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On the wave-like character of periodic precipitates

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1. Introduction

The similarity between wave patterns and periodic precipitates was remarked upon nearly thirty years ago by St. Leduc[1]. The suggestion of a possible physical basis for such similarity is conveyed in Wo. Ostwald's "diffusion-wave" theory of the formation of the Liesegang precipitates; in this theory, Ostwald[2] postulated the existence of three diffusion waves in the system corresponding to the external and internal electrolytes and the soluble product of the reaction. More recently the idea of a diffusion wave has been applied by Michaleff[3] and his co-workers in order to interpret an important feature of the observed pattern, namely, the widening of the space between the successive rings which corresponds with the slowing down of the diffusion occurring as we proceed outwards from the centre of the pattern. Christiansen[4] and Woulff have gone further and suggested a physical connection between the formation of the periodic precipitates and the De Broglie matter waves associated with the diffusing ion. Nikiforoff[5] and Kharamonenko find additional support for the wave idea in the observation that any point in the diffusion field can become the centre of a ring system; they have made experiments which show that the front of a ring system is 'refracted' in the optical sense when passing across the boundary between gels of different concentration.

When it is completely formed, a Liesegang pattern is a static structure and is therefore scarcely to be regarded as a wave phenomenon in the usual sense, as the latter involves a movement or periodicity in time. It may be permissible however to describe a periodic precipitate as a wave-like phenomenon, meaning thereby, that it presents some analogies in its spatial distribution to the configuration at a particular instant of a periodic train of waves. Even here a difficulty presents itself when we remember that in a periodic wave-train the disturbance may be either positive or negative whereas the density of a precipitate is of necessity a positive quantity. Indeed the essence of a wave is the fact just mentioned, namely, that its amplitude can have either sign, on which depends the possibility of the interference effects which occur when superposed trains of waves reinforce or destroy each other. It is thus clear that the analogies between a wave and a periodic precipitate would be without physical content unless it can be shown by investigation that superposition effects can be observed in periodic precipitates analogous to interference and diffraction phenomena in acoustics and optics. Indeed, the existence of such superposition effects, if established, would enable the wave-like character of Liesegang precipitates to be regarded as an established fact besides giving it a real physical significance.

Three years ago, one of us (K Subba Ramaiah) undertook systematic studies on periodic precipitates with a view to ascertain whether the particles in these precipitates had any specific crystal orientation. Observations made in the course of these studies by us in collaboration made it clear that superposition effects of the kind referred to in the preceding paragraph are actually exhibited by Liesegang precipitates, thus establishing their wave-like character. A general account of the observed phenomena and of their interpretation on the wave-hypothesis, together with the photographs illustrating the present paper, were laid before the Indian Academy of Sciences at Bangalore in a lecture delivered by the senior author on the 12th of November 1936. The hopes which were entertained of developing a mathematical theory of periodic precipitates on a wave-basis led to the printing of the lecture being deferred. The results were however included in the thesis for the doctorate submitted by K Subba Ramaiah to the Madras University in October 1938. A preliminary note summarising them also appeared as a letter to *Nature* (*London*) in its issue of August 20, 1938. Owing to various circumstances, it has not as yet been possible so far for either of us to devote much further attention to the subject. It has therefore been considered desirable to publish our work of 1936 substantially as presented in the Academy lecture of that year.

2. Superposition of wave-trains of equal amplitude

In the theory of interference and diffraction phenomena, attention is usually paid only to the distribution of the intensity in the field, and not to the actual position of the wave-fronts in space at any given instant. This is natural, as the variation of intensity is the very essence of the theory of interference and in optical and acoustical phenomena is the feature accessible to direct observation. The configuration of the wave-fronts is indeed unobservable without special experimental aid, and the employment of stationary waves or alternatively of stroboscopic methods is necessary to reveal the position of the individual waves. In fact, the details of the wave-pattern in interference and diffraction phenomena are most readily grasped by examining stroboscopic photographs of ripples on water or of ultrasonic vibration within liquids. In relation to our present problem, the consideration of such features is even more important than that of intensity, for the reason that though the density of a precipitate may be qualitatively estimated or even quantitatively measured, it is a simpler matter to observe the geometric configuration of the precipitate. We shall therefore proceed to consider a few typical cases of superposition which, as we shall see presently, have an application to observable effects in periodic precipitates.

