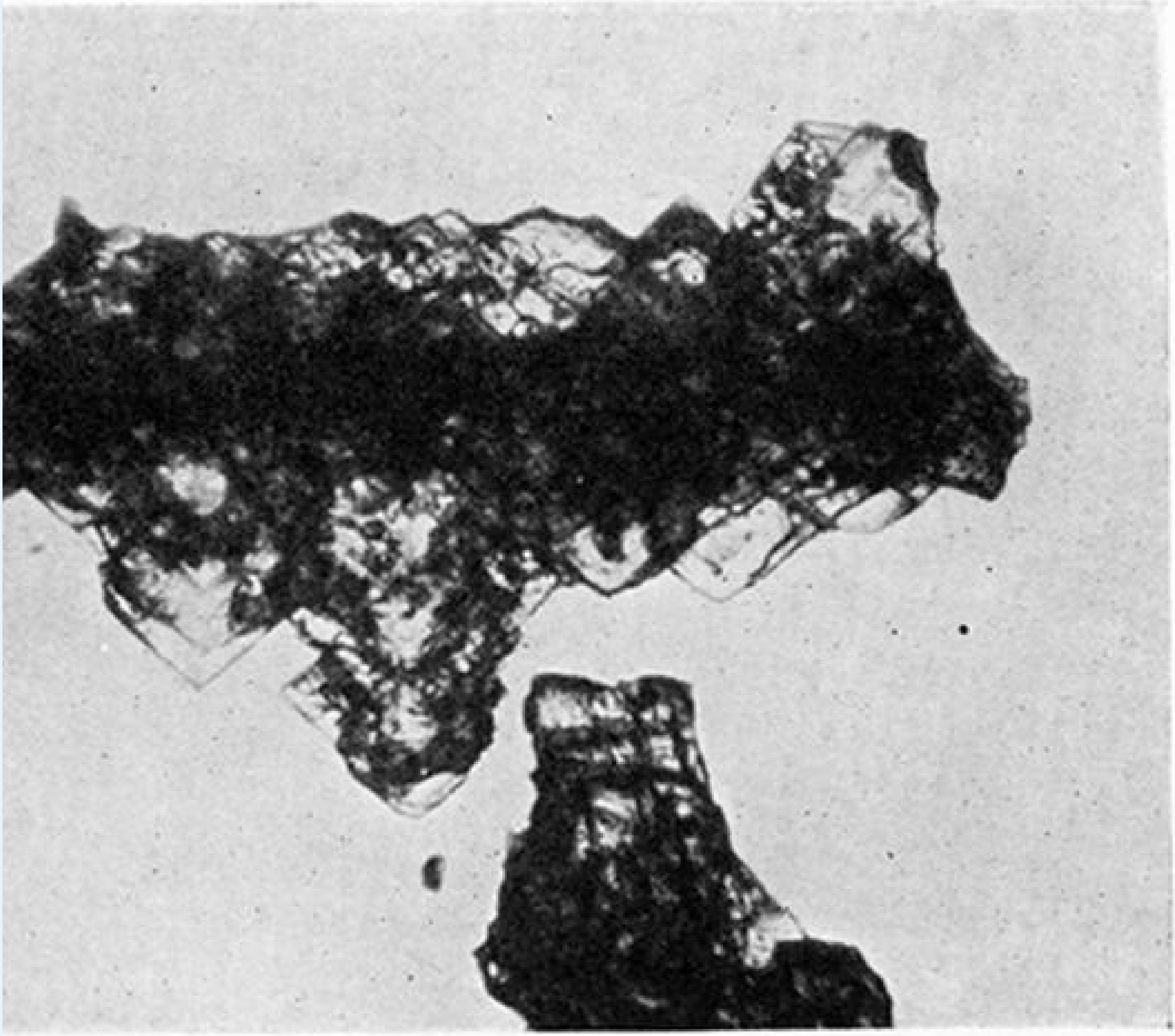
