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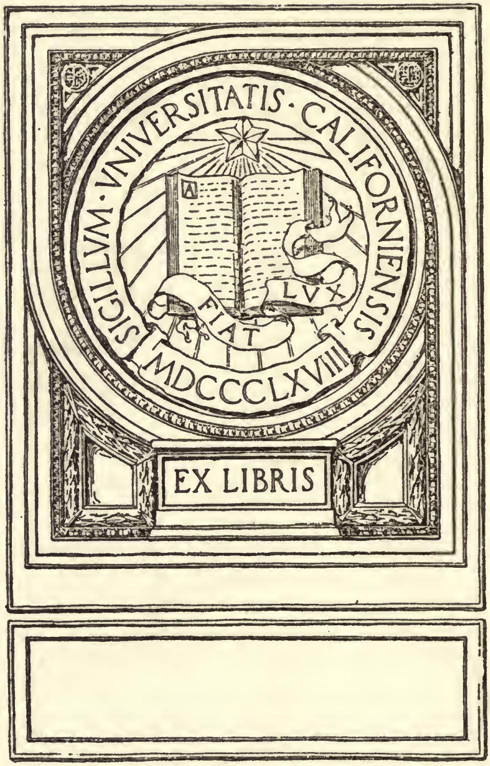
The Silver Bromide Grain of Photographic Emulsions

By A. P. H. Trivelli *and* S. E. Sheppard

Monographs on the Theory
of Photography, from the
Research Laboratory of the
Eastman Kodak Company

No. 1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Monographs on the Theory of Photography

THE SILVER BROMIDE GRAIN OF PHOTOGRAPHIC EMULSIONS.
By A. P. H. Trivelli and S. E. Sheppard.

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Preface to the Series

The Research Laboratory of the Eastman Kodak Company was founded in 1913 to carry out research on photography and on the processes of photographic manufacture.

The scientific results obtained in the Laboratory are published in various scientific and technical journals, but the work on the theory of photography is of so general a nature and occupies so large a part of the field that it has been thought wise to prepare a series of monographs, of which this volume is the first. In the course of the series it is hoped to cover the entire field of scientific photography, and thus to make available to the general public material which at the present time is distributed throughout a wide range of journals. Each monograph is intended to be complete in itself and to cover, not only the work done in the Laboratory, but also that available in the literature of the subject. A very large portion of the material in these monographs, however, will naturally be original work which has not previously been published. The monographs are written by those specialists in the Laboratory who are best qualified for the task, each monograph being edited by the Director of the Laboratory and by Mrs. Schramm, who is the active editor of the series.

Rochester, New York
April, 1921

Preface

The fundamental units of the sensitive materials used in photography are the small grains of silver halide which, imbedded in gelatine, form the emulsion.

Since these grains are of very small size, and are, furthermore, precipitated in a colloid medium, they have usually been treated simply as colloid aggregates.

As a result of a complete crystallographic study involving photomicrographic work of a high order, it has been possible not only to confirm the fact that the grains of high-speed emulsions are definitely crystalline, but to identify their crystalline form and to show that all the grains, though having several distinct shapes, belong to the same crystalline class. The grains being thus established as micro-crystalline, their formation in the emulsion can be studied by the aid of the recent physico-chemical theories of precipitation and especially of the dispersion theory of Von Weimarn, according to which the dispersity of the initial precipitate will be determined by the concentration of the solutions and other physical conditions. The changes in the dispersity of the original precipitate during ripening, which will follow from the laws of surface energy, is now found to be related to changes in the content of adsorbed impurities, and in connection with this the effect of ammonia upon the grains has been studied.

The catalysis of crystallization by nuclei is suggested as an explanation of some of the effects produced by the admixture of silver iodide with silver bromide in an emulsion, and the fact that traces of colloidal silver make the grains color-sensitive is believed to be related to this.

A study of the relations existing between the sizes of the grains and their photographic properties is reserved for a future monograph.

Rochester, New York
April, 1921

The Silver Bromide Grain of Photographic Emulsions

CONTENTS

The Silver Bromide Grain of Photographic Emulsions

CHAPTER I

The Influence of Ammonia on Photographic Emulsions and a Theory of Ripening

The use of aqueous ammonia in the ripening of photographic silver halide emulsions was introduced by Johnston[1] and is well known to photographic technologists, particularly through the later work of J. M. Eder.[2]

Eder states that exposing a dry gelatino-bromide plate for a few minutes to the vapor from strong ammonia immediately before using in the camera results in a marked increase in sensitiveness. On the other hand, Gaedicke[3] concluded that fuming prior to exposure diminished the sensitiveness, but that, subsequent to exposure and prior to development, it increased the developability of the latent image, resulting in an effective sensitizing. This action he considered to be one on the latent image, not an acceleration of the action of the developer. Sheppard and Mees[4] found that certain plates gave a higher inertia, or lower speed, with ferrous oxalate developer than with organic developers, while a larger group gave practically the same speed with both developers. For the latter, however, a slight fuming with ammonia increased the inertia, i. e., decreased the speed, when ferrous oxalate was used as developer. In addition to these relatively invisible effects, the accounts of which exhibit rather contradictory conclusions, it was observed by Eder that, if moist silver bromide plates were exposed under a bell-jar to ammonia vapor for a considerable time, they became more sensitive to light and coarser-grained, ultimately forming a network of coarse-grained silver bromide with relatively empty interspaces resembling frost figures.

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[1] Johnston, J., Gelatino-bromide of silver emulsions treated with ammonia. Brit. J. Phot. Almanac 1877: 95. 1877.

[2] Eder, J. M., Beiträge zur Photochemie des Bromsilbers. Sitzungsber. Akad. Wiss. Wien. **81**: 679. 1880.

[3] Gaedicke, J., Ammoniakräucherung bei Trockenplatten. Jahrb. Phot. **27**: 62. 1913.

[4] Sheppard, S. E., and Mees, C. E. K., Investigations on the theory of the photographic process.

Englisch[1] found that a partial development of the latent image was possible, for by treating an exposed plate with strong aqueous ammonia the unexposed parts were apparently more rapidly dissolved away than the exposed parts. He attributed this to a lesser solubility of the exposed halide in ammonia. Lüppo-Cramer,[2] repeating the experiments, came to a different conclusion. Under suitable experimental conditions he found that the exposed portions at first apparently dissolved out more rapidly than the unexposed, but that this relation was reversed on continuance of the ammonia "development." Lüppo-Cramer modified Englisch's experimental conditions by using ammonia vapor instead of aqueous solutions. This has advantages in that the action is slower and therefore can be better observed, and that there can be no actual removal of dissolved silver bromide from the plate. Proceeding in this way, and with the help of the microscope, Lüppo-Cramer concluded that ammonia development is really a reaggregation or "ripening" process which proceeds at different rates, according to the exposure to light of a given part of the plate.

Lüppo-Cramer considers that this supports the theory that light brings about a certain disintegration of the silver halide. He ascribed the "developability" with ammonia to the increased "inner dispersity" of the silver bromide grains. He finds that at first the exposed parts show a coarsened grain, and concludes that, in consequence of disintegration, the exposed silver bromide particles have on the whole a greater solubility in ammonia, whereby at first an immediate Ostwald ripening occurs. This, however, is reversed on further treatment, the unexposed parts becoming later relatively coarser-grained than the exposed parts. This he attributes to the "disintegration by light" affording a greater number of crystallization nuclei, whence, with greater number of crystals formed, the ultimate size will be smaller, since the mass of material per unit area is the same. Lüppo-Cramer later supported this view with experiments in which the "chemical latent image" was completely (?) destroyed, but could still be developed with ammonia.

It does not appear that this reasoning is either necessary or sufficient. To begin with, if the first effect in the more exposed parts is essentially an increased solubility and solution of the disintegrated particles of the original silver halide grains, whence come the subsequently invoked greater number

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[1] Englisch, E., Zeits. wiss. Phot. 2: 416. 1905.

[2] Lüppo-Cramer, Photographische Probleme, p. 83.

of crystallization nuclei? And also, where, at the same time, are the relatively larger crystals which, according to the Ostwald ripening theory, must be present to increase at the expense of the smaller crystals? There appear to be mutually incompatible requirements here, since the increased crystal fragments must disappear—by solution—to give the postulated initial Ostwald ripening in the more exposed parts, and yet, to explain the apparent reversal effect later, must also have been there all the time.

The experiments now to be described show, we believe, that the facts are capable of a less involved explanation. They show:

(a) That there is no ammonia development of the latent image, properly so called, but only an ammonia development of the visible image, no effect being obtainable with exposures to light much lower than those which give the least visible photochemical effect;

(b) That the actual development can be more simply explained by a simple recrystallization effect, not involving directly, but only (if at all) as a very subsidiary factor, any Ostwald ripening;

(c) That the development or ripening nuclei are due not to disintegration, but to the photochemical decomposition products of the silver halide—probably colloid silver adsorbed to silver halide—and to similar decomposition products from the reducing action of the ammoniacal gelatine on the silver halide.

In addition to correcting what appears to us the incorrect and unnecessary conclusions drawn by Lüppo-Cramer in his otherwise valuable and interesting papers, the experiments are noteworthy because this ripening with ammonia affords a cross-section of the ripening process in general, particularly as convection currents within the emulsion are eliminated. At the same time, it is believed that they indicate the causes for some of the natural limitations and peculiarities in the ripening process.

FUMING OF UNEXPOSED LAYERS

The experimental method followed was in the main similar to that of Eder and Lüppo-Cramer, namely, fuming with ammonia vapor evolved from strongest aqueous ammonia. Some side experiments with ammonia solutions applied direct showed that far less control was obtainable in this way. The aqueous ammonia—S. G. 0.90–0.92—was contained in deep crystallization dishes, the plates to be fumed being laid film down over them, so that an unfumed surround was obtained in each case. Care was taken that the distance between the ammonia solution and the plate was kept constant, unless purposely varied. For convenience the fuming was conducted under a hood in a dark room. Illumination and inspection during the experiments were facilitated by placing the carefully leveled dish over a dark-room lamp laid on its back, so that red light was thrown upward through the dish and plate. In all, some hundred experiments were performed, using Seed 23 and Seed Process Plates, Cine Positive film, and Lantern Plates.

In repeating some of the experiments previously described, an initial phase of the action of ammonia on the silver halide emulsion was noted, which appears to have attracted little, if any, attention. On fuming Seed Process plates, unexposed to light and unmoistened, in the manner described above, it was observed that the first visible differentiation of the fumed from the unfumed area is a uniformly diminished opacity; this was such that in one hour—the actual time varies both with the kind of plate and with its relative moisture content—the film had become almost transparent by transmitted light, but showed a light bluish gray turbidity by reflected light.

Fig. 1

Print through fumed plate on unfumed plate. Crescent shows untreated portion.

Fig. 2

Print on fumed plate through unfumed plate. Crescent shows untreated portion.

The extent of this induced transparency is shown by the photograph in Fig. 1, which gives the result of printing a negative through a plate so treated on to another one unfumed.

The part made transparent becomes, photographically,[1] greatly reduced in speed and density-giving power, as is shown by Fig. 2, which gives a direct print from the negative shown in Fig. 1 on the partially fumed plate. The unfumed surround is overexposed long before the fumed part gives a developable impression. On development the image frequently shows considerable irregularly distributed surface fog of a dichroic nature. Microscopic investigation of the fumed transparent area showed that in this state the emulsion has a fine and very uniform grain, apparently considerably finer than the original. The reduction of opacity, however, is due not solely to this diminution in grain size, but largely to an approximation of the refractive index of the grains to that of the gelatine.

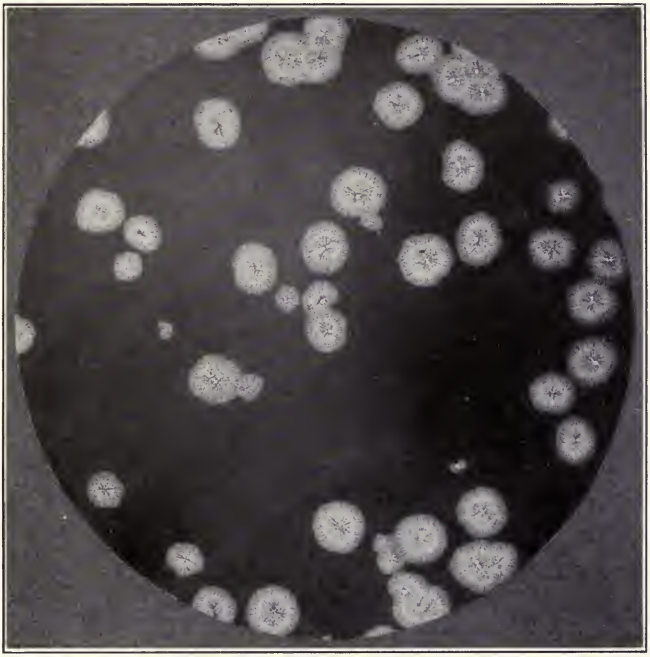

FIG. 3
Ammonia fuming, early stage

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[1] The photographic speed- and density-giving power of an emulsion on exposure and development must not be identified with the photochemical sensitiveness giving rise to a visible image.

It is very probable that at this stage a double compound of silver halide and ammonia is formed. (See p. 25.) The change of grain size is, however, not very pronounced as compared with later stages. This is evident in that at this stage the change is largely reversible. On being removed from the ammonia atmosphere the emulsion regains opacity to near its former value, this being accelerated by an air current. The next phase (on continued fuming), is an irreversible ripening, in the sense of increase in size of grain, in which large crystal aggregates are formed. They commence at isolated points (see Fig. 3), and radiate from these until the respective recrystallization circles or domains meet, when boundaries which tend to be straight lines are formed, so that the original recrystallization areas become polyhedral, as illustrated in Figs. 4 and 5.

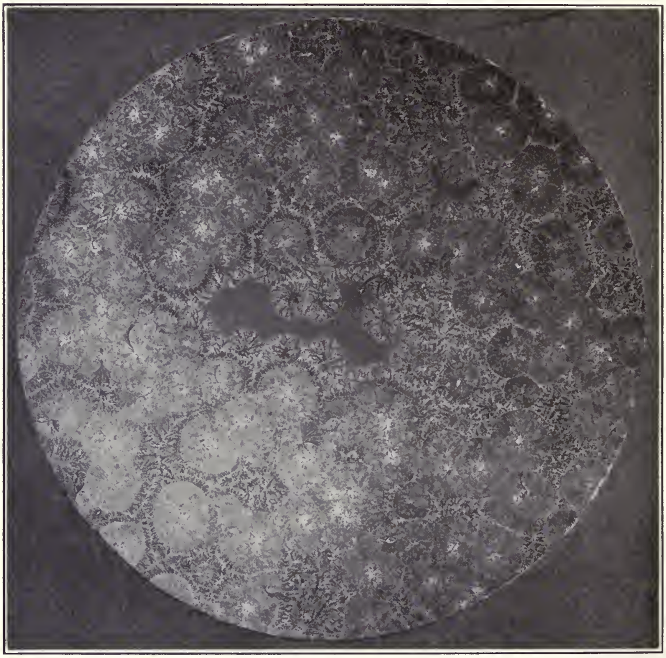

Fig. 4
Ammonia fuming, middle stage

It will be seen that the final stage is a complete filling up of the area fumed with a number of polyhedral cells enclosing a sort of efflorescence of trichites and crystal aggregates. The figures so far given are from natural size contact prints from contact negatives made direct from the original preparations; hence the appearance of the original preparations is reproduced as accurately as possible. Photomicrographs dealing with certain aspects of this recrystallization process will be given later in connection with the discussion of the theory.[1] At this point it is necessary only to note that the beginning of nucleation, under the conditions given, is to a certain extent accidental. In any case, it commences at the boundary where the film is in contact with the ammonia container, but in the fumed area dust particles or other casual nuclei seem to serve. As scratching the sides of the container starts crystallization from solutions, so a stress mark made with a glass rod on the emulsion induces ammonia development along the trace.[2]

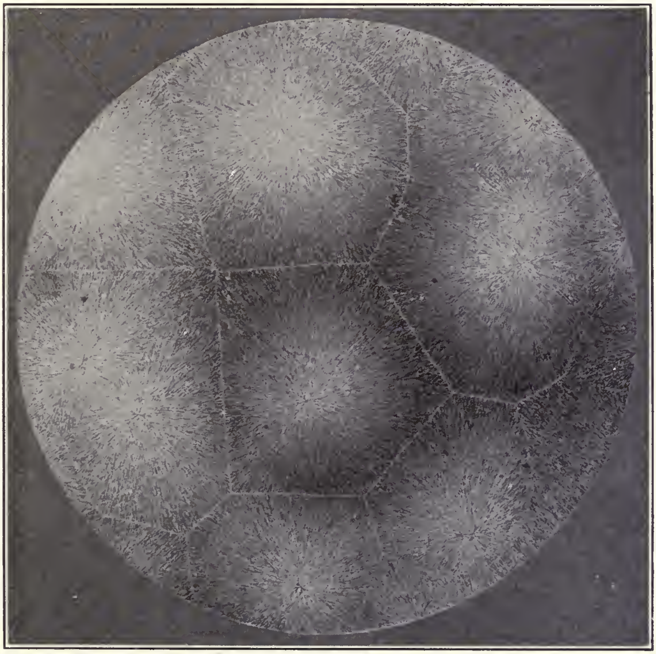

FIG. 5
Ammonia fuming, final stage

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[1] Examples of this have been given by Eder (l.c.) and Lüppo-Cramer, Kolloidchemie und Photographie. XII. Koll.-Zeits. **9**: 240. 1911.

[2] Cf. Lüppo-Cramer, Kolloidchemie und Photographie, l.c. This was confirmed in the present investigation.

FUMING EXPOSED PLATES

The plates were exposed behind a scale negative—a sensitometer strip—to a 100-watt lamp for definite times and at definite distances. From density measurements of the scale negative the relative exposures could be calculated, but it is unnecessary to give these within this scale, because it was found that precision in the matter of gradation within the scale was neither important nor practicable to determine. As has been pointed out under conditions of fuming, there is no actual increase or decrease of material within a given area, exposed or unexposed, but only changes of aggregation or dispersity and of refractive index, which produce an apparent change of density or opacity. Plates were exposed both moist and dry. In preparing the moist plates the plate was soaked for a brief period in water, and superfluous water blotted off. The plates were weighed dry and wet to determine the amount of water absorbed.

The general effect of moisture was greatly to accelerate the action of ammonia vapor. Although a definite proportionality of effect could not be ascertained, it was evident that excessive swelling in water produced more irregular effects. The most marked difference between dry and moist plates, in line with the acceleration, was the much coarser grain produced in the wet or moistened plates, as will be evident from figures to be given later.

EXPOSURE NECESSARY FOR AMMONIA DEVELOPMENT

A result of importance, in view of earlier pronouncements on the "development of the latent image by ammonia," was that the exposures to light necessary to obtain a developed image were of an entirely different order, being very many times greater than those required to obtain a developable image by ordinary development.

Thus with Seed Process plates the exposure necessary to obtain ammonia development of an image of the scale was some 150 times that necessary to give an image developable with pyro-soda. With Cine Positive film, the corresponding figure was about 250 times as long an exposure; and similar results were obtained with other emulsions. (With lantern plate, 190 times.) Under these conditions, which imply exposures well toward the ordinary solarization limit, it appears incorrect to speak of a development of the latent image by ammonia. And, in fact, close inspection showed that ammonia development of an image is possible only from an exposure which is either the same or but little below the threshold value of exposure to give a visible image. Of course this threshold varies very considerably with the visibility conditions, and it is generally possible to detect with the microscope definite evidence of photochemical changes well below the visible threshold of image formation.

Fig. 6 shows the slight indication of image formation after ammonia-fuming a Seed Process plate, dry, for some seventeen hours, the plate having received an exposure 130 times that necessary to give a full scale with pyro-soda development. The ammonia development here has proceeded to the stage of reversal already referred to, but has brought out nothing further on the scale. An unfumed control plate as well as the plate used showed a threshold visible image within a field or two of the lowest developed by ammonia.

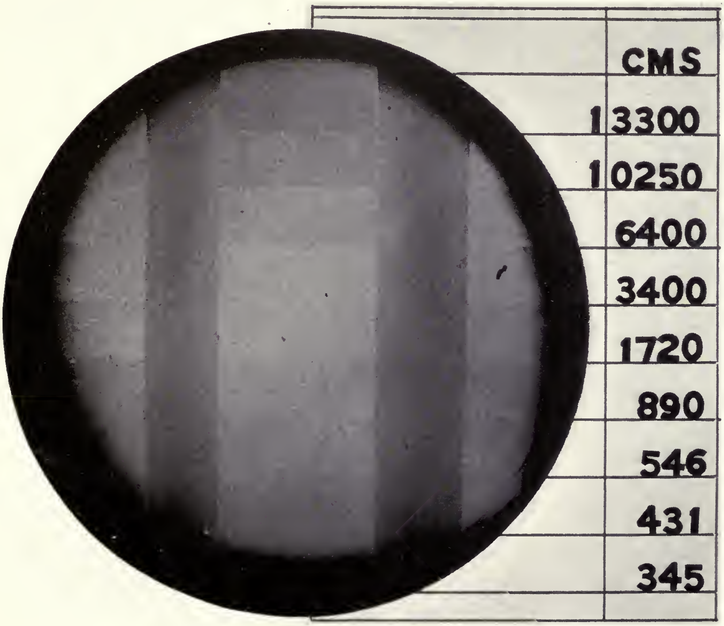

Fig. 6
Exposed plate, fumed dry; exposures in candle-meter-seconds

EFFECT OF MOISTURE

If the plate is moistened by swelling in water, fuming with ammonia produces an effect earlier, but the developable threshold exposure is much higher. Thus the result shown in Fig. 7 was obtained after soaking a plate for one minute in water and fuming fifteen minutes; but the ill-defined differentiation or development covers only part of the scale covered in Fig. 6 and implies about nine times as great an exposure, the normal image being visible over a greater range. Further development with ammonia in this case only filled the plate with crystal aggregates and obliterated the primary differentiation between exposed and unexposed portions. The faint indication of an image obtained in this way is shown in Fig. 7.

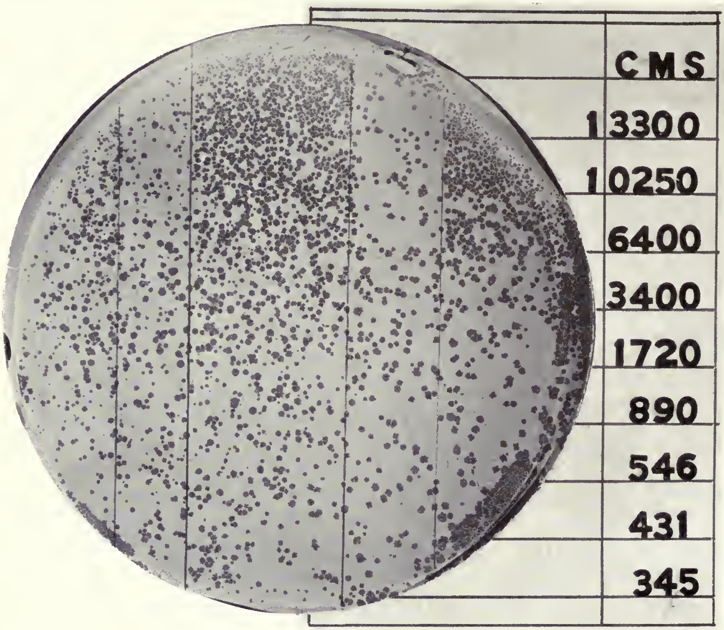

Fig. 7
Exposed plate, fumed moist; exposures in candle-meter-seconds

REVERSAL

The appearance of reversal observed by Lüppo-Cramer is clearly indicated in Fig. 8. It is to be noticed that more than one type of reversal, as regards relative optical density, is apparent in the process. The exposed portions, as compared with the unexposed, appear at first more transparent, and later, less transparent, than contiguous unexposed portions. This is due, first, to the new silver bromide-ammonia complex having a lower refractive index than silver bromide; second, to the varying stages of dispersity of the new and old phases. Reversal with increased exposure to light for the same time of development (fuming) indicates that the optical opacity at first increases with the number of nuclei, reaches a maximum, and then diminishes. (See Fig. 8.) Reversal with increase of time of fuming is more apparent than real, being dependent upon the relations between the stages of recrystallization in two contiguous fields. Finally, this is affected by a third factor—partial or complete reconversion of the silver bromide-ammonia complex into silver bromide, leaving pseudomorphs of silver bromide by evaporation of ammonia.

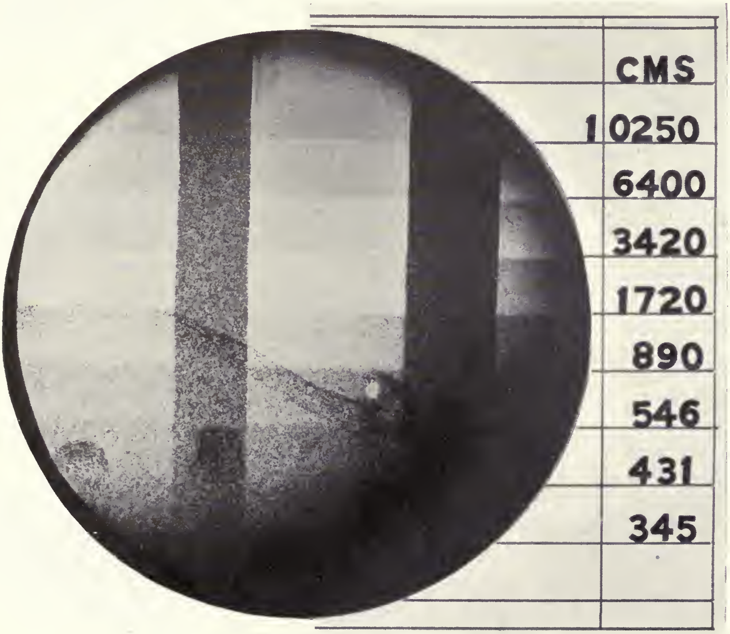

Fig. 8
Exposed plate, showing appearance of reversal

EFFECT OF AMMONIA-FUMING ON DIFFERENT EMULSIONS

As already noted, the rate and sensibility of ammonia-fuming is very dependent in one and the same emulsion on the actual state of the plate in respect of moisture content. It is very difficult to bring different emulsions to the same state in this respect, hence reliable comparisons between different emulsions are anything but easy to obtain. It was hoped at one time that ammonia-fuming might be used as a method of investigation and control of the "grain" of an emulsion when coated, somewhat in the manner of the etching reactions in metallurgy; but it is evident that, even if it should be possible, much more work on the control of conditions will be necessary. Taken by and large, however, the results showed that the finer-grained emulsions react, or rather reaggregate, more rapidly on fuming with ammonia than the coarser-grained ones. Their sensibility in the matter of the development of an image by ammonia after exposure to light appears to be entirely a matter of their photochemical sensitiveness. The rate at which ammonia-ripening takes place is a function of the size of the grain, the character of the emulsion, and the moisture content.

THEORY OF AMMONIA DEVELOPMENT

Reference has already been made and certain objections raised to Lüppo-Cramer's theory that ammonia development is due to a disintegration of the silver halide grains by light. The fact that in the absence of light action the reaggregation by fuming starts at the point of contact of the vessel used with the emulsion layer, or within this at casual dust particles or other nuclei, suggests that it is unnecessary to postulate either disintegration of silver halide grains by light, or Ostwald ripening. The simplest explanation is that reaggregation and recrystallization are initiated by nuclei furnished by light. Since the development practically only commences with exposures giving the threshold of a visible image, it is evidently unnecessary to look for these nuclei further than the photochemical decomposition product, most probably colloid silver adsorbed to residual silver halide, forming photo-halide. Accepting this, and in view of the absence of ammonia development for exposures much, if at all, below the visibility threshold of light action, it appears that the nuclei in the range of the so-called latent image are either not large enough or possibly still too "protected" by residual silver halide to function in ammoniacal recrystallization. This, however, is only in line with the fact that the threshold values of exposures above which it is possible to develop physically by an acid silver developer is very much higher (particularly in coarser-grained plates), than that for ordinary chemical development.

The evident reversal on prolonging development is simply a consequence of the variation of light transparency with the phase of the recrystallization process and the dispersity of the reaggregated silver halide. In the first noticed phase of apparent homogeneous peptization and increased transparency, new crystal nuclei of an ammonia-silver halide complex start to form about nuclei furnished by light. Then the size of these nuclei increases, and at first therewith the opacity. But in less exposed regions, and *a fortiori* in non-exposed ones, the number of initial foreign nuclei is, at the start, proportionately less; hence the grain size on reaggregation can overtake that in the exposed regions where there are a greater number of nuclei.[1] But a limit is set to this and a tendency to neutralize the initial differentiation formed by the fact that prolonged action of ammonia on the gelatino-silver halide results in a chemical reduction, thus furnishing colloid silver nuclei which are sometimes evident as a silver stain after fixing, but which are generally developable with a silver intensifier after careful fixation and washing. Lüppo-Cramer's chief argument for the disintegration hypothesis is the possibility of ammonia development after destruction of the image, as evidenced by incapacity for development with free silver, the destruction being brought about by bromine. In repeating these experiments it was found, first, that the threshold exposure which could be differentiated by ammonia was much raised by this treatment, and, secondly (as stated by Lüppo-Cramer), that the differentiation, or development, is very imperfect after this treatment. This result is in no way a necessary consequence of the disintegration theory. It is equally well and perhaps better accounted for on the colloidal silver nuclei theory here proposed. While bromination tends to re-halogenize the photochemical decomposition product, the silver halide thus formed is not physically homogeneous with the original silver halide grains, but, as altered material, may itself furnish nuclei for the ammonia recrystallization. Further, and perhaps more effective, is the local reaction on the gelatine.

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[1] If the plate is fumed moist, then dried out again, the visual opacity of the exposed regions is usually higher than that of the unexposed region, and increases to a limit with exposure. If the plate is fumed dry, and further dried out after fuming, the opacity of the lower exposures is usually less than in the unexposed region adjacent, reaches a minimum, and then increases again, but usually does not reach that of the adjacent unexposed region. The phenomena are further varied by the nature of the emulsion and the original size of the emulsion grains.

The conception that the new phase formed by photochemical decomposition could furnish the nuclei for this recrystallization was tested indirectly in two ways. First, a plate was given an exposure just sufficient to form a latent image, i. e., one developable with a chemical developer, but not, as already stated, with ammonia. This image was just developed, very faintly, but not fixed. After washing and drying, the plate was fumed with ammonia, whereupon a well-defined image was developed up, showing that the silver nuclei furnished by development could function as nuclei for ammoniacal recrystallization. See Fig. 9.

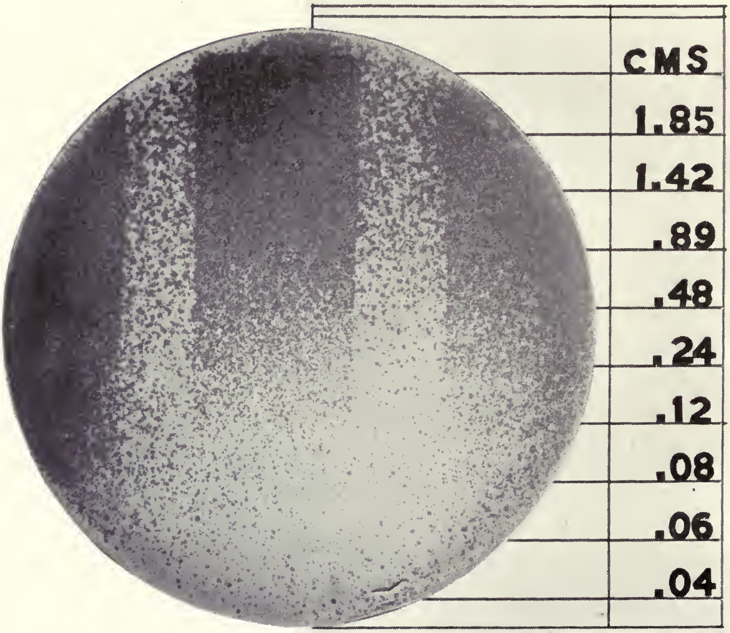

Fig. 9

Normally exposed plate, developed to appearance of image in diluted developer, then fumed with ammonia

As a second indirect support of the theory advanced, the development of colloidal gold nuclei by ammonia-fuming can be brought forward. By marking a plate with a glass rod dipped in gold chloride solution and drying down, then washing well and drying again, a very faint deposit of colloidal gold is left. On fuming with ammonia, this is developed by recrystallization on the traces of gold.