(i) *Two intersecting trains of the same wavelength and of the same amplitude*—This is the typical case which shows in the clearest possible way how interference modifies the geometric configuration of a wave-pattern. If there were *no interference*, the wave-pattern at any instant would consist of two continuous and intersecting sets of parallel straight lines cutting each other obliquely and dividing the whole field into a net of similar rhombus-shaped figures, in the two pairs of parallel sides of which we recognise the two intersecting wave-trains. Interference completely alters this picture. We observe a pattern in which the two interfering wave-trains are no longer distinguishable, as these cohere with each other, forming wave-fronts which are everywhere parallel to the longer diagonal of the rhombus, while the lines of interference maxima and minima run parallel to the shorter diagonal, in other words perpendicularly to the direction of the resultant wave-fronts. It is important to notice that the wave-fronts are not continuous: the lines of maximum *positive* disturbance are to be found in each *alternate* rhombus, while the lines of maximum *negative* disturbance are to be found in the intervening ones, the two being separated by the *interference lines of zero amplitude*. In other words, if we consider only the waves of maximum positive displacement or only those of maximum negative displacement, *their fronts run discontinuously*, the interference lines of zero disturbance forming the terminations, and the wave-fronts on the other side of such interference line *being displaced by half a wavelength with respect to each other*. This is an effect very characteristic of interference, and taken together with the fact that the two separate sets of wave-fronts become indistinguishable is a complete demonstration of the wave-like nature of any phenomenon in which such features are noticed.

(ii) *Two intersecting trains of different wavelength and of equal amplitude*—This case is very similar to the preceding one, except that the superposed wave-trains would form a net of parallelograms with unequal sides instead of rhombuses. The wave-fronts and interference lines would therefore be inclined to each other instead of being perpendicular. The wave-fronts would exhibit discontinuities similar to those already referred to in the preceding case. Another new feature of the case now considered would be the secular movement of the interference lines in a direction parallel to themselves. This would give rise to the phenomenon of "beats" if we consider the variation of the disturbance at any point of space as a function of time. The wave-fronts as they move parallel to themselves and pass through any given point undergo periodic changes of amplitude, thus breaking up the disturbance into periodic groups. We are not however concerned with these secular aspects, if we confine attention to the form of the wave-pattern at a *particular instant*.

(iii) *Two parallel trains of unequal wavelength and of equal amplitude*—In this case again, the two wave-trains (supposed to be of harmonic type) completely cohere and become indistinguishable, being replaced by a single train of intermediate wavelength which however is broken up into groups of waves separated by interference lines of zero-disturbance. The group-length is twice the distance between such successive interference lines, there being a sudden reversal in the phase of the resultant waves as we pass a line of zero disturbance. Half-way between the lines of zero intensity, we have the group maxima in which the amplitude of the individual waves is the sum of the amplitudes of the two superposed disturbances.

3. Superposition of wave-trains of unequal amplitude

The results stated in the preceding section would be modified in a significant way if the superposed wave-trains are of unequal amplitudes. We shall consider first the typical case of two intersecting trains of the same wavelength. As the result of the inequality of the amplitudes, the interference minima will cease to be of zero amplitude, and the discontinuous changes of phase occurring at these minima must therefore disappear and be replaced by rapid but continuous changes of phase. The positions of the interference maxima and minima will however be unaltered as these are determined only by the relative phases of the two waves. We can easily indicate the changes to be expected in the forms of the wave-fronts by taking a case in which one of the interfering wave-trains is assumed to vanish and assuming its amplitude to be gradually increased to the full value, while that of the second wave-train is correspondingly diminished until it finally vanishes. It is obvious that in the two extreme cases when one or the other wave-train is non-existent, the resultant disturbance would have a continuous wave-front identical with that of the survivor. It follows that there would be continuity of wave-fronts also in the intermediate cases, such continuity being secured by a small rotation of the wave-fronts near the interference maxima accompanied by a marked curving round in the vicinity of the interference minima, so that they join up continuously with the neighbouring wave-fronts on the other side of the minima. It is clear that when one of the interfering waves has a greater amplitude than the other, the resultant disturbance would follow more closely the outline of the stronger wave. The direction of the rotation and curvature of the wave-fronts must therefore undergo reversal when the stronger wave becomes the weaker, and *vice versa*. In the limiting case, therefore, when the waves are of nearly equal amplitude, we should have a bifurcation or forking consisting of very steeply inclined lines which connect up the wave-front more or less symmetrically with its two nearest neighbours on the other side of the interference minimum. This forking is replaced by a discontinuity of the wave-fronts when their amplitudes are exactly equal.

The features referred to above and deduced from general geometrical reasoning are readily to be noticed in any good photograph of interference effects with capillary waves on water or with ultrasonic waves in liquids. Figure 1 is a drawing made from a ripple photograph and exhibits clearly the effects mentioned. They may be explained in full detail by considering the configuration of disturbance as has been done by G L Datta[6] from whose paper the accompanying drawing of a small area of the central part of an interference field (figure 2) due to two similar centres of disturbance has been reproduced. The figure shows clearly the displacement of half a wave in the positions of the wave-fronts on either side of the interference lines, as well as the appearance of prongs or forks joining up these fronts. By drawing such figures for the case in which the amplitudes of the interfering waves differ greatly, we may illustrate the smaller and less abrupt changes of phase which then occur and the unsymmetrical curving of the wave-fronts which results therefrom, as may be seen in outlying parts of the field in figure 1.

