STUDIES IN PHOTOGRAPHIC SENSITIVITY.

I.

THE DISTRIBUTION OF SENSITIVITY AND SIZE OF GRAIN IN PHOTOGRAPHIC EMULSIONS.*

BY

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THE problem of the " latent photographic image " has not infrequently excited curiosity and interest outside purely photographic circles. It has been an " imponderable," in some ways less susceptible of exact measurement than atom or electron. Arguments in favor of a chemical or physical nature have held the field without the deadlock being broken. To the problem of the " latent image " there has been added that of " sensitivity." On the one hand, it has been recently suggested that, at least in one and the same emulsion, this is nothing but an affair of geometry and probability.[1] Sensitivity, on this view, is only the *chance* of a grain, or connected group of grains, being hit by a light-quantum, hence, for unshadowed grains, is strictly a matter of projective area. On the other hand, chemists and emulsion-makers have arrived at a substantial theory of sensitiveness which in its most recent developments [2] tends to identify the substances of " sensitiveness " with both the latent and the developed image, as dispersed or colloid silver. As noted in more detail later, it may be assumed that in the silver bromide grain of emulsions there exists, owing to reducing conditions in preparing the emulsion, a specific, or even individual, distribution of a photocatalyst.

This is very feasibly a nucleation of colloid silver amicrons, dispersed in the silver halide lattice. Differential sensitivity of grains, on this view, depends upon this distribution of sensitizing nuclei; any probability function found valid either for variation of sensitivity amongst grains of the *same size,* or relating sensitivity to size of grain, enters in the process of emulsion preparation, rather than in that of exposure.

We propose, in this and subsequent papers, to examine these hypotheses, to note wherein they lead to similar conclusions, and as far as possible to test experimentally between them. The hypothesis of a discrete structure of light is of great theoretical significance; practically, the problem posed is of fundamental importance in the photographic industry.

In this paper is presented (1) a statement of the problem, with a discussion of some previous work on the photochemical law for the silver halide grain; (2) a correlation theory of the size-frequency of photographic emulsions and their sensitometric characteristics; (3) a comparison of theories of the relation of sensitivities and size distribution to the density exposure function. The material of part (2) will be dealt with more fully in another place and connection.[3]   Its presentation is necessary in order that the very varied " disperse " character of photographic emulsions may be realized, as also the broad statistical basis of the connection of grain size with emulsion speed.

I. STATEMENT OF THE PROBLEM.

It has already been pointed out that in earlier work (H. and D., etc.) consideration of individual variations of the grains of silver halide emulsions was lacking. It is now known that the elementary grains are definite crystals of one system and class, but that in a given emulsion they vary:

1. In total size or volume;
2. In cross-section or projective area;
3. In shape.

It may be further considered possible, even probable, that wide variations of " sensitivity " exist among the grains of one and the same emulsion. We may initially define " sensitivity " as the

[3] Cf. *J. Phy. Chem.,* in press.

reciprocal of the energy required to make a grain developable by a developer of given reduction potential. It is generally accepted at present that the condition for developability is a nucleus, *i.e.,* that the photo-effect, whatever its nature, is localized in the grain. The most concrete development of this is that the nuclei consist of colloid silver, either provided (in part at least) by photolysis of silver halide, or formed by condensation of pre-existent colloid silver amicrons to submicrons. This latter hypothesis is due to F. F. Renwick. His primary contention, that the sensitive substance is not silver halide at all, but colloid (metallic) silver has recently received support from some remarkable experiments of F. Weigert.[4] In any case, if we attribute a definite sensitivity to a grain, this means that a certain finite increment of energy is necessary for developability. In the general problem of chemical reactivity, what has been termed the *critical energy increment*[5] of a molecule is analogous to this " inertia " of the grain, the reciprocal of its sensitivity.

Considering the variable of sensitometry, the density D, it must be remembered that to a near approximation grains contribute, on complete development, to density in proportion to their number and size conjointly, or again, to a slightly lower approximation, to their number and projective area. The quotient

$$\frac{\triangle D}{\triangle E} = \frac{\text{density increment}}{\text{energy increment}}$$

reckoned per unit area, would appear *a priori* to be independent of the size of grain, assuming a continuous wave-front. But if conditions permit a local concentration of energy related to the size of grain, the magnitude of the above quotient will depend upon the distribution of grain sizes in unit area.