The minutiae of the recrystallization and reaggregation process induced by ammonia-fuming will be discussed later in connection with the general theory of ripening. Apart from the general interest of the phenomena in question, the phase of increased transparency first noted may be worth investigating sensitometrically. If a homogeneous peptization is effected, the resolving power and solarization limit should be markedly altered. Another point of interest is the relation of this ammonia recrystallization to the ripening of emulsions. The reaggregation or alteration of dispersity will be discussed later, but it should be mentioned here that the existence of direct chemical reduction of the silver halide by ammonia and gelatine combined was found. It is probable that this plays a determining role in the occurrence of both ripening fog and aging fog in gelatino-bromide emulsions.

The chemical composition and constitution of the silver halide-ammonia compounds is quite fully discussed by Ephraim[1] in his studies on auxiliary valences. He concludes that a maximum of three ammonia molecules can become attached to the silver atom, so that for salts saturated with ammonia the composition will be $AgHal: 3NH_3$, while the constitution may be any one of the following:

I. $[Ag(NH_3)_3\,X]$; II. $[Ag(NH_3)_6\,AgX_2]$; or III. $[Ag(\overset{X}{NH_3})_3]$.

At ordinary temperatures the tri-amine is not stable, passing over to the di- and mono-amines as the temperature is increased or as the pressure of ammonia is diminished.

SUMMARY

1. The general course of development of silver halide emulsions by ammonia was found to be similar to that described by Eder and Lüppo-Cramer.

2. It appears to be incorrect to speak of "development of the latent image" in this connection, as the ammonia development does not begin much, if at all, below the threshold of the visible (print-out) image.

3. It is concluded that the process consists primarily in recrystallization of the silver halide as a silver halide-ammonia complex on nuclei furnished by the visible photochemical image; it is therefore unnecessary to assume either a mechan-

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[1] Ephraim, F., Ueber die Natur der Nebenvalenzen. XIX. Ammoniakate des Silbers. Ber. chem. Gesell. **51:** 706. 1918.

ical disintegration of the grains by light or Ostwald ripening as factors in the effect.

4. The following results appear of importance for the general theory of emulsions: The opacity to light of a mass of silver halide increases at first on recrystallization with the number of independent nuclei. Independent nuclei can be furnished by foreign substances, such as colloidal silver or gold, or probably even altered gelatine. Under the combined action of ammonia and gelatine silver bromide is reduced with production of colloidal silver.

CHAPTER II

Von Weimarn's Theory and the Determination of the Dispersity of Silver Bromide Precipitates

The sensitive silver halide preparations used in photography may be divided into two main classes:

A. Silver halide formed in the presence of excess silver salt. This includes wet collodion, collodion emulsion, and most printing-out emulsions. The function of excess silver salt here is probably chiefly that of a chemical sensitizer, i. e., as a halogen absorbent;

B. Silver halide formed in the presence of excess soluble halide. This includes both positive and negative gelatine emulsions for chemical development. While development emulsions for printing (developing-out papers) and positives depend chiefly upon silver chloride and combinations of silver chloride and silver bromide in which the after-process of ripening plays a relatively small part, the fundamentally important negative emulsions are composed of silver bromide and silver iodide, the silver bromide in considerable excess and seldom used alone. By ripening is understood the increase in speed and change in other sensitometric properties induced by certain digestion processes, either by heat, with excess of soluble bromide present (boiling process), or at lower temperatures by ammonia. This treatment generally involves an increase in the average size of the grains, or, in the terms of colloid chemistry, a decrease in the dispersity. It was at one time associated with the flocculation of colloid particles,[1] but later has been more generally regarded as a case of Ostwald ripening. By this is meant the growth of larger crystalline particles at the expense of smaller ones, on the presumption that the latter have a greater solubility. Before considering either the general grounds for this thesis or its specific applicability to photographic emulsions, it should be pointed out that modern high-speed emulsions, relatively coarse-grained, are not produced by the ripening of emulsions which would otherwise be slow and fine-grained. The two types are produced under relatively different initial conditions, and, as pointed out by Lüppo-Cramer[2] and Mees,[3] are practically discontinuous.

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[1] Cf. Quincke, G., Die Bedeutung der Oberflächenspannung für die Photographie mit Bromsilbergelatine und eine Theorie des Reifungsprozesses der Bromsilbergelatine. Jahrb. Phot. **19:** 3. 1905.

[2] Lüppo-Cramer, Photographische Probleme, l.c.

[3] Mees, C. E. K., The physics of the photographic process. J. Frankl. Inst. **179:** 141. 1915.

It may be said that fundamentally the production of such different emulsions depends upon certain general principles for regulating the dispersity, or average grain size, of a solid precipitate. In a certain measure specific applications of these principles have been familiar for a long time to both analytical and industrial chemists. But it is only in recent years, with the development of colloid chemistry, that they have been reduced to definite and general laws, capable to a certain extent of mathematical expression, and equally concerned with the genesis of colloids and of crystals. While the conditions for crystallization from liquid melts by cooling have become known largely through the researches of Tammann,[1] the determination of similar principles governing the dispersity or internal subdivision of a new phase separating from supersaturated solutions, particularly where the new phase is solid, is due to the Russian investigator, von Weimarn.[2] His contentions as to the "vectorial" character of phases of matter usually termed amorphous will be noted later. Meanwhile the kernel of his work will be briefly reviewed, as it is of considerable experimental and practical importance.

It is a fact well known to chemists that not only does the form and subdivision of a precipitate vary in different substances, but that variations in the conditions of precipitation will alter the character of the precipitate for one and the same substance. Thus, Stas[3] distinguishes certain "modifications" of the silver halides, reference to which is made in many text-books of photography.[4]

Von Weimarn's first postulate is that the actual form and internal subdivision of a new solid phase are determined by two sets of factors:

1. Unilateral influence of the vectorial molecular forces on the molecules forming the free (crystal) surface. By this is meant a directing or orienting force of the molecules separating as a new phase on those forming the free surface of the crystalline individuals of this phase. It is considered that the molecules in the free surface of a crystal are imperfectly oriented, or imperfectly ordered in respect of the space lattice determining the crystal system and form. Since the smaller the crystal, the greater its surface as compared with its volume, the crystalline ordering would tend to be overwhelmingly deviated from if it were not for this factor. It is considered

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[1] Tammann, G., Krystallisieren und Schmelzen.

[2] Weimarn, P. von, Zur Lehre von den Zuständen der Materie.

[3] Stas, J. S., Recherches de statique chimique au sujet du chlorure et du bromure d'argent. II. Ann. chim. phys. V. **3**: 145. 1874.

[4] Eder, J. M., Ausführliches Handbuch der Photographie, Vol. III, p. 13.

as giving rise to a "capillary pressure" additive to the general hydrostatic pressure on the surface, and increasing with increasing dispersity. Hence, in general, it increases the crystalline solid character, raising the melting point as the size of the grain diminishes for substances for which pressure does this, while for the relatively few substances, like water: ice, the opposite obtains;

2. The second factor or group of factors is considered to be always tending to bring the substance to the fluid state—i. e., one of relatively unordered molecular movement—and is sometimes identified with ordinary dynamic surface tension.

The conception that the form and size of a crystal depend upon a balance of internal and external forces is itself logical, and will be considered from a slightly different angle later. It should be noted at this point, however, that von Weimarn contends that all so-called amorphous solid precipitates are essentially crystalline in the character of their unit particles, cellular and flocculent textures being due to secondary causes. The crystallinity of the particles may be ultra-microscopic (krypto-crystalline), but it exists as a reality determining the trend of their changes.[1] Since a crystal is regarded essentially as a phase of definite composition, this standpoint is in apparent contradiction with the general view of such precipitates as "absorption-compounds," i. e., as phases of variable composition.[2] The explanation is that the purity or composition of a crystal is largely a function of its size. The smaller the crystal, the larger its relative surface, and the more it is liable to contamination with dissolved and adsorbed foreign molecules. Hence, the composition of a solid crystalline dispersed phase is a function of the dispersity.

The composition of the surface layer may be expressed as $X_n\ Y_m\ Z_p$, i. e., X_n molecules of the dispersed substance, Y_m molecules of the solvent (or dispersing medium), Z_p molecules of co-existing solutes. N, m and p need stand in no rationally fixed ratio; thus Y_m may be nearly eliminated by drying, while Z_p will increase with the dispersity of X_n proper. These combinations form the class of adsorption compounds or "capillary combinations."

It is desirable to add to this exposition of von Weimarn's theory that, as a result of other work, we regard the "attachment" of the components Z_p and Y_m as varying from a state of true solution in the crystal to one of entirely super-

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[1] Cf. von Weimarn, l. c., vol. I, p. 13.

[2] Bemmelen, J. M. van, Die Absorption.

ficial combination by chemical (residual) affinity.[1] In general, however, the contamination will be ruled by the following characteristics:

a. Equilibrium is reached very rapidly;
b. The reverse separation by washing with pure solvent proceeds very slowly, adsorption being in most cases practically irreversible;
c. For low concentrations of the adsorbed substance (in the solution) relatively greater amounts are adsorbed than at high concentrations.

Von Weimarn considers that these characteristics are largely explainable by the fact that the surface layer of a crystal behaves in a measure like a strongly compressed viscous liquid.

Coming now to a more specific consideration of precipitation, he points out that the actual aggregation of the molecules of a new phase depends upon a considerable number of proximate factors, e. g., its solubility, its latent heat of condensation, the pressure on the medium, viscosity, and the concentration of reactants. Of these, solubility and concentration demand first attention, and it is assumed concerning them that aggregation of a new phase may be divided into two stages, the first (a) consisting in the formation of amicroscopic "germs" or nuclei, the second (b) in the growth of these particles, chiefly by diffusion of dissolved molecules into the sphere of their attraction. This division is common to Tammann's theory of crystallization from super-cooled melts and von Weimarn's theory of crystallization from supersaturated solutions. The latter proposes the parallel forms:

SUPERSATURATED SOLUTIONS	SUPER-COOLED LIQUIDS
a. (1st stage)	
$W = R\,\dfrac{\textit{Condensation pressure}}{\textit{Condensation resistance}}$	$W = R\,\dfrac{\textit{Super-cooling}}{\textit{Latent Heat}}$
$= R\,\dfrac{Q-S}{S} = P/S$	$= R\,\dfrac{T-T^1}{L}$

Where W = velocity of condensation
Q = total available molecules in solution
S = normal solubility of coarse-grained phase
Hence $Q-S$ = actual supersaturation
P/S = specific supersaturation at initial condensation

b. (2nd stage)	
$V = \dfrac{D}{d} \cdot Z(C-c)$	$v = \dfrac{H}{d} \cdot Z(t-T)$, where
Where V = velocity of crystallization	v = velocity of crystallization

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[1] Cf. Langmuir, I., The constitution and fundamental properties of solids and liquids. I. Solids. J. Amer. Chem. Soc. **38**: 2221. 1916; II. Liquids. *ibid.* **39**: 1848. 1917.

D = diffusion coefficient
d = diffusion path length
c = saturation concentration (solubility) for a given dispersity
Z = total surface

H = heat conductivity
d = diffusion path length
t = melting temperature

The expression for the second stage is essentially identical with that for the so-called Nernst theory of heterogeneous reactions,[1] which may be considered an adaptation of Wilderman's formula.[2]

Nernst's modification consisted in supposing that, in heterogeneous chemical reactions, the reaction itself was accomplished with practically infinite velocity and adjacent to the boundary surface between phases, and that the velocity measured was that of diffusion across a layer d having a concentration gradient varying from saturation to that general in the solution.[3] Hence, for the velocity constant k he substituted D/d, D being the diffusion coefficient.

This conception has been keenly criticized,[4] and in fact is only partially adequate for a limited number of cases. Its insufficiency will be specifically noted later. As regards the second stage of crystallization, Wilderman's generalized expression,

$$V = k\,Z\,(C - c) \mp K,$$

(where $C - c$ expresses the concentration difference, or distance from equilibrium, and K is a characteristic "instability constant"), may be substituted without affecting von Weimarn's thesis.

The following important deductions are made:

I. Provided that the product (volume x concentration) be kept constant and sufficient time allowed, individual crystal magnitudes are inversely proportional to W, the initial condensation velocity;

II. With increasing W the number of nuclei increases, but for very high W adhesion of these occurs—i. e., groups or clumps of crystal nuclei cohere, forming a single crystalline aggregate termed by von Weimarn aggregation crystallization.

In any case, the initial stage of separation of a new phase is the formation of a colloid solution (suspensoid or emulsoid). This, however, may be so transient as to escape notice, depending upon the relation between the velocity of initial condensation and that of crystalline growth.

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[1] Nernst, W., Theoretische Chemie.

[2] Wilderman, M., On the velocity of reaction before complete equilibrium and before the point of transmission, etc. Phil. Mag. VI. 2^{2}: 50. 1901.

[3] Cf. W. Nernst, l. c.

[4] Cf. M. Wilderman, l. c.

The important factor here is not the absolute, but the specific supersaturation P/S. Thus, with a given value of P (say a few grains per 100 cc.) a very soluble substance (e. g., sodium chloride in water), will deposit nothing at first, even for considerable supersaturation, since not only is the solubility of coarse-grained crystalline sodium chloride very considerable, but that of the amicrons is even greater.[1] Hence the initial velocity of condensation is small compared with, for instance, silver chloride.

However, the value of P, the absolute supersaturation, is still of considerable importance. The resulting precipitate will be very different, according as a given value of P/S $(= V)$ is due to large or small S. In the one case, a large amount of the precipitate is formed, in the other, little. If V be large, the former case gives a gelatinous precipitate, or gel; if V be small, a large number of dispersed particles, therefore a solution. Thus by suitable alteration of P or S, or both, we can ensure the initial separation of the dispersed phase in any desired form.

The stability of the new phase in the initial condition is dependent, to a large extent, upon conditions expressed in the formula for the second stage.[2] The smaller the existent supersaturation $C-c$, and the smaller the value of V, the greater the stability. Decrease of D, the diffusivity, helps this. Hence, for stable suspensoid hydrosols there are required:

Large values of $P=Q-S/S$ and
Small values of S

so that V may be large, giving many nuclei.

An example along these lines, worked out in detail by von Weimarn, is barium sulphate. The solubility in water at 18° C. is .00024 gms. per 100 cc. This is large enough so that, with ordinary solutions of barium salts with sulphates, the values of P do not give large values of V and hence barium sulphate is obtained in an immediate microcrystalline form. But from more concentrated solutions of more soluble barium salts, e. g., barium sulphocyanide and manganese sulphate, the barium sulphate may be obtained either as a cellular gel or a translucent hydrosol.

Summarizing von Weimarn's postulates at this stage:

1. With very soluble substances, suspensoids are obtained only for large values of V, resulting in a gel. If V be small, the suspensoid is transitory.

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[1] The presumption of a higher solubility of finer grained particles will be discussed later.

[2] It must be understood that these stages are, as regards the general rate of change and the total mass in course of change, continuous and, to some extent, simultaneous. The differentiation is mainly important as affecting the character of the precipitate.

2. With substances of small but measurable solubility (from 4 to 10 gms. in 100 cc.), the suspensoid stage is reached for both large and small values of *V*, the former resulting in a gel, the latter in a dilute hydrosol.
3. With substances practically insoluble the suspensoid stage is not recognizable for small values of *V*. With large values of *V*, dilute sols are obtained.

THE DETERMINATION OF THE INITIAL GRAIN SIZE OF PRECIPITATES IN RELATION TO VON WEIMARN'S THEORY

As a first application of von Weimarn's principles, the precipitation of silver bromide at different initial concentrations was studied with $V \times C$ kept nearly constant. Equivalent amounts of silver nitrate and potassium bromide solutions were mixed at a temperature of 20° C. A deviation was made, simulating emulsion practice, in that steady mechanical agitation was employed. The vessels were dimensionally similar cylinders with proportionate Wulff (centrifugal) agitators. Under these conditions it was not found that the dispersity of the precipitate was markedly affected whether the silver nitrate was added to the potassium bromide or conversely. However, the photochemical sensitiveness (visible darkening) was higher in the latter case.[1]

The results obtained are shown in the following table:

EQUIVALENT CONCENTRATION (*Normal*)	DISPERSITY	REMARKS
.0002	Clear hydrosol	↑
.0004	Clear hydrosol	
.0010	Clear hydrosol	
.0025	Cloudy sol, settles somewhat	Decreasing
.025	Turbid suspension, settling	dispersity
.25	Flocculent → crumbly ppt.	
.75	Flocculent $\rightarrow\left\{\begin{matrix}\text{milky above}\\ \text{curd below}\end{matrix}\right\}\rightarrow$ silt	
1.50	Flocculent ppt. → silt	↓
3.00	Curdy → crumbly ppt.	Decreasing
4.50	Curdy, quasi-cellular voluminous gel	dispersity

See outside curves in Figs. 10, 11, 12.

These results are mainly qualitative and will be studied quantitatively later. They show, however, that as the initial concentration of reactants is increased, the dispersity passes through a minimum, the precipitate here obviously approaching the crystalline condition. And for lower and higher concentrations it tends to give colloid sols and gels respectively.

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[1] As has been indicated by Mees (The Physics of the Photographic Process, l. c.), many properties of the emulsion probably depend not simply on the dispersity (grain-size), but on the distribution of sizes, or "dispersity gradient."

Now the extent to which the variation of dispersity thus offered by change of initial concentration is photographically useful is limited. For one thing, it is not practicable to keep the volume concentration constant; for another, the practicable range of amount of precipitate per unit volume of emulsion is limited. Hence, in any case, other factors must be introduced; and these are superposed upon variation of initial concentration within a certain limited practicable range.

CHAPTER III

Accessory Factors Influencing the Dispersity of Silver Bromide Emulsions

In von Weimarn's theory, the grain size of precipitates is considered as being regulated essentially by the initial concentration of the reactants. In point of fact, there are a number of modifying factors, frequently as important as concentration, which may, for convenience, be termed accessory dispersal factors. These factors, in so far as silver bromide emulsions are concerned, are:

1. The colloid emulsifying medium, and variation of its concentration and condition;
2. Effect of mixture of silver halides;
3. Addition of solubilizing reagents, in particular excess of bromide or ammonia;
4. Addition of other soluble ingredients acting either on the silver halide or on the gelatine or on both, and, modifying all these, temperature and agitation.

Taking these up in detail:

1. EFFECT OF COLLOID MEDIUM UPON DISPERSITY

The influence of colloid media such as gelatine upon the silver halide precipitate is far-reaching. To begin with, silver halide precipitated in the absence of such a medium is, except where certain special precautions are taken, practically immediately reducible by developers. That is, it is not only mechanically, but also chemically, unsuitable for photographic purposes. It was suggested by Sheppard and Mees[1] that the most probable explanation of this form of the protective function of gelatine is that it acts as a filter against nuclei (development germs), and this view is strongly supported by Lüppo-Cramer.[2] Apart from this, however, it affects the dispersity (or size of grain) and the form and composition of the individual grain.

Considering dispersity first, we have at present only qualitative indications. It is well known that, in the presence of gelatine, silver bromide is still obtained as a colloid hydrosol at concentrations of the reagents which would otherwise give a coarse-grained precipitate. Generally, it appears that if the relation between concentration of precipitants and dis-

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[1] Sheppard, S. E., and Mees, C. E. K., l.c., p. 206.

[2] Lüppo-Cramer, Kolloidchemie und Photographie. XIII. Koll.-Zeits. **10:** 182. 1912. Cf. Reinders, W., and Nieuwenburg, J. van, Gelatine und andere Kolloide als Verzögerer bei der Reduktion von Chlorsilber. Koll.-Zeits. **10:** 36. 1912.

persity of new phase is represented by a curve of the type shown in Figs. 10, 11 and 12, i. e., passing through a minimum dispersity, then the effect of a protective colloid is to flatten out the curve and shift the minimum more or less considerably to regions of higher concentration. This effect will in general be the more pronounced the greater the concentration of the gelatine, so the emulsion-maker can control the dispersity to a considerable extent by varying the concentration of gelatine present at mixing, supplying the rest as required.

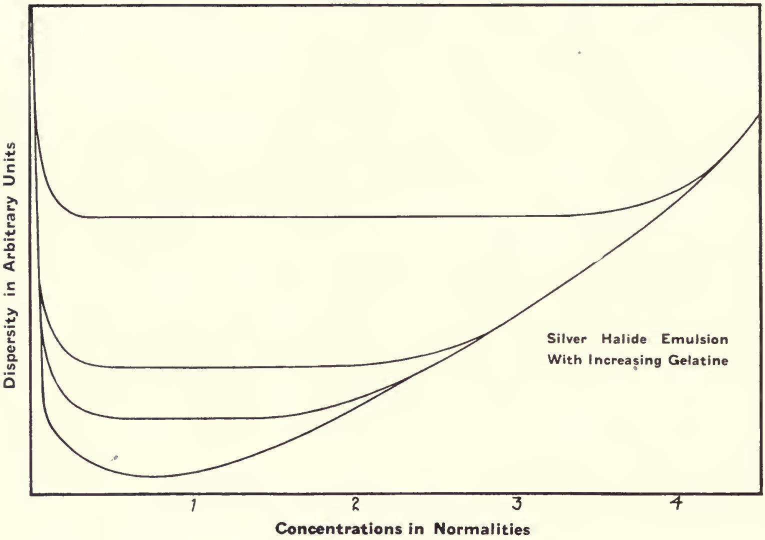

Fig. 10

It is probable that part at least of this effect is due to the increase of viscosity, or inner friction, of the medium. Reverting to von Weimarn's theories, it will be seen that the effect might be attributed chiefly to this factor, which would have the result of increasing the number of nuclei. It can be shown, however, that while viscosity counts for much, the protective action of the colloid is not due to this alone, since solutions of different bodies of equal viscosity give very different results. There is here a definitely selective action, dependent upon the colloid chemical character of the medium, and largely specific in respect of the substance precipitated or dispersed. Provisionally, we shall regard this as a capillary chemical or adsorption effect, and discuss its nature more fully both experimentally and theoretically.

Technically, it is well known that different kinds of gelatine are by no means equivalent for preparing silver halide emulsions. Without trenching on the colloid chemistry of gelatine, or on the nature of the colloid condition of its sols and gels, it is to be noted that the condition of a given gelatine will depend to a considerable extent upon its thermal history, and also upon its content of electrolytes. The affinity of gelatine for water—as shown particularly by its absorption as gel, and also by its behavior as sol—is increased greatly by small amounts of acid and alkali. Again, it is affected by salts, some of which increase, others decrease, its affinity for water. In considering the effect of additions upon a gelatino-halide emulsion, not only the direct effect on the silver halides must be considered, but also the indirect effect, by way of their action on the gelatine.

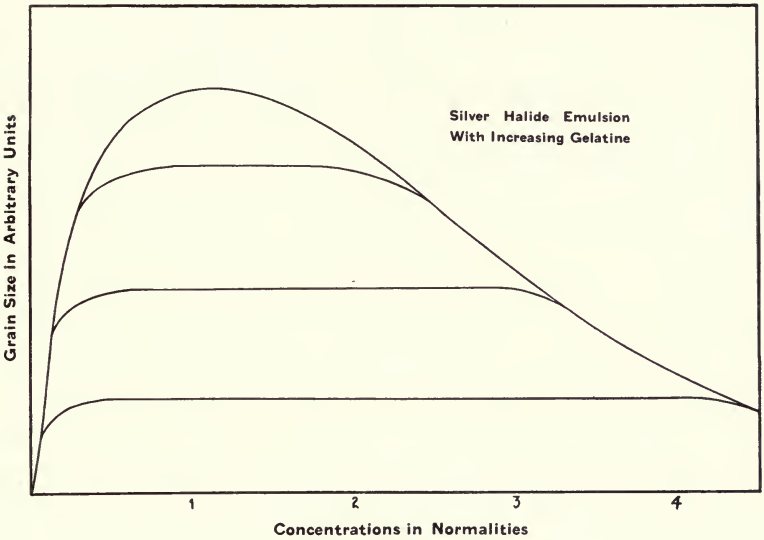

FIG. 11

We may at this point anticipate the results given in a later chapter by stating that while it is very possible, even probable, that in the preparation of emulsions, particularly in the ripening process, a combination of some kind between the gelatine and the silver halide occurs, we know little or nothing as to its character or extent. We have found, following Eder,[1] that silver bromide precipitated in gelatine and

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[1] Eder, J. M., l. c., Vol. III, p. 11.

centrifuged out at 1,000 to 2,000 revolutions per minute carries with it, after rapid washing with warm water, about two per cent of gelatine. Similar figures were obtained with silver halide emulsions. However, the greater part of this is probably mechanically retained and it is most probable that the amount of "combined" gelatine in the ripened high speed emulsions is of the order of the dyes retained in sensitizing.

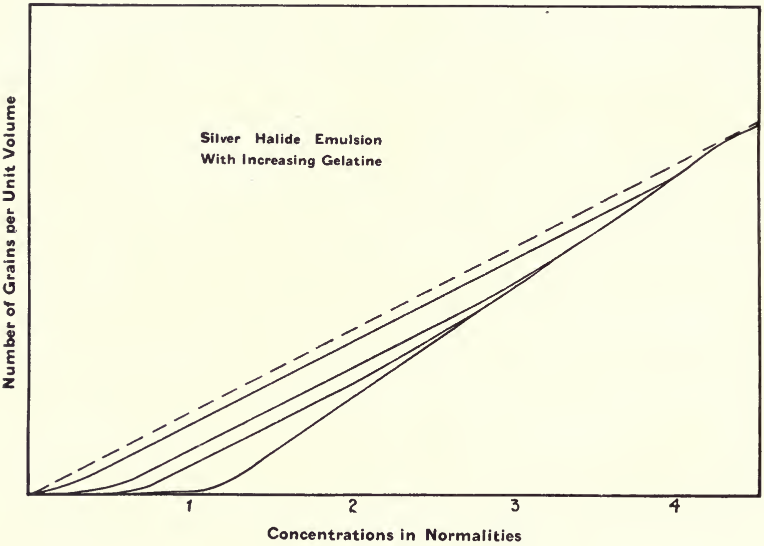

FIG. 12

For low-speed and positive emulsions the nature of the combination between the gelatine and the silver halide is probably even less definable. Nor do we know whether or not there is a solution or adsorption of the gelatine as a whole, or whether there is a selective (preferential) solution, sorption or combination of amino-acid anhydrides which may be considered as the potential structure-units of the gelatine solution aggregate, or of protein derivatives.

Influence of Temperature. The general conclusions outlined here—the shape of the dispersity-concentration curve, etc.,—are much modified by change of temperature. By reducing the amount of gelatine and raising the temperature to near the boiling point, the zone of minimum dispersity is markedly enlarged, so that by adding the first part of the precipitating silver solution drop by drop, thus forming (according to the principles discussed), a nucleus solution, then adding the remainder relatively rapidly and stirring well, a well defined crystalline precipitate is obtained. The principle is, of course, familiar in analytical chemistry in the control of precipitations for gravimetric analysis.[1]

Colloid Medium and Crystal Form. We must, however, notice that the effect of a colloid medium upon the dispersity of a precipitate is closely connected with its effect upon the form of a crystal. This will be readily understood in view of the fact that it affects not only the condensation but the rate of crystal growth.

This may be studied in its most pronounced form when crystallization occurs at rest. Generally, of course, agitation tends to diminution of the size of crystals, quiescence to increase. The object being to obtain a uniform, relatively fine-grained material, silver halide emulsions are continuously and thoroughly stirred.

Studying, for maximum contrast, the conditions of crystallization at rest with a colloid present affecting crystal growth, there are, from one point of view, the following possibilities:[2]

a. Total inhibition of crystallization;

b. Suppression of some of the lines of growth;

c. Extension of the crystal to abnormal proportions, forming a compound crystal;

d. Gyrating and curving direction of growth.

Of these, the first need not be considered here. The others will be discussed in order.

(b) Suppression or repression. It is supposed that currents are set up to and from growing crystals—i. e., micro-convection currents due to gravity changes, as well, probably, as convergence of diffusion lines, which are again affected by the rate of crystallization and viscosity. These currents are likely to become more accentuated and well defined for a medium at rest, and one of high viscosity.[3] Hence, any tendency to irregularity of growth will be facilitated in so far as these currents are favored. This important question will be taken up later.[4]

(c) Extension of the crystal to abnormal dimensions, forming a compound crystal. The accompanying photomi-

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[1] Cf. Brother, G. H., Suggestions on some common precipitates. J. Amer. Leather Chem. Assoc. **13**: 159. 1918.

[2] Bowman, J. H., A study in crystallization. J. Soc. Chem. Ind. **25**: 143. 1906.

[3] Viscosity must have a limiting or maximum influence here, for it tends to decrease gravitational convection currents.

[4] Cf. Chapter IX.

crographs (Figs. 13-16) of silver halide ripened *in situ* by fuming gelatino-bromide plates with ammonia illustrate both (b) and (c). In some cases there are filiform and dendritic structures, due largely to factors of the type (b)—i. e., greater rapidity of condensation with very imperfect orientation. In others, there is a definite tendency to form an imperfect skeletal example of a much larger compound crystal, the constituent crystallites being oriented in planes at definite angles to each other.

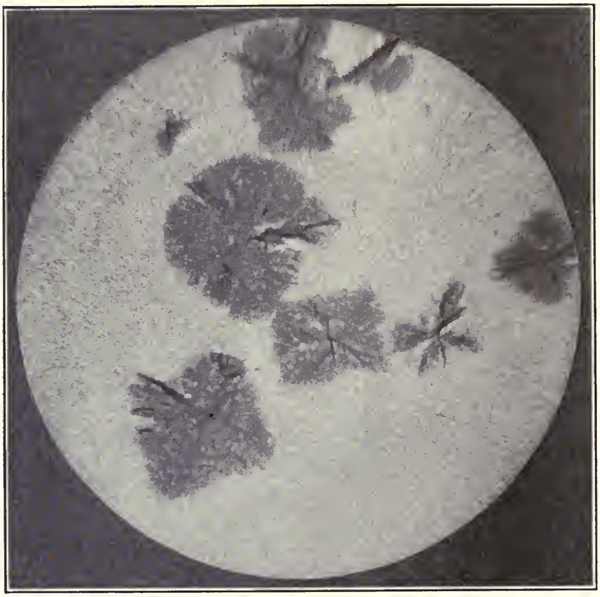

Fig. 13
Crystal aggregate, magnified 40 diameters

In some cases, within the same diffusion sphere (or condensation-halo) it will be seen that on one side the condensation tendency has prevailed, giving a dendrite, and on the other, the orientation tendency, giving an aggregate-skeleton, or compound crystallo-crystalline aggregate.

These types of growth (b) and (c) at rest are both compatible with what Bowerman terms the relay principle,—i. e., a growing point is pushed forward into the supersaturated mass and becomes a new focus or nucleus.

(d) Finally, curving or gyrating occurs where the crystallizing force is so nearly balanced by the resistance to growth that this takes place along the lines of least resistance. There are reasons for stating that in a system at rest this will generally approach a logarithmic spiral.

Taken altogether, the phenomena in a colloid gel (at rest) indicate that the supply, as fixed by the diffusion potentials of the supersaturated field, is more or less divided in distribution between local condensation and uniform orientation of the crystallizing molecules. There results, then, a particular equilibrium between the former tendency to increased density in phase (condensation) and the latter tendency to oriented or ordered distribution in phase (crystallization *per se*), which is possible only in systems at rest, where the diffusion sphere may be large[1] (cf. Fig. 5). Agitation destroys this condition,

FIG. 14
Crystal aggregate, magnified 40 diameters

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[1] The principle here outlined is an application of Gibbs' theorem on the homology of macro-canonical and micro-canonical ensembles, as given in Elementary Principles of Statistical Mechanics. On formation of skeletons and crystal growths in general, see R. Brauns, Chemische Mineralogie, p. 130, and O. Lehmann, Molekular Physik, Vol. I, p. 337. Lehmann's explanation of the local concentration gradients along the lines of auto-intensification applies to the growth forms (dendrites), but our contention is that these are characteristically antithetic to the skeletal forms, and that this difference is explicable on the differentiation pointed out by E. Riecke (Ueber Wechselwirkung und Gleichgewicht trigonaler Polysysteme, Ann. Physik. IV. 3: 543. 1900). Riecke considers that the growth of a crystal depends, inherently, on the exertion of both attractive (condensing) and orienting (ordering) forces by the original nucleus on the crystallizing substance. This subject will be discussed more fully in a later chapter.