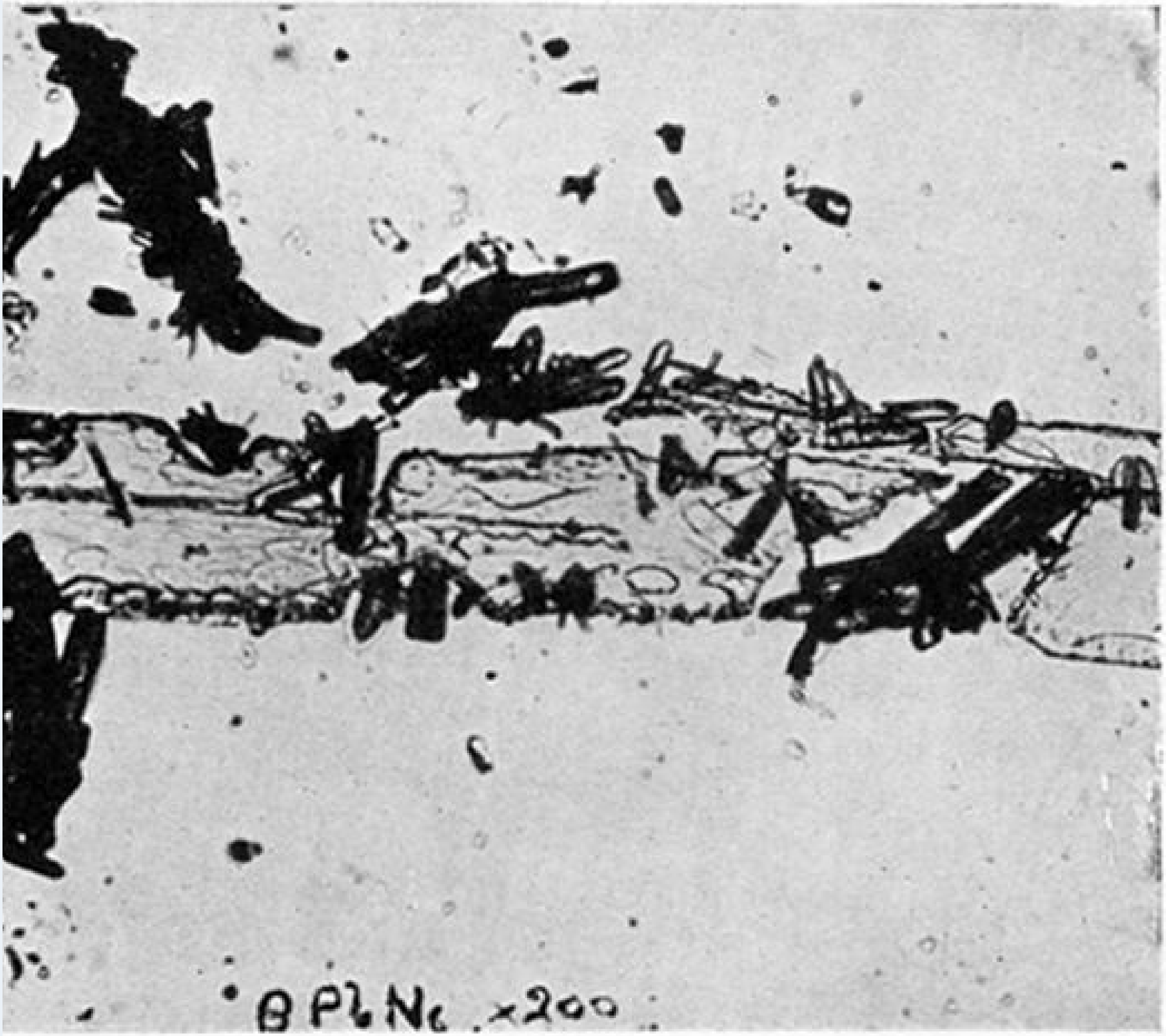