It is unnecessary to discuss in detail the case of two intersecting trains of unequal wavelength and unequal amplitude, as the features then to be expected would naturally be similar to those already discussed above. In the case of two parallel trains of unequal wavelength and of unequal amplitude, the groups of waves would no longer be separated by lines of zero disturbance with a discontinuous reversal of phase. We would have, instead, regions of maximum

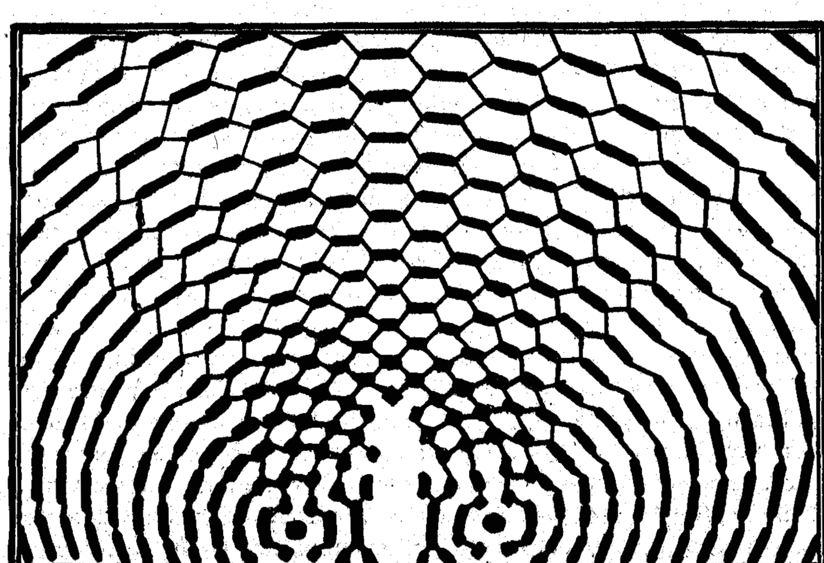


Figure 1. Drawing from ripple photograph.

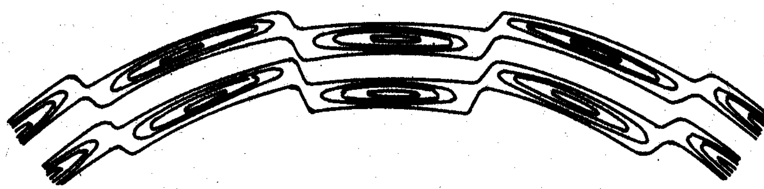


Figure 2. Contours of equal amplitude.

and minimum disturbance in which the wavelength, amplitude and phase all exhibit changes as we pass through different parts of the field. We shall not however consider these points in detail.

4. Interference of wave-groups

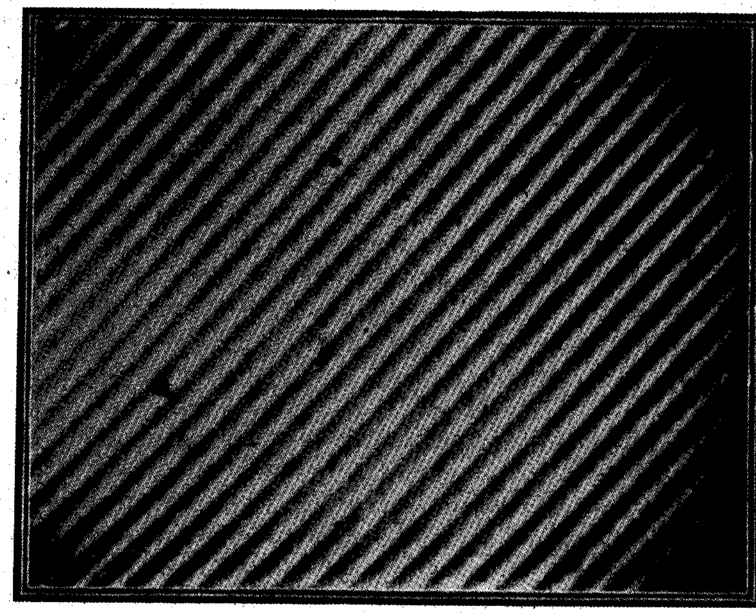
If a source simultaneously emits two wave-trains of equal amplitude but of slightly different wavelength, the resulting disturbance would consist of a succession of wave-groups separated by regions of zero amplitude. If a second and similar source also emits such groups of waves and if the two trains traverse the field intersecting each other, it is clear that their superposition would give, besides the individual waves and groups emerging from the two sources separately, a further superposition effect, namely, two interference patterns corresponding to the two wavelengths emitted by each of the sources separately. These interference patterns would be on different scales corresponding to the two different wavelengths, and as these would again be superposed on each other, and as the phases of the wave-fronts change by a half period across each interference line, the result of such superposition would be a simple interference pattern corresponding to the mean wavelength, and further overlying this we would have a "group interference pattern" in which the interference lines would run parallel to those in the "wave interference pattern" but would be much more widely spaced. This "group interference pattern", which is here regarded as arising from the superposition of the two "wave interference patterns" may equally well be regarded as the result of the mutual interference of the two groups of waves emitted by the two sources separately. Such interference would be possible as the phase of each group as a whole reverses across each line of minimum disturbance in it. The two groups would thus tend to cancel each other's effects where their phases are opposite and to reinforce each other where they are in agreement. The length of the group being much greater than the length of the individual waves, the spacing of the interference lines in the group pattern would be correspondingly greater than the spacing of the interference lines in the wave pattern.