—i. e., reduces aggregation-crystallization to a relative minimum depending upon chance of collision of crystal nuclei, which increases with total concentration of reactants, and decreases with the viscosity of any colloid present.

Actually, then, agitation under certain conditions may favor crystallization, for by eliminating certain types of aggregation-crystallization it increases the chances of development of individual crystals. The system to which the crystal belongs can be supposed to be determined inherently by its chemical constitution, or, if polymorphic, by conditions of pressure and temperature.

Fig. 15

Ammonia recrystallization of silver bromide, exfoliatory aggregation, magnified 30 times

The facts just described may be partially accounted for by certain considerations of the influence of capillarity upon crystal form, a topic which will be discussed in a subsequent chapter. (See pp. 57 et seq.)

2. EFFECT OF MIXTURE OF SILVER HALIDES

The Condition of Co-precipitated Silver Halides. When two relatively insoluble compounds with a common ion, such as silver chloride and silver bromide or silver bromide and silver iodide, are precipitated together, the proportions in which they are formed in the precipitate depend upon:

1. The solubilities of the compounds in water;
2. The solubilities of the compounds in excess of the precipitants;

3. The relative proportions and absolute excesses of the precipitants;
4. The possible formation of definite compounds in between the precipitated substance.

These conditions, expressed in terms of the mass law, determine true equilibrium for a given temperature.[1] We must, however, bear in mind the possibility of the end-state in a given case being a "false equilibrium," owing to quasi-mechanical adsorption factors, etc., so increasing the inner friction that true equilibrium is not reached.[2] There are

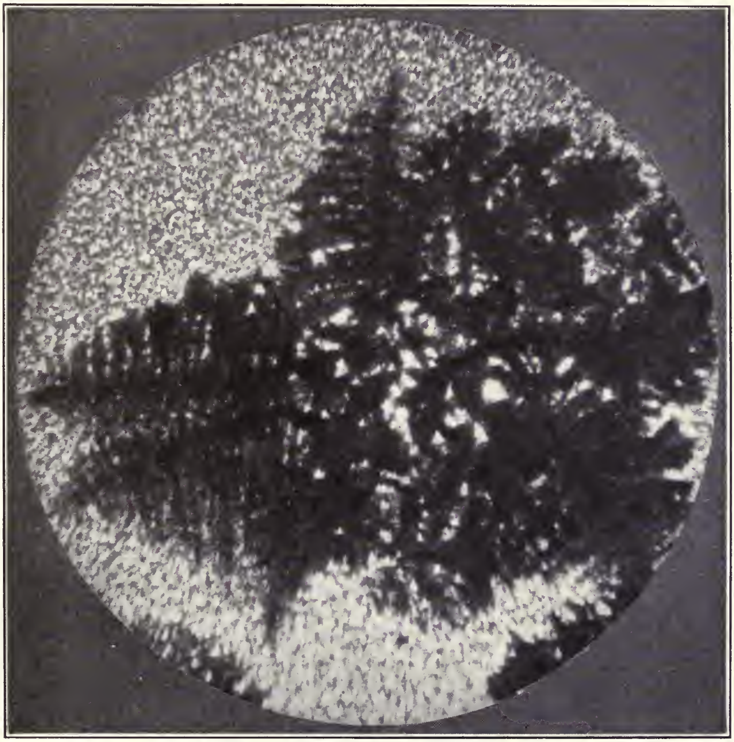

Fig. 16
Silver bromide aggregate, recrystallized by ammonia fuming. Compound dendritic and cubic aggregate structure

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[1] See F. W. Küster, Ueber Gleichgewichtserscheinungen bei Fällungsreaktionen. Zeits anorg. Chem. **19**: 81. 1898.

[2] Duhem, P., Traité élémentaire de mécanique chimique, fondée sur la thermodyna mique. Vol. I, p. 4.

several phenomena in the formation and ripening of silver halides which point to this as a probability. The experimental test of false equilibrium is that different end-states are reached on proceeding from opposite directions. It is possible that the discontinuity between low-speed and high-speed emulsions depends to some extent upon this condition.

An important investigation in which the precipitation relations of the silver halide pairs, silver chloride-silver bromide and silver bromide-silver iodide, were examined is due to Thiel.[1] The object of the research was the investigation of reversible electrodes of the second kind with mixed depolarizers. The so-called second kind of galvanic elements are concentration cells in which the electrodes are of the same element, having the same solution tension, but bathed in solutions of a slightly soluble salt of the electrode initial in equilibrium with a soluble salt of another metal with the same anion. These combinations are then reversible with respect to the anion, and the polarization-preventing salt of the electrode metal is termed a depolarizer.

Thiel pointed out that elements of the second type might be formed in which the metal is surrounded by a depolarizer which is not a single solid body of constant valency, but a homogeneous mixture of the body giving the anion with another, thus being analogous to an amalgam. If silver bromide-silver chloride, silver bromide-silver iodide, silver chloride-silver iodide formed homogeneous mixtures, this objective could be realized with silver. Conversely, potential measurements with such combinations give information as to the homogeneity of the mixtures of the co-precipitated silver halides under varying precipitation conditions; and this is naturally the consequence of present interest. Thiel's observations and results of most importance in this connection were as follows:

1. When mixtures of silver bromide and silver iodide were precipitated together, noteworthy peculiarities in the color were observed. While the precipitated silver bromide was pale yellow, and the silver iodide only a slightly deeper yellow, mixtures showed a much deeper color, varying from lemon yellow to that of egg yolk. No direct connection between the color and composition could be observed, as the color obtained in mixtures of different proportions would often be the same, while it might vary in equivalent mixtures;

2. In the precipitation of pure silver iodide the presence of a trace of free iodine was evident. To keep this down as

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[1] Thiel, A., Umkehrbare Elektroden zweiter Art mit gemischten Depolarisatoren. Zeits. anorg. Chem. **24**: 1. 1900.

much as possible, the acidity (from sulphuric acid) was kept as low as was compatible with obtaining pure precipitates.[1] The color in the solution was discharged by a few drops of sodium thiosulphate.

From this Thiel at first concluded that the color of the mixtures might be due to a trace of free iodine in the precipitate. However, treatment with thiosulphate failed to remove it, so it is probable that it depends in some way upon the condition of the precipitate—presumably the dispersity;

3. Investigation of the pair silver chloride-silver bromide showed that they formed homogeneous mixtures in all proportions—that is, have unlimited miscibility;

4. On the other hand, silver bromide-silver iodide have only limited miscibility. In this case, silver bromide in excess is able to dissolve silver iodide up to thirty per cent, whereas silver iodide is able to dissolve silver bromide only up to five per cent. Thus, if we have altogether ten millimols of silver halides precipitated and saturation for silver iodide just reached, the precipitate would contain three parts silver iodide to seven parts silver bromide. If now sufficient potassium iodide were added to the solution to form four parts silver iodide at equilibrium in the precipitate, the solid phase would consist of a saturated solution of silver iodide in silver bromide (2.5 : 5.9) and a saturated solution of silver bromide in silver iodide (0.1 : 1.5);

5. On comparing the amounts of silver bromide-silver iodide in mixed precipitates with the theoretical quantities given by the solubility relations,[2] it was found that more of the silver than calculated was always present. There is a tendency to preferential precipitation of the less soluble component.

In so far as these results bear on photographic emulsions it may be noticed that the presumption formerly was that either specific addition compounds of the silver bromide and silver iodide were formed (Eder) or that silver bromide and silver iodide were miscible to an unlimited extent.[3] Supposing the precipitates crystalline, Thiel remarks that the behavior of silver chloride-silver bromide mixtures indicates a high but not perfect degree of isomorphism, while with silver

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[1] In precipitating silver halide the solution must be acid rather than neutral or alkaline, as otherwise contamination with silver oxide may ensue. In any case, the only permissible alkali generally would be ammonium hydroxide, which redissolves silver oxide. (Compare the two methods for making emulsions, on p. 27.) On the other hand, where iodides are used it is evident that if free, strong acid (high hydrogen-ion dissociation) is present, free iodine, which is strongly adsorbed by silver iodide, will be formed.

[2] Cf. Thiel, l. c., p. 60-63.

[3] Bancroft, W. D., l. c., p. 650.

bromide-silver iodide mixtures there is either only a low grade of isomorphism, or isodimorphism.

Although the proportion of silver iodide in silver halide emulsions is well within the range of homogeneous mixture (or solid solution), it is probably sufficient to markedly affect the crystalline habit and growth in view of the generally anomalous behavior of the silver bromide-silver iodide mixtures of the silver bromide.[1]

While it is not entirely permissible to compare separations from liquid melts with precipitations from supersaturated solutions, yet a contingency for the same substances is obvious. Thus it is of interest to note that Stoltzenberg and Huth[2] concluded from thermal analysis of fused silver halides that all three are capable of forming a liquid crystal phase, the transition temperature of regular silver bromide to liquid crystal being 259° C. Below the transition points they show considerable plasticity. As against this, Tubandt and Lorenz[3] conclude, from their studies of the application of conductivity determinations to polymorphy of single compounds and to the state of binary salt mixtures, that there is no definite evidence for a liquid crystal phase with the silver halides. Further, as regards mixtures of the halides, they find that:

1. Mönkemeyer's[4] conclusion of unlimited miscibility between silver bromide and silver iodide is incorrect. There is only a restricted miscibility from both sides, with series of regular and hexagonal mixed crystals;

2. The saturation line of regular mixed crystals cuts the crystallization curve as the proportion 80% silver bromide-20% silver iodide. It is probable that here the combination 4AgBr : AgI separates. The region between 20 and 100% silver bromide probably consists of homogeneous mixtures of this compound (4AgBr : AgI) with silver bromide. Thus, in this region, no transition phenomena are observed, which indicates stability of form;

3. Silver iodide-silver chloride gives complete mixed crystals up to 90% silver chloride, with marked transition phenomena;

4. The crystals from melts containing 80% and more silver bromide are strongly birefringent;

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[1] Cf. Chapter IX.

[2] Stoltzenberg, H., and Huth, M. E., Ueber kristallinisch-flüssige Phasen bei den Monohalogeniden des Thalliums und Silbers. Zeits. physik. Chem. **71:** 641. 1910.

[3] Tubandt, C., and Lorenz, F., Das elektrische Leitvermögen als Methode zur Bestimmung des Zustandsdiagramms binärer Salzgemische. Zeits. physik. Chem. **87:** 543. 1914.

[4] Mönkemeyer, K., Ueber die Bildung von Mischkrystallen der Blei-, Silber-, Thallo- und Cupro-halogene aus Schmelzfluss. Neues Jahrb. Mineral. Geol. **22:** 1. 1906.

5. It may be concluded that the only alternative to the presence of the combination 4AgBr : AgI is that a third stable modification of silver iodide is present in the region 80% - 100% silver iodide, such as that indicated by Tammann[1] as stable at very high pressures. From the conductivity phenomena this is not probable.

Now, although we can not infer directly that the molecular state of a solid phase from a homogeneous liquid melt will be identical with a solid phase of the same composition obtained by precipitation from supersaturated solution, yet it is very probable that the state of the solid phase from the liquid melt represents the equilibrium condition to which that from the supersaturated solution tends to approach. Hence it is possible that some of the color anomalies of silver bromide-silver iodide mixtures observed by Thiel may depend upon the completeness of formation of the compound 4AgBr : AgI, and that this again may be concerned in ripening phenomena. It is particularly interesting to note that birefringence in the crystals of silver halide emulsions is now well established.[2] In regard to the general influence of a co-precipitate like silver iodide upon silver bromide or silver chloride, Tubandt and Lorenz remark that the "simple silver iodide molecules may transfer their oscillation condition to simple silver bromide or silver chloride molecules executing other but similar oscillations, and thus help order them in the same space lattice."

3. ADDITION OF SOLUBILIZING AGENTS

The influence of solubilizing agents on the dispersity of silver bromide in emulsions need not be discussed here, as it consists in intensifying or otherwise modifying the saturation factor of von Weimarn's theory; and also because it will be considered in more detail from the point of view 1) of thermodynamic theory in the discussion of capillarity and crystal growth (Chapter V), and 2) of molecular theory in the discussion of crystallization catalysis (Chapter IV).

4. ADDITION OF SOLUBLE INGREDIENTS OTHER THAN SILVER HALIDES

The concluding statement of section 2, with regard to mixed silver halides, indicating what may be termed a mutual induction effect in crystallization, brings us to the heart of the problem of photochemical sensitizing of the silver halides, including both ripening effects and the so-called optical sensitizing by the use of certain dyes.

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[1] Tammann, G., Das Zustandsdiagramm des Jodsilbers. Zeits. physik. Chem. **75**: 733. 1911.

[2] Cf. Chapter X.

CHEMICAL, OPTICAL AND PHASE SENSITIZERS

The original photochemical conception of sensitizers, due to Vogel,[1] was that they acted as absorbents of decomposition products,—e. g., silver nitrate as absorbent of bromine from silver bromide gives silver + bromine,—a function, as pointed out by Bancroft,[2] similar to that of depolarizers electrochemically, and as such indicated by Grotthus.[3]

At first gelatine was supposed to be superior to collodion as a medium because of higher halogen absorption power. But it was pointed out by Lüppo-Cramer[4] that the superiority could not rest on this property alone, and that ordinarily chemical sensitizing of this form probably plays only a small part in the field of gelatino-halide emulsions. The discovery of optical sensitizers by Vogel brought forward a new photochemical problem. Why should certain—quite a limited number—dyes make silver halides sensitive to their own absorption region? There have been two explanations for this. One is that a chemical decomposition of the dye is effected, which is either extended to the silver bromide before development, or provides a nucleus for development. The other supposes that the internal vibrations of the dye molecules in absorption of light affect the silver halide in the same way as its own direct absorption of light.

It is evident that the crux here is very similar to that for the developability (latent image issue) of the silver halides *per se*. This is a region where chemical and physical change overlap. The theory of radiation-transformation, or radiation catalysis, has received powerful support from the work of Chapman and his collaborators[5] on the photochemical induction of chlorine,[6] and has been extended to chemical catalysis in general by Lewis.[7] In the case of the silver halides and dyestuffs it has been made more precisely applicable by the work of Stark and his collaborators[8] on "latent fluorescence" and "ultra-violet fluorescence."

[1] Vogel, H. W., Handbuch der Photographie. 4th edition, Vol. I., pp. 193-195.

[2] Bancroft, W. D., The electrochemistry of light. J. Phys. Chem. **12**: 209, 318, 417. 1908; and **13**: 1, 181, 449, 538. 1909.

[3] Grotthus, F. von, Physisch-chemische Forschungen.

[4] Lüppo-Cramer, Photographische Probleme, l. c., p. 33.

[5] Burgess, C. H., and Chapman, D. L., The interaction of chlorine and hydrogen. J. Chem. Soc. (Trans.) **89**^{2}: 1399. 1906. Chapman, D. L., Chadwick, S., and Ramsbottom, J. E., The chemical changes induced in gases submitted to the action of ultra-violet light. J. Chem. Soc. (Trans.) **91**^{1}: 942. 1907. Chapman, D. L., and MacMahon, P. S., The interaction of hydrogen and chlorine. J. Chem. Soc. (Trans.) **95**^{1}: 135. 1909. Chapman, D. L., and MacMahon, P. S., The retarding effect of oxygen on the rate of interaction of chlorine and hydrogen. J. Chem. Soc. Trans.) **95**^{1}: 959. 1909.

[6] See also Sheppard, S. E., Photochemistry.

[7] Lewis, W. C. M., Studies in Catalysis. V. J. Chem. Soc. (Trans.) **109**: 796. 1916.

[8] Stark, J., Zur Energetik und Chemie der Bandenspektra. Physik. Zeits. **9**: 85. 1908; Steubing, W., Fluoreszenze und lichtelektrische Empfindlichkeit organischer Substanzen Physik. Zeits. **9**: 493. 1908.

Recent research on selective absorption and fluorescence has shown that the absorption spectrum and the fluorescence spectrum of a substance are potentially equivalent, but that much of the fluorescent spectrum is easily rendered "latent" owing to re-absorption and degradation by adjacent layers of the same molecules. The fluorescence spectrum is excited in its maximum extension and intensity for layers practically one molecule deep. This is strikingly borne out by R. W. Wood's work[1] on the resonance spectra of sodium, potassium, etc.

Again, fluorescence is not limited to the visible region, but may exist in both the ultra-violet and the infra-red. Stark's theory is substantially that optical sensitizing is due to ultra-violet fluorescence from a layer of dye one molecule thick, and that excess of dye interferes by excessive absorption.

However, there is one difficulty in the way of this hypothesis. The dyes which sensitize are quite limited. Yet practically all dyes containing a benzene ring with unstable auxo-chromes or auxo-fluors should be capable of ultra-violet fluorescence. It appears probable that something more is necessary—namely, a marked and selective capacity for sorption and solid solution by the silver halide. The importance of this will be more fully evident on considering, on the one hand, the theory of the nature and genesis of the crystalline condition; and on the other, the experimental researches (particularly those of Retgers, Reinders and Marc), on the influence of additions on crystallization.

It is agreed that a crystal is a homogeneous assemblage of ultimate particles of a substance, such that each particle is similarly situated and similarly environed by identical particles, and that the typical distribution may be referred to a regular group of points or space lattice.

It may be pointed out at this stage that one reason for the importance of crystallization in the formation of sensitive halide emulsions is the increased probability of the extension by resonance of the perturbation (from light) of a single molecular layer throughout the mass of a uniform crystal.

Further, however, it is not agreed as to whether the "ultimate crystalline particles" are molecules or associated aggregates of molecules, or, as indicated by X-ray crystal analysis, whether crystallization involves loss of molecular individuality.[2] In any case, it appears to be a manifestation

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[1] Wood, R. W., Researches in physical optics.

[2] Cf. I. Langmuir, l. c.

of the same intra-molecular force which we term "chemical affinity" and which is now identified with the radiation field proper to atom or molecule.[1] A consistent theory of the genesis of crystallization based on this view has been suggested by Beckenkamp.[2] He considers that crystallization is regulated by approach to equilibrium of the inner radiation fields of atoms or molecules, in particular by very short wave-length ether vibrations (wave-length fractions of molecular diameter). Interference between these forms a system of stationary waves, (the permanence of which would obviously depend upon reduction of thermal energy, e. g., molecular kinetic energy), the nodal points of which by mutual attraction (resonance) determine the crystallization of simple forms, twinning, etc. An analogy will make this clearer. It is supposed that the atoms (or molecules) are marshalled in symmetrical space lattices by stationary ether wave systems, just as the particles of talc or lycopodium are arranged in symmetrical patterns by stationary sound wave systems in Lissajou's experiments. As differing from the analogy, however, the determining stationary wave system is not external, but internal and inherent, emanating from the atoms (or molecules) themselves. In other words, a crystal is a concrete manifestation of an actino-chemical equilibrium. It becomes conceivable, then, that if a substance is to act effectively as an optical sensitizer, in that its specific absorption is to disturb the actino-chemical equilibrium, it must also be able to accommodate itself to the space lattice of the material sensitized. Now it will be seen later that, to effect this, substances must either be so constitutionally similar as to be more or less isomorphous, or be capable of the colloid condition, wherein the tendency to pronounced crystalline form is a minimum, that to molecular net-works (gels) a maximum.

The operation of a sensitizer may be regarded in respect of either wave-length or phase. It would be very possible for a crystalline substance to absorb only a limited amount of light of suitable wave-lengths, but of such irregular phase ordering that the equilibrium radiation field of the crystal would get only partially in resonance. We can conceive then that a non-crystalline body in solid solution or absorbed would increase the photochemical sensitiveness, acting as a resonance complement. Thus colloid silver acts as a panchromatic

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[1] See Wyckoff, R. W. G., The nature of the forces between atoms and solids (J. Wash. Acad. Sci. **9**: 564. 1919,) particularly Classification of Crystalline Solids. "The crystalline state furnishes the greatest condensation of the fields about the individual particles (atoms or molecules, depending upon the type of solid)."

[2] Beckenkamp, J., Der tetrakishexagonale oder oktaedrische Typus der Kristalle. Ann. Physik. IV. **39**: 346. 1912.

sensitizer for silver halides. The behavior of traces of calcium, bismuth, etc., in developing phosphorescence in the alkaline earth sulphides is a similar case.[1] If the above conception is true it is possible that silver iodide acts both as a wave-length sensitizer and as a phase-sensitizer for silver bromide, as well as acting as an independent source of silver nuclei by its direct photolysis. However, these contributions are likely to be of less total importance than its stabilizing influence as a crystallization buffer substance on the crystallization of co-precipitated silver bromide.

It has been shown that a fundamental relation exists between photochemical catalysts, positive and negative, and crystallization catalysts. This relation may be summed up as follows: Crystallization is a process of approach to a complete (static) equilibrium of the radiation fields (chemical affinities) of the component atoms and constituent molecules. The attainment of static equilibrium may be accelerated or retarded by alien substances, or crystallization catalysts, which, from the actino-chemical nature of crystallization, are consequently likely to be also photochemical catalysts, affecting the transformation and redistribution of incident light energy. That is, they affect the way in which light energy is redistributed by a molecule or aggregate M. This may be represented thus:

$$\text{Light energy—M}\left\{\begin{array}{l}\text{Fluorescence}\\ \text{Phosphorescence}\\ \text{Photochemical change}\\ \text{Photo-electric effect}\\ \text{Heat}\end{array}\right\}\begin{array}{l}\text{Distribution}\\ \text{of energy}\\ \text{largely}\\ \text{determined}\\ \text{by catalysts}\end{array}$$

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[1] Cf. S. E. Sheppard, l. c., p. 400.

CHAPTER IV

Crystallization Catalysis

We can conveniently include all the effects of additive substances upon the crystallization of a new phase under the term crystallization catalysis. By this we shall understand both the positive actions leading to fully developed crystals and the negative ones retarding crystallization and leading to well developed colloids. It follows from what has been said that the seat of crystallization catalysis is primarily the interface between growing crystal and mother liquor.

In the simplest case, positive catalysis of crystallization is effected by substances which form more soluble, but readily dissociable compounds with the crystallizing substance. Thus the soluble bromides and ammonia act in this way to silver bromide. Substances forming very stable soluble complexes, such as thiosulphates and cyanides, do not have this effect. On the contrary, especially if they form less soluble stable complexes, such bodies are strong negative catalysts, such as, with silver bromide, bodies like mercuric bromide or lead bromide (or other mercuric and lead salts). These substances, it should be noted, produce strong congelation of silver halide hydrosols. A more complex case of crystallization catalysis exists where a consolute substance affects the habit of the growing crystal. A striking example is the effect of urea upon the crystallization of sodium chloride. In water alone sodium chloride crystallizes in cubes, but if urea be added, octahedra are formed.[1] An important and interesting series of investigations on crystallization from aqueous solution have been made by Marc and collaborators.[2] Marc found that, while with some substances the rate of solution is equal to the rate of crystallization up to the greatest velocities of stirring, there are others which show a great difference; and with these the rate of crystallization may be only one-sixteenth that of solution, indicating a slow change practically independent of diffusion as to speed. In any case, however, crystallization may be brought to a standstill prematurely by the presence of dyes, while the rate of solution of the crystals is either not affected or only somewhat retarded. The taking up of dye by the crystals in general follows the

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[1] Cf. Retgers, J. W., Beiträge zur Kenntnis des Isomorphismus. V. Zeits. physik. Chem. **9**: 257. 1892.

[2] Marc, R., Ueber die Krystallization aus wässerigen Lösungen. Zeits. physik. Chem. **79**: 71. 1912.

adsorption formula, but shows the phenomenon of "saturation"—i. e., with concentrations above a certain value there is no increment of adsorption. Marc considers that the surfaces of the crystal become saturated, and attributes the checking of crystal growth to the slowness of diffusion of the dye in the solid crystal, with which it tends to form a solid solution.

Generally, colloids are readily adsorbed,[1] but not so crystalloids—unless either isomorphous or chemically combining. Between the amounts of different substances which can saturate a given crystal surface,[2] quantitative relations exist which are conserved for other surfaces. The saturation indicates that an absolute minimum of surface energy is reached. Such saturated surfaces have lost all "free" surface energy, and therewith the capacity to act as germ or catalyst.

This last corollary perhaps indicates a relation to photographic solarization, where the halide grains progressively lose capacity to function as a "germ" for chemical development.

That colloidal silver can be taken up by crystallizing silver halides was shown by Reinders.[3] He concludes that colloidal silver forms solid solutions with the silver halide, not simply a surface adsorption layer. The photo-halides are normal salts of silver colored by small amounts of colloidal silver, the color depending upon the dispersity of the latter. Certain dyes, and albumenoids such as gelatine, are also absorbed by the crystallizing silver halides, and it is noteworthy that gelatine and similar colloids check or completely prevent the taking up of colloidal silver. This is a confirmation of Sheppard and Mees' filter theory of the value of gelatine as an emulsifying medium. Colloidal gold behaves similarly to colloidal silver.

The panchromatizing effect of colloidal silver is very probably responsible for a remarkable panchromatizing effect discovered by J. G. Capstaff of the Eastman Research Laboratory. Mr. Capstaff found that, if an ordinary dry plate or film[4] be bathed a short time in a two per cent sodium bisulphite solution ($NaHSO_3$), then subjected to prolonged washing in faintly alkaline water and allowed to dry spontaneously, it becomes more or less panchromatically sensitized. Although the result is not yet capable of precise control, it has been found that the extension of spectral

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[1] Marc, R., Ueber Absorption und gesättigte Oberflächen. Zeits. physik. Chem. **81**: 641. 1912.

[2] Marc worked with micro-crystals, so this does not specify a habit surface.

[3] Reinders, W., Studien über die Photohaloide. Zeits. physik. Chem. **77**: 213 and 357. 1911.

[4] Most of the experiments were made with Eastman Portrait Film.

sensibility runs parallel with duration of washing with ordinary (hard) tap water. Thus, only a slight extension of sensibility was found after five to fifteen minutes' washing; very considerable after one to five hours' washing; and after twenty-four to thirty hours' washing, sensibility was extended to nearly 800$\mu\mu$. (See Fig. 17.) The time of washing may be greatly shortened, five to ten minutes being sufficient to develop strong sensitizing action, if the wash water is made faintly alkaline with sodium carbonate (Na_2CO_3). (See Fig. 17, 4.)

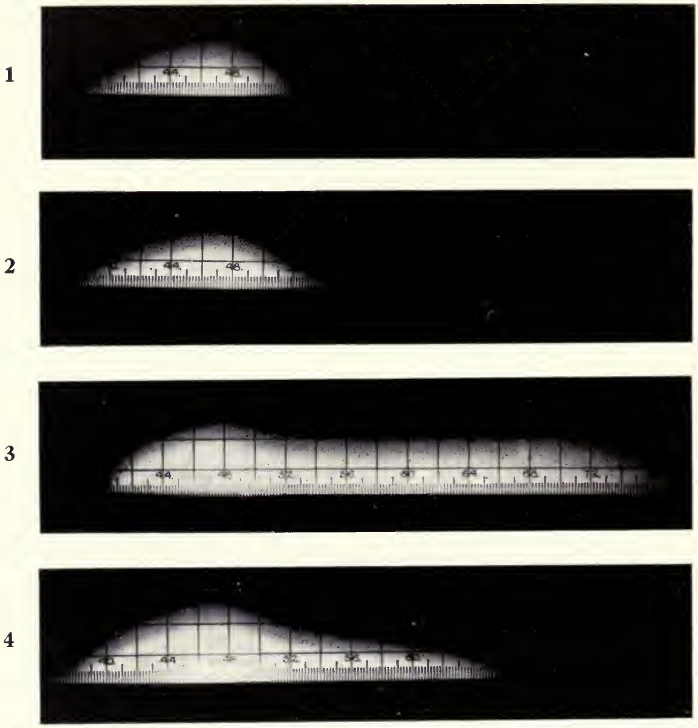

Fig. 17

Capstaff panchromatizing effect, showing stages in the development of color sensitizing with time of washing in hard water

The nature of the sensitizing action will be evident from Fig. 17[1] (1, 2 and 3), which shows phases of its progression to

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[1] Taken with a wedge spectrograph.

full panchromatic sensibility. It is evident that the sensitizing action differs markedly from that conferred by sensitizing dyes, since the action commences not with a new band, but by lateral extension toward the red end of the usual sensitivity curve. There is at the same time a small decrease in the blue sensitiveness, but this is more than compensated for by the increase in general sensitiveness; hence the speed to white light is greatly increased.

As regards chemical conditions, those at present evident are as follows:

a. The effect can be induced by sulphurous acid, as well as by acid bisulphites; it is then due immediately to sulphurous acid (H_2SO_3);
b. If this is washed out with distilled water, little or no sensitizing action is observed;
c. An alkaline after-bath or wash is necessary to develop the induced or presensitizing effect;
d. A very small amount of soluble bromide—e. g., potassium bromide (KBr) at a concentration of .004 per cent—in the sensitizing bath, is able to kill the effect;
e. "Chemical fog" increases progressively with the sensitizing effect although not reaching very high values—e. g., $D = 0.6$ at the limit.

Provisionally, the existing facts appear to be compatible with the view that a small amount of reduction of ionic to metallic silver is effected by or in the presence of sulphurous acid, as a presensitizing effect; that this is inhibited by soluble bromide; and that the alkaline after-bath is necessary to peptize this silver to higher dispersity, by which the panchromatizing effect is fully developed.[1]

In view of the similarity of the adsorption phenomena of the colloidal metals and dyes, particularly the fact that silver halides can be panchromatically sensitized with colloidal silver, there seems a measure of probability in the view that exposure to light produces a substance which is itself capable of accelerating the reaction to light of the wave-length in question. Such a presensitizing effect would be an example of a specific auto-catalysis. However, we are straying somewhat from the main theme. It is sufficient to point out that there is some probability that in ripening a certain amount of adsorption of gelatine, or of hydrolytic derivative of gelatine, occurs. Also, there is a possibility that a very slight initiation of reduction occurs, which, however, is rapidly succeeded by spontaneous fogging. Again, it is equally possible that the most important fact in ripening is a recrystallization, involving

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[1] It is interesting to note that a visible yellowish-orange discoloration increases progressively with the washing treatment; this runs approximately parallel with the sensitizing action.

a purification of the silver halide. Bancroft's theory[1] that ripening involves progress of the gelatino-silver halide grain to a certain optimum composition of silver halide-gelatine-water, but that therefore size of grain is entirely unimportant, would, according to this view, be only partially correct. For first, only by progress from the suspensoid colloid to a micro-crystalline suspension of lower dispersity could adsorbed free bromide be completely washed out. It is a mistake to suppose that any amount of washing will completely remove every trace of a stabilizing electrolyte from a colloid precipitate. Several peculiarities of emulsions are no doubt connected with this.

Secondly, any further phenomena of purification—e. g., degelatinization—can not be independent of the size of grain in more advanced recrystallization as in negative emulsions, particularly high-speed emulsions, because purification and increase of size go largely together, as is brought out by Marc's investigations. What seems most probable for the critical stage, when an emulsion is nearing the point of "going over"—i. e., becoming liable to spontaneous fog—is that a process of degelatinization of the silver halide crystal is going on *pari passu* with a taking up of colloidal silver formed by interaction of silver halide with decomposition products of the gelatine; for, as shown by Reinders, taking up gelatine excludes the taking up of colloidal silver. The point at which the protective effect of the gelatine is passed (due to weakening by hydrolysis) is the point of going over.

This view would seem in some degree incompatible with Reinders' observation that silver halides crystallizing from gelatine solutions are much more sensitive—i. e., that taking up gelatine increases sensitivity. But it must be reiterated that this refers to photochemical sensitiveness—i. e., photolytic production of visible darkening or coloration. Photographic developability is a phenomenon of another order, in which excess of gelatine in the grain will impede the chemical reduction of the grain by the developer by lessening the contact action of the nuclei, while presence of a minimum trace of colloidal silver may lower the quota of developability per grain to be added by exposure to light.