Fig. 12—Lead bromide, slow crystallization from 0·25% gum-arabic solution ×35



ig. 13—Lead azide, showing β → α change
× 200

Fig. 14—Aggregation on (001) × 75

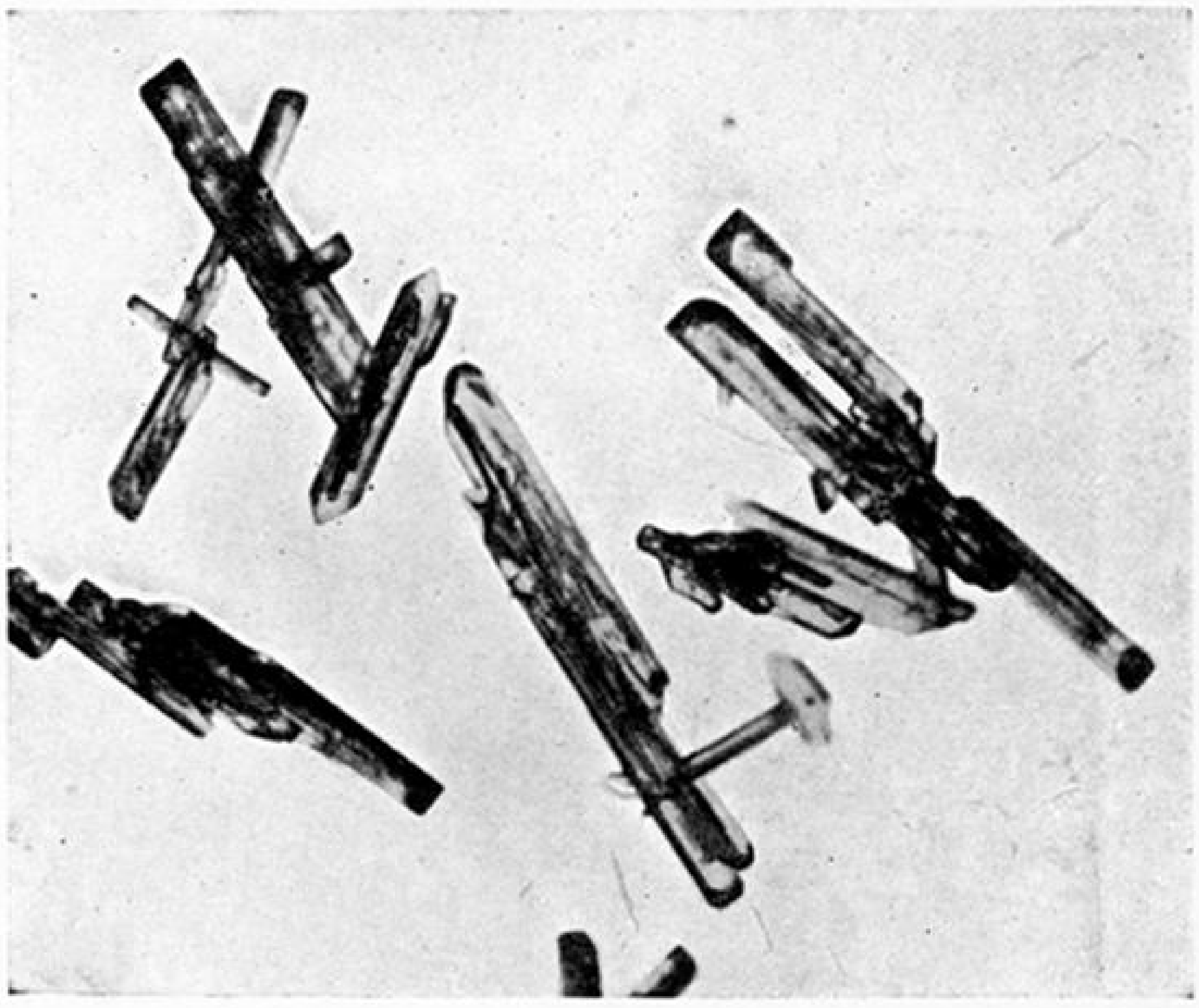


Fig. 15—Rapid crystallization, no colloid, 50° × 150

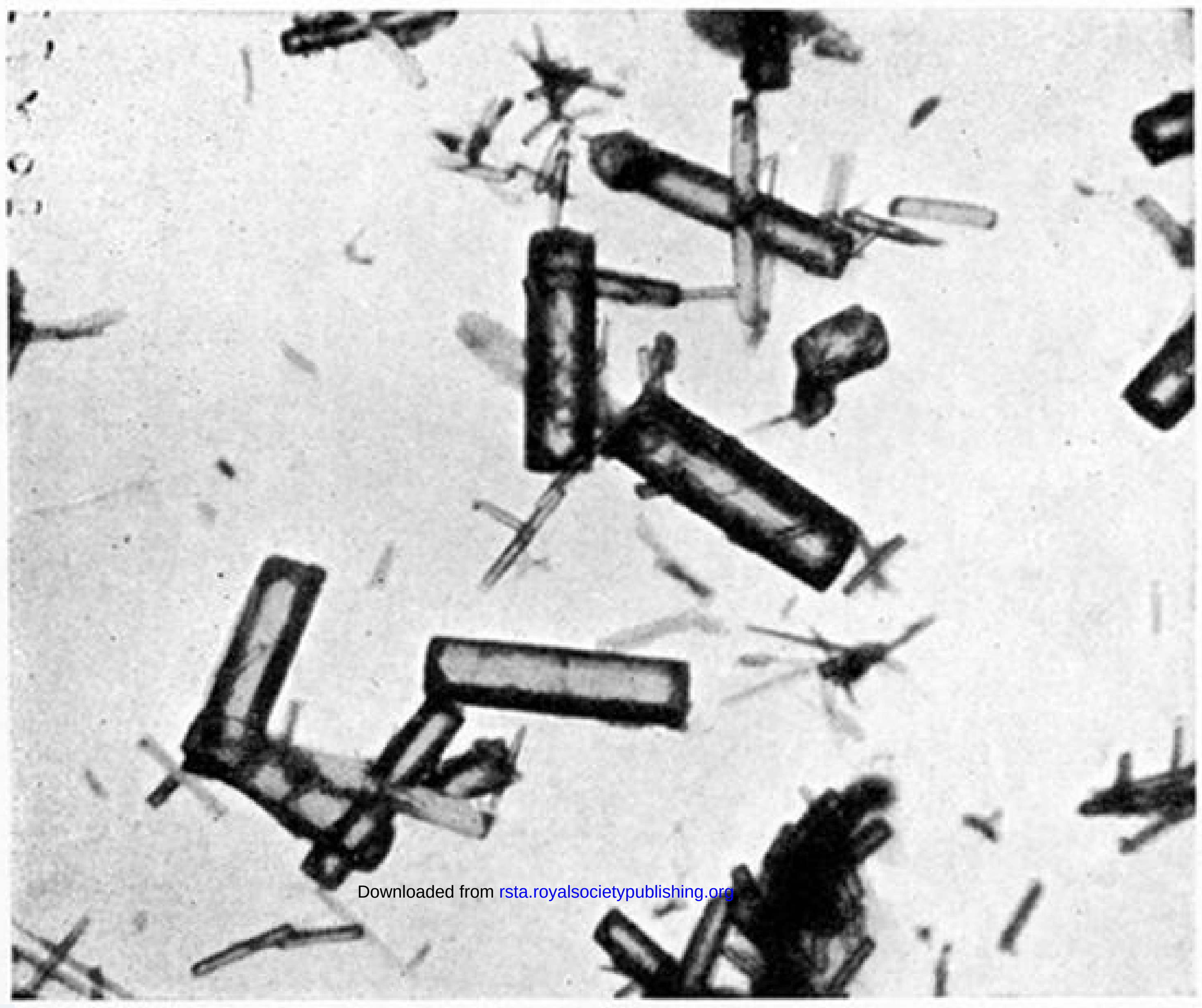