Supposing a continuous wave-front, that is, *not* a quantum-like or discrete structure of radiation, local condensation of the energy to the critical increment might be effected in the material: (1) By reason of a variable distribution of a photochemical catalyst in the material, or specifically, among the grains. The probability of a grain reaching the critical increment would then depend upon its having a certain amount, and perhaps individual distribution, of the catalyst, the primary function of which would

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[4] *Sitz. ber preuss. Akad. Wiss.,* 1921, p. 641.

[5] W. McLewis: " System of Physical Chemistry," vol. iii, p. 140.

be to increase the energy density of absorbable type.[6] Colloid silver submicrons supply a concrete example. Alternatively, it may be supposed that the silver halide is itself relatively inert, and with Renwick that the colloid silver particles are the true photosensitive material. In either case, the distribution of the " catalyst " could depend on the size of the grains, *e.g.*, the probability of a grain having sufficient catalyst might be proportional to its mass. *In this case, the sensitiveness-variation curve would coincide, to a first approximation, with the size-frequency curve,* for one and the same emulsion. (2) Local condensation and a sensitivity variation might be effected, as suggested in Toy's paper,[7] by optical conditions of refraction, reflection, etc., within the grain but depending on chance orientations and concentrations of the crystalline grains. Such a hypothesis is difficult to prove or disprove, but the statistical data being accumulated may strengthen or weaken its plausibility.

There remains, by exhaustion, the possibility of local, or granular, concentration of energy not by virtue of inherent factors of the sensitive material, not by accidental circumstances in its disposition, but as a necessary consequence of a discrete structure of the energy itself.[8]

The mathematical development of this assumption has been dealt with by Dr. L. Silberstein. It may, however, be pointed out here that to a large extent it gives the same relation between effective sensitivity variation and size-frequency distribution as that previously discussed on the hypothesis of a photocatalyst distributed amongst grains with a probability varying as their masses. On the quantum theory, however, it is the projective area which is fundamental rather than the mass. The important modifying factor of "clumping," or secondary aggregation of the primary grains, will be noted in connection with the results of measurements of size-frequency.

We advance later an approximate theory of the photochemical law for the single silver halide grain. Hence it appears desirable to examine more closely the experimental results of R. Slade

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[6] Cf. W. McLewis: " System of Physical Chemistry," vol. iii, p. 140 (1919).

[7] *P. J.,* **61**, 417 (1921). We may note here, in connection with the data given later, that in *thick* grains the *position* of a photocatalytic centre might vary in grains of same size and shape.

[8] Cf. F. E. Ross: *Astrophys. J.,* **52**, 96 (1920).

and G. I. Higson,[9] since they propose as a result of these an empirical formula expressing "the photochemical law of the silver halide grain." Further, Higson has used these results, and this formula as a basis for deduction of density-exposure functions and ideal characteristic curves.[10] Essentially, their data consist in counts of numbers of grains in a one-grain layer made developable by increasing exposure, impressed either by increasing intensity for constant time, or by increasing time for constant intensity. They considered that in the emulsion used all the grains were of the same size, which appears doubtful to us, in view of our results with similar emulsions. But, passing this by, they advance a further postulate.[11] "All experimental evidence leads to the conclusion that all grains in one emulsion behave identically if they are of the same size." This is contrary to results of Svedberg [12] and has since been directly rebutted by Toy,[13] yet it is quite fundamental to their argument and mode of presenting their data.

They state,[14] "If (following Einstein) it is assumed that light is discrete in its nature, and that it is only necessary for one of these light quanta to be absorbed by a grain to make it developable, then if there were a number of grains, a, present on the plate, and they were exposed to a light of intensity, I, for a time, t, after which time x grains had been made developable,

$$\frac{dx}{dt} = kI(a - x)$$

and integrating between limits 0 to t and 0 to x

$$ln \frac{a}{a - x} = kIt,$$

or

$$x = a(1 - e^{-kIt}).$$

If the grains were of different sizes, the probability of their obtaining a nucleus would vary, the larger grains being more

[9] R. Slade and G. I. Higson: *Proc. Roy. Soc.*, **98A**, 154 (1920).

[10] G. I. Higson: "The Action of Light on the Photographic Plate," *Phot. J.*, **61**, 35 (1921), and *Ibid.*, p. 144.

[11] See p. 156, *loc. cit.*

[12] The. Svedberg: *Phot. J.*, **62**, 180 (1922).

[13] F. C. Toy: *Phot. J.*, **61**, 417 (1921).

[14] See p. 157, *loc. cit.*

likely to be affected; k would therefore have a different value for each size of grain.