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[1] Bancroft, W. D., The photographic plate, l. c., p. 650.

CHAPTER V

Capillarity and Crystal Growth

The original work in this direction is due to Gibbs.[1] From his investigation of the equilibrium of heterogeneous substances he deduced that the forms which are in equilibrium for crystals under the influence of capillary forces are those in which the surface energy is at a maximum or a minimum. Assuming that each crystal face has its specific capillarity constant, measured by the work of increasing the face by the unit of area, this deduction may be expressed by assuming that

$$A_1S_1 + A_2S_2 + A_3S_3 + \ldots A_nS_n$$

is a maximum or minimum, the areas of different faces being denoted by S_1, S_2, etc., the capillarity constants by A_1, A_2, etc. Gibbs, however, qualified this theorem by the statement that the tendency of a crystal to take up the form set by this capillarity equilibrium is inversely proportional to its linear dimensions. He states that "On the whole, it seems not improbable that the form of very minute crystals in equilibrium with solvents is principally determined . . . by the condition that

$$A_1S_1 + A_2S_2 + \ldots A_nS_n$$

shall be a minimum for the volume of the crystal, . . . but, as they (the minute crystals) grow (in a solvent no more supersaturated than is necessary to make them grow at all), the deposition of new matter on the different surfaces will be determined more by the nature (orientation) of the surfaces and less by their size and relations to the surrounding surfaces."[2]

It is in fact probable that the surface energy principle ceases to be regulative for crystals of a given substance above a certain size—i. e., beyond a certain dispersity—though we do not know whether this is absolute or is relative to the nature of the substance. Although Gibbs was the originator of this principle, it is better known from the work of Curie[3] and Wulff.[4] Since it is closely interwoven with all questions of crystal size and growth, and with the so-called "Ostwald

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[1] Gibbs, J. W., Scientific papers, Vol. I., pp. 320-326.

[2] Gibbs, J. W., l. c., p. 325, footnote.

[3] Curie, P., Sur la formation des cristaux et sur les constantes capillaires de leur différentes faces. Bull. franç. minéral. **8:** 145. 1885.

[4] Wulff, G., Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Krystallflächen. Zeits. Kryst. u. Mineral. **34:** 449. 1901.

ripening," it is desirable to consider more closely its consequences and the experimental results. Considering a crystal in its mother liquor, only the surface energy is variable, and its growth will be in that form for which the total surface energy is a minimum. Furthermore, each surface must have its own specific capillarity, otherwise a sphere would be formed.

For substances like silver bromide and silver chloride crystallizing in the regular system, the condition for a right quadratic prism is as follows: Let x be the side of the base, y the height of the prism, A the capillarity of the (equivalent) side faces, and B of the base, then the surface energy $E = 4xyA = 2x^2B$.

Since the volume of the prism is $V = x^2y =$ constant, we have $\delta(x^2y) = o$, and equilibrium will occur when E is a minimum. The necessary condition for this is $A(x\delta y + y\delta x) + Bx\delta x = o$ for any variations satisfying $V =$ constant,—i. e., $x\delta y + 2y\delta x = o$. This gives at once $Ay = Bx$; or $x/y = A/B$, which means that the capillary constants of the prism surfaces and bases are inversely proportional to the lengths of the sides. Similar calculations can be made for a cube or an octahedron. A regular octahedron can occur only if A_{100}: $A_{111} > \sqrt{3}$; a cube if $A_{100}:A_{111} < 1/\sqrt{3}$.

Wulff and Hilton[1] have reduced the principle of minimum surface energy to another form, formulating a generalized connection between the capillarities of the various faces and their distances from the center of the crystal for undisturbed growth. This is expressed in the following theorem:

The perpendiculars on the faces of a crystal from a certain point within it are proportional to the capillarities of the faces, thus:

$h_1 : h_2 : h_3 \ldots . h_n = k_1 : k_2 : k_3 : \ldots . k_n$, where h = the perpendiculars, k = the capillarities, and n the total number of faces.

This holds for 22 of the 32 crystal classes. But for the other ten there are an indefinite number of points equidistant from all faces of the same form. Wulff[2] considers that his work on the rates of growth of the faces of Mohr's salt, $(NH_4)_2Fe(SO_4)_2.6H_2O$, established the theorem, but his proof has been called into question by Hilton;[3] and it has been pointed out by Friedel[4] that Wulff obtained the same results with crystals of different habits, thus showing that a distorted crystal does not tend to approach an ideal form.

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[1] Hilton, H., Mathematical Crystallography.

[2] Wulff, G., l. c.

[3] Hilton, H., l. c., p. 105.

[4] Friedel, G., Examen critique de la théorie de Curie-Wulff sur les formes crystallines. J. chim. phys. 11: 478. 1913.

Marc and Ritzel[1] reached the same conclusion from their work, which showed that there are different velocities of solubility on the octahedral and the cubic surfaces of these crystals. Since in the case of silver bromide crystals in photographic emulsions one is dealing only with octahedral faces, the Gibbs-Curie-Wulff law may be applied without limitation, providing that no other crystallization conditions arise, and that the crystals are obtained from very slightly supersaturated solutions. Ostwald considered that his experiments on red and yellow mercuric oxide[2] gave a quantitative proof that the solubility (equilibrium condition) is a function of the size of grain, and this was supported by Hulett's experiments[3] with gypsum ($CaSO_4$).

Hulett placed aqueous solutions of gypsum in contact with large gypsum plates and found that equilibrium occurred when the concentration reached 15.33 millimols per litre. Then, if very fine gypsum powder was added to the saturated solution, the concentration increased, in one case reaching 18.2 millimols per litre. This high solubility decreased very rapidly at first, then more slowly, until after 168 hours the concentration again became 15.33 millimols.

A similar experiment with very finely powdered baryta showed a sudden increase of about 80 per cent in the saturation concentration, which, as with gypsum, decreased to the normal amount after long standing.

The size of the gypsum grains varied from 0.2 to 0.4μ. The baryta grains averaged about 0.1μ. These dimensions are at the limit of microscopic resolving power, and should therefore be accepted with caution.

The experiment with gypsum was further complicated by the presence of a monoclinic α-dihydrate and a rhombic β-dihydrate, into which the α-dihydrate passes over when left for a considerable time in the concentrated solution. The solubility of the β-dihydrate is approximately 30 per cent less than that of the α-dihydrate.

The results of Hulett's experiments have been mathematically worked out by Valeton,[4] as follows:

If r is the length of a certain crystal edge, the volume of a crystal grain of the form under consideration ur^3, the surface

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[1] Marc, R., and Ritzel, A., Ueber die Faktoren, die den Kristallhabitus bedingen. Zeits. physik. Chem. **76:** 584. 1911. Cf. critique by Kuessner, H., *ibid.* **84:** 313. 1913; and Ritzel's reply, *ibid.* **86:** 106. 1913.

[2] Ostwald, W., Ueber die vermeintliche Isomerie des roten und gelben Quecksilberoxyds und die Oberflächenspannung fester Körper. Zeits. physik. Chem. **34:** 495. 1900.

[3] Hulett, G. A., Beziehungen zwischen Oberflächenspannung und Löslichkeit. Zeits. physik. Chem. **37:** 385. 1901.

[4] Valeton, J. J., referred to by Gross, R., Sammelkristallization in Beziehung zum Atomfeld der Kristalle. Jahrb. Rad. u. Elekt. **15:** 270. 1918.

ur^2, the energy per cu. cm. i and the surface tension per sq. cm. γ, then the total energy contained in a grain having length of side r is—

$$E_r = iur^3 + \gamma ur^2 \; .$$

Further, if g is the specific gravity of the crystal and M the gram-molecular concentration of the solution, then $\frac{M}{g}$ is the molar volume and $\frac{M}{gur^3}$ the number of crystal grains contained in one mol. The total energy in one mol is then

$$u_r = i\,\frac{M}{g} + \gamma\,\frac{M}{g}\,\frac{1}{vr^3}\,ur^2 \; .$$

If one takes $\frac{u}{v} = K$,

$$\text{then} \quad u_r = i\,\frac{M}{g} + \gamma\, K\,\frac{M}{gr} \; .$$

For grains having the edge-length $r = \infty$,

$$u_\infty = i\,\frac{M}{g} \; .$$

The difference $u_r - u_\infty$ is the work necessary to powder one mol of infinite size to grains of a size corresponding to the edge-length r.

Now, if the very large grains are in equilibrium with concentration c_∞, then there is, according to thermodynamic conditions for equilibrium, a concentration c for saturated solutions in contact with the grain size r, of which the osmotic work in one mol is increased by an amount corresponding to the difference between c and c_∞. This is developed as follows:

In the case of dilute solutions the osmotic work may be represented approximately by the equation—

$$RT = \frac{p}{c}, \text{ where}$$

p = osmotic pressure, T = absolute temperature,
R = gas constant.

Therefore,

$$RTlnc_1 = RTlnc_\infty + \gamma K\,\frac{M}{gr},$$

$$\text{or} \qquad c_1 = c_\infty \,.\, e^{\frac{\gamma K}{RT} \cdot \frac{M}{gr}} \; .$$

On the basis of these relations Valeton has worked out a diagram (Fig. 18) by substituting the pairs of values found by

Hulett for grain sizes 2 and 0.2 and the corresponding concentrations of 15.33 and 18.2 millimols per litre.[1]

It will be remembered that the conclusion that solubility is a function of the size of grain is incorporated in von Weimarn's theory of precipitation. It has also been very generally accepted as applying to the ripening of photographic silver halide emulsions. As already stated, procedure here is broadly divided into (a) the boiling process, using excess soluble bromide in slightly acid solution, and (b) the ammonia process, carried out at lower temperatures. In either case, a particular type of solvent for silver bromide is present, the action of which will be considered specifically. The presence of solvents tending to form complexes does not necessarily affect the argument as to Ostwald ripening.

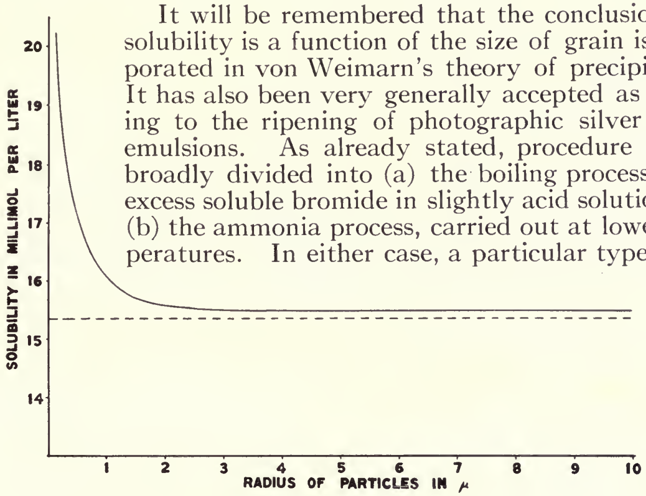

Fig 18

The first to attempt a microscopic and semi-quantitative survey of the photographic ripening process were Bellach and Schaum.[2] As a first result Bellach observed that in certain stages of ripening, beside relatively shapeless to spherical grains, definite crystalline polyhedra, apparently tetragonal, were present. As pointed out by Bancroft,[3] this had been previously observed by Banks[4] and has been fully confirmed by other observers.[5] Bellach at first assumed that this occurred only in mixed emulsions, but later found it in pure silver bromide emulsions prepared by himself. Crystallization was observed after a certain time both when the boiling process was employed, and with ammonia ripening.

At the same time, the average size of grain increased, the photomicrographs showing this to concur with the disap-

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[1] For a critique of this work, see Gross, R., l. c.

[2] Bellach, V., Die Struktur der photographischen Negative, l. c.

[3] Bancroft, W. D., The photographic plate, l. c.

[4] Banks, Remarks in discussion of paper by Hurter and Driffield on the latent image. Phot. J. **22:** 159. 1898.

[5] Dyer, Note under *Emulsionsbereitung*. Jahrb. Phot. **18:** 437. 1904. Sheppard, S. E., and Mees, C. E. K., l. c., p. 51. Lüppo-Cramer, Phot. Prob., l. c.

pearance of small grains. There appears to be evidence that for certain straight silver bromide emulsions a definite Ostwald ripening occurs. It must be noticed, however, that in practice variable amounts of silver iodide are also present, and the influence of this will have to be considered separately. We may note that *per se* it appears to show little or no ripening in gelatine.[1]

EXAMPLE OF OSTWALD RIPENING WITH MERCURIC IODIDE

An apparently well developed example of Ostwald ripening was observed by us in an experimental study of the photochemistry of mercuric iodide. Previous investigators (notably Lüppo-Cramer), working with this compound observed that, when precipitated in gelatine, it appears first as the yellow, unstable modification, which crystallizes in the rhombic system and which passes over to the stable red iodide, crystallizing in the tetragonal system, normally below 127° C.,[2] the transition temperature. Lüppo-Cramer tried various colloid media, finding that with gum arabic the red stable form is immediately produced—which indicates a lower protective effect. When the iodide is precipitated in gelatine in presence of excess of potassium iodide, it appears first as a yellow, very finely divided colloidal suspension, which on being digested at 70-90° C. in presence of excess of potassium iodide passes over to the regular form.

The emulsion used in our experiments was in general prepared as follows:

a.	10 gms. soft gelatine	in	400 cc. H_2O
b.	10 gms. $HgCl_2$	"	100 cc. H_2O (hot)
c.	10 gms. KI	"	50 cc. H_2O
d.	20 gms. hard gelatine	"	60 cc. H_2O

Emulsion H - 24

(a) and (b) are mixed together at 60-70° C., then (c) is added with careful stirring. The emulsion was ripened by heating at 70-90° C. for 60 to 190 minutes. Samples were removed at definite intervals for centrifugal analysis. The setting gelatine (d) was added before washing and coating. The progressive change or ripening effected could be followed visually by the color change from yellow through salmon pink to deep red. At the same time the increase in size of grain

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[1] Lüppo-Cramer, Phot. Prob., l. c., but this depends on presence of excess of soluble iodide. From this crystallization occurs readily.

[2] Reinders, W., Ueber die Bildung und Umwandlung der mischkrystalle von Quecksilberbromid und Quecksilberjodid. Zeits. physik. Chem. **32:** 494. 1900.

and probably also in density was evident on centrifuging samples of the emulsion at different stages. The following table illustrates this (see Fig. 19):

			CENTRIFUGE	
NO.	TEMPERATURE	TIME OF COOK	TIME	R. P. M.
1	43° C.	0	5 mins.	1000
2	78° C.	5 mins.	5 mins.	1000
3	75° C.	15 mins.	5 mins.	1000
4	85° C.	40 mins.	5 mins.	1000
5	88° C.	60 mins.	5 mins.	1000
6	90° C.	80 mins.	10 mins.	1000
7	90° C.	100 mins.	10 mins.	1000
8	90° C.	120 mins.	10 mins.	1000
9	90° C.	140 mins.	10 mins.	1000
10	90° C.	140 mins.	10 mins.	1000

The progress of ripening is also shown microscopically in an increase in size of grain and concurrent disappearance of smaller grains. This is shown by the accompanying photomicrographs. (Fig. 20.) The changes are also shown by the centrifugal separations.

Here, then, there appears a definite example of Ostwald ripening, in the sense of the "eating up" of smaller grains by larger ones, fairly well formed tetragonal octahedra of mercuric iodide being formed. At the same time the emulsion acquired higher sensitiveness and density-giving power, although, of course, still much inferior to silver bromide. It must be considered, however, before regarding this as establishing a clear case of Ostwald ripening, that another factor is present. This is the initial appearance of mercuric iodide in the yellow form, belonging to the rhombic system, and stable only above 129.5° C. The colloid gelatine has acted here as agent of retarded transformation. In this connection it is important to note that silver iodide also is polymorphic, crystallizing in the hexagonal form below 145° C., and in the regular above this temperature. There is, therefore, an obvious possibility that silver iodide precipitated in gelatine or, generally speaking, under conditions favoring retarded transformation, may occur initially in the unstable form, passing over, similarly to mercuric iodide, to the stable form on digestion. There are certain phenomena in straight silver iodide emulsions which point to this. Reciprocally, if precipitated with silver bromide, this potentiality may be of importance.

The condition or mode of combination of silver iodide with silver bromide, important *per se*, may, however, be only accessory to two other important roles of this substance in emulsions. First, as relatively less soluble in either excess potassium bromide or in ammonia, it will function in recrystal-

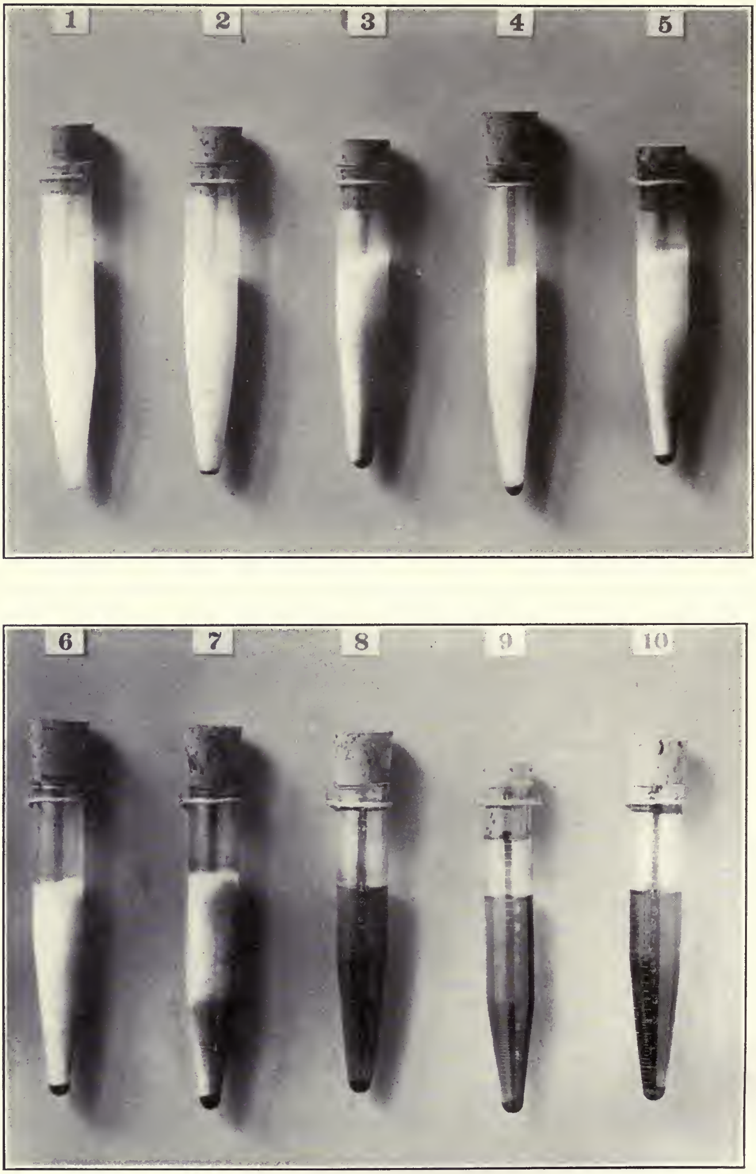
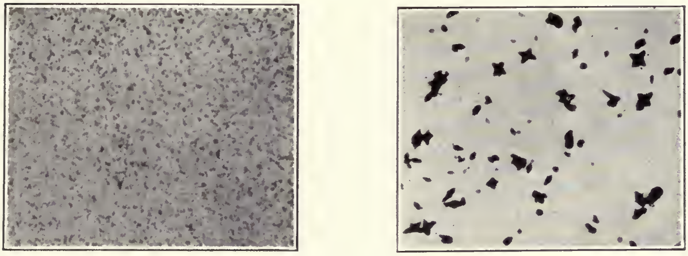
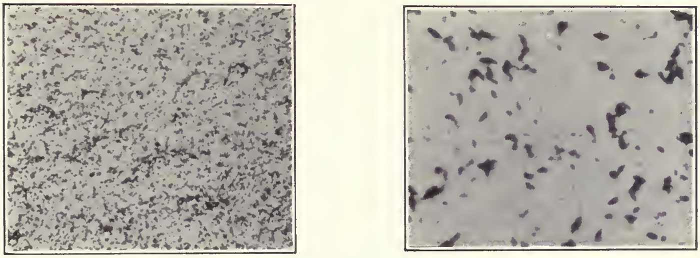


Fig. 19
Ripening of mercuric iodide emulsion. Progressive accumulation of the red stable form shown by centrifuging



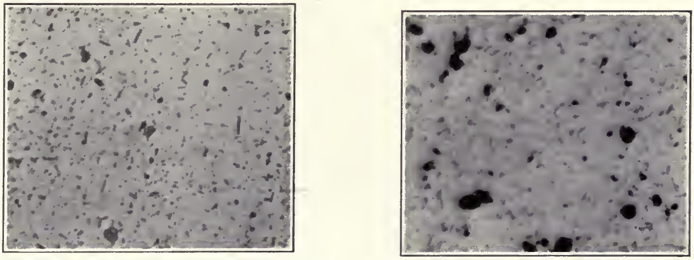
X 1000. 0-5 minutes.

X 1000. 160 minutes.



X 1000. 5-15 minutes.

X 1000. 120 minutes.



X 1000. 40 minutes.

X 1000. 60-80 minutes.

Fig. 20

Progress of ripening, showing increase in size of grain lization as a buffer substance, tending to conserve and regulate the number of nuclei. It has been shown in Chapter I that relatively foreign substances can act as nuclei for recrystallizing silver halides, and one function of silver iodide is very probably of this character. Another may well consist in the greater adsorptive power of silver iodide, which can be operative both in emulsion preparation in the matter of taking up other sensitizers, and in development after exposure in affecting the adsorption of the developer.[1]

Before concluding this discussion, it is desirable to point out that the principle of minimum surface energy can lead to other phenomena than Ostwald ripening in recrystallization; that in fact this is by no means the necessary consequence. Since this is of considerable importance in regard to the possibility of making fairly fine and uniformly grained emulsions of high speed we shall include a brief account of the effect of the principle of minimum surface energy upon the variability of habit, or of the preferential growth of certain faces of the crystal.

It has been shown that this principle necessarily implies different capillarity constants for different faces. This, however, involves different solubilities for different faces, for otherwise it appears impossible to conceive how a distorted crystal can assume the equilibrium form (with minimum surface energy) unless certain faces dissolve while others grow. The most complete discussion of this experimentally still unsettled point is due to Ritzel[2] and Kuessner.[3] Ritzel applied Freundlich's corrected form of Ostwald's formula for the solubility of small particles as related to surface tension.[4] For a substance crystallizing in cubes the formula gives the solubility of a cube (C_w) of length of side A in relation to that of an infinitely extended cube as (reference being to perfectly developed forms):

$$C_w = C_{w_\infty} \cdot e^{\frac{M}{RT} \cdot \frac{4S_w}{Pa}}$$

where M = Molecular weight,
R = Gas constant ($.8316 \times 10^{\cdot 8}$),
T = Absolute temperature,
S_w = Surface tension on cube face,
P = Density.

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[1] See Sheppard, S. E., and Meyer, G., Chemical induction and photographic development. J. Amer. Chem. Soc. **42**: 689. 1920; Phot. J. **60**: 12. 1920.

[2] Ritzel, A., Die Kristalltracht des Chlornatriums in ihrer Abhängigkeit vom Lösungsmittel. Zeits. Kryst. u. Mineral. **49**: 152. 1911.

[3] Kuessner, H., l. c.

[4] Freudlich, H., Kapillarchemie, p. 47.

Following Wulff and Hilton, it is more convenient to take as characteristic parameter of the crystal not a but the distance of a surface from a middle point, $A = a/2$, when the formula becomes

$$C_w = C_{w\infty} \, . \, e^{\frac{M}{RT} \cdot \frac{2S_w}{PA}}$$

While for octahedra, taking the distance B from a middle point, since total surface $O = 12 \sqrt{3} \, . \, B^2$, mass $m_o = P.4 \sqrt{3} \, . \, B^3$,

$$C_o = C_{o\infty} \, . \, e^{\frac{M}{RT} \cdot \frac{2S_o}{PB}}$$

where $S_o =$ surface tension of octahedral surface. Kuessner finds that, for equilibrium, the parameters A and B must be proportional to the respective capillarity constants. The minimum of surface energy then entails, however, an equality of solubilities of all faces, otherwise the combination could not be in equilibrium. It is found, by executing a cyclic process of transference and equating work terms, that the same solubilities must be possessed by

1. A cube of parameter A;
2. The cubo-octahedron, with parameter A for the cube face, and $A.S_o/S_w$ for the octahedral face; and
3. The octahedron with parameter $B = A.S_o/S_w$.

But this leads to a contradiction. It is shown that under given conditions only one form can be stable, since the minimum of surface energy can exist for only one configuration. The single stable form is a cubo-octahedron if $\frac{S_o}{S_w}$ is between $\sqrt{3}$ and $1/\sqrt{3}$; a simple hexahedron if $S_o > \sqrt{3}\, S_w$; a simple octahedron if $S_o < S_w/\sqrt{3}$; and only then is thermodynamic stability ensured.

Finally, it is pointed out that a paradox results in that the stable form is that with the greater solubility; for only then can the other be transformed into it by way of the cubo-octahedron. There is, however, no real contradiction here, in that the stable, more soluble form may dissolve in a common solution and the other less stable form will grow, for this must by growth transform into the stable form, so that the total result would be a single crystal of the stable form. Hence it follows that the principle of Ostwald ripening, by solubility decrease with size of crystal, must be applied with caution. It will be seen that recrystallization may well occur between cubical and octahedral forms of a regular system without reference to growth of large crystals at expense of small. If, as suggested in this paper, the importance of recrystallization in ripening is less concerned with increase of size (size being principally determined by initial condensation conditions) and more with the inner adjustment of composition, the possibilities indicated here are significant.[1]

Equally relevant to the problem of the scope and function of crystallization in silver halide emulsions is the relation of dispersity to the twinning of crystals. It has been shown experimentally by Johnsen[2] that, compared with simple forms, twin crystals are a labile phase. Pawlow[3] has tried to show that the free energy of twins is greater than that of single crystals of equal mass, but smaller than that of two simple crystals which, combined, would be of equal mass. It will be seen that twin forms might occur as an intermediate stage between ultra-microscopic crystals and larger microcrystals, or more generally, as pointed out by Niggli,[4] we can make the following statement: In a system of definite dispersity (surface/volume), twins represent a labile phase relative to single crystals; or, a fine crystalline precipitate consisting entirely of twin forms will be of higher dispersity than a precipitate of single crystals of the same individual mass.

Reverting to von Weimarn's analysis of the crystallization process, it appears probable that the genesis of twin forms may be predicated as entirely determined in the amicroscopic stage of the dispersed phase. This conception is entirely in harmony with the influence of solution factors on twinning, regarded as operative by way of surface forces. The influence of these solution factors is necessarily greater, the higher the dispersity.

We have seen that the initial formation of the labile (yellow) rhombic form of mercuric iodide in gelatine, which is stable only above 129.5° C., and which is converted into the stable (red) form on keeping the emulsion melted, is in line with Ostwald's law of stages. According to this a new phase appears first in the form involving the least loss of free energy. Now since the regular form of silver iodide is stable

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[1] The results of the present investigation (Chapter VIII), of the crystal forms of silver bromide in normal gelatine-bromide emulsions show only octahedral forms. Hence, either the above-noted factor would be imperative for silver bromide emulsions, or limited to the submicroscopic stage. The reported preparation of fine-grained highly ripened silver bromide emulsions in albumen is interesting in this connection. See Lehmann, E., and Knoche, P., Plate-grain and albumen emulsions. Brit. J. Phot. **61**: 759. 1914.

[2] Johnsen, A., Untersuchungen über Kristallzwillinge und deren Zusammenhang mit anderen Erscheinungen. Neues Jahrb. Mineral. Geol. **23**: 237. 1907.

[3] Pawlow, P., Ueber die Bildung, das Gleichgewicht, und die Veränderungen des Kristalles im isothermen Medium. Zeits. physik. Chem. **72**: 385. 1910.

[4] Niggli, P., Kolloidchemie und Zwillingskristalle. Koll. Zeits. **10**: 268. 1912.

only above 145° C., an initial appearance of silver iodide in this form would mean a greater relative retention of free energy than in the case of mercuric iodide, but might tend to happen more readily in the presence of greater protection afforded by co-precipitation with excess silver bromide. Silver bromide alone has not been obtained in any other than the regular system. But the tendency to assume a form proper to a relatively labile system might limit the effect to twinning as the immediate sequence of the suspensoid stage. Indeed, Mugge[1] has suggested that twinning in any case indicates an accommodation of the crystal to a different space grating, corresponding to an earlier or later energy condition. Since this would involve a condition of internal strain, it should result in an optical anomaly, such as birefringence in uniaxial crystals, a phenomenon which has been shown to occur in silver bromide emulsion crystals.[2]

It is possible (though this awaits determination), that this occurrence of optical anomaly, or, better, of anomalous optical activity, is the very focus of ripening in relation to speed, etc. If so, and if it should be found to be connected with twinning, the conditions determining the occurrence and governing the—relatively—temporary fixation of this labile stage merit earnest consideration.[3]

Going back to the broadest generalization governing the morphogenesis of a new phase, we have Ostwald's law of stages. Now there are two ways in which the law could operate in crystallogenesis. One form may be stated thus. Every given crystal individual in its growth (evolution to most stable form) tends to pass through every stage of its possible range of forms; each transition reduces its free energy, but each transition is such as to make the necessary reduction of free energy a minimum at each step. For example, a substance which normally crystallizes in the regular system as rigid crystals, but at higher temperatures and normal pressures in the rhombic, might also be capable of plastic and liquid crystalline forms at both higher temperatures *and* pressures, as asserted of silver iodide. In forming a new phase, especially of a new component, the individuals would then pass through the sequence;

Liquid → liquid → plastic → rhombic → tetragonal
droplet crystal crystal crystal crystal,

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[1] Mugge, O., Ueber die Zwillingsbildung der Kristalle. Fortschr. Mineral. **1:** 38. 1911.

[2] The interpenetration of gelatine and the co-crystallization of silver iodide have also to be considered in this connection.

[3] Because indicating that the intensified development and stabilization of this stage is the direction in which high speed fine-grained emulsions must be sought. In existing emulsions, examined microscopically, but few instances of twinning were observed. But investigation of the sub-microscopic stage is lacking.

the latter stable stages being chronologically later. This represents a linear evolution.

On the other hand, there is an alternative possibility. At the initiation of the new independent component, nuclei of every possible phase of the new component are formed simultaneously, the transitions observed representing the relative dominance of each there present with resorption of the regressive stages, and the progression of form being determined chiefly by factors influencing dispersity in the amicroscopic state. At any relatively permanent stage, all possible forms are present, but in quantities determined by conditions regulating dispersity-equilibrium.

This view indicates that we should generally observe and study not the apparent linear evolution in time of pseudo-individual crystals, but the mutation in space of the collective mass. Where we expect to see the chronologically sequent steps of a linear evolution we really section off displacements of the mobile equilibrium between simultaneous forms, the equilibrium among which is above all determined by the tendency to forms of minimum free surface energy.[1] It will be seen, as an important consequence, that according to this view the new component and new phase, at their very inception (in the amicroscopic suspensoid condition), must be regarded as heterogeneous.

For an average uniform degree of dispersity (isopsegmaty), the individual particles will consist of arbitrary crystalline aggregates, polysynthetic twins, twins, and single crystals.[2] From this start progress to equilibrium by reduction of free energy will lie in displacement in favor of single crystals, aggregates and twins reducing to these as shown by Johnsen's experiments.

CONDITIONS FAVORING TWINNING AND OTHER MULTIPLE FORMS

Since twins are not a stable form, it is important to consider the conditions favoring their occurrence. Following von Weimarn's analysis and Johnsen's specific experiments, it is evident that their occurrence is primarily determined in the amicroscopic stage, partly by collision of ultra-microscopic crystals. Barmhauer[3] has pointed out that in the evaporation

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[1] With the progress of dispersimetry, this mutation theory will find a large field in metallurgy. The isolation of single quasi-individual crystals, instructive as it may be, indicates the resultant arrest of one line of mutation. We require also the mass resultant.

[2] Together, of course, with "dissolved" (molecularly dispersed) molecules (or the mother phase , liquid crystallites and droplets, and, if another crystalline system is possible, a duplicate set of aggregates, etc.