Fig. 16—Rapid crystallization from 0·25% dextrine solution at 80° × 200

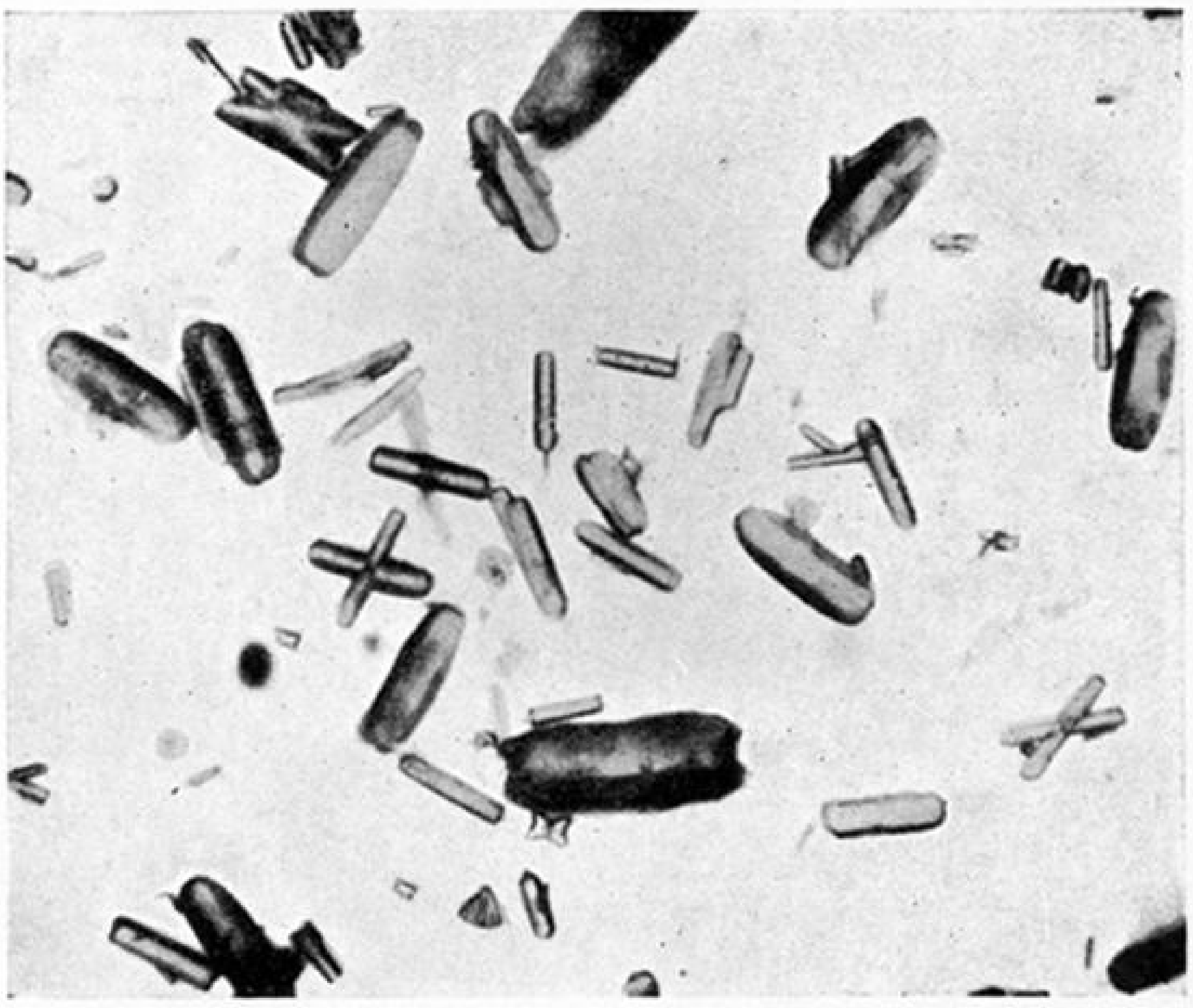