"The present investigation has shown that k *has* a larger value for larger grains, but also that it is not generally true that the number of grains changed is a simple function of the product It. *It is therefore impossible that the mechanism of the process is the absorption of light in discrete quanta, as has been assumed above.**

"In this investigation of the photochemical law of the silver halide grain, plates were prepared from an emulsion containing grains which were, as nearly as possible, all the same size. The emulsion was coated on the plate in such a thin layer that there was only one layer of grains. These plates were exposed either to varying intensities for the same time or to the same intensity for varying times. The source of light used was monochromatic blue light from the mercury arc in some cases, and white light (continuous spectrum) in others.

"If the total number of grains present is a, and x is the number changed after exposure for a time t, to a light of intensity, I, then

$$\frac{dx}{dt} = P(a-x),$$

where P is the probability of any grain being made developable in unit time, and is a function of I and of t.

"Integrating

$$\int_0^x \frac{dx}{a-x} = \int_0^t P \cdot dt,$$

therefore

$$\ln \frac{a}{a-x} = \int_0^t P \cdot dt,$$

"This, however, does not make it possible to evaluate P as a function of I and t without making other assumptions."

But, although an equation of the type $x = a(1 - e^{-kIt})$ is de-

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* Italics are ours.

ducible by application of the discrete theory of light,[15] it is also obtained by other considerations not involving this, but simply the assumption that the grains do differ in quality, *i.e.*, inherent sensitivity. The result, if confirmed, that the above expression did not hold, would not contradict the hypothesis of sensitivity-variation —it would only show that the distribution of sensitivity assumed [16] was inadequate. When Slade and Higson proceed still to evaluate

$$\int_0^x \frac{dx}{a-x} = \int_0^x \frac{dN}{N-n} \ as = \int_0^t P \, dt$$

where P is "the probability of any grain being made developable in unit time and is a function of I and t," it appears to us that they thereby assume tacitly, just the contrary to their statement (p. 158), "In the emulsion used . . . all the grains were of the same size, *and experimental proof has been obtained that they were all of the same quality.*" [17] It is difficult to see—on this basis, and accepting the principle that a grain made developable is completely developed (in three minutes, under their conditions with one-grain layers)—how *any* function of the type

$$\int_0^x \frac{dx}{a-x}$$

could be evaluated. For all these grains, of identical size and "of the same quality" should become simultaneously developable for some one and the same exposure (although this unique exposure need not be that regulated by the reciprocity law $E = It = $ constant) *unless the mechanism of the process is the absorption of light in discrete quanta.* For, if grains of identical size *and quality* are exposed to radiation of discrete structure, then the "hits" will be regulated by some probability function.
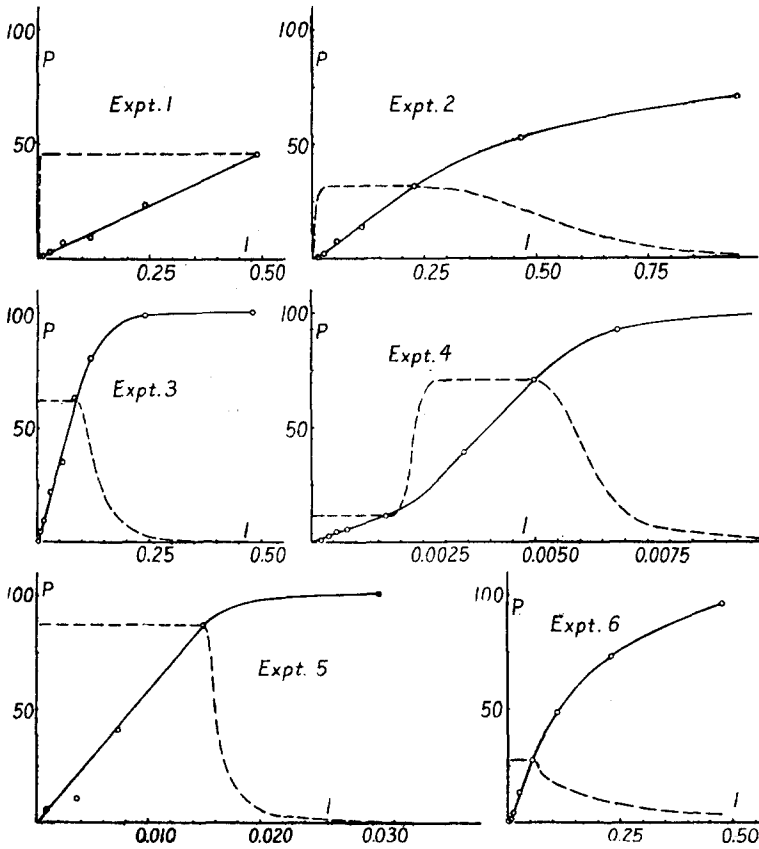
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[15] Cf. F. E. Ross: *Astrophys. J.*, **52**, 95 (1920).