The discussion thus shows that when there are two similar sources emitting groups of waves, we have two kinds of interference pattern, one on a fine scale for the individual waves, and another on a much larger scale for the groups of waves. The two patterns would co-exist, but would be entirely separate and distinguishable. Further, we would also have the usual discontinuities of the wave-fronts in the wave interference patterns, and similar discontinuities of the group fronts in the group interference pattern but on a much larger scale. It should be remarked that the "group fronts" and the "wave-fronts" would everywhere run parallel. If, however, the discontinuities are replaced by continuous curves, forks or branches, the wave-fronts and group fronts would not be parallel to each other in the vicinity of the interference minima. The deviations from parallelism should be specially noticeable in the vicinity of the group interference minima, as these are on a relatively larger scale.

5. Wave-interferences in Liesegang patterns

In the examples of rhythmic precipitation which illustrate the treatment of the subject in treatises on colloid chemistry and even in special monographs, we usually observe only a few unequally spaced bands of which the width is small compared with their mutual separation. The suggestion of a resemblance between such precipitates and the infinite train of harmonic waves postulated by the mathematician would seem indeed rather far-fetched. The case is however, different when we consider the rhythmic precipitates of silver chloride or silver phosphate in gelatin which are described more fully in the following paper. In these cases, we observe under the microscope thousands of rings following each other in regular succession, and the width of the rings is everywhere comparable with their spacing. Such a periodic precipitate indeed strikingly suggests an analogy with an extended harmonic wave-train. The analogy becomes more specific if we compare the regions where the precipitate appears with the parts of the wave where the amplitude is positive and the empty spaces without deposit to the negative part.

Figure 3 in plate I illustrates a small area in a rhythmic precipitate of silver chloride in gelatin, reproduced from a photomicrograph with a magnification of 160 diameters. In this area, we have a remarkably uniform and uninterrupted periodicity of the deposit. This however is the exception rather than the rule. Usually, even when the preparation is made with very careful technique, the rings exhibit non-uniformities of a very significant character, illustrations of some of which are reproduced as figure 4 in plate I and figures 5 and 6 in plate II. In figure 4, the interruption takes the form of a succession of forks running somewhat obliquely across the lines of the deposit near the centre of the field. A short distance away from this region of the forking, the lines of deposits become very sharp and straight and also much more intense than in the region of the forks. It will also be seen that the lines of deposit on the left side when produced correspond with the dark regions of no deposit on the right and *vice versa*. In the extreme left-hand top and the right-hand bottom corners, the forkings broaden



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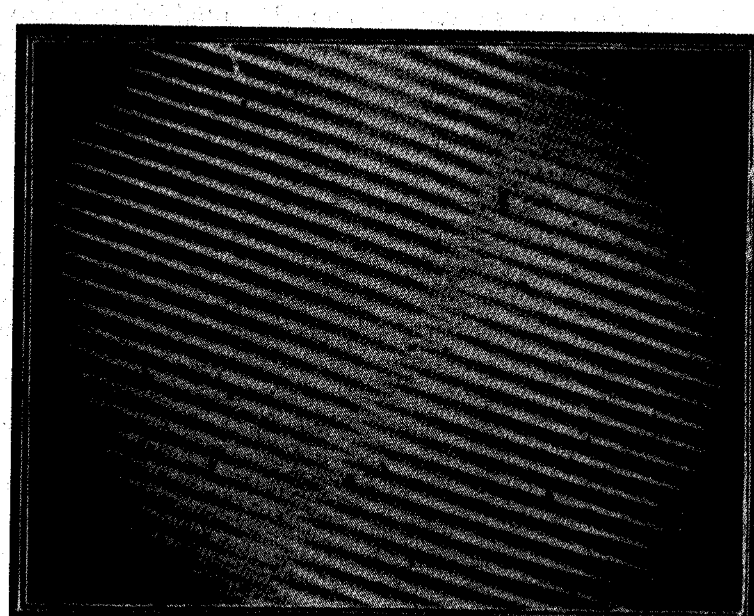