Fig. 17—Rapid crystallization from 0·5% dextrine solution at 50° × 200

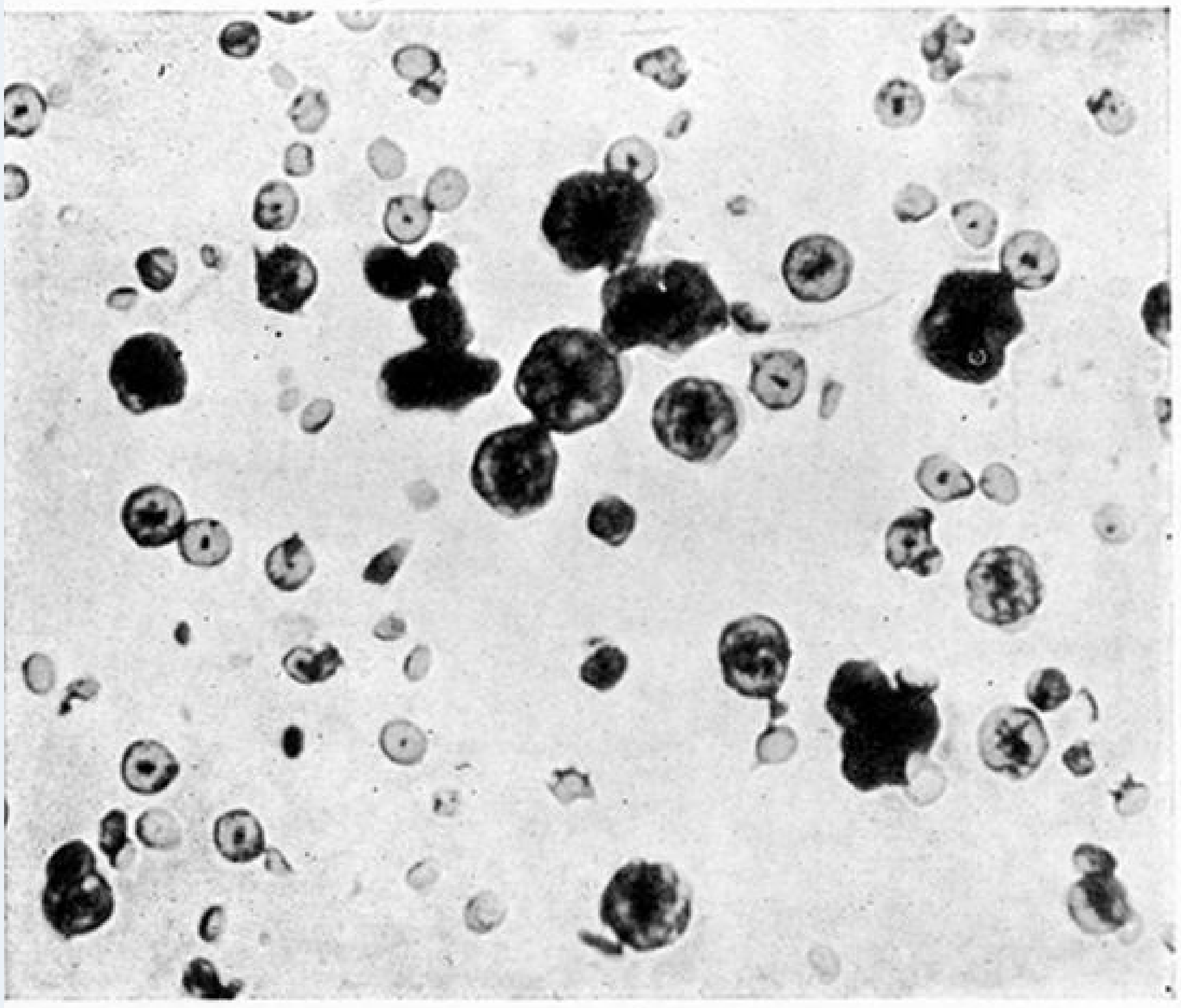


Fig. 18—Rapid crystallization from 0·5% dextrine solution at 20° × 200