[16] v. infra, p. 18.

[17] Our italics.

Since their premises, argument, and conclusions do not seem to fit together, it appeared desirable to reconsider their data from a different basis. Instead of forming the logarithmic quotient $ln\dfrac{a}{a-x}$

FIG. 1.

Slade and Higson's data replotted.

as dependent variable, which *assumes* either heterogeneity in the material or discreteness in the radiation—it is reasonable to plot the usual accumulation curve, *i.e.,* the number of grains changed, as ordinate, against either the *intensity,* for constant time of exposure, or the *time* for constant intensity. We have done this for Slade and Higson's data, with the results shown in Figs. 1, and 2, Intensity Scale.

In experiments 1, 2 and 3 (Fig. 1) (with monochromatic Hg. blue light) it will be seen that the number of grains changed is a linear function of the intensity up to 30 per cent. or more of the total, when the " rate of change " becomes less. To bring

FIG. 2.
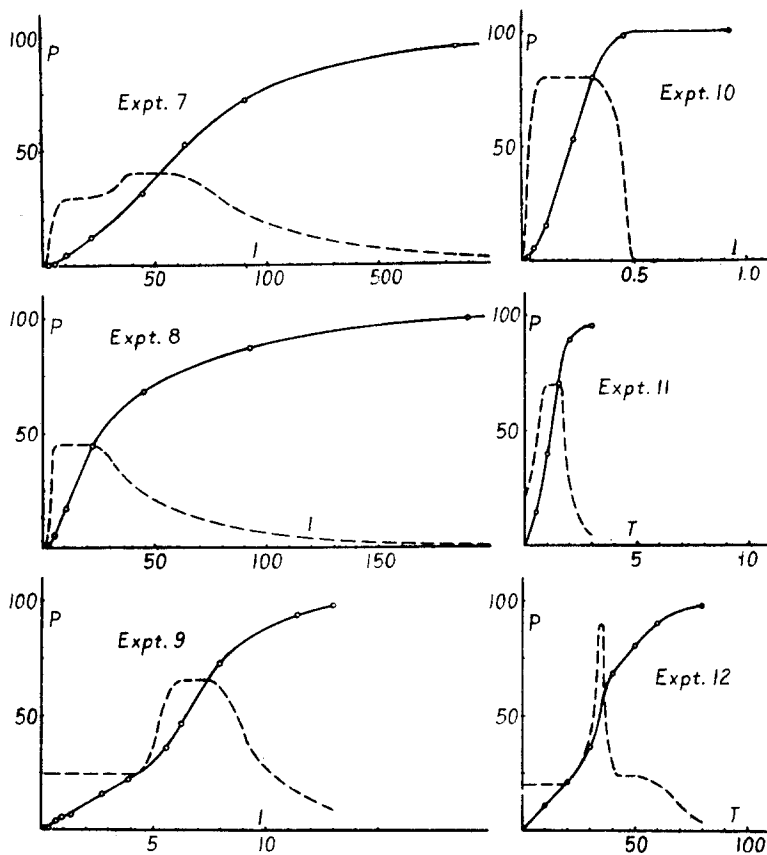
Slade and Higson's data replotted.

out these features, we have also plotted the first derivatives of the curves, *i.e.*, as noted later, the " rate curves."

An interesting feature of these replotted curves is that the " white light " intensity curves show on the whole a greater similarity to the " monochromatic " time curves than to the " monochromatic " intensity curves. All of these show a well-marked " initial acceleration," corresponding to autocatalysis.