[3] Barmhauer, H., Die neuere Entwicklung der Krystallographie, p. 121.

of unsaturated solutions of potassium sulphate (which allows slow crystallization), only simple crystals are formed, whereas by rapid cooling of a hot concentrated solution, giving high supersaturation and rapid crystallization, there are formed a great number of twins. Further, infiltration of alcohol into a cold concentrated solution gives rise to great numbers of the most multifariously shaped twins, and if a cold concentrated solution thickened with gelatine is evaporated, there is again a large production of variously shaped twins and triplets.

Production of twins, etc., is less easy with less soluble substances, which of course agrees with the influence of a higher degree of supersaturation, and it is obviously possible that this would be affected by the solubilizing factors in emulsion-ripening. A supersaturated solution probably already contains the whole permutation of crystal germs in equilibrium with molecularly dispersed substance (dissolved molecules), and hence not growing, but contributing to the "colloidal" properties of such solutions. On rapid cooling or increased supersaturation, the stages are fixed under the dominance of primary inoculation. And here the nature of the medium and the initial concentration play the chief role. Under the foregoing conditions, a special type of twinning may predominate, corresponding to specific alteration in solubility of single faces, as already noticed. Preferential twinning on specific faces has been frequently observed by mineralogists.

The effect of inoculation was studied by Johnsen in relation to degree of supersaturation with enantiomorphous crystals of sodium uranyl acetate, with the following results:

SUPERSATURATION (1 = SATURATED)	NO. OF CRYSTALS		INOCULATION EFFECT D/L
	L.	D.	
1.00	13	29	2.23
1.03	10	23	2.30
1.09	10	25	2.50
1.14	7	22	3.14
1.20	1	40	40.00
1.26	1	45	45.00
1.31	1	45	45.00
1.34 labile	14	11	.79
1.34 labile	5	20	4.00

It will be seen that the effect increases at first with the degree of supersaturation, and decreases immediately when the solution is labile. This comprises the view of the predetermination of forms in the highly dispersed stage.

In general, then, the twinning conditions are closely related to those conditions of separation of a new phase which lead to colloids, and the control of twinned forms is essentially a problem of dispersoid chemistry, depending upon the methods used to produce systems of great dispersity.

Becke[1] has pointed out that in general twinned crystals grow more rapidly than simple ones. This may be attributed to the multiplication of the force of crystallization, or rate of growth, at the boundary where common directions of growth radiate.

These conditions have also a bearing on the formation of pseudomorphs and mimetic twinning. Increased supersaturation will usually involve nearer approach to a transition point, and consequently, as suggested by Mugge, increased tendency to orientation in an altered space lattice.

The conception that, just before crystallization, solutions consist often not only of different particles of one modification but of polymorphic particles of different modifications is in agreement with Smits' theory of allotropy.[2] He has shown that, where two modifications of a substance (e. g., mercuric iodide, silver iodide) may exist, under certain conditions both modifications are present in a definite equilibrium over a wide temperature interval about the transition point (compare p. 62). The transition point is thus a point of separation of a mixture, analogous to the "cracking" temperature of an oil-water emulsion.

SUMMARY

Our review of the factors in the preparation and ripening of silver halide emulsions thus returns to the point of departure. Beginning with the dispersion theory of von Weimarn, it connects up the peculiarities of "slow" and "rapid" emulsions with this analysis. But while the slower positive emulsions remain short-circuited in the region of the purely colloidal phenomena of peptization and pectization, high-speed emulsions require a traverse of very definite crystallization phenomena. In this connection it is suggested that decreased dispersity and increased grain size is determined chiefly by initial precipitation conditions, and that ripening by way of recrystallization depends mainly on elimination of adsorbed impurities. It is pointed out that degelatinization favors adsorption of colloidal silver, setting a limit to ripening. The hypothesis of Ostwald ripening is discussed in connection with the law of minimum surface energy, and it is shown that

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[1] Becke, F., Ueber die Ausbildung der Zwillingskristalle. Fortschr. Mineral. **1:** 68. 1911.

[2] Smits, A., Eine neue Theorie der Erscheinung Allotropie. Zeits. physik. Chem. **76:** 421. 1911.

mere increase in size is not the sole outcome of this, but that equilibrium relations between different habits are involved.

At this point, leaving the field of colloid chemistry for that of crystallography, the relation of twinning and habit variation to the initial conditions of dispersity is discussed, and it is shown that conditions similar to those regulating the colloid state determine the formation of twinned crystals and anomalies of crystallization. The relation of twinning to intra-crystalline strain and anomalous optical activity is pointed out, and the suggestion made that this relation may be of great importance in the theory of emulsions and their preparation. Thereby the problem is brought back into the ambit of the analysis of initial precipitation and colloid chemical regulation of dispersity. The gamut of silver halide emulsions from the slowest gas-light to ultra-rapid may be conceived as disposed on a helix, the axis of which is this colloid chemical regulation of dispersity—that is, ratio of surface to volume—since all the auxiliary factors of sensitizers and desensitizers, of size of grain, of individual crystal habit and eventual twinning, of optical anomaly and strained space-lattice, are dependent thereon.

None the less, although this dispersoid theory envisages and embraces emulsion phenomena in their entirety, collectively and distributively, it will be obvious from the foregoing that its function is limited to that of a regulative principle, operating statistically through the principle of minimum surface energy. The intimate relation between grain structure and photographic properties is, however, fundamentally a matter of crystallographic investigation, and as such is dealt with in the following chapters.

Considering that initial precipitation conditions determine very much the type of emulsion in the case of development emulsions precipitated with excess halide, and considering also the ripening or after treatment, the following factors are involved:

(a) The precipitate is $[(AgBr)_x : (AgI)_y]\ m\ (KBr)_n \quad (Gel_3 : H_2O)_o$;

(b) Silver bromide-silver chloride readily form continuous solid solutions in all proportions;

(c) Silver bromide-silver iodide form only restricted solid solutions; it is probable that mixtures containing up to 20% silver iodide contain the compound four parts silver bromide-one part silver iodide, or tend to form this compound;

(d) Silver iodide acts as a crystallization buffer-substance, a brake on speed of recrystallization. In particular, remaining undissolved by the ripening agent, it tends to conserve the original number of nuclei, and hence restrict increase in size of grains. It can also affect adsorption;

(e) Sorption of the soluble additions is higher, the higher the dispersity;

(f) This sorption, lowering reactivity in development, is not entirely removable by washing;

(g) It is reduced by recrystallization in ripening;

(h) Ripening in colloid silver halide emulsions is mainly a flocculation phenomenon;

(i) Ripening in suspensions proper is mainly a recrystallization process;

(j) This recrystallization process increases homogeneity of the silver halide in the grain, reduces absorbed bromide, and probably gelatine;

(k) Recrystallization, in so far as it affects ripening, is limited by formation of saturated surfaces, and very probably by colloid silver formation (incipient reduction). It is not known at what stage colloid silver is formed, but it may occur early, and thus afford nuclei for recrystallization, as shown in ammonia development (Chapter I) in the case of ammonia-ripened emulsions;

(l) When the experimental conditions regulating the three primary factors (1) dispersity-distribution, (2) recrystallization, and (3) sorption, (both adsorption and desorption), are completely known, scientific control of the characteristic curve—i. e., of speed, latitude, and density—will be possible.

These results show that a consideration of the dispersity and distribution of the silver halide precipitate is insufficient to account completely for all the facts. It therefore becomes necessary to study intensively the crystalline form and habit of the individual silver halide grains, and thus endeavor to determine in what way this factor of fundamental structure is related to the facts reviewed in the preceding pages.

CHAPTER VI

Experimental Study of the Crystallization of Silver Bromide

Microscopic examination of emulsions used for sensitive photographic plates reveals a definite crystalline structure of at least a large number of the silver bromide grains. F. W. T. Krohn,[1] who was apparently the first to recognize this structure, made his observations between 1892 and 1901, though his conclusions were not published until 1918. Banks' is the first recorded observation.[2]

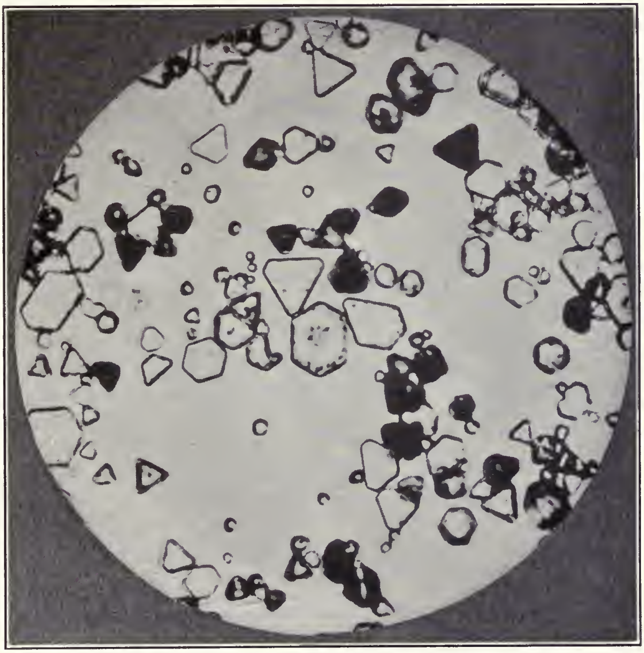

FIG. 21

Special silver iodo-bromide emulsion, magnified 1350 diameters

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[1] Krohn, F. W. T., The mechanism of development of the image in a dry-plate negative. Phot. J. **58:** 193. 1918.

[2] Banks, E., Remarks in discussion of Hurter and Driffield's paper on the latent image. Phot. J. **22:** 159. 1898.

Bellach[1] and Lüppo-Cramer[2] observed this structure somewhat later, though their published accounts, which appeared in 1903 and 1907 respectively, preceded Krohn's description.

In Figs. 21 and 22 are shown photomicrographs of an emulsion (magnified 1350 diameters[3]), which was prepared for this special purpose, and which is distinguished by a number of relatively very large grains, the largest having a diameter of $6-8\mu$. Fig. 23 is a photomicrograph of a "Radio-bromide" emulsion (magnified 2,500 times), made by Guilleminot of Paris, and Fig. 24 shows a similar magnifica-

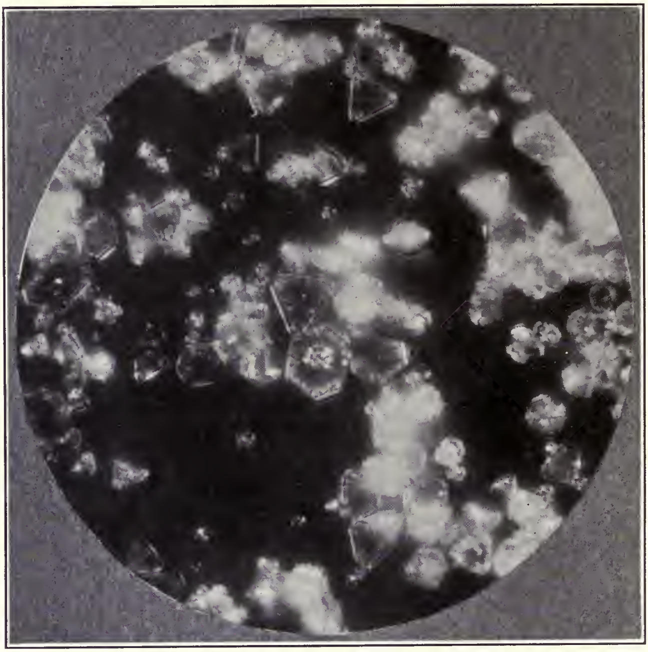

FIG. 22

Special silver iodo-bromide emulsion, between crossed nicols. Magnification, 1350 diameters

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[1] Bellach, V., l. c.

[2] Lüppo-Cramer, Photographische Probleme, p. 51.

[3] For description of the apparatus used see pp. 82-83.

tion of Seed 30 emulsion prepared by the Eastman Kodak Company.

It will be noticed in all these figures that the largest grains are polygons with angles of 60° and 120°. There is an obvious tendency to round off the edges and corners in the small grains—a phenomenon which is repeatedly observed in the formation of crystals in a colloid matrix—so that the smallest grains generally appear more or less spherical.

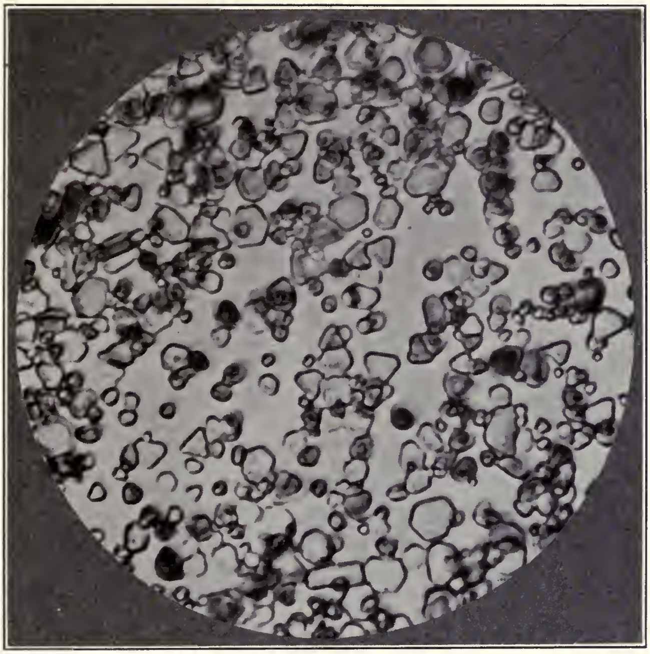

FIG. 23
Guilleminot's Radio-bromide emulsion,
magnified 2500 diameters

It will also be noted that there are apparently two kinds of grains, those which are clear and therefore absorb little transmitted light, and those which appear nearly black and therefore absorb considerable transmitted light. In the original negative, however, these "dark" grains do not show uniform light absorption. Instead, there seems to be a network of more or less dark portions, the details of which are not shown in the reproduction. As may be clearly seen in Fig. 21, these dark bodies exhibit the same crystallographic habit as the transparent grains, so that, for the present at least, there is no justification for the assumption that these represent two different substances.

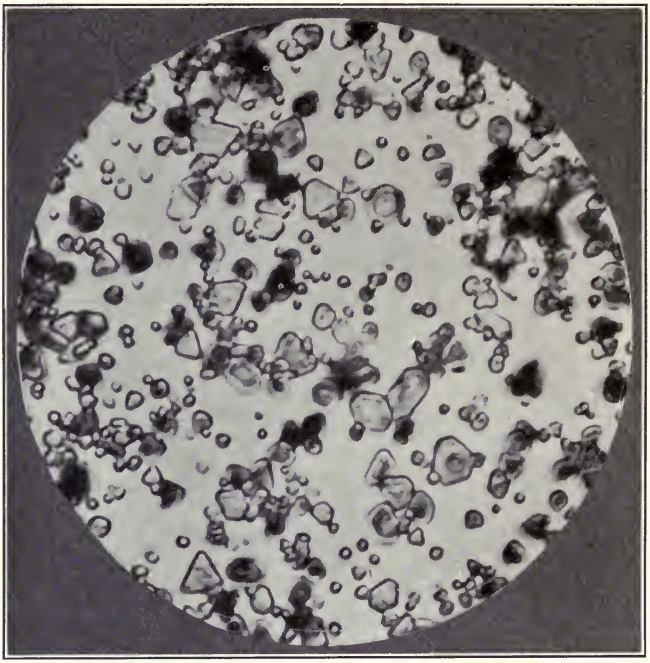

Fig. 24

Seed 30 emulsion, magnified 2500 diameters

The ratio between the number and the size of the round and the polygonal grains and between the clear and the opaque grains is not constant, but may vary considerably in the different emulsions. Thus, for instance, Lüppo-Cramer[1] prepared a photomicrograph of an emulsion in which there

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[1] Lüppo-Cramer, Photographische Probleme, p. 54.

were no well-developed crystal forms, all the grains being spherical. This must not be interpreted as meaning that these spherical bodies are not crystals, however, for that which determines whether or not a given body is crystalline is structure, not habit. The typical polygonal form of a well developed crystal is merely one manifestation of its structure.

The above-mentioned emulsions (and this may be said of practically all highly sensitive emulsions), contain in addition to the silver bromide a certain quantity of silver iodide, which varies in different emulsions. But there is never any indication that either the bromide or the iodide crystals are precipitated alone—i. e., without an admixture of the other.

In investigating this question, 122 photomicrographs of as many emulsions, prepared in various ways and magnified 2,500 times, were examined without finding one instance of separate precipitations of the iodide and of the bromide,—i. e., of hexagonal silver iodide and regular silver bromide. For silver iodide is polymorphous and, as the p.-t. diagram of Bakhuis-Roozeboom[1] shows, the stable phase at normal temperatures is hexagonal, the transition point into regular silver iodide being about 145° C. And it is very improbable that silver iodide for emulsion purposes is precipitated at 145° C. or higher.[2] Renwick[3] is of the opinion that the hexagonal silver iodide determines for the most part the crystalline form of the silver iodo-bromide grains, and thus forces the silver bromide to crystallize according to the hexagonal system. But this is not in agreement with the facts, as will be shown in later paragraphs.

Thiel[4] has determined by electrical measurements that, at 25° C., silver iodide can form solid solutions with silver bromide up to 30 molar per cent. This opens the question as to whether all the indications of isomorphism mentioned by Mitscherlich actually occur below these limits. As a means of investigating this, very carefully purified silver iodide was dissolved in ammonia (D. = 0.897) and the solution allowed to evaporate at room temperature in an open vessel. The crystalline precipitate obtained showed micro-

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[1] Bakhuis-Roozeboom, Heterogene Gleichgewichte, Vol. I, p. 128. See also Gmelin-Kraut, Handbuch der anorganischen Chemie, Vol. II, p. 115.

[2] It may, however, tend to occur initially, at high dispersity, in the unstable regular form, as is the case with mercuric iodide precipitated in gelatine. (See Chapter V, p. 62.) Being, in this form, isomorphous with silver bromide, co-precipitation with the bromide would favor this condition. However, at ordinary temperatures this form would be thermodynamically unstable, and, on any application of heat, would tend to pass to the stable form, thus setting up strain in the associated silver bromide crystals.

[3] Renwick, F. F., (Discussion of Krohn's paper). Phot. J. **58**: 195. 1918.

[4] Thiel, A., l. c.

scopic tabular crystals of the regular system of the form {100} and the combination {111} with {100}, which became faintly brownish in the light. Thus at room temperature silver iodide separates from ammoniacal solution in a metastable phase.

Mixtures of silver iodide and silver bromide which were dissolved in concentrated ammonia crystallized in octahedra of the regular system. For silver bromide alone the regular forms {111} and {100} and combinations are known. Hence it may be said that regular metastable silver iodide can, within certain limits, produce isomorphous mixtures with regular stable silver bromide.

Since the quantity of silver iodide in emulsions falls below these limits, silver iodide crystals of photographic emulsions may very well belong not only to the same crystal system, but also to the same crystal class as silver bromide. The classification of silver bromide would then be determinative for the silver iodo-bromide crystals of emulsions.

EARLY CRYSTALLOGRAPHIC INVESTIGATIONS OF SILVER BROMIDE

All crystallographic investigations of silver bromide confirm the existence of regular silver bromide. The crystals of natural silver bromide (bromyrite) show forms {111} and {100.}

Investigators have interpreted their observations differently, as shown in the following:

Roscoe and Schorlemmer[1] reported that silver bromide crystallizes from aqueous solutions of hydrobromic acid and mercuric nitrate in octahedra; Bellach[2] described "tetrahedral forms" of silver bromide; and mention is made of hexagonal forms of silver bromide, as follows:

Elsden[3] says: "The crystals have no influence upon polarized light when lying flat, but they appear to be doubly refractive when the rays pass obliquely through them, as if they belong to the hexagonal system"; Baur[4] records that amorphous silver bromide, dissolved in concentrated ammonia, is precipitated in hexagonal tablets upon diluting the solution

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[1] Roscoe, H. E., and Schorlemmer, C., Treatise on chemistry, Vol. II., p. 472.

[2] Bellach, V., l. c.

[3] Elsden, J. V., On the formation of a chemical compound of ammonia with silver bromide. Phot. News **25**: 174. 1881.

[4] Baur, E., *Silber* in Abegg's Handbuch der anorganischen Chemie, Vol. II, Part 1, p. 684.

with five parts of water; and Renwick[1] writes: "Silver bromide could occur both in the cubic and in the hexagonal crystalline systems." Krohn[2] also mentions hexagonal silver bromide, but he probably means by that octahedral silver bromide of the regular system which crystallizes in hexagons.

The only classification of silver bromide crystals is by Groth,[3] who assigns silver bromide crystals to the hexakis-octahedral class of the regular system. (See the concordance of symmetry classes, p. 131.)

THE PREPARATION AND EXAMINATION OF THE MICROSCOPE MOUNTS[4]

The Materials Used. The following chemicals were used in the precipitations:

Silver nitrate made by the Eastman Kodak Company;
Potassium bromide 'Analyzed,' from Kahlbaum;
Potassium bromide U. S. P. IX from Merck;
Ammonia (D = 0.897) purified double-distilled, from Powers-Weightman-Rosengarten Co., Philadelphia;
Distilled water from the laboratory.

These substances are recognized as the purest utilized for practical purposes. A special chemical analysis was not undertaken, because it was believed that possible impurities have no effect on the classification of crystals. Indeed, impurities are sometimes desirable, since their presence may alter the free energy between the crystal surfaces and the mother liquor, and new forms thus appear. Since the class to which a crystal belongs is determined by the highest symmetry common to the different crystals, it is desirable to have quite a large quantity of crystals of various forms. For this reason a large number of crystals were precipitated in the presence of various supplementary agents, which, however, led to no different result than that already obtained by the crystallization of the silver bromide from unadulterated solutions.

Preparation of Crystals. A solution of potassium bromide was added to a silver nitrate solution, the precipitated amorphous silver bromide was washed several times in a beaker with boiling distilled water, and the surface liquor removed by decantation. Finally the precipitate was washed on filter

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[1] Renwick, F. F., l. c.

[2] Krohn, F. W. T., l. c.

[3] Groth, P., Chemische Krystallographie, Vol. II., p. 200.

[4] Higson has recently published an article (Photomicrography in photographic research, Phot. J. **60**:140. 1920), in which a similar method of preparing microscope mounts is described.

paper and dried. The silver bromide in slight excess was put in a bottle with ammonia, and, to obtain equilibrium, was allowed to stand for a week (being frequently shaken) at a temperature of 20° C. This stock solution was then used in the preparation of the silver bromide crystals.

After being washed the crystals were placed on a slide, dried, covered with Canada balsam and a cover-glass, and heated in a drying oven at 70° C. for at least twelve hours. If microscopic examination showed that new forms had appeared, the precipitation was repeated and the new preparation heated, often as high as 90° C.

As a result of this treatment the crystals are so massed together that it is possible to observe and photograph only a few isolated crystals. Better results are obtained if, after washing, the crystals are suspended in a three per cent water solution of gelatine and then spread on the slide.

In all, 192 slides of silver bromide alone and 73 of silver bromide crystals precipitated in the presence of various foreign substances were prepared. Each preparation contained on the average about 2,000 crystals, so that altogether more than 500,000 crystals were prepared.

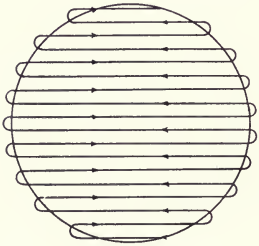

FIG. 25
Method of examining the preparations of silver bromide crystals under the microscope.

The best and most interesting preparations were selected and carefully examined under the microscope. The slide under observation was moved back and forth in such a way as to give the effect of moving the objective in the manner shown in Fig. 25. The distance between the two successive back and forth movements was thus in every case much smaller than the diameter of the microscope field.

Apparatus used.

a. *In the examination.* The instrument used in the investigation was a large model Zeiss microscope with an illuminating attachment and a Bausch and Lomb camera mounted on a large horizontal standard. An arc lamp of 12 amperes and 110 volts, with a rheostat and an Abbé aplanatic condenser (N. A. = 1.40) served as the illuminant.

For the 800 diameters magnification a Zeiss 2 mm. oil-immersion apochromat (N. A. = 1.4) and Zeiss compensating ocular No. 4 were used: for magnification of 1350 diameters, a Bausch and Lomb 1.9 mm. oil-immersion objective (N. A. = 1.3) with Zeiss compensating ocular No. 6; for magnifying 2,500 times, a Bausch and Lomb 1.9 mm. oil-immersion objective (N. A. = 1.3) and Zeiss compensating ocular No. 12. In every case a Wratten G filter was used, and the degree of magnification was ascertained by means of a Bausch and Lomb stage micrometer ruled to 10μ and 100μ.

b. *In preparing the photomicrograph.* Since silver bromide is yellow, and it is desirable to show as many details as possible in the photomicrograph, a yellow filter (Wratten G) was used. There is an additional advantage in this, as the silver bromide decomposes very rapidly in the strong illumination in the microscope, and shutting out the blue and violet rays retards this decomposition, although it does not entirely prevent it.

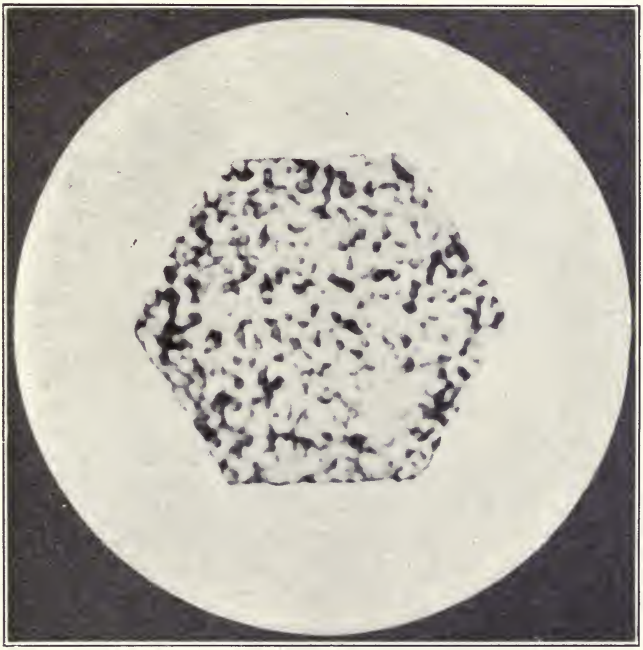

Fig. 26
Photochemical decomposition on the octahedral surfaces of silver bromide crystals. Magnification, 2500 diameters

Figs. 26 and 27, which are photomicrographs of two different crystals taken after less than two minutes' exposure to unfiltered light, show how rapidly decomposition proceeds in unfiltered light. This photochemical decomposition does not take place simultaneously over the entire surface of the crystal, but begins in isolated points from which it spreads over the whole crystal until the crystal disappears (as has been observed by Lorenz[1]). In this respect, therefore, the direct photochemical decomposition of silver bromide crystals seems to proceed in a manner comparable to the formation of the developed image as demonstrated by Scheffer[2] and Hodgson.[3]

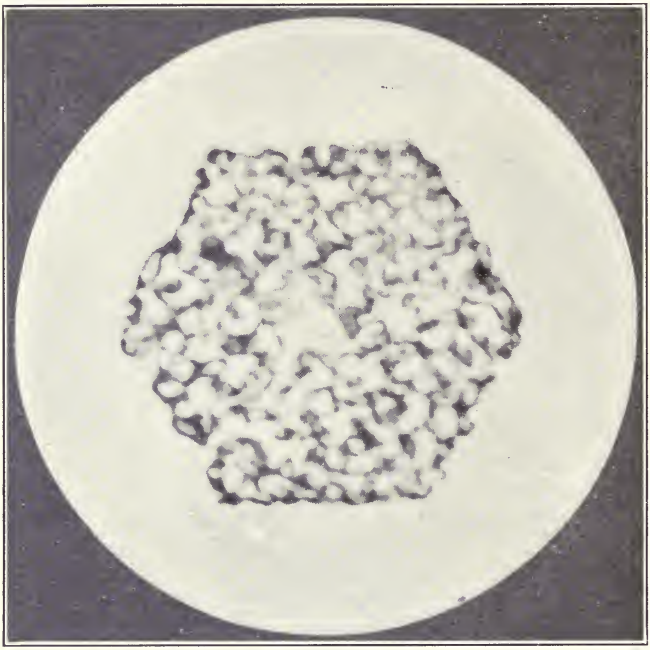

Fig. 27

Photochemical decomposition on the octahedral surfaces of silver bromide crystals. Magnification, 2500 diameters

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[1] Lorenz, R., Kolloidchemie und Photographie. Koll. Zeits. **22:** 103. 1918.

[2] Scheffer, W., Microscopical researches on the size and distribution of the plate grains. Brit. J. Phot. **54:** 116. 1907.

[3] Hodgson, M. B., The physical characteristics of the elementary grains of a photographic plate. J. Frankl. Inst. **184:** 705. 1917.

The presence or absence of colloids such as gelatine does not affect the progress of this photochemical decomposition, and it will be seen that most of the photomicrographs contain dark spots caused by this decomposition.

The use of the Wratten G filter made it necessary to use yellow-sensitive plates; and as it was desirable to obtain negatives which would intensify delicate details, Wratten panchromatic plates (M-plates), were used and developed for 2¾ minutes at a temperature of 18-20° C., in the following developer:

Metol	2.2 gr.
Hydroquinone	8.8 gr.
Sodium sulphite	4.8 gr.
Sodium carbonate	4.8 gr.
Potassium bromide	0.88 gr.
Water to	1000.00 gr.

(It was demonstrated in the physical section of this laboratory that it is possible under these conditions to obtain a degree of development where $\gamma = 2.4$ without danger of appreciable fog.)

SILVER BROMIDE CRYSTALS

Of the various known solvents of silver bromide, such as hydrobromic acid, potassium bromide, mercuric nitrate, ammonia, etc., ammonia has been found the most convenient. Not only can the various crystal forms of silver bromide in photographic emulsions be accurately identified when crystallized from ammoniacal solutions, but also a large quantity of other forms which are valuable for crystal determinations.

METHODS OF PREPARATION

There are three different methods for crystallizing silver bromide from ammoniacal solution: (a) by diluting the solution with water; (b) by evaporation of the ammonia; (c) by cooling the solution.

The first method was used by Elsden in his above-mentioned work on silver bromide; the second was utilized by Reinders[1] for obtaining crystallized photo-chloride; and the third was undertaken at our suggestion by Mr. Schneider.

None of these methods gave uniform results, crystals of various forms being always obtained. No rule could be established for the appearance of any one crystal form, for everywhere were all possible grades and transitions. This was probably due to the impossibility of obtaining identical

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[1] Reinders, W., l. c.

conditions throughout the solution during the process of crystallization. In the more concentrated solutions crystals of silver bromide-ammonia compounds, which frequently produced singularly beautiful pseudomorphs, also appeared.

The methods of preparation will be taken up in order, and the silver bromide-ammonia pseudomorphs and means of detecting them will be treated in a later section.

(a) *Dilution of ammoniacal solution.* The dilution was made as rapidly as possible and at room temperature (about 20° C.). The crystals separated throughout the solution and fell to the bottom. In reflected light they showed a lively play of colors, due to the interference phenomena of thin layers. (The majority of these crystals were laminate.)

For the various conditions under which the precipitation was made and the results obtained, see the following table:

Original Solution		Dilution with H_2O	Crystal Faces	Special Forms	Well-defined Dimensions	Numbers of Preparations Examined
% NH_3	% AgBr					
29.4	0.4	1:2	O, C	d, s, p, l	1, 2, 3	2
29.4	0.4	1:2½	O	d, p, l	1, 2, 3	3
29.4	0.4	1:3	O	l	2, 3	2
29.4	0.4	1:5	O	l	2, 3	8
29.4	0.4	1:10	O	l	2, 3	11
23.5	0.4	1:2	O	l	2, 3	3
23.5	0.4	1:5	O	l	2, 3	3
23.5	0.4	1:10	O	l	2, 3	6
20.5	0.34	1:5	O	l	2, 3	3
20.5	0.34	1:10	O	l	2, 3	3
17.6	0.26	1:10	O	l	2, 3	3
14.7	0.25	1:10	O	l	2, 3	3

O = octahedron
C = cube
l = lamelliform
p = pseudomorph
d = dendrite
s = skeleton
1 = needle
2 = plate
3 = ordinary crystal

As is evident from the above, octahedra predominate. Only the first preparation contained a few cubes, and they were very irregular. The first preparation also showed the greatest variety of crystal forms, which is readily comprehensible, since it was impossible to obtain identical crystallization conditions throughout the solution because of concentration changes due to the evaporation of the ammonia. In order to have the conditions as nearly uniform as possible, however, the crystallization was carried out in closed vessels.