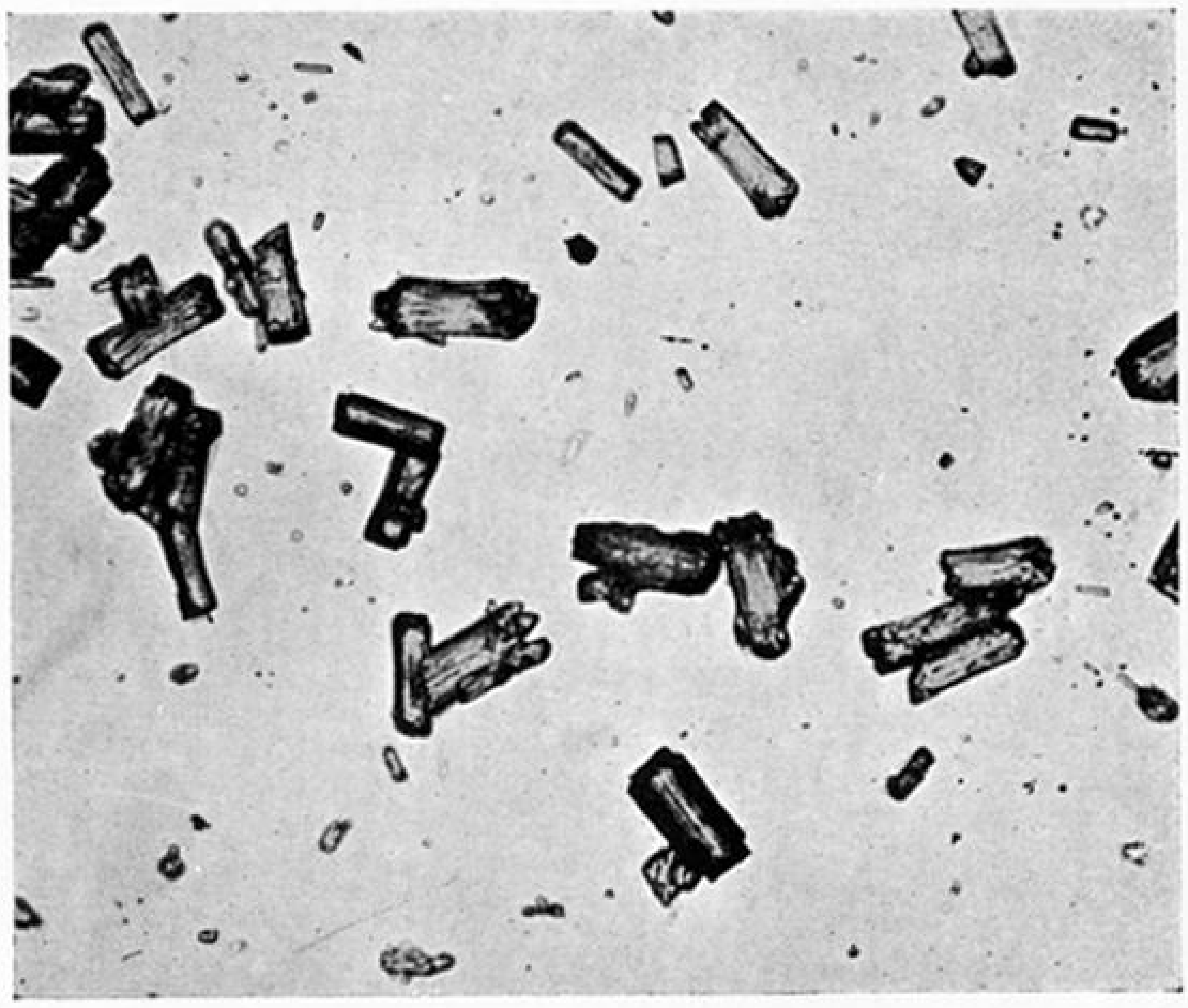


Fig. 19—Showing incipient spherulitic growth × 250

Photomicrographs of Lead Azide