On the whole, the data agree with the view that the rate of photochemical change in the single grain, leading to a sufficient accumulation of the photoproduct to induce developability, follows a law of the type

$$\frac{dm}{dA} = k_1 A + k_2 f(m)A \ ,$$

where $A =$ light absorbed, k_1 is the coefficient of absorption of

FIG. 3.
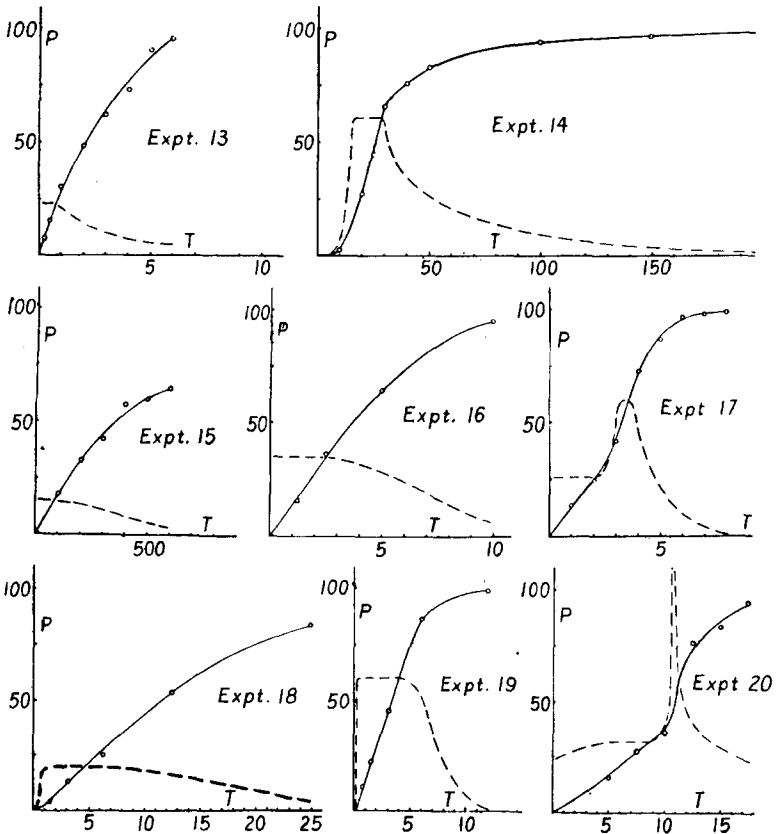
Slade and Higson's data replotted.

unchanged halide, k_2 is the coefficient of absorption of the photoproduct, $f(m)$ a function of its mass and distribution in the grain. Now we may suppose k_1 is small compared with $k_2 f(m)$, and that $f(m)$ varies initially from grain to grain. We can write

$k_2 f(m) = K$ and obtain the same type of " fundamental reaction formula " (for the single grain) as noted later, in which case the " first derivative " indicates the " frequency curve of inertias." *But* the present data do point to this " frequency curve " as not being entirely inherent, *i.e.*, preëxistent to exposure, but liable to be modified and induced by exposure itself, *as would result from an autocatalytic effect* of the photoproduct varying from grain to grain. Stress has been laid on this factor by one of the writers in a recent paper on the optical sensitizing effect of soluble iodides on the silver bromide emulsion.[18] Although in the subsequent portion of this paper it is neglected, the evidence from Slade and Higson's data, while not complete, decidedly indicates that this aspect requires further consideration. The more marked occurrence of the " initial acceleration " with both the " white light " intensity curves and the " monochromatic " time curves is perhaps connected with it; photosensitizing, for the same time period, but with different intensities, would be more probable with white light pulses than with the more regular trains of waves of " monochromatic " blue light, except when these were allowed to act for increasing periods of time.

In a paper on " The Photographic Efficiency of Heterogeneous Light,"[19] F. C. Toy has given incidentally results of further experiments tending to confirm Slade and Higson's formula as to intensity. He states,[20] " Slade and Higson have shown that the relation between light intensity, I, and the effect produced A, is given by

$$A = \alpha I (1 - e^{-\beta I})$$

where α and β are constants, so that if the intensity is small, A varies as I^2." Later, he gives a table showing good correspondence between values of A calculated, and values observed.

These observations could be more valuable if the quantity A, termed " the photographic effect," were more precisely defined. It can only be presumed, in view of reference to their paper, that it refers to percentage number of grains made developable in a one-grain layer plate of grains of approximately equal size, and,

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[18] *P. J.*, **62**, 89 (1922), " The Action of Soluble Iodides and Cyanides on the Photographic Emulsion," S. E. Sheppard.

[19] F. C. Toy: *Proc. Roy. Soc.*, A, **100**, 109 (1922).