The dilutions indicated in the table are about the limits within which one can obtain well-developed crystals.

(b) *Evaporation of ammonia.* Eleven different concentrations of ammonia were prepared, each being diluted with ten per cent more water than the preceding one. They were treated with a slight excess of silver bromide and left in closed vessels for a week. When equilibrium was established, several drops of the solution were put on a slide, and the ammonia allowed to evaporate. Then the crystals were heated. In this way thirty-five slides were prepared. The highest concentrations gave pseudomorphs in addition to octahedra in the form of the usual crystals and plates. Also, there were the same dendritic and lamellate-formations as in the diluted ammoniacal solution.

(c) *Cooling the ammoniacal solution.* A given quantity of ammoniacal silver bromide solution was put in a bottle and enough boiling distilled water added to fill the bottle. It was then sealed so that no air would be in contact with the liquid. The cooling was accomplished by means of a stream of ice-cold water, and the rate of cooling was regulated by using bottles of different volumes. Too rapid cooling produced too small crystals, and too slow cooling gave only well-developed crystals. Very good results were obtained by using a 50 cc. bottle and a 10 cc. and a 14 cc. pipette. Crystals obtained under these conditions showed the greatest variability of forms,—i. e., skeletons, lamellate-formations on the crystal surfaces, etc.

The various conditions under which the crystallization was carried out are given in the table below:

Solution		Degree of Cooling (°C.)	Rapidity of Cooling	Crystal Faces	Special Forms	Well-defined Dimensions	Numbers of Preparations
% NH_3	% AgBr						
0.6		95° – 4° 96° – 5°	c				1
1.18	0.01	95° – 22°	a, b, c	r, c, o	s, l	1, 2, 3	21
1.76	0.02 (–)	95° – 5° 94° – 6°	a, b	c, o	s, l	1, 2, 3	12
2.35	0.02 (+)	95° – 22° 96° – 5°	a, b, c	o, p	l	1, 2, 3	6
2.94	0.03	95° – 21° 95° – 4°	a, b, c	o, p	l	1, 2, 3	35
5.88	0.06	95° – 20°	a, b, c	o	l	2, 3	5

a = vessel of 50 cc.
b = vessel of 10 cc.
c = slow cooling at room temperature in a 50 cc. bottle

o = octahedra
c = cubes
r = rhombic dodecahedra
p = pentagonal dodecahedra
s = skeletons
l = lamellate-formations

1 = needles
2 = plates
3 = ordinary crystals

SILVER BROMIDE-AMMONIA COMPLEXES

According to Bödländer and Fittig,[1] silver bromide in ammoniacal solution is present as the complex compound $Ag(NH_3)_2Br'$, in which $Ag(NH_3)_2$ is the complex cation.

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[1] Bödländer, G., and Fittig, R., Das Verhalten von Molekularverbindungen bei der Auflösung. Zeits. physik. Chem. **39**: 597. 1902.

These silver bromide-ammonia compounds separate from solution in a solid phase, the following compounds being produced:[1] $Ag_2(NH_3)_3Br_2$; $AgNH_3Br$; $Ag(NH_3)_3Br$. Therefore, in the crystallization of silver bromide from ammoniacal solutions, it is not impossible to obtain a complex compound which may lead to entirely erroneous results. But Bödländer has shown that these complex compounds are very unstable, and in contact with air or water dissociate into their constituents, thus forming pseudomorphic forms of silver bromide.

The following characteristics were tested as to their reliability for distinguishing the silver bromide from the ammonia compound:

$AgBr$	$Ag_n(NH_3)_mBr_n$
1. Yellow.	1. Colorless.
2. Sensitive to light.	2. Insensitive to light.
3. Unchanged in ammonia-free water.	3. Becomes turbid in ammonia-free water.
4. Microscopically unchanged after being heated to 70° C.	4. Becomes opaque microscopically after being heated to 70° C.
5. Shows simple refraction between crossed nicols.	5. Shows double refraction between crossed nicols.

1. The yellow color of silver bromide crystals is so intense that it can be perceived even in crystals of $\pm 1\mu$ in diameter, and it is, therefore, a useful means of distinguishing silver bromide from the colorless ammonia-compounds.

2. The complex silver bromide-ammonia compounds are unchanged after being in the sunshine in the presence of ammonia for a day. As soon as the ammonia-pressure becomes too low, however, a photochemical decomposition of the disengaged silver bromide sets in. This gives the impression that the complex compound is sensitive to light, as the light-decomposed ammonia compound is very similar to photochemically decomposed silver bromide. Therefore, this test is not recommended for practical purposes.

3 and 4. These tests, the effect of ammonia-free water and the effect of heat, may be combined. First, the crystals are well washed with distilled water; if they remain unchanged during the washing (the ammonia-compound becomes turbid), they are heated to 70° C., or even higher, for at least twelve hours. In this heating the pseudomorphic crystals become opaque, due to loss of ammonia, and may therefore be readily detected, as the silver bromide crystals are unaffected.

5. The double refraction of light by the various silver bromide-ammonia compounds has not been definitely estab-

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[1] Ephraim, F., l. c.

lished. Elsden[1] examined only one of the complexes—which one is not known—and found that it belonged to the tetragonal system. Hence too little is known regarding this test to consider it reliable.

SUMMARY OF OBSERVATIONS

Crystal forms observed. In the various preparations the forms observed were as follows: $\{111\}$, $\{110\}$, $\{100\}$, $\{210\}$, of which $\{111\}$ and $\{100\}$ appeared as single crystals, and of which the following combinations were found: $\{111\} + \{100\}$; $\{111\} + \{110\}$; $\{111\} + \{210\}$.

The rhombic dodecahedra, which were seldom seen, occurred only as small strips on the edges of the octahedra.

Special forms observed. Among the forms observed, needles, plates, "dark" grains and pentagonal dodecahedra merit special mention.

Silver bromide needles. In a microscopic study there was found a developed and fixed photographic plate which under the microscope showed very remarkable developed grains in the form of needles. Figs. 28 and 29 show two such grains, magnified 2,500 times, which measured respectively 21μ and 12μ in length.

FIG. 28

Needle-shaped grain occurring in a silver iodo-bromide emulsion; enlarged 2500 diameters.

FIG. 29

Needle-shaped grain occurring in a silver iodo-bromide emulsion; enlarged 2500 diameters.

The usual developed grains of photographic plates are somewhat larger than the original silver iodo-bromide crystals, and generally have a different form. (A photomicrograph,

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[1] Elsden, J. V., l.c.

published by M. B. Hodgson,[1] shows developed grains which retain the form of the original crystals only in those cases where the crystals were very large. The change in form is so slight in proportion to the size of the grains that the form of the crystal is but little affected.)

When there is an accumulation of silver iodo-bromide crystals in the emulsion, or when the distance between the crystals is very small, the developed grains coalesce, which makes them appear very much larger than the original crystals. The needles shown in Figs. 28 and 29 may be linear aggregations of silver iodo-bromide crystals, or may be developed from small needles.

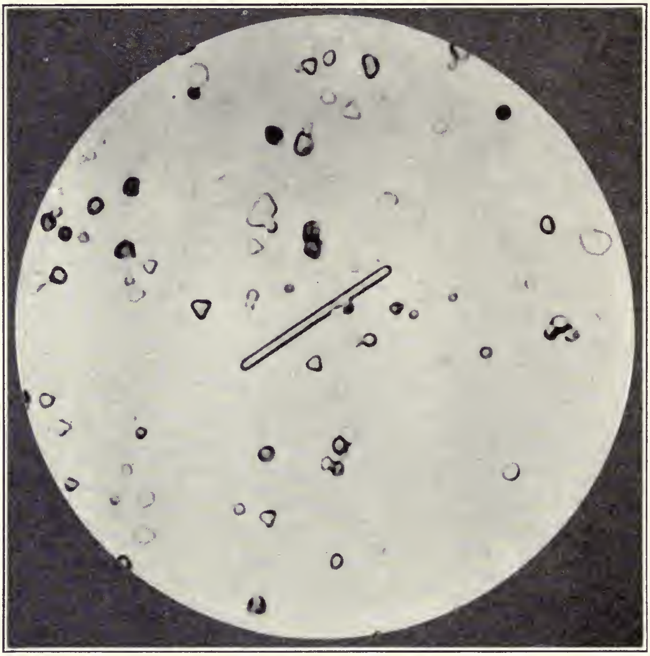

Fig. 30

Crystalline needles in a silver iodo-bromide emulsion, enlarged 2500 diameters

A microscopic examination of the original emulsion showed various needle-shaped crystals, some of which were photographed. (Figs. 30 and 31.) However, needles were found

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[1] Hodgson, M. B., l. c.

not only in this emulsion but also in a large number of commercial plates, though in the latter the needles were not of such unusual size.[1] Needles were also found in emulsions containing silver bromide alone. Between crossed nicols these needles show exactly the same optical behavior as the other grains. This observation is not new, as Lüppo-Cramer[2] published a photomicrograph of an emulsion needle in 1907.[3]

FIG. 31
Crystalline needles in a silver iodo-bromide emulsion, enlarged 2500 diameters

To make a more accurate determination of the crystalline form of these needles, various crystalline precipitates were examined microscopically and needles were found which showed not only octahedral faces (Fig. 32) but cubical faces as well.[4] Where there were cubic faces, the combination

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[1] The lengths of the needles in the different emulsions varied from 3μ to 25μ.

[2] Lüppo-Cramer, Photographische Probleme, p. 49.

[3] Wallace also refers to the presence of "spicular crystals" in certain emulsions.

[4] There was abundant needle-formation in a preparation which contained 0.05% aluminium bromide, and good needle-formation in one to which 0.5% strontium bromide had been added.

$\{111\} + \{100\}$ frequently appeared (Fig. 33). Needles were also obtained by subliming silver bromide, but their faces could not be determined on account of the rounded corners. Octahedral needles were also found in one of the above-mentioned preparations of silver bromide from potassium bromide solution. The needles are, therefore, not unique modifications of silver bromide, but must be regarded as the result of a special development of the silver bromide crystals.

Figs. 32 and 33
An octahedral and a cubic needle of silver bromide, precipitated from ammonical solution. Magnification of 2500 and 800 diameters, respectively.

Silver bromide plates. It was to be expected that, in addition to the ordinary silver bromide crystals, developed more or less in accordance with the three co-ordinates, and the needles, which show a marked growth in only one direction, plates, or crystals which develop in two directions, would also appear. This was true in most cases where the silver bromide was crystallized from ammoniacal potassium bromide solution. There were relatively few instances where the crystals developed well in all three directions.

That most of the crystals are plates may be shown as follows:

1. By focusing down with a 2 mm. Zeiss oil-immersion apochromatic objective (N. A. = 1.4) and compensating ocular No. 12 with the diaphragm of the condenser (N. A. = 1.4) wide open. The small depth of focus of this system made it possible to obtain a very sharp focus on the thin surface of the object. The crystals well developed in three directions were distinguished in that they could be sharply seen in more than one focus. Plates, on the contrary, appeared suddenly sharp and distinct, and vanished almost immediately on changing the focus;

2. When the crystals are in Canada balsam, one may turn them over and look down at right angles to the edges of the crystals, most of which are thinner than one μ;

3. The lively play of colors in the silver bromide crystals in reflected light and the pale colors in transmitted light, in which gray of the first order in Newton's color series was often identified, is explainable only by the interference phenomena of thin layers.

How thin these crystals may be is shown by the fact that, according to the well-known formula,

$$\frac{{}^{n}\mathrm{air}}{{}^{n}\mathrm{AgBr}} = \frac{\lambda\mathrm{AgBr}}{\lambda\mathrm{air}} \quad \begin{array}{rl} (\text{where } n = & \text{refractive index,} \\ \lambda = & \text{wave-length of light}), \end{array}$$

the wave-length in silver bromide is less than half as long as the wave-length of the corresponding colors in the air. Now, if it is remembered that air layers 0.3μ thick can produce marked interference colors, it may be readily understood that silver bromide plates 0.13μ thick can produce the same effect. (These facts first directed our attention to plate-formation in photographic emulsions.) Koch and du Prel[1] stated that whether the silver bromide crystals in photographic emulsions are plate-shaped or tetrahedral is yet to be determined.

After this form had been verified, Krohn's article[2] was published (in 1918). In this article Krohn stated that previous to 1901 he had been able to observe emulsion grains from all directions because of their Brownian movement, and had come to the following conclusion: "The crystals are lammellar and almost hexagonal and are probably imperfectly developed octahedra such as one gets with chrome alum crystallized in a shallow dish;"

4. Measuring the total volume of silver bromide in a photographic emulsion, determining the number of grains in one cc. of the emulsion, and calculating the mean diameter of the grains gives the data for computing the average thickness of the silver bromide crystals in the emulsion. To do this, a given quantity of emulsion was spread on a definite area of film. Pieces were then taken from five different regions of the film and by means of a microtome three cross sections of each of 5μ (± 0.06) in thickness, were prepared and used for the microscope preparations. This process was repeated for five different emulsions, each containing a dif-

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[1] Koch, P. P., and du Prel, G., Ueber das Korn der photographischen Platte und eine Methode zu einer Untersuchung. Physik. Zeits. **17**: 536. 1916.

[2] Krohn, F. W. T., l. c.

ferent quantity of silver bromide, so that there were 75 preparations in all. One hundred and fifty photomicrographs (magnification 1176.4 diameters) were taken, using a paraboloid condenser. The use of dark field illumination makes it possible to define each grain sharply, so that the number of grains in the emulsion can be counted. The number in these emulsions varied from 16 to 43×10^{10} per cc. One emulsion contained $16 \times 10^{10} \pm 0.5 \times 10^{9}$ grains. The diameter of the grains averages about 1.5μ. Assuming that all the grains are truncated tetrahedra, the average thickness may be reckoned as 1/14 of the diameter. In other words, most of the grains in photographic emulsions are plates.

The dark grains. As shown in Fig. 22, these grains show very intense light between crossed nicols. This may be due either to a thicker layer of silver iodo-bromide or to a greater reflection of light. Also, there is a layer-by-layer variation in the definition of these dark grains as the focus of the microscope is changed. All this indicates that these dark grains are crystals more or less well developed in all three dimensions, and that the effect of dark color is probably produced by the strong light-reflections in the crystal, due to the unusually high refractive index, as has been observed in crystals of thallium salts and of gold-barium acetate.

The pentagonal dodecahedra will be discussed later. (See page 95.)

FACES OBSERVED

The following faces were observed in the different crystal forms:

Usual crystals	{111}		{100}
Combinations	{111}	+	{100}
	{111}	+	{110}
Plates	{111}		{100}
Combinations	{111}	+	{100}
	{111}	+	{210}
Needles	{111}		{100}
Combinations	{111}	+	{100}

Etching.

In order to study the etch-figures which appeared on the larger octahedral faces after treatment with ammonia, the crystalline precipitate obtained by cooling the ammoniacal solution was kept in the closed bottle at room temperature without removing the ammonia. The solubility increased with the higher temperature and very beautiful etch-figures, in the form of triangles with rounded corners, resulted. It was thought that these figures would aid in determining symmetry-ratios, but in this case they gave no criterion for classification.

CHAPTER VII

THE CLASSIFICATION OF SILVER BROMIDE CRYSTALS

From the crystal forms observed, it would seem that the symmetry-relations of silver bromide crystals are less than is now assumed. An accurate method of investigating this relation by the determination of different physical constants in various directions in the silver bromide crystals, which would be adapted to the extremely small dimensions of the silver bromide crystals, is not yet perfected.

The pentagonal dodecahedra obtained by cooling the ammoniacal solution are so important for the classification of silver bromide that they merit closer study. These forms occurred only in combination with the octahedra, as shown in Figs. 34 and 35. This combination is well known in SnI_4, FeS_2, CoAsS, $Cs_2Al_2.(SO_4)_4.24H_2O$ and $(NH(CH_3)_3)_2.Al_2(SO_4)_4.24H_2O$. Unfortunately, the combinations of pentagonal dodecahedra and octahedra are not very clear in the accompanying reproductions, in which the combinations resemble quintettes. But a careful study of the original preparations leaves no doubt that these crystals, especially those in Fig. 35 d and f, are combinations of true pentagonal dodecahedra with octahedra.

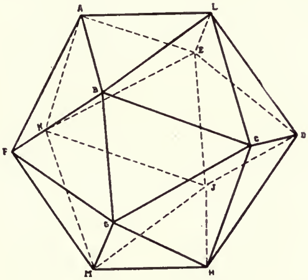

FIG. 34

Diagram showing fully developed combination of octahedron and pentagonal dodecahedron.

The pentagonal dodecahedra are distinguished from the usual silver bromide crystals in that there is a strong tendency to plate-formation, while the faces ABF, BGF, BCG, CHG, CDH, DJH, DEJ, EKJ, EAK and AFK show a much greater rapidity of growth in the direction of their normal than the other faces. The resulting lack of development of these latter faces produces a five-sided pyramid which in Fig. 35a is lying with one of the triangular faces on the slide.

In Fig. 35a and b are pictured two combinations $\{111\} + \{210\}$ in which the upper and lower pyramids are about the same size. Since, as Fig. 34 shows, the corners of the two pyramids do not coincide, but are about 36° apart and are

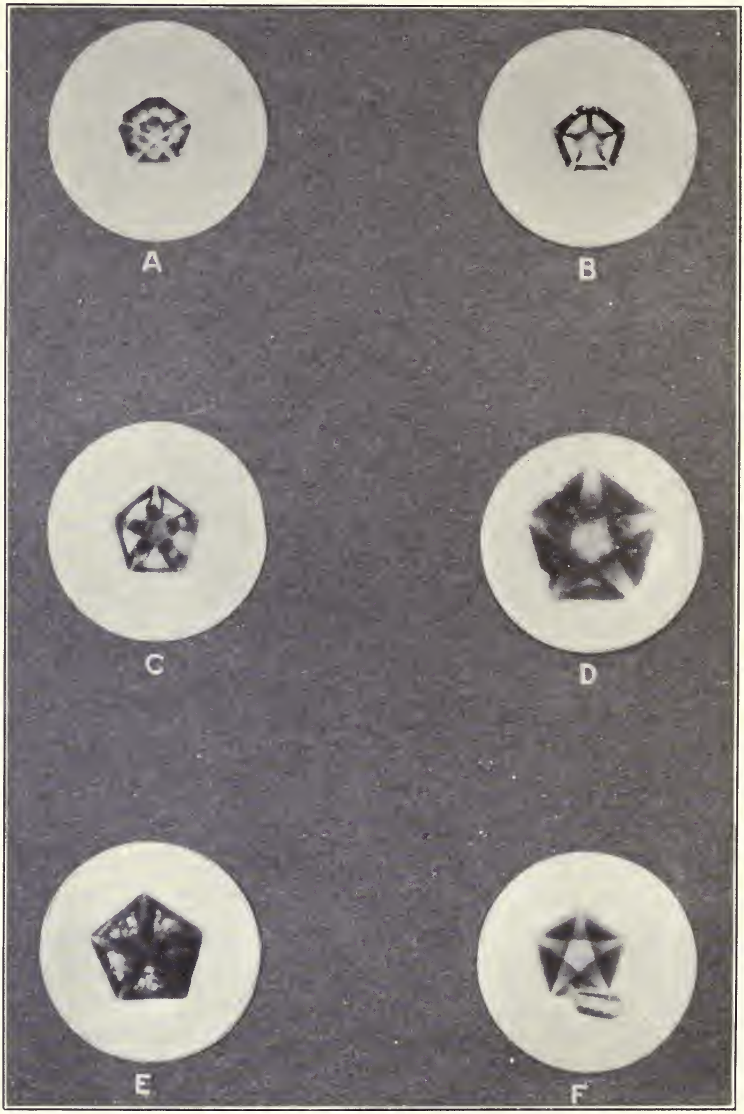

FIG. 35
Combinations of octahedra with pentagonal dodecahedra of silver bromide. Enlarged 800 diameters

flattened, the resulting truncation produces a decagon in projection.

The occurrence of pentagonal dodecahedra shows that silver bromide crystals belong only to the tetrahedral-pentagonal-dodecahedral or the dyakisdodecahedral class.[1] However, there is no evidence of the hemihedrism of silver bromide crystals. What have been described by many authors as tetrahedra of silver bromide in photographic emulsions are triangular octahedral plates (see below). Inasmuch, therefore, as this hemihedrism is not proven, we must place silver bromide in the dyakisdodecahedral class.

THE CLASSIFICATION OF SILVER CHLORIDE AND SILVER IODIDE

It has been mentioned that silver iodide in limited quantities can form homogeneous mixed crystals with silver bromide. This indicates that the metastable silver iodide, crystallized in regular form from solutions at ordinary temperatures, may be placed in the same class as silver bromide.

Groth[2] placed silver chloride in the hexakisoctahedral class, in accordance with his observations of the faces of natural crystals. But these crystals may be as logically placed in the dyakisdodecahedral class. Furthermore, Thiel[3] has demonstrated, by the continuous change of potential of silver chloride-silver bromide mixtures, that silver chloride forms homogeneous mixtures with silver bromide in all proportions. So in all probability silver chloride belongs to the same crystal class as silver bromide.[4]

THE POSSIBILITY OF MODIFICATIONS OF SILVER BROMIDE

Even though the reasons for assuming the existence at ordinary temperatures of a stable or metastable hexagonal silver bromide in addition to the regular silver bromide are insufficient, the fact that silver bromide crystallizes in the dyakisdodecahedral class indicates that it is possible for it to crystallize in right and left pentagonal dodecahedra, so that a kind of enantiomorphism, as in quartz, sodium chlorate, etc., may exist. This is not to be interpreted in a purely geometrical sense, i. e., that optical differences, such as the opposite

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[1] See concordance, p. 131.

[2] Groth, P., l. c., Vol. I., p. 200.

[3] Thiel, A., l. c.

[4] Crystals were also identified from silver cyanide and silver sulphocyanide as octahedra of the regular system. These investigations, however, have not been carried further.

rotation of circularly polarized crystals, can occur here, but rather, as Marbach[1] found in the case of pyrite and cobaltite, that these crystals belong in the thermo-electric electromotive series partly beyond positive antimony and partly beyond negative bismuth: so that a pyrite crystal of the first kind which is united with a similar crystal of the second kind produces a stronger thermal current than antimony with bismuth. In this sense it is possible for silver bromide to form two modifications.

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[1] Marbach, cited by Groth in Physikalische Krystallographie, p. 193. (Third Edition.)

CHAPTER VIII

The Silver Bromide Crystals of Photographic Emulsions

As is well known, in photographic emulsions the silver bromide is precipitated in the presence of a protective colloid (gelatine) and therefore one has to do with a case of colloidal precipitation. Since there are distinct silver bromide crystals in the melted emulsion and in plates, a transformation in the sense of colloidal silver bromide to crystalline silver bromide must have taken place.

This transformation is, however, simply a special case of the thermodynamic principle according to which the system tends to reduce its surface-energy,[1] and which (as has been indicated in Chapter V), is the starting point of the Gibbs-Curie-Wulff law; for, as stated, this conversion takes place more quickly in the presence of a solvent of silver bromide, such as potassium bromide, ammonium hydroxide, etc. Further, the rapidity of the transformation increases with rise in temperature. Whether the colloidal silver bromide consists of an aggregation of unusually small crystals, or of purely amorphous silver bromide—i. e., in the molecular state—makes no difference, since the surface-energy of colloids is very large in proportion to the surface-energy of the single silver bromide crystals. It is probable therefore that the velocity of solution of colloidal silver bromide is greater that that of the crystalline silver bromide. Thus a transformation occurs in the solvent by which the crystalline silver bromide is formed while the colloidal form disappears. This is essentially the same as the principle discussed above to indicate the relation between the size of the crystal and the decreased solubility, which in photographic literature is known as "Ostwald Ripening."[2]

Therefore in photographic emulsions one finds, certainly for a number of the grains if not for all, the same conditions as in ordinary processes of crystallization; and this does not prevent our applying the Gibbs-Curie-Wulff law to at least the larger silver bromide grains which have definite crystalline structure.

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[1] In general, small crystals dissolve more quickly than larger ones because, in the transformation of many smaller crystals into one larger, the surface energy is diminished.

[2] Ostwald, W., l. c.

The question of the influence of gelatine on crystallization processes, already discussed in part, will be dealt with in another relation in a later chapter.

FORMS OF SILVER BROMIDE CRYSTALS IN EMULSIONS

The forms of the silver bromide crystals in photographic emulsions are very varied, though all belong to the same crystallographic system and the same class. In 122 different emulsions which were examined at a magnification of 2,500 diameters, only octahedra could be positively identified. Higson (l. c.) says he found cubic crystals in silver bromide emulsions. In the work described here this observation could not be confirmed, and the presence of cubes and of combinations of cubes with octahedra or other forms could never be definitely determined. It is possible that Higson's cubic crystals were obtained from precipitations from dilute ammoniacal solutions.

The octahedra appear:

a. In crystals more or less well developed in three directions—dark grains;

b. In plates, which are most markedly developed in two directions; and

c. In needles, which are developed principally in one dimension.

(Those grain-aggregations and groups which come only within the range of probability will be disregarded.)

Each of these forms exhibited variations, for which the plates are especially noticeable, though the needles and ordinary crystals showed similar differences to a less marked degree. We will, therefore, limit our discussion here to the plates, since they are in the majority in photographic emulsions.

Plate-forms are so numerous that it is impossible to describe them all. Here we shall discuss only definite types as observed in the emulsions, remembering that the other forms represent all possible transitions between the types described, and that all are variations of one and essentially the same crystal form.

Fig. 36 represents an octahedron (ABCDEF) which is lying with one face on the paper. In parallel projection a hexagon is obtained. Now, if the capillary constant between the mother liquor and the crystal is different for different faces,[1] so that, for example, K_1 of the face AED and K_2 of

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[1] Cf. Chapter V.

the face BCF are much smaller than K_3 of the face ACD, K_4 of the face CDF, K_5 of the face DFE, K_6 of the face FEB, K_7 of the face EBA, and K_8 of the face BAC, then the conditions necessary for the formation of a plate or tablet are established.[2]

An equilateral regular hexagon is produced if

$$K_1 = K_2, K_3 = K_4 = K_5 = K_6 = K_7 = K_8,$$
$$K_1 < K_3.$$

These plates are thinner the greater the ratio K_3/K_1. For one emulsion the mean value of K_3/K_1 has been determined as 14.

On the other hand, if

$$K_1 = K_2, K_3 = K_5 = K_7, K_4 = K_6 = K_8, \text{ and}$$
$$K_1 < K_3 < K_4 < 2K_3,$$

a scalene but otherwise regular hexagon will result, as shown in Fig. 37. Here AED is the upper and BCF the lower octahedral face of the tablet.

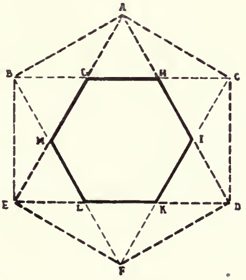

FIG. 36

Diagram showing the formation of a tabloid equilateral hexagon from an octahedron.

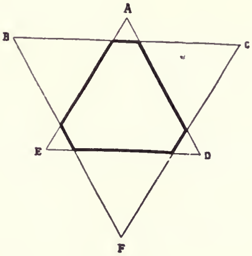

FIG. 37

Diagram showing the formation of a tabloid unequilateral hexagon from an octahedron.

If the following conditions obtain during development, $K_4 \geqq 2K_3$, a triangular plate will be formed, as shown in Fig. 38. Since the growth of three of the side-faces is two or more times as rapid as that of the other three, the latter are suppressed.

Another scalene but otherwise regular hexagon which is often to be seen in emulsions is formed when

$$K_1 = K_2, K_3 = K_4 = K_6 = K_7, K_5 = K_8, \text{ and}$$
$$K_1 < K_3 < K_5 < 2K_3.$$

---

[2] For the sake of simplicity, K_1 is assumed as equal to K_2. Small differences between K_1 and K_2 obviously do not affect this and the following results. It is also assumed that K does not change during growth.

Irregular forms appear when K_3, K_4, K_5, K_6, K_7, and K_8 are more or less unequal.

One very remarkable form occurring in emulsions is the trapezoidal lamina (Fig. 39) which appears in the most varied modifications. The conditions for its formation are:

$K_1 = K_2$, $K_3 = K_5 = K_7 = K_8$, $K_4 = K_6$,
$K_1 < K_3$ and $K_4 \geqq 2K_3$.

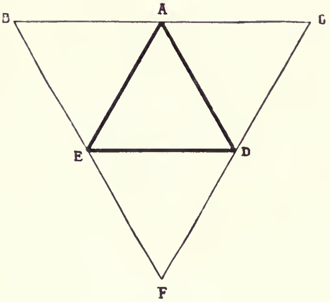

FIG. 38

Diagram showing the formation of a tabloid equilateral triangle from an octahedron.

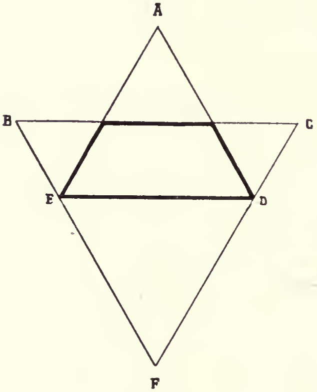

FIG. 39

Diagram showing the formation of a tabloid trapezium from an octahedron.

Modifications result when:
$K_5 = K_8$, $K_5 < K_4$; $K_8 < K_4$, $K_3 = K_7 < K_4$, or if under the same conditions:
$K_3 = K_7$, $K_3 < K_4$, $K_7 < K_4$, $K_5 = K_8 < K_4$, etc.

A pentagon (Fig. 40) with angles of 60° and 120° and therefore of a form quite different from the faces of the pentagonal dodecahedron appears when:

$K_1 = K_2$, $K_3 = K_4 = K_6 = K_7 = K_8$,
$K_1 < K_3$ and $K_5 \geqq 2K_3$.

Modifications are obtained when K_3, K_4, K_6, K_7, and K_8 are more or less unequal, but always remain smaller than K_5.

A rhombus (Fig. 41) with angles of 60° and 120° appears when two parallel side faces are suppressed on account of too great velocity of development, when therefore:

$K_1 = K_2$, $K_3 = K_4 = K_6 = K_7$, $K_5 = K_8$,
$K_1 < K_3$ and $K_5 \geqq 2K_3$.

Modifications may appear when K_3, K_4, K_6, and K_7 are more or less varied, but always remain smaller than K_5.

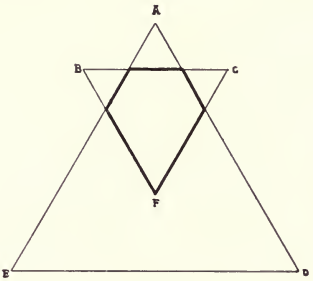

FIG. 40
Diagram showing the formation of a tabloid pentagon from an octahedron.

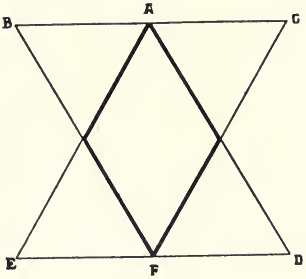

FIG. 41
Diagram showing the formation of a tabloid rhombus from an octahedron.

A different development phenomenon is responsible for the needle formations, which develop when the free energy of the base is greater than that of the prism-faces, so that the crystal grows most rapidly in the direction of the base. The multiplicity of plate-forms is induced by the greater velocity of growth of one side-face between two other side-faces having an inferior development. The formation of plate-shaped crystals by convection-currents in the mother liquor is not possible in silver bromide emulsions, since the grains are suspended and in slight Brownian movement, which reduces the convection-currents, on the one hand, and these are further reduced by the viscosity of the mother liquor on the other. An octahedral needle results when two contiguous side-faces develop more rapidly than the other side-faces. (Fig. 42.) However rapid this growth may be, these latter faces can never disappear. But if the capillarity constant of one of these rapidly growing faces decreases during growth, the development of the entire needle in one direction is interfered with.