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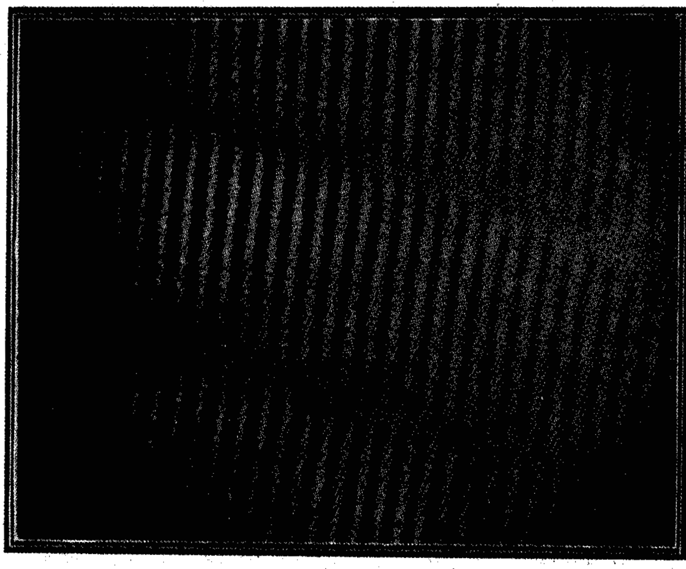
Plate I



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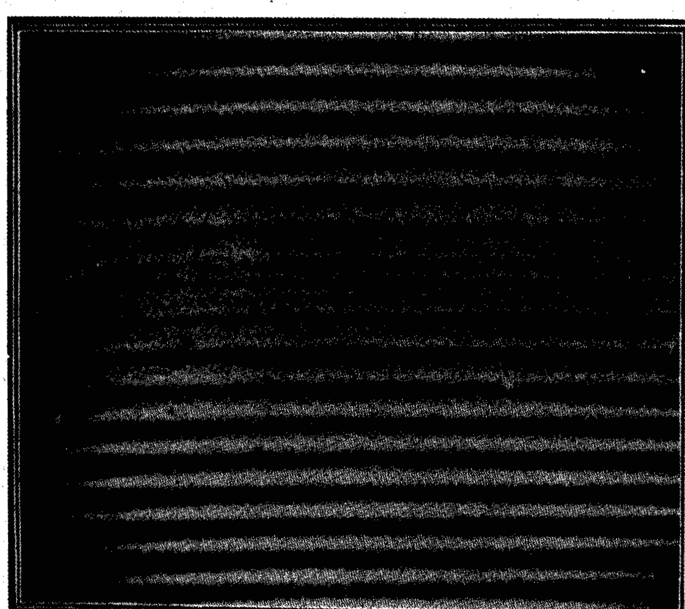

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Plate II

giving rise to a distinct doubling of the lines of deposit. These features when considered together leave little doubt that we are here observing the effects of the "coherent interference" of two "periodic waves" of deposit of slightly different wavelength and direction and of nearly equal amplitude superposed on each other as discussed in sections 2 and 3 of this paper.

Further confirmation of this view is furnished by figure 5. One of the effects indicated by the theory of interference is that when the area over which two intersecting wave-trains are superposed is sufficiently extended, we should observe a succession of equidistant interference lines running parallel to each other. Observation of the silver chloride precipitates shows that parallel and equidistant or nearly parallel and equidistant lines along which there is a sharp break or dislocation of the lines of precipitate occur so frequently as to exclude the possibility of their being accidental. Figure 5 is an example of two such "interference lines" running parallel to each other and cutting across some thirty or more "waves" of the deposit, the wave-front exhibiting a sharp bend or a forking at each point of intersection.

Examination of silver chloride deposits shows that still another effect is common in them, namely, that of a succession of interference lines running parallel to the wave-fronts, due evidently to parallel "waves of precipitation" of slightly different wavelength having been superposed. Figure 6 is a photomicrograph of a portion of the field exhibiting such an effect. Over the greater part of the field, the two series of waves are "coherent" and form single sharp lines of heavy deposit, while in those regions where the waves are out of step, the deposits are relatively light. In the regions of light deposit, the individual waves and in the manner in which they fall out of phase can actually be observed in the distribution of the precipitate. Though this particular feature does not support the "interference" theory, it is not inconsistent with it, in view of the fact that the distribution of the precipitate is evidently not of the simple harmonic type. Superposition of two waves which are not of harmonic type and which resemble periodic "pulses" would result in changes of form being observable in the vicinity of the intensity minima analogous to those actually seen in figure 6.

6. Groups and group-interferences in rhythmic precipitates

The peculiar fine structure of periodic precipitates of silver chromate and the circumstances in which it is observable have been fully discussed in the following paper by one of us. The present trend of opinion appears to be that the so-called secondary structure of very finely spaced rings is due to presence of impurities in the gelatin leading to the formation of closely-spaced silver chloride or phosphate rings. Reasons have however been given in the paper* in support of the

*K Subba Ramaiah, *Proc. Indian Acad. Sci.* A9 467–478.

view that such impurity is probably not essential for the formation of secondary structure, the items of evidence being: (1) a thoroughly washed gelatin which shows only a slight turbidity but no rings with silver nitrate, produces both secondary and primary rings when pure potassium chromate is added to it; (2) the spacing of the secondary silver chromate rings is not so close as that of the silver chloride rings; and (3) the primary and secondary rings form a continuous periodic system observable everywhere in the field. An explanation has also been offered for the fact in certain circumstances the primary rings may be obtained without the secondaries being present.