[20] *Loc. cit.*, p. 110.

as assumed by Slade and Higson " identical quality." Since no statement as to this or other such effect is made, we cannot feel that this places Slade and Higson's formula beyond criticism; it does not seem to us compatible with Toy's own independent results, of the variable sensitivity of grains of the same emulsion, of the same shape and size. Neither a variable chance distribution of sensitizing nuclei, nor a quantum hypothesis of exposure gives such a relation, so that it remains in conflict with both types of hypothesis discussed here.

Under these conditions, an uncertainty cannot but be felt as to the conclusiveness of Toy's otherwise probable result " that over the spectral range used . . . radiations of different frequencies do not act independently in producing the photochemical change, but probably simply as a total amount irrespective of any difference of quality;" a result contrary to Slade and Higson's conclusion from their data that the same amount of energy as a monochromatic radiation has more photographic activity than as complex radiation such as " white light."

The existence of differential " sensitivity " amongst grains of the same size in one and the same emulsion was confirmed and extended to grains of the same geometrical shape by Toy.[21] Since his data did not extend below 30 per cent. developability, it is not profitable to compare the curve of *percentage* grains against *exposure* with Slade and Higson's results. It must suffice to point out again that this result does not seem to be compatible with the premises on which Slade and Higson found their formula.

II. TENTATIVE THEORY OF THE RELATION OF SENSITIVITY VARIATION TO THE CHARACERTISTIC CURVE.

The sensitometric characteristics of an emulsion are expressed in their entirety by the characteristic, or H. and D. curves, with the proviso, that the curves will possibly differ accordingly as an intensity or a time scale of exposures is impressed on the plate or film. If Schwarzschild's relations hold, they will differ only in the density ordinate by a common factor p and have the same form. The conclusions of Slade and Higson that intensity enters into the density-exposure function as I^2 for small values of I (and large values of t) and as I for large values of I (and small values of t) do not for the reasons cited appear to us conclusively proven.

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[21] F. C. Toy: *Phot. J.*, **61**, 417 (1921).

Assuming, provisionally, that the incident energy is represented with sufficient accuracy either by It_c when t is constant, or by I_ct when I is constant, then the sensitometric characteristics deducible from the curves are:

D_{max}	Maximum density developable
γ_∞	Maximum slope
i	Inertia if no regression occur
or a and b	Nietz's coefficients of the time-gamma convergence point
Lat.	Latitude
K	Velocity-constant of development

The empirical comparison of size-frequency curves with the characteristic curves and the derived values has only a limited value, however. It is desirable to have at least an orienting theory of the general relation of sensitivity-variation to the density-exposure function as a whole. We shall only assume at first that a statistical variation of sensitivity exists among the grains of the same emulsion, without prejudice as to its origin or explicit nature.

The conception of statistical variation among reacting units—*prima facie* of one chemical species—has not entered much into general chemical dynamics. Statistical variation of gas molecules as to velocity has been from the first, however, a feature of the kinetic theory of gases. Through statistical mechanics and radiation theory this has begun to react powerfully on the theory of chemical kinetics. While we may utilize conceptions developed in this field, notably by W. Mc. Lewis, R. C. Tolman and E. K. Rideal, it is in the field of biochemistry [22] that the application of variation to reaction velocity has been made most definite; this is most notable in regard to problems of the immuno-chemistry of cells and unicellular organisms. Biologically the existence of variation has to be admitted *de facto*, without, so far, any satisfactory theory of its origin prevailing.

Whether we are dealing with molecules, grains or cells as reacting units, variation of sensitivity (reactivity) amongst the units will greatly affect the course of the reaction, so that it may depend chiefly on this, and only secondarily upon the course of the fundamental reaction.

Now the actual progress of the reaction may be expressed graphically in two ways. First, as the usual accumulation or

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[22] Cf. S. C. Brookes: *J. Gen. Physiolog.*, I, 61 (1918).

time curve, the amount changed being plotted as ordinate, against time as abscissa. For dispersed granules or cells, we could plot number x volume against time. There is also the rate curve, the ordinates being the amount of substance changed per unit time $\frac{\Delta x}{\Delta t}$ plotted against time. The former is the more usual in reaction kinetics, while the latter is the "mortality curve" of vital statistics. The latter curve is evidently the first derivative of the time curve, and we can pass from the *rate* curve to the *time* curve, either empirically by graphic integration, or algebraically, if the differential equation expressing the rate curve is known and integrable. Conversely we can obtain the rate curve from the time curve by differentiation.