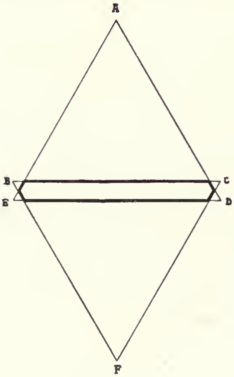

FIG. 42
Diagram showing the formation of a needle from an octahedron.

Among needles, one must differentiate between well-developed needles of approximately equal thickness and width, and plate-like needles. The first type appears as octahedra when $K_1 = K_2 = K_5 = K_8$. The second appears as octahedra when $K_1 < K_5$. These distinctions could not be made in photographic emulsions, however, because of the limits of microscopic resolving power.

The conditions for the formation of a needle are:

$$K_1 = K_2,\ K_3 = K_4 = K_6 = K_7,\ K_5 = K_8, \text{ and } K_3 < K_5.$$

Now it is possible that needles do not develop with equal rapidity in two opposite directions—e. g., K_3 and K_4 may be very much greater than K_6 and K_7. But this does not affect the results in the least.

Only slight indications of tabular octahedral twinning, such as was frequently observed in ammoniacal silver bromide crystal-formation (Fig. 43), were to be seen in completed photographic emulsions.[1]

THE RELATION BETWEEN THE LIGHT-SENSITIVITY AND THE SURFACE-ENERGY OF SILVER BROMIDE CRYSTALS IN EMULSIONS

Only very general statements can be made on this subject, as very little is known about it. If a change in light-sensitivity is produced by an increase or decrease of the surface-energy of silver bromide emulsion crystals, then in general it may be assumed that larger emulsion grains have a different sensitivity from smaller. In practice, indeed, it often seems that the coarse-grained emulsions are more sensitive than the fine-grained. But that this is not always the case is shown by the following:

An experimental emulsion was prepared, the grains of which measured up to 8μ in diameter and which had an H. and D. speed of only 38. In comparison with this emulsion a "Royal Standard Lightning Plate" from Kodak Ltd. was tested, the grains of which averaged up to 2.8μ in diameter, and of which the H. and D. speed was 728. Thus it appears that emulsions containing grains of approximately one-third the linear dimensions are more than nineteen times as sensitive. This is true also of individual grains in the same emulsion. After a quantitative investigation of this question, Koch and du Prel[2] concluded that it is not possible to formulate a definite relation between grain-size and sensitivity with the information at present available, but that it is certain that the largest grains in an emulsion are by no means the most sensitive.

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[1] See Chapter V, p. 68.

[2] Koch, P. P., and du Prel, G., l. c.

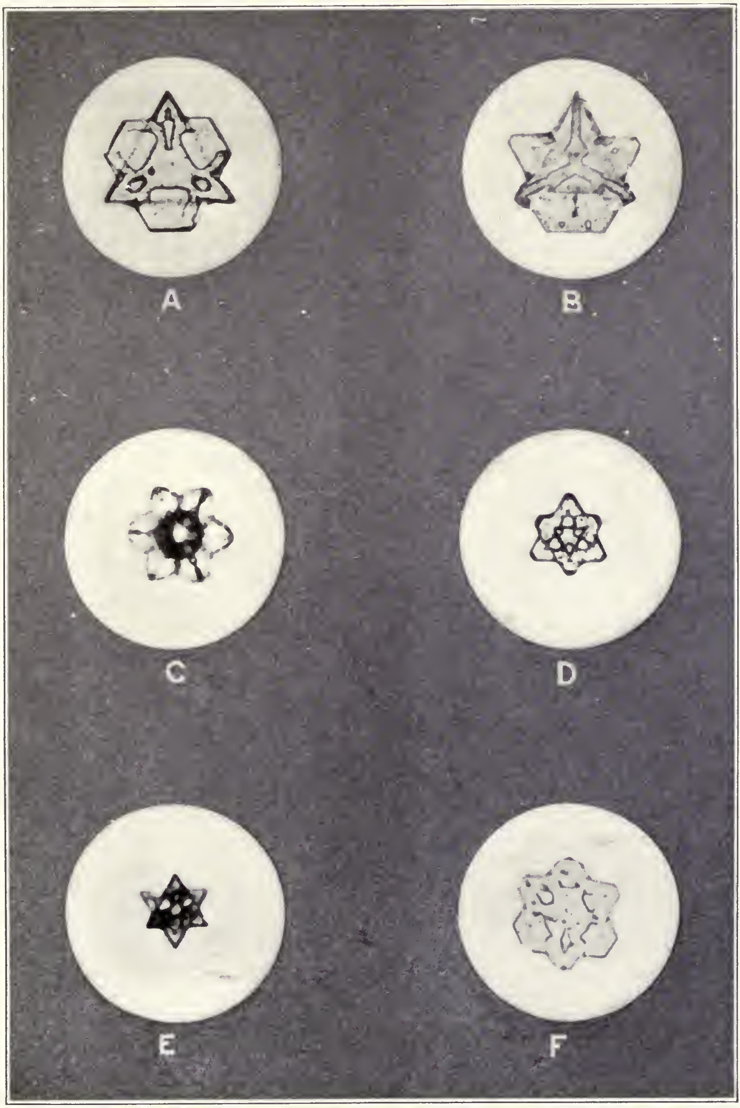

FIG. 43
Twin forms on octahedral faces of silver bromide. A-E, magnified 800x; F, 2500x

Lehmann and Knoche[1] also demonstrated that ripening increases the sensitivity of silver bromide-albumen emulsions without noticeably altering the size of the grain.

Now, if one considers the ripening process as a purely thermodynamic one, entirely independent of light-sensitivity,[2] (i. e., as a process in which the surface-energy of the grains tends to reach a minimum), Lüppo-Cramer's remarks[3] to the effect that the sensitivity of colloid emulsions may be increased to but a relatively slight degree, and that the initial stage of emulsion-making (the conditions under which the silver bromide is precipitated), is of much greater importance than the later steps of the process, become more intelligible.

In other words, the increase in sensitivity is determined not so much by the ripening process as by the conditions under which the silver bromide precipitation was accomplished. (See particularly Chapter II, p. 27.)

Luther's statement, made independently, that the laws of thermodynamic equilibrium are not applicable to photochemical equilibrium, and that therefore there is no definite connection between thermodynamics and photochemistry,[4] is in entire agreement with this view.

Thus we come to the conclusion that the high sensitivity of some photographic emulsions may be somewhat influenced by variations in the surface-energy, but can certainly not be entirely determined thereby. In agreement with Lüppo-Cramer's statement above, we must very probably seek these conditions in the crystal structure of the silver bromide on the surface of the grains.[5]

From the crystallographic standpoint only one method of investigation in this direction is possible without methods of X-ray crystal analysis. That method is to determine the directions of most rapid growth relative to the characteristics of the crystal lattice, an observation which is especially significant in the case of the silver bromide octahedra. And since these octahedra occur in three forms,—as ordinary crystals, plates, and needles—it is possible to investigate the directions of greatest growth not only in volume, but even on the octahedral faces.

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[1] Lehmann, E., and Knoche, P., Plate-grain and albumen emulsions. B. J. Phot. **61**: 759. 1914.

[2] The H. and D. interpretation of light sensitivity is intended here.

[3] Lüppo-Cramer, Phot. Prob., p. 35.

[4] The formation of a thermodynamically more stable form of silver bromide does not indicate that such a form is less sensitive to light, as R. Abegg (Die Silberkeimtheorie des latenten Bildes. Arch. wiss. Phot. **1**: 18. 1899) and V. Bellach (l. c., p. 37) assume.

[5] W. D. Bancroft (The photographic plate, l. c.) and W. Reinders (l. c.) attribute the high sensitivity to the presence of gelatine. But it must be borne in mind that emulsions of unusually varied sensitivities may be prepared from the same gelatine—which may be explained by differences in structure.

CHAPTER IX

THE DIRECTIONS OF MOST RAPID GROWTH IN SILVER BROMIDE CRYSTALS AND THE OCCURRENCE OF ANOMALOUS FORMS

1. *In the ordinary octahedra.* According to Lehmann,[1] the directions of most rapid growth are along the line of greatest acumination. Since in octahedra these directions coincide with the three principal crystallographic axes of the crystal, the former are indicated by the latter. Lehmann has also shown that skeletons grow in these directions, and silver bromide skeletons which were formed exactly like the framework of the three co-ordinate axes were repeatedly found.

2. *In octahedral plates.* To determine the direction of most rapid development here, either of two methods may be followed:

a. By observing the direction in which the skeleton develops;

b. By very rapid but suddenly disturbed crystallization.

In addition to the skeletons which coincide with the crystal axes, there is in plates one form of skeleton the rays of which coincide with the edges of vicinal faces, and which may be termed surface skeletons.[2] They must not be regarded as special needle-combinations, for they always appear in uniform and entirely regular star-shaped figures from which three definite rays emanate at angles of usually 120°. These skeletons often form the framework of plates, when they have three, six, nine, or twelve rays. Four rays usually appear only in trapezoidal plates, and five in octahedral pentagonal plates.[3]

Structural anomalies occurred so frequently that they merit special attention. Crystal-development is possible only when the mother-liquor is slightly supersaturated. The surplus quantity of the crystalline substance in solution is deposited and thus the concentration of that part of the liquid in the vicinity of a crystal is decreased. By the liberation of the latent heat of solution and the decrease in satur-

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[1] Lehman, O., cited by Groth in Physikalische Krystallographie, p. 284.

[2] The ice-skeletons of snow flakes may be classified here.

[3] These trapezoidal rays can be crystallographically constructed from a vicinal triakis-octahedral plate (triangle) in which one of the edges between two vicinal faces is truncated by a vicinal-ikositetrahedron. Similarly, the five rays of the octahedral pentagon may be explained by the appearance of two vicinal ikositetrahedra. The octahedral rhomboids occur so seldom that their rays have not been satisfactorily determined.

ation, the solution becomes specifically lighter and local concentration and convection currents set in.

According to Lehmann,[1] these local concentration-currents are the cause of the formation of structural anomalies and skeletons, and Wulff[2] considers them the cause of the formation of vicinal faces.[3]

Among the plates obtained from ammoniacal solution were a large number of structural anomalies, a few of which are illustrated in Figs. 44 and 45. That such lamellar-structures actually are produced may be demonstrated by the variations in the Newton colors. That vicinal faces having absolutely no connection with the crystal faces may be simulated in this way is shown, e. g., in Fig. 44a, where there are indications of an unusually flat ikositetrahedron, while the other plates and those in Fig. 45 show traces of unusually flat triakisoctahedra. Fig. 46 shows the same much more sharply defined, and Fig. 46d is especially remarkable for the combination of a triakisoctahedral skeleton[4] with an octahedral plate. Thus one has here a transition to the skeleton. That these skeletons may appear isolated is shown in Fig. 47, where twelve triakisoctahedral silver bromide skeletons are reproduced. In addition to these, a large number of ikositetrahedral skeletons of silver bromide were found, twelve of which are pictured in Fig. 48. Ikositetrahedral skeletons in octahedral plates are shown[5] in Fig. 49, and combinations of triakisoctahedral and ikositetrahedral skeletons in octahedral plates in Fig. 50, among which Fig. 50f is noteworthy because of the indications of a right and left dyakisdodecahedral skeleton in combination with the triakisoctahedral and the ikositetrahedral skeleton in an octahedral plate.

The attempted classification of skeletons does not pretend to be conclusive, because of the difficulties of establishing an

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[1] Lehmann, O., Molekular Physik. Vol. I., p. 354; and Groth, P., l. c., p. 284.

[2] Wulff, J., l. c.

[3] H. A. Miers (An enquiry into the variations of angles observed in crystals. Phil. Trans. A. **202:** 459. 1903), attempted to destroy the concentration-currents by stirring the liquid (a solution of alum) but even so obtained vicinal faces. Then he demonstrated by refractometric measurements that the refractive indices of the solution which is in contact with the crystals is the same as that of a strongly supersaturated solution. This adsorption-layer is, of course, quite different from the solution itself, so the real nature of the vicinal faces is still not entirely clear.

[4] So far as we know, crystallographers have not introduced any especial differentiations nor a nomenclature for skeletons. The silver bromide skeletons are here designated according to the theoretical vicinal faces of which they may form the edges, without, however, considering them capable of being classified crystallographically.

[5] Ikositetrahedral skeletons in octahedral laminae are very seldom obtained in the above-described methods of precipitation. Those reproduced here were obtained by adding a mixture of gum arabic and dextrose in varying quantities to the solution, and heating it to not higher than 60° C.

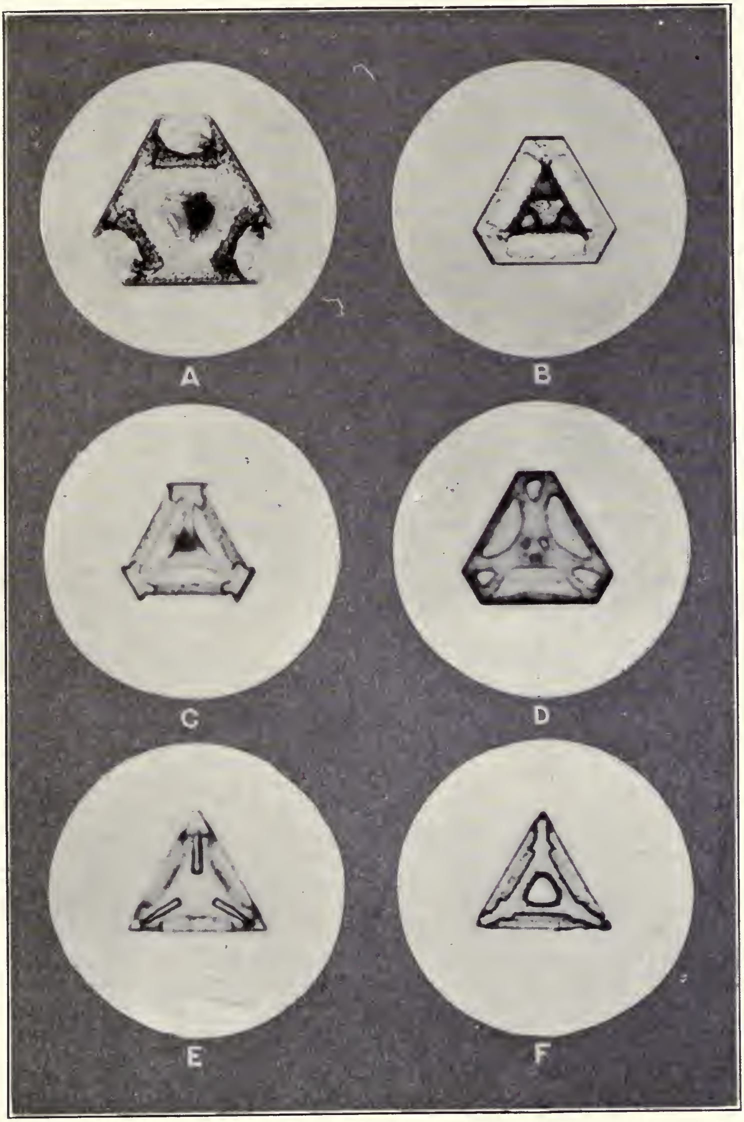


Fig. 44
Lamellae formations on octahedral faces of silver bromide.
Magnification, 800 diameters.

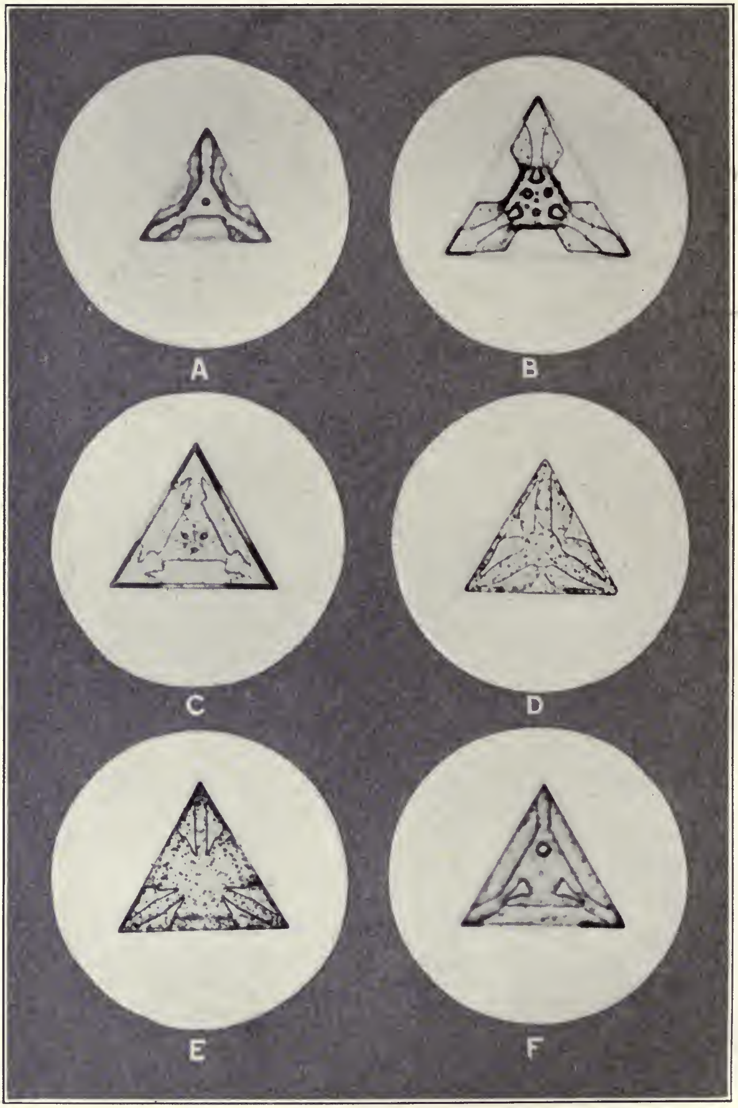


FIG. 45
Lamellae formation on octahedral faces of silver bromide.
Magnification, 800 diameters

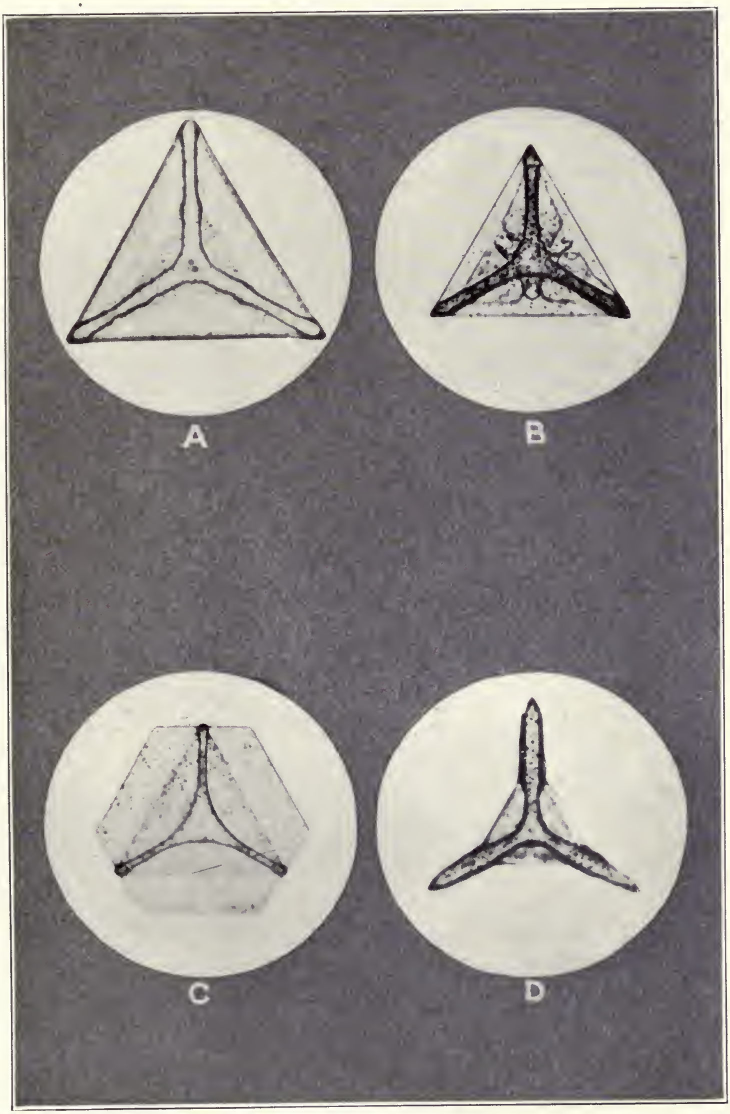


FIG. 46
Ikositetrahedral skeletons on octahedral faces of silver bromide crystals. Magnified 800 times

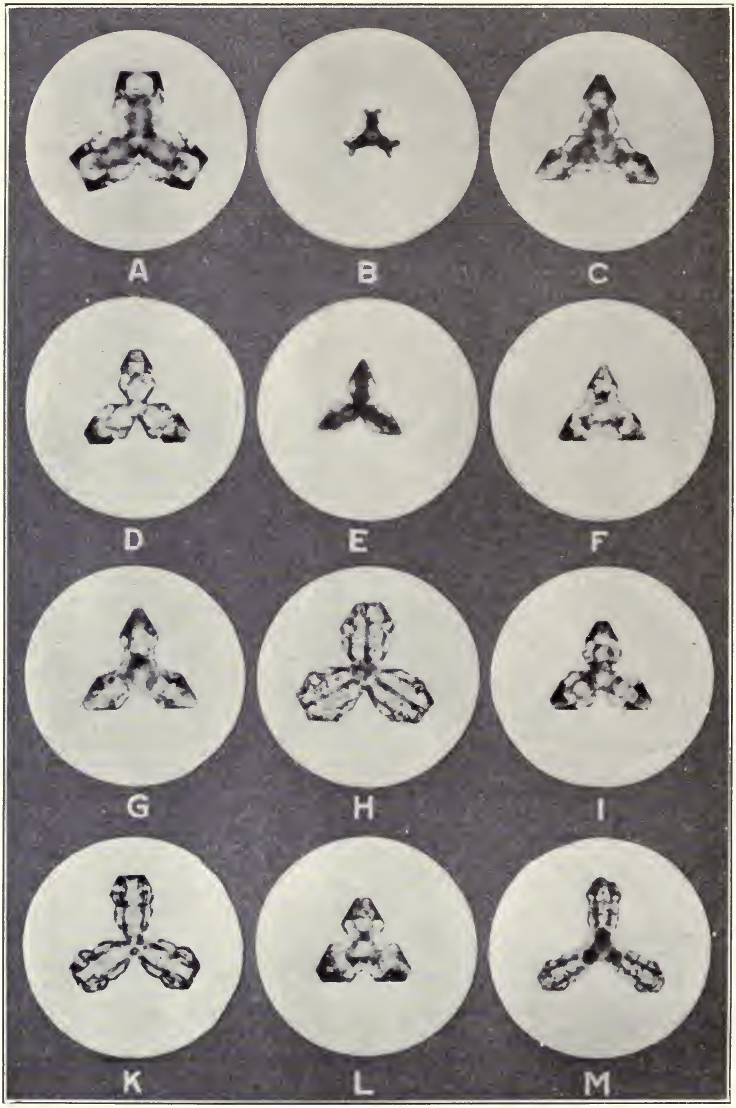


FIG. 47
Triakisoctahedral skeletons of silver bromide, enlarged 800 diameters

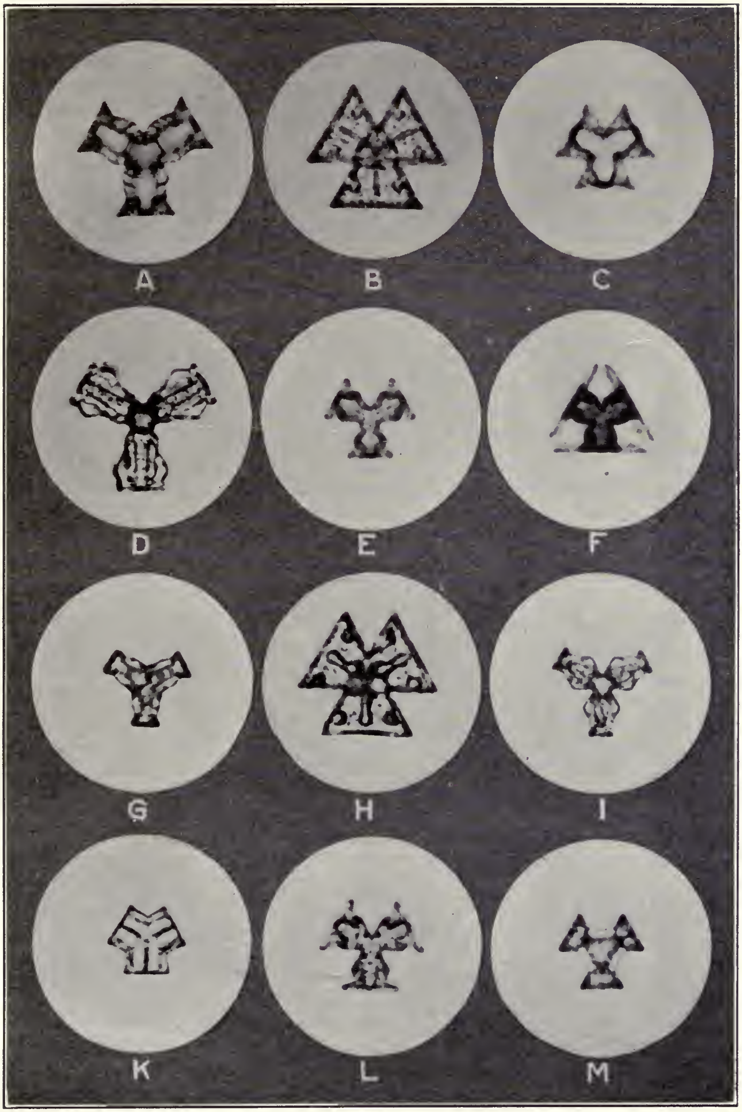
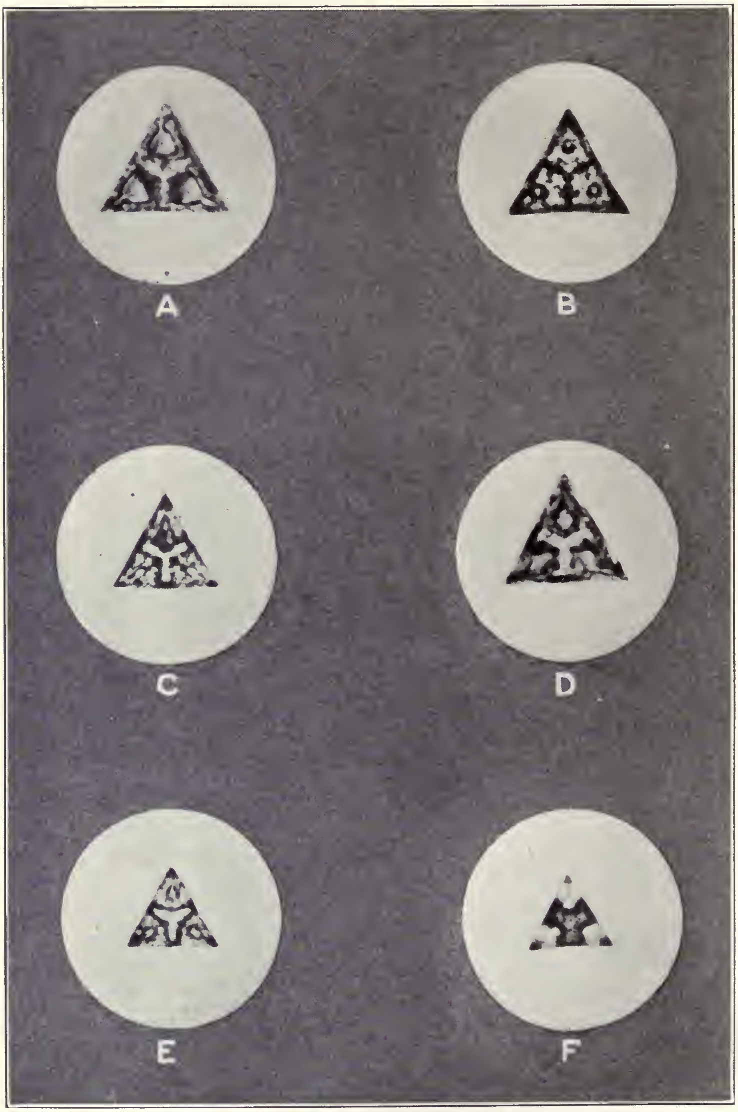


FIG. 48
Ikositetrahedral skeletons of silver bromide, enlarged 800 diameters



No. 49
Ikositetrahedral skeletons on octahedral faces of silver bromide crystals. Magnified 800 times

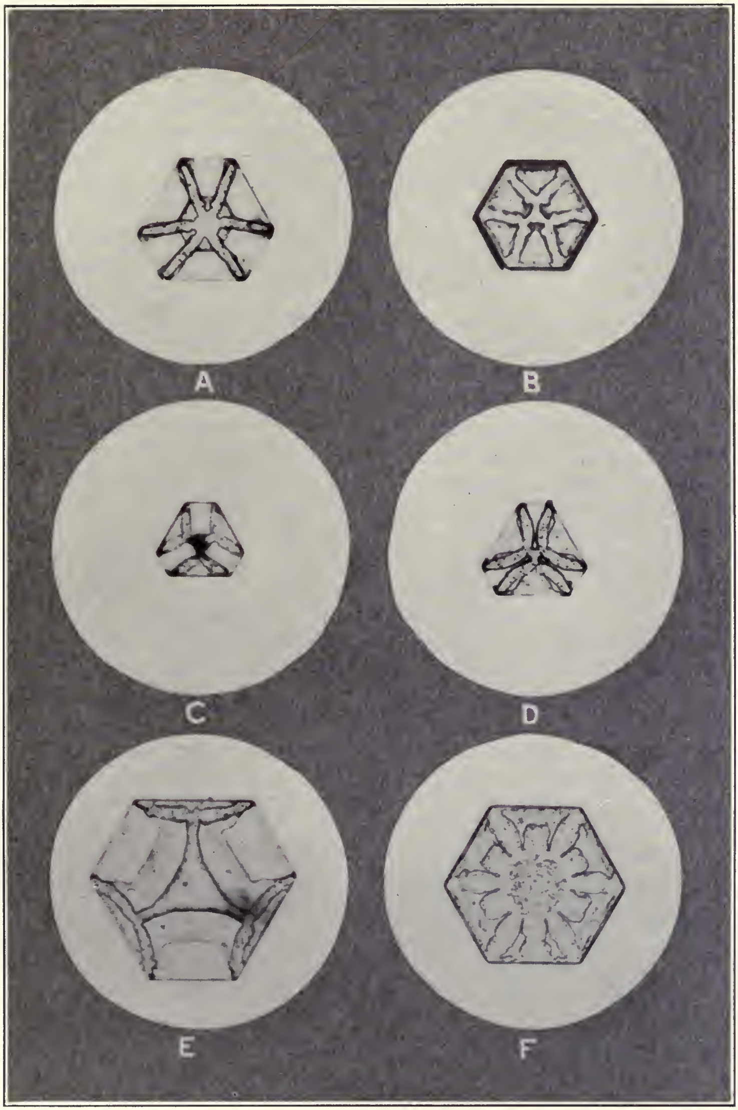


FIG. 50

A-E, Combinations of triakisoctahedral and ikositetrahedral skeletons on octahedral faces of silver bromide, magnified 800 times.

F, Diagrammatic combination of triakisoctahedral, ikositetrahedral, r- and l- dyakisdodecahedral skeleton on an octahedral face of a silver bromide crystal. Magnification, 800 diameters.

exact classification; for instance, the differences between triakisoctahedral and ikositetrahedral skeletons are not always evident. The ends of the rays vary, being either pointed or blunt. Skeletons having pointed rays have been attributed to the triakisoctahedra, those having blunt rays to the ikositetrahedra. To which of these groups Fig. 47c belongs is not clear; but, since the writer was able to observe this skeleton as a plate with an octahedral face, it has been assigned to the triakisoctahedra.