A careful examination of the silver chromate rings in gelatin in various circumstances of formation reveals a variety of interesting effects, which fit beautifully into the theory of wave-interferences and group-interferences developed earlier in this paper. It should be remarked that this interpretation is wholly independent of any decision on the question whether or not the presence of a minute quantity of impurity in the gelatin is essential for the production of a periodic precipitate and on the question whether or not, such impurity plays an important part in the spacing and distribution of the precipitate. We shall base ourselves solely on the observed facts regarding the configuration of the rings in various circumstances. Figures 7 and 8 in plate III, figures 9 and 10 in plate IV and figures 11 and 12 in plate V are photomicrographs of small selected areas in silver chromate precipitates intended to illustrate the relationship between the so-called primary and secondary ring systems and the appearance of interference phenomena in them. Figures 13 and 14 in plate VI, figure 15 in plate VII and figure 16 in plate VIII are enlargements of the Liesegang patterns themselves; these are of the type from which selected areas have been enlarged and reproduced as figures 7–12. Figures 13–16 are in fact intended to explain and illustrate the physical origin of the effects shown in figures 7–12. A careful study of the plates shows that the configuration of the rhythmic precipitates is strikingly influenced by the initial geometrical distribution of the precipitating agent. In figure 13 we have a small circular drop of silver nitrate solution starting the precipitation; in figure 14 we have an elliptical drop, while in figure 15 we have two circular drops running into an oval figure; in figure 16 we have two separate drops separated by an interference dead space. Even in the case of the apparently circular drop illustrated in figure 13, we notice radial dislocations in the rings running outwards from the margin of the drop. The very striking perturbations of the rings seen in figure 14 with the elliptical drop indicate clearly that the form of its boundary is responsible for these effects. Further, in figures 15 and 16, the perturbations in the form of the rings are most prominent in the central regions where the effects of the two drops are superposed, and less prominent in the marginal areas where they are practically independent.

A study of the Liesegang patterns illustrated in figures 13 to 16 brings out the following interesting facts. Firstly, where the primary rings run most regularly, that is, without inflections or changes of curvature, the secondary rings run most nearly parallel to the primaries; on the other hand, where the primaries bend

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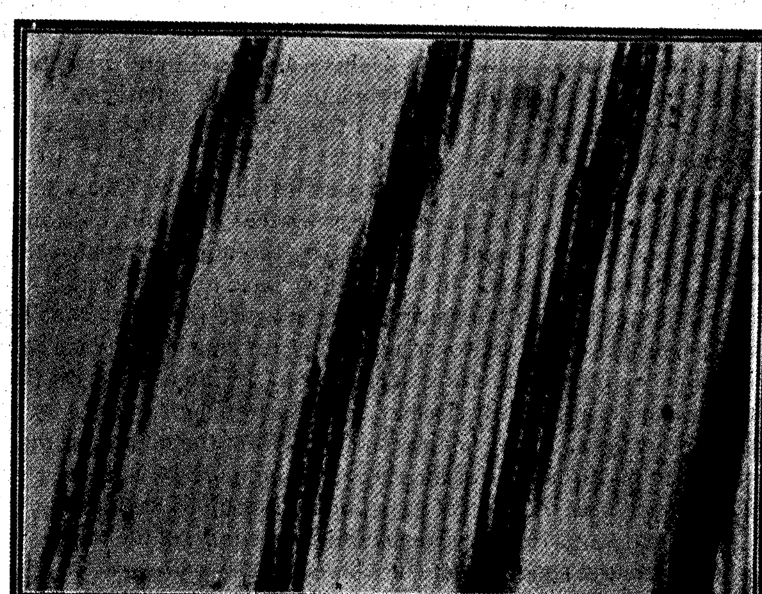