Essential to the present argument is the fact that under certain conditions the *rate* (or mortality) curve may be identical with the variation (or frequency) curve of individual resistivities (inertias, reciprocals of sensitivities). Supposing the time curve replaced photographically by an exposure curve

$$D = f(E),$$

then with certain restrictions to be discussed, the first derivative of this

$$\frac{dD}{dE} = f'(E)$$

would give the variation curve of inertias of the reacting particles, or correlatively, the sensitivity-frequency curve.

The importance of the first derivative of the characteristic curve was first noticed by Nutting, Jones and Mees [23] for positive emulsions. It was introduced as dependent upon finite groups of grain sensitivities by Ross [24] in a theoretical discussion of the density-exposure function, and attention was a little later drawn to the subject in respect of negative emulsions by F. F. Renwick.[25] The latter's statement of the fundamental property of the derived curve appears to agree to a large extent with the conclusions reached here. " Since every ordinate of the derived curve represents the amount of silver bromide which has just attained the developable condition at the corresponding exposure, it is evident that we might regard each ordinate as a measure of the quantity

[23] *P. J.*, **54**, 342 (1914).
[24] *J. Opt. Soc. Amer.*, **4**, 255 (1920).
[25] *P. J.*, **61**, 10 (1921).

of silver bromide in the film having that particular true inertia value." It is now evident that if for "quantity" we substitute "number of particles per unit area" that the first derivative becomes the statistical frequency curve of inertias—provided there is no reduction of intensity through the film, as noted by Renwick, but also provided that the relation of grain size to grain sensitiveness is explicit.

Considerable modifications are necessary before these premises can be applied to actual sensitometric curves—obtained normally as

$$D = \phi \, (\text{Log } E),$$

with first derivative

$$\frac{d\,D}{d\,(\text{Log } E)} = \phi' \, (\text{Log } E).$$

To facilitate this application we have developed an approximate theory of the density-exposure function for very restricted conditions. The direct theoretical development of a function for the characteristic curve is beset with difficulty. Application of the calculus to a system composed of finite discontinuous units, such as silver halide grains, is itself contestable, and the difficulty becomes greater if statistical variation of the grain-sensitivities is admitted. The following device has been adopted for an indirect attack. A relatively simple photochemical reaction is assumed in an ideal homogeneous system. In the reaction equation obtained, the heterogeneity or variation factor is then introduced by replacing the reaction-constant of the function first obtained by various sensitivity or inertia variations.

The formula developed for photochemical change in a homogeneous layer is based on the Grotthus-Draper law that the rate of change is proportional to the energy absorbed by unchanged photolyte. The fundamental premise is therefore the same as that of Hurter and Driffield; no account is taken, however, of the absorption by altered silver halide for reasons discussed in a fuller paper. The expression obtained, for the general case of moderate absorption is:

$$e^{-K\delta x} = e^{-K\delta a} + (1 - e^{-K\delta a} e^{-KkI_o t}). \tag{1}[26]$$

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[26] Deduction of this expression is dealt with in a fuller paper on this phase of the subject. J. Plotnikoff's integration (*Zeit. wissent. Phot.*, **19**, 238 (1920)) of a similar differential equation leads to a different result and appears to us incorrect.

Where $k =$ coefficient of absorption of supposed monochromatic radiation
$\delta =$ thickness of layer
$a =$ original concentration of photolyte per unit volume
$x =$ amount of photoproduct per unit volume

Before applying any considerations dealing with the heterogeneity of the actual system considered, we may note that this expression reduces to two much simpler forms:

(a) When the absorption factor $k\delta$ is very large:

Equation 1 may be written

$$ln \frac{\left[e^{K\delta x} - e^{-K\delta(a-x)}\right]}{\left[1 - e^{-K\delta(a-x)}\right]} = KkI_o t \qquad (2)$$

which, if $e^{-k\delta}$, approaches 0, becomes

$$ln\,(e^{K\delta x}) = KkI_o t$$

whence $\delta x = kI_o t \qquad (3)$

a linear relation between amount of photoproduct and exposure.

(b) When the absorption factor $k\delta$ is very small, functions of the type $e^{-K\delta(\ )}$ can be expanded and reduced to:

$$e^{-K\delta(\ )} = 1 - K\delta(\ )$$

so that we have from equation 2

$$ln \frac{K\delta a}{K\delta(a-x)} = ln \frac{a}{a-x} = KkI_o t$$

$$x = a(1 - e^{K'I_o t}) . \qquad (4)$$

This equation is of the so-called monomolecular form as found for the " dark reactions " and proposed by Elder for the density-exposure function.   Its insufficiency *per se* for representation of this function has been exposed by Ross.   According to present considerations, it could only be valid for a homogeneous material with very low absorption.   The course of the reaction in such a homogeneous system may tend to approach either the linear form (equa. 3), when absorption is high (*e. g.,* the maximum of the wave-length sensitiveness curve) or the logarithmic form, when absorption is low (*e.g.,* the limits of the wave-length sensitiveness curve).   But, in any case, photographic emulsions are heterogeneous systems.