The connection between skeleton forms and structural anomalies due to lamination is thus very evident in the case of silver bromide. There is, therefore, no objection to Lehmann's theory that these forms are the results of special growth conditions caused by local concentration currents. But it must be remembered that under these special growth-conditions regularities appear which can be conditioned only by the lattice structure of the crystals, as, for example, the directions of the rays of the skeleton. Then these rays probably represent the directions of most rapid development. The diagram in Fig. 50f contains all the skeletal radiations thus far verified; from which we conclude that in the octahedral face there are twelve possible directions of most rapid growth, which form angles of 30° with one another.

The second method for determining the direction of most rapid growth, by the sudden interruption of unusually rapid crystallization processes, consists in greatly diluting the ammoniacal silver bromide solution with water. (See table on page 86.) The crystals obtained in this way show growth phenomena at the edges of the octahedral plates, as indicated in Fig. 51. The directions of growth of the triakisoctahedral and ikositetrahedral skeletons of the octahedral plates are represented in the center of gravity of the triangle, but for the sake of clarity the development directions of both dyakisdodecahedral skeletons are omitted. If one transposes the directions of growth at the corners so that they start from the center of gravity, it is obvious that they coincide exactly with those of all skeletal forms.

3. *In octahedral needles.* In needles the direction of most rapid growth obviously coincides with the needle axis. In ordinary needles this direction coincides with one of the principal crystallographic axes. If a, b, and c are the three main axes, having development-velocities of V_a, V_b, and V_c, then to form a needle only one of the three need have a much greater velocity of growth than the other two, i. e., $V_a = V_b$, $V_b < V_c$.

The directions of most rapid growth in laminate needles (see Fig. 42) may be determined from the octahedral hexagon, since these needles are distorted hexagons. As is readily seen, this direction coincides with one of the rays of the triakisoctahedral or of the ikositetrahedral skeleton.

The octahedral silver bromide needles thus show no other directions of most rapid growth than have already been found in the usual octahedra and the octahedral plates.

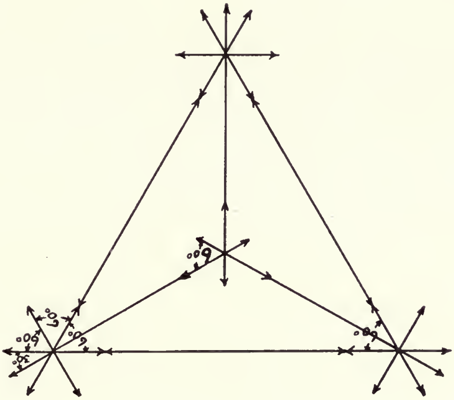


FIG. 51
Diagram showing directions of most intensive growth of an octahedral plate

4. *In other crystal forms of silver bromide.* In addition to octahedra, prisms and plates of pentagonal dodecahedra and of rhombic dodecahedra have been found in silver bromide. That there are rhombic dodecahedral skeletons with rays which coincide with the sides of the rhombus could not be proved.

The pentagonal dodecahedra, which appear only in combination with octahedra, are formed in large numbers when one or two per cent gelatine or about 0.005 per cent of agar-agar is added during the process of precipitation from suddenly cooled, highly concentrated solutions. Skeletons were often observed of which the rays coincided with the sides of the pentagonal pyramids which are so characteristic in these combinations. The rays of these skeletons formed angles of about 72° with each other. No dimensions can be given, as it was impossible to measure the skeletons on account of their crude formation.

A large number of cubes and cubic skeletons were observed, of which fifteen different forms are reproduced in Fig. 52. Here combinations with the octahedra may be clearly seen in f and h. Whether these were plates or the ordinary crystals could not always be determined with certainty. Presumably a to f are plates. The only ones that could be positively identified as ordinary crystals are g to p. Cubes could readily be identified by turning them over, when the different dimensions could be definitely seen. They are approximately mathematically true cubes.

It is difficult to say in which direction the most rapid growth of fully developed cubes takes place. Many axial skeletons were observed which coincided with the main axes and had cubic faces at the ends. This may be the case with skeletons which coincide with the diagonals of the cube, but so far such skeletons have not been observed.

The most rapid growth in cubic faces is clearly shown in the skeletons b to e in Fig. 52. These coincide with the diagonals of the rectangle, and this direction is also shown in the laminated structure on the cube surfaces g to p; so that, presumably, the skeleton was formed first, and then developed into the complete crystal. The surfaces k to o (Fig. 52) show growth also in directions parallel to the sides of the cube. This is very clearly shown in Fig. 52m. However, these directions are the same as those already mentioned, which coincide with the main axes.

It is obvious that the direction of greatest growth of cubic needles coincides with one of the main axes. A cubic needle without an octahedral point, although not impossible, has not yet been observed in silver bromide. But the fact that these cubic needles may have only one octahedral point, the other being (e. g.) cubical, leaves unsettled the question as to whether the growth in one direction is to be attributed to the greater octahedral acumination.

SUMMARY OF THE OBSERVATIONS CONCERNING THE DIRECTION OF THE MOST RAPID GROWTH OF SILVER BROMIDE CRYSTALS

The principle enunciated by Lehmann that the directions of greatest development are generally coincident with the place of greatest acumination of the crystals may, therefore, not apply to all silver bromide crystals.

The principle applies to the following forms:

Octahedra;
Octahedral axial skeletons;

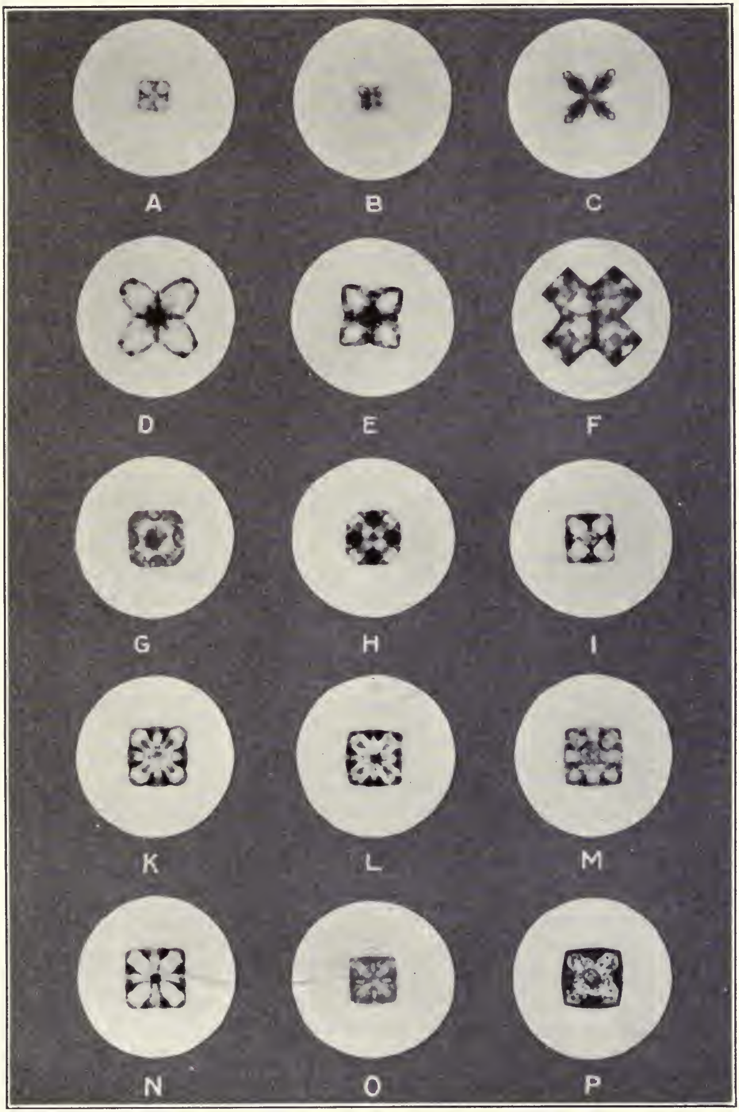


FIG. 52
Skeletons and cubes of silver bromide. A-B, 2500 diameters' magnification; C-P, 800 diameters'

Octahedral plates with triakisoctahedral skeletons;
Triakisoctahedral skeletons;
Cubic plate skeletons;
Cubic plates.

The principle as definitely does not apply to the following forms:

Octahedral plates with ikositetrahedral skeletons (see Fig. 48f);
Ikositetrahedral skeletons;
Octahedral plates with triakisoctahedral and ikositetrahedral skeletons;
Octahedral plates which have dyakisdodecahedral skeletons.

The principle is doubtful in regard to cubes and cubic needles.

A law concerning the direction of most rapid growth can not yet be formulated. It may coincide with the angles of greatest acumination, or it may coincide with the corners of more obtuse points, or even with the normals of the surfaces. That the capillary constant may play a very important part here has already been intimated. The extreme complexity of the problem is evident from the fact that, in many cases, a certain direction of growth may suddenly change during the process of crystal-formation without it being certain that this was caused by a modification of the conditions under which the crystallization proceeded.

CHAPTER X

THE BEHAVIOR OF SILVER BROMIDE AND SILVER IODO-BROMIDE CRYSTALS IN POLARIZED LIGHT

Since the polymorphism of silver bromide is of the greatest importance in the theory of the photochemical processes in photographic plates, a large number of the silver bromide hexagons were microscopically examined in polarized light.

If these hexagons belong to the hexagonal crystal system, they can not be other than a combination of hexagonal prisms with the pinacoid as basis. Such a combination crystal shows simple optical refraction only in the direction of the principal axis. In every other direction it is said to show double refraction between crossed nicols. In fact this was observed by Elsden, and may perhaps be the reason for his mention of hexagonal silver bromide.

Polarization of light in these crystals is, however, quite different from that which is caused by anisotropism of the crystals of other than the regular system. Higson (l. c.) has obtained only negative results from the examination of crystals of the regular system in polarized light. In the different crystal plates, which are of various thicknesses, the polarization is always approximately the same, and it is difficult to see the characteristic Newton color series. This phenomenon shows clearly that here one is dealing with polarization due to reflection, and not with double refraction produced by the crystal structure. This reflection is very strong in preparations of microscopic crystals mounted in Canada balsam on account of the great differences in the refractive indices. For silver bromide at $\lambda 431$, $n = 2.360$; at $\lambda 656$, $n = 2.2336$;[1] and for Canada balsam,[2] $n = 1.528 - 1.532$.[3]

But the silver iodo-bromide crystals of photographic emulsions behave quite differently. Between crossed nicols they show, beside the unavoidable reflections, a distinct double refraction, as may be seen in Fig. 22. This figure is a photomicrograph of exactly the same area of the same emulsion as that in Fig. 21, and is taken at the same magnification.

In some emulsions even a colored axial figure was observed, which, in combination with the cloud-like distribution of the

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[1] Landolt's Physikalisch-chemische Tabellen, p. 983 (Fourth Edition, 1912).

[2] *Ibid.*, p. 981.

[3] It would be simplest to examine the axial image in convergent polarized light. However, on account of the difficulty of mounting a Bertrand lens in a microscope, and of obtaining a petrographic microscope during the war, these methods were dispensed with.

light spots in the crystal, shows that here one is dealing not with a normal crystallographic anisotropism of silver bromide, but with an optical anomaly which is caused by tensions in the crystal structure. This has no connection with the polymorphism of silver bromide. It shows only that the crystalline structure of silver bromide in photographic emulsions is more complicated than that of silver bromide alone, not in so far as that one has to do with another lattice structure, but rather that the crystal lattice contains more or less regularly distributed foreign bodies which greatly affect the optical properties of silver bromide and, as Reinders[1] has demonstrated, probably exert a very great influence on the light-sensitivity of the bromide.

The above-mentioned examination shows that at present we know only regular silver bromide in the stable phase at regular temperatures. This greatly simplified the present work, as it made it possible to distinguish the different crystals direct without troublesome goniometric measurements. Various necessary measurements,—e. g., of the silver bromide skeleton—are not possible on account of the small size of the crystals (10–30μ) on the one hand, and the impossibility of observing the same crystal in different positions on the other. One method, to obtain the crystals suspended in different positions in gelatine, does not give satisfactory results on account of the large aberration due to the depth of the necessary optical system, and the great diversity of the skeletons.

THE ANOMALOUS OPTICAL ACTIVITY OF SILVER IODO-BROMIDE CRYSTALS IN PHOTOGRAPHIC EMULSIONS

Only two methods are known by which it is possible to change a mono-refractive medium into a doubly refractive one: a) by placing the medium in an electric or magnetic field of high intensity; and b) by subjecting the medium to an internal or external mechanical strain.

The first method is practically impossible in the case of the silver halide crystals of photographic emulsions. Even if there is a contact potential between the silver halide and the gelatine, it can not be more than a few volts, which is much too low to produce double refraction between crossed nicols. For the present, then, we must attribute the double refraction of the silver halide crystals to mechanical strain.

Brauns[2] has shown that alum crystals are mono-refractive only when they are chemically pure, and that isomorphic mixtures are made doubly refractive by even a slight content

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[1] Reinders, W., l. c.

[2] Brauns, R., cited by Groth in Physikalische Krystallographie, p. 513.

of another alum. Because of the different intervals between the alternately superimposed atoms in the crystal structure, an internal tension is produced which causes double refraction.

Later the same phenomenon was observed in other salts.

In view of the fact that the silver halide crystals of photographic emulsions may, within certain limits, be considered as isomorphous mixtures of regular silver iodide and silver bromide, the anomalous double refraction may be partly accounted for.

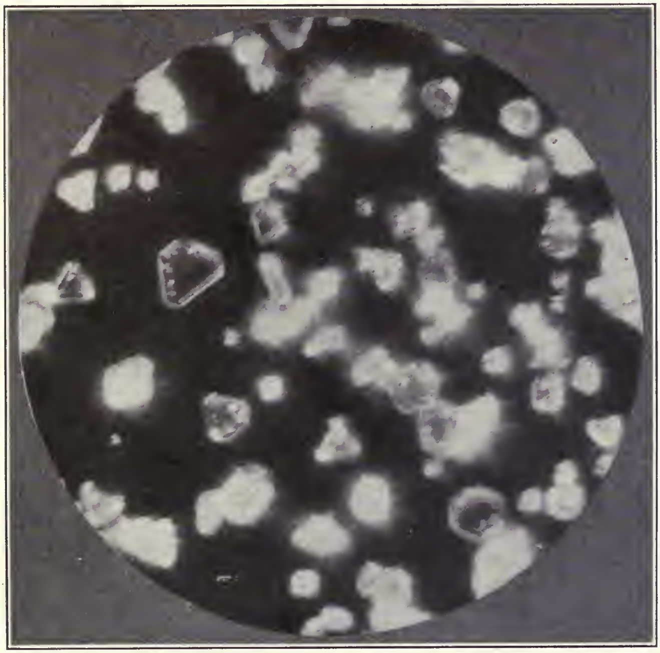

FIG. 53A
Silver iodo-bromide emulsion between crossed nicols, showing the effect of mechanical strain in the gelatine around the grains

In order to prove this experimentally, silver iodide was added to an ammoniacal solution of silver bromide. The solution was shaken frequently until, after 24 hours, it was supposed that equilibrium between the solid and the liquid phase was established. 5 cc. of this solution were mixed with 40 cc. of water heated to 95° C., and cooled in a closed bottle set in ice-water (temperature 4° C.). The crystals formed were washed, put on a slide in Canada balsam, and covered with a cover-glass. The anomalous double refraction between crossed nicols is very distinct in Fig. 53a, which is a photomicrograph of this preparation at 500 diameters' magnification. However, this does not quite solve the problem, because pure silver bromide emulsions, specially prepared in this laboratory, also show polarization phenomena between crossed nicols.

It is possible that in the drying of the plates the surrounding gelatine exerts a pressure on the silver halide grains. This external strain should be present in the gelatine around the crystals, and should be visible between crossed nicols. Indeed, faint indications of this were noticed in very coarse-grained emulsions, such as that shown in Fig. 22 at 1,350 diameters' magnification. Therefore, to make the phenomenon more visible, some emulsions were dried more rapidly and at a

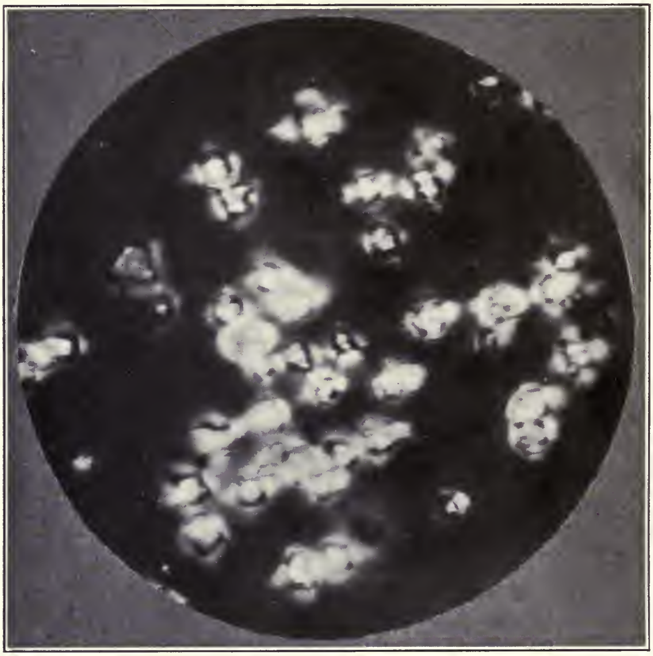

Fig. 53B

Silver iodo-bromide emulsion between crossed nicols, showing the effect of mechanical strain in the gelatine around the grains. It is possible that in this case these radial effects are due to scattering of light reflected by the flat surfaces of the crystals, which is not the case in emulsion grains.

higher temperature. The result is shown in Fig. 53b. There are, therefore, external strain lines which radiate from the silver halide grains into the colloidal matrix. But the silver halide grains and even the silver bromide grains of photographic emulsions still showed anomalous polarization phenomena between crossed nicols when they were freed from the surrounding gelatine by boiling with dilute sulphuric acid. So this experiment presented no definite solution of the problem.

Therefore, the only remaining explanation is in the structure of the silver halide grains.

That the grains of photographic plates do not consist of pure silver halide, but of a system of gelatine and silver halide (plus water plus salts?), is a thesis which has already been discussed. (Chapter III.) Quincke[1] advanced a theory concerning the colloid-chemical structure of silver halide grains in photographic emulsions. Bellach[2] found that careful drying sometimes reduces the average size of the grains. When testing one of Eder's emulsions he found a contraction of 0.65 x 10^{-5} sq. mm. per grain, which indicates a complex structure. Hodgson,[3] however, could not observe, even at the highest magnification, any swelling of the grains when soaked in water.[4] This, however, does not contradict Bellach's observation, in view of the fact that for changes in volume of the silver halide grains, not only is the presence of gelatine essential, but the manner in which it is distributed in the grains is also of importance. If there is a regular distribution of hermetically sealed gelatine particles in the grains, their swelling is not to be expected under any circumstances. If, on the other hand, there is a continuous network of gelatine in the grains, it is quite possible to effect a change of volume if the internal gelatine is in contact with the external gelatine, and if the elasticity of the layers of the silver bromide crystals resisting displacement is not too great. The greater the resistance of the silver bromide to changes in volume, the greater the internal tension in the grains.

With the recognition of the crystalline structure of silver halide grains in photographic emulsions, the conception that

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[1] Quincke, G., Niederschlagmembranen und Zellen in Gallerten oder Lösungen von Leim, Eiweiss, und Stärke. Ann. Physik. IV. **11:** 449. 1903. Die Bedeutung der Oberflächenspannung für die Photographie mit Bromsilbergelatine. *Ibid.* IV. **11:** 1100. 1903.

[2] Bellach, V., l. c.

[3] Hodgson, M. B., l. c.

[4] We repeated Hodgson's experiment at a magnification of 2,500 diameters, using the emulsion pictured in Fig. 21. This emulsion was poured out in a very thin layer (of one grain in thickness) and dried. The emulsion side was turned toward the condenser and a photomicrograph of the grains taken. If the condenser is removed very carefully, one can moisten the emulsion and again photograph it. This procedure showed no difference in the dimensions of the grains in the dry and the wet emulsion.

these crystals are a binary system disappeared. Lüppo-Cramer[1] expressed himself differently at different times regarding the structure of the silver halide grains. First, he assumed that the crystals are free from gelatine. In his later work, however, he vigorously and often defends the theory of the heterogeneity of silver halide grains in photographic emulsions. So he probably differentiates between two different kinds of silver halide grains in emulsions: crystalline grains and colloidal grains. W. D. Bancroft[2] is also of the opinion that the whole question of the high sensitivity of photographic plates depends on the system silver halide-gelatine.

The possibility of gelatine in silver halide crystals was first demonstrated experimentally by Reinders.[3] He showed that silver chloride, crystallizing in the presence of various colloids, such as colloidal silver, gelatine, albumen, casein, etc., has the capacity of taking up and homogeneously distributing these colloids in the crystals. With gelatine this effect was noticeable even in concentrations of 1 mg. gelatine in 10 liters of water.[4]

If the anomalous double refraction of silver halide crystals is caused by this enclosed gelatine, then silver bromide crystals from ammoniacal silver bromide solutions containing gelatine should show double refraction, since colloid-free silver bromide solutions apparently can yield only simply refractive crystals. But no definite double refraction could be detected experimentally.

However, this experiment is not conclusive, because the conditions of crystallization in photographic emulsions are entirely different from those in ammoniacal solution. In photographic emulsions there is, first, a suspension of colloidal silver halide which consists of more or less fine flakes of silver halide of varying size and structure. The diameters vary from submicroscopic to $\pm 1\mu$. In the presence of a silver halide solvent (such as potassium bromide or ammonia), the colloidal silver halide passes over into the more stable crystalline silver halide. Gelatine is continually absorbed during the formation of the crystal, throughout which it is homogeneously distributed (Reinders).

But the silver halide flakes also contain some microheterogeneously distributed particles of gelatine which remain in

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[1] Lüppo-Cramer, Photographische Probleme, l. c.

[2] Bancroft, W. D., The photographic plate, l. c.

[3] Reinders, W., Studien über die Photohaloide, l. c.

[4] This visible decomposition is distinct from the latent effect of light. Therefore, the laws concerning visible photochemical decomposition can not be applied to the latent effect of light.

the crystal and form a structure different from that described by Reinders. The grains of sensitive plates have a diameter of 2 to 3μ and more. Hence there must be another factor concerned than the simple conversion of flakes into crystals. The increase in size of the grains may be due either to the combining of several single flakes during the crystallization process, or to the crystallization of smaller flakes on larger. However this development-process is regarded, the gelatine structure of the flakes is not necessarily lost in crystallization, but may pass over into the crystals. There may be a change in structure, depending upon the treatment of the emulsion. In fact, the gelatine structure depends upon the conditions of the precipitation and the subsequent treatment of the emulsion. (Hodgson vs. Bellach.) This microheterogeneous structure, which does not occur when silver bromide is precipitated from ammoniacal gelatine-containing solutions, may be the cause of the tensions in the emulsion crystals, to which the anomalous double refraction is to be ascribed.

If, however, a mono-refractive medium contains microscopic or submicroscopic suspensions of dielectrics, the double refractivity may not be the only cause of the abnormal phenomenon seen between crossed nicols. Diffuse reflections can, under these conditions, illuminate the dark field. But it is hardly conceivable that this may produce polarization phenomena which resemble the axial images sometimes found in emulsions. However, these images are possible if strains are present.

Thus we must conclude that the anomalous optical activity of silver-iodo-bromide crystals in photographic plates may be the result of any of several factors:

a. The tensions resultant from the isomorphic mixture of silver iodide and silver bromide (cf. Chapter V);

b. The mechanical strain exerted to a small degree by the gelatine surrounding the silver iodo-bromide crystals;

c. The probable mechanical strain of microheterogeneously distributed gelatine particles in the silver halide crystals;

d. The probable diffuse reflections in microheterogeneously suspended gelatine in the silver halide crystals.

Hence we must regard sensitive photographic emulsions not only as suspensions of silver halide crystals in gelatine, but also as a probably very much more complex suspension of gelatine in crystalline silver halide. A fuller discussion of this aspect of the question has been given in Chapter IV.

The probable complexity of this suspension has been indicated by a distinction between a homogeneous and a microheterogeneous suspension, which refers only to a different degree of distribution. Therefore, these terms should be interpreted only in a relative sense.[1] As a matter of fact, both types of distribution lie beyond the limits of microscopic resolving power. Therefore, both could be interpreted equally well as homogeneously distributed gelatine. Gibbs has emphasized the fact that the conceptions "homogeneous" and "heterogeneous" are relative. That is to say, one can not make a sharp distinction between the two because there is a continuous transition between homogeneous and heterogeneous, according to the point of view. Take, for example, the photographic emulsion. Microscopically considered, it is heterogeneous; but macroscopically it is homogeneous. The purest crystal medium is homogeneous in ordinary light but heterogeneous in the X-ray. Hence the grades of distribution of gelatine in silver halide crystals, as mentioned above, can be interpreted as both homogeneous and heterogeneous, or one as homogeneously, and the other as heterogeneously distributed, according to one's point of view.

THE GELATINE ENCLOSING THE SILVER IODO-BROMIDE CRYSTALS OF PHOTOGRAPHIC EMULSIONS

The radial distribution of the tension exerted by the gelatine around the crystals in photographic emulsions indicates a complex effect. This appears not only in gelatine, but also, as Fig. 53B shows, in Canada balsam. This balsam is a very viscous liquid, which makes the phenomenon appear even more complex. The cause is unknown. Possibly the following observations may suggest a solution.

In some preliminary experiments on the adsorption of colloids by silver bromide crystals, colloidal dyes were used. If the entire process of crystallization takes place in the presence of such dyes, then the Reinders' distribution of colloid in crystal can be directly (microscopically) proven.[2] An analogous phenomenon was noticed, especially with the sodium salt of 1-naphthol-4-sulphonic acid-azo-β-napthol. An excess of this dye coagulates around the silver bromide crystal in the form of rays which may vary greatly under different conditions.

For gelatine, therefore, the phenomenon may be explained as follows: By a ray-like coagulation of the gelatine around

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[1] Where differences in space distribution of the same kind of material are concerned, the terms "iso-psegmatic" (equal-grained) and "allo-psegmatic" or "poly-psegmatic" (vari-grained) are more suitable.

[2] Cf. also Marc's experiments, cited on page 52.

the grains, spots of greater or less density occur in the gelatine. The drying of the gelatine has a different effect in different places because of this structure, as the rays will tend to dry more quickly than the rest of the gelatine. All strain will be neutralized by internal displacements if the drying is slow. But if the drying is rapid, there is not sufficient time to compensate the resultant strain, and a double refraction of gelatine may be seen through crossed nicols.

This presupposes that gelatine possesses a solidification structure which persists in dry gelatine, and which originates in a manner analogous to that of the solidification of liquids to crystalline aggregates in which radially arranged structures (spherolites) may be observed. Still this leaves unexplained the same phenomenon in the viscous Canada balsam. Here, however, one is entering the province of pure colloid-chemical investigation, which is outside the scope of the present discussion.

GENERAL SUMMARY OF THE CRYSTALLOGRAPHIC STUDY OF SILVER BROMIDE CRYSTALS

1. It has been shown that silver iodide is precipitated from ammoniacal solutions in the metastable regular form, which is isomorphous with silver bromide, and that the crystallographic classification of silver bromide may apply also to the silver iodo-bromide crystals of photographic emulsions.

2. The occurrence of silver bromide pseudomorphs was investigated, and methods for recognizing silver bromide-ammonia complexes described.

3. All the crystalline forms of silver bromide obtained were identified.

4. The faces of needles and plates of silver bromide were studied, and shown to be growth-modifications of octahedra and cubes.

5. Etch-figures were obtained on the octahedral faces of silver bromide.

6. Silver bromide was assigned to the dyakisdodecahedral class of the regular system.

7. Because of their isomorphism, silver chloride and regular silver iodide were placed in the same class as silver bromide.

8. The possibilities of modifications of silver bromide were discussed.

9. The occurrence of needles, plates, and ordinary crystals of silver iodo-bromide in photographic emulsions was demonstrated.

10. It was shown that the Gibbs-Curie-Wulff law is applicable to photographic emulsions, and that thereby all octahedral forms appearing in these emulsions may be explained.

11. The directions of most rapid growth were determined for the various crystalline forms of silver bromide.

12. It was shown that Lehmann's theory concerning the direction of most rapid development of crystals does not always apply to silver bromide crystals.

13. The examination of the characteristic optical properties of silver bromide crystals in polarized light showed that the so-called hexagonal silver bromide is really regular.

14. The possible causes of the anomalous optical activity of silver halide crystals of photographic emulsions in polarized light were studied, and it was suggested that these crystals are the center of various mechanical strains.

15. It was suggested that there are two different gelatine structures in the crystals of photographic emulsions.

16. The structure of the gelatine surrounding the grains in photographic emulsions was more closely studied and a radial coagulation of gelatine around the grains observed.

In conclusion we wish to express our great appreciation of the co-operation of Messrs. W. H. Davis, F. A. Elliott, G. H. Norris and L. Schneider, who assisted in the experimental part of this investigation, and of Professor A. C. Gill, of Cornell University, who read the manuscript and made helpful criticisms and valuable suggestions.

CONCORDANCE OF POSSIBLE SYMMETRY CLASSES OF SILVER BROMIDE

Inasmuch as the forms included in the regular system, to which silver bromide belongs, are variously named by different authorities, a correlation of the terminology is given below:

	Authorities				Number of faces in general form
Symbol	Hilton Schonfliess	H. A. Miers	E. S. Dana	Other Names	
T	Tetartrohedry	XXVIII Tesseral Polar	5 Tetartrohedral	Pentagonal dodecahedral	12
T_h	Paramorphic hemihedry	XXX Tesseral Central	2 Pyritohedral	Parallel faced hemihedry Pentagonal hemihedry Dyakisdodecahedral	24
T_d	Hemimorphic hemihedry	XXXI Ditesseral Polar	3 Tetrahedral	Hexakistetrahedral Inclined faced hemihedry	24
O	Enantiomorphous hemihedry	XXIX Tesseral holoaxial	4 Plagihedral	Gyroidal hemihedry Pentagonikositetrahedral	24
O_h	Holohedry	XXXII Ditesseral Central	1 Normal	Hexakisoctahedral	48

MONOGRAPHS ON THE THEORY OF PHOTOGRAPHY

The Silver Bromide Grain

Abbreviations adopted in citations of serial publications.

Astrophys. J.	The Astrophysical Journal
Arch. wiss. Phot.	Archiv für wissenschaftliches Photographie
Ann. Physik	Annalen der Physik
Ann. chim. phys.	Annales de chimie et de physique
Ber. chem. Gesell.	Berichte der deutschen chemischen Gesellschaft
Bull. soc. franç. mineral.	Bullétin de la société française de minéralogie
Brit. J. Phot.	The British Journal of Photography
Brit. J. Phot. Almanac	The British Journal of Photography Almanac
Fortschr. Mineral.	Fortschritte der Mineralogie, Krystallographie, und Petrographie
J. Amer. Chem. Soc.	Journal of the American Chemical Society
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association
J. Chem. Soc. (Trans.)	Journal of the Chemical Society (Transactions)
J. chim. phys.	Journal de chimie physique
J. Frankl. Inst.	Journal of the Franklin Institute
J. Phys. Chem.	The Journal of Physical Chemistry
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry
J. Wash. Acad. Sci.	Journal of the Washington Academy of Science
Jahrb. Phot.	Jahrbuch für Photographie und Reproductionstechnik (Eder's)
Jahrb. Rad. u. Elektr.	Jahrbuch der Radioaktivität und Elektronik
Koll.-Zeits.	Kolloid-Zeitschrift
Neues Jahrb. Mineral. Geol.	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie
Phil. Mag.	The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science
Phil. Trans.	Philosophical Transactions of the Royal Society of London
Phot. J.	The Photographic Journal
Phot. News	Photographic News
Physik. Zeits.	Physikalische Zeitschrift
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wien
Zeits. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie
Zeits. Kryst. u. Mineral.	Zeitschrift für Krystallographie und Mineralogie
Zeits. physik. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre
Zeits. wiss. Phot.	Zeitschrift für wissenschaftliches Photographie

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