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Plate III

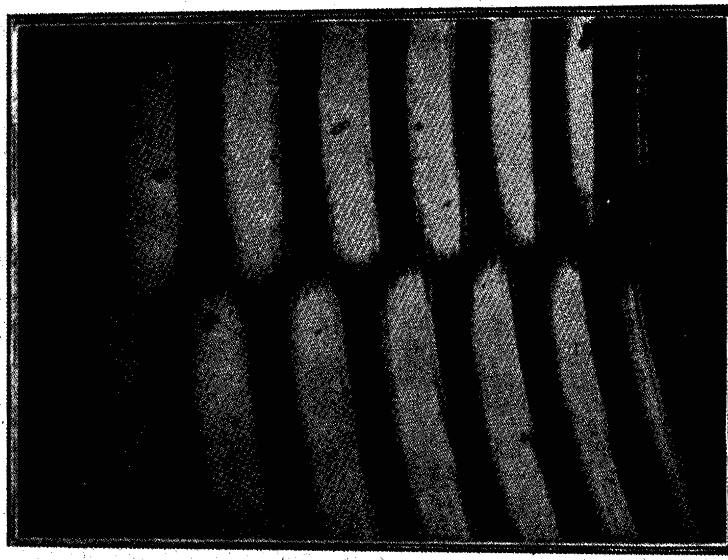

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Plate IV

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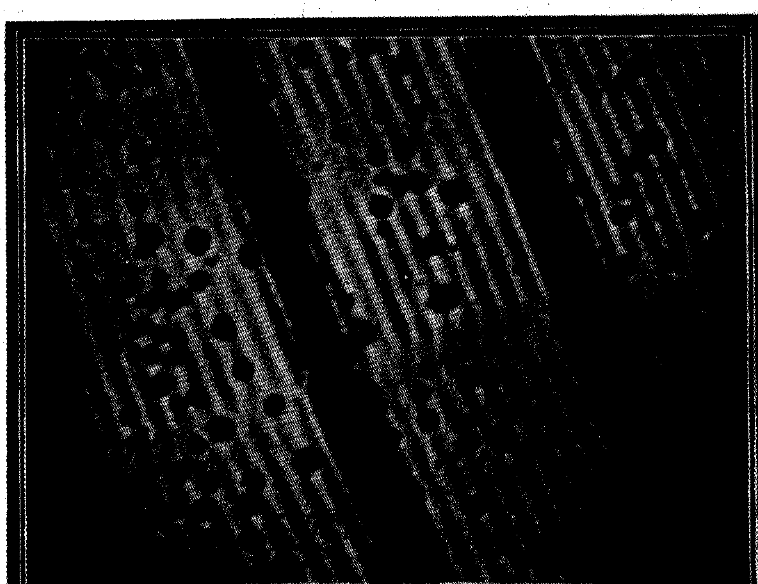

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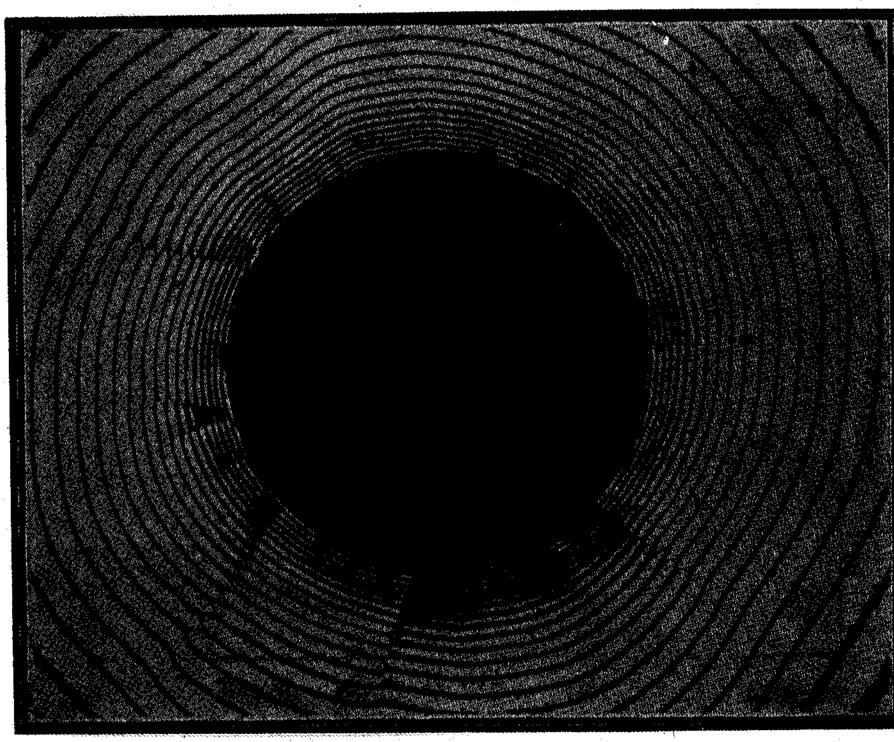
Plate V



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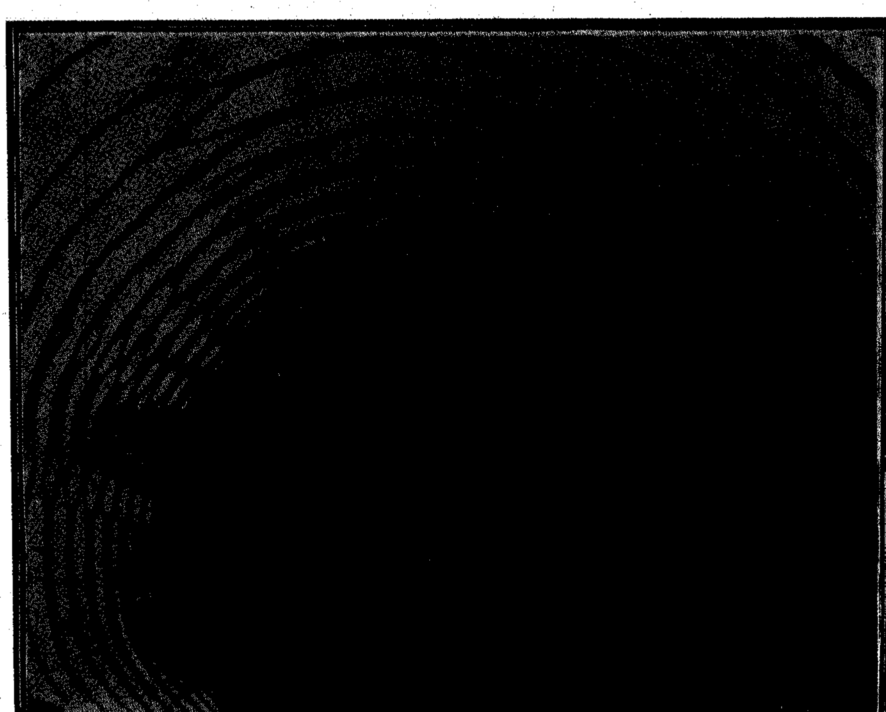

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Plate VI

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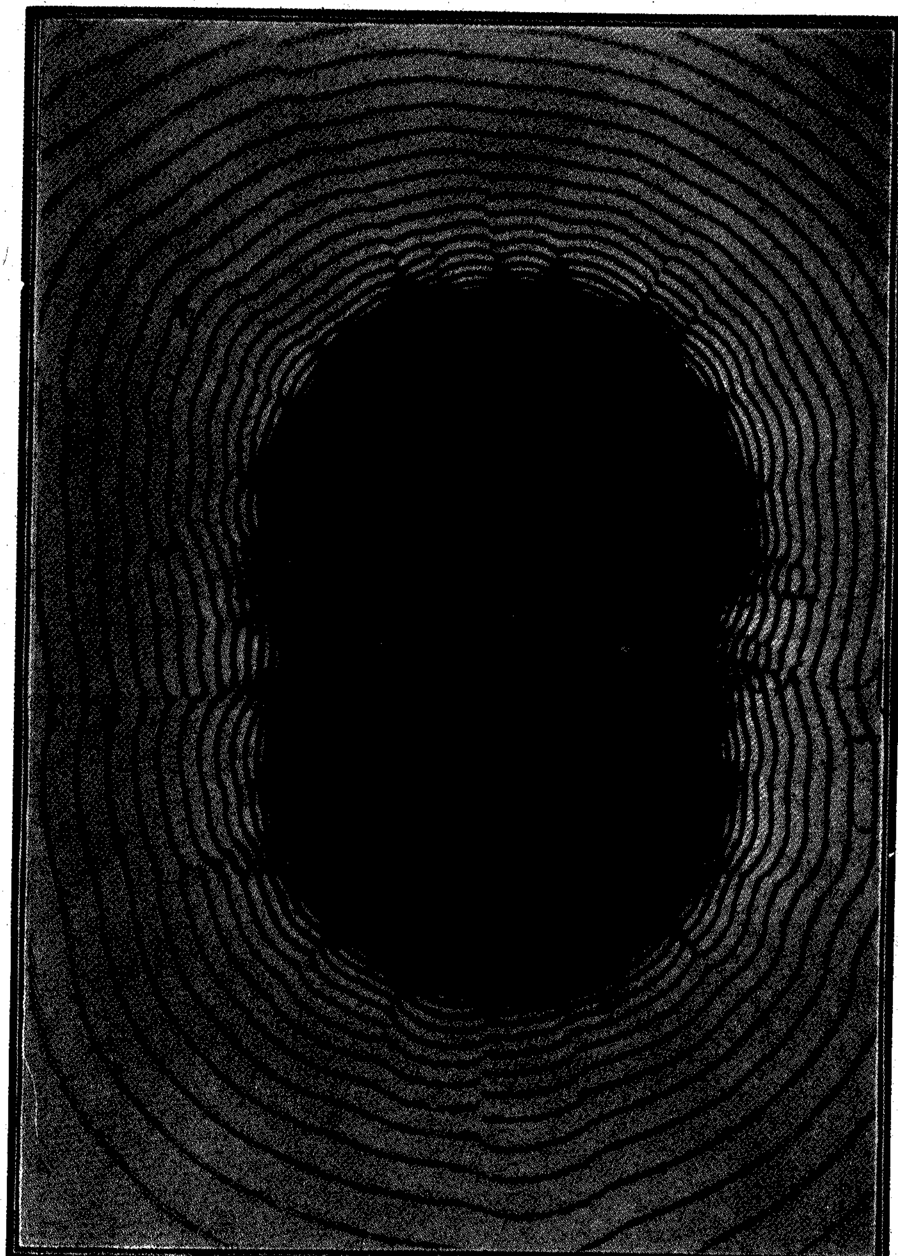

Plate VII