Effect of Heterogeneity of Material.

We do not propose at this stage to consider the effect of modifying assumptions proper to the homogeneous reaction, *e.g.*, allowing for absorption by the altered silver halide, for limited autocatalysis by the photoproduct, etc.[27]   It has appeared to us more important to proceed to consideration of sensitivity variation.

Consider the simplest case of sensitivity distribution, *viz.*, negligible deviation from a certain average value. The sensitivity-variation curve, corresponding to the rate curve, would be a straight line perpendicular to the abscissa. Its integral, the time curve, would, if the fundamental reaction is supposed uniform (of zero order), follow the axis to this point of intersection, then rise perpendicularly. That is, all grains would become developable at the same exposure, whatever the photochemical law for the single grain.

Apart from inherent and "quantum" sensitivity variations, in thick layers absorption of light in the upper layers involves an apparent gradient of sensitivity through the film. This is partly allowed for in the deduction of a reaction formula, which remains, however, of complicated form except for very high or very low values of the absorption factor. (See previous section.)

Following Ross, we may combine this absorption factor with inherent variation of sensitivity. Before resorting to this artifice it will be simpler to limit consideration at first to one-grain layers.

Suppose the photochemical absorption proper to be of such large or such small magnitude as to give the limiting cases obtained for the ideal reaction:

a. $x = kE$ Uniform rate

b. $x = a(1 - e^{-kE})$ Monomolecular rate

Then let us assume that the material is broken up into "microsystems," each obeying one or other of the above formulæ, but in either case having different individual values of k—the velocity constant—distributed according to some probability function, *e.g.*,

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[27] The changes in developability of the grain, with different developers, with solarization, with iodide, etc., are not consistent with so simple a view as that adopted, but these are secondary properties. The evidence from Slade and Higson's data (see p. 492), shows, however, that the possibility of autocatalysis being a primary factor requires further consideration.

the normal law of error. In either case, if k does not vary, all "grains" would become developable at the same exposure. We must then equate the actual rate to the distribution function of the k's—the sensitivity distribution. For immediate convenience in testing the "size variation" hypothesis of sensitivity, we have selected distribution functions of type found experimentally to represent our actual size-frequency data. The general progressive increase of "speed" with grain size shown in our data (p. 514) warrants such an attempt.

In general, if the granular material does not cover the whole of a given area, say 1 sq. cm., for which the reaction is being considered, the available exposure will be that falling on the normal grain surface or projective area, S, i.e., according to previous considerations.

a. $$\frac{dx}{dt} = kI.S; \quad x = kS.E$$

b. $$\frac{dx}{dt} k'I.S(a-x); \quad x = a(1 - e^{-k'SE})$$

provided the grains have the same sensitivities (or inertias), and $S = \sum_{0}^{n} s$, the sum of areas of n grains per sq. cm. Now we may obviously have two extreme cases for the function $k = f(i)$, the variation of inertia, in relation to size of grain. These are:

Case I.—$k = f(i)$, totally independent of grain size. Then, if the grains are the *same size,* integration has to be extended only to inertias, if of different sizes, to both inertias and grain sizes.

Case II.—$k = f(i)$ is a function of grain size. For example, the sensitivity may vary directly as the grain size, or the inertia be inversely proportional thereto. This is the simplest possibility, integration over a range of sizes being at the same time integration over sensitivities.

According to the argument developed, either of these cases may be conjoined with the fundamental "molecular" equations a or b. This procedure is developed, to illustrate the modifications, in the following synopsis:

EQUATION TYPE A.

Fundamental reaction.	Variation function of inertias.	Size Condition.	Integral, or Exposure function.
	$\dfrac{dx}{dE} = k$	$k = y = y_0$	All same size
I. $\dfrac{dD}{dE} = k$	$f(i) = y = y_0$	S	$D = kEB\,s$
II. $\dfrac{dx}{dE} = k$	$k \quad f(i)$	S	$D = s\displaystyle\int f(i)\,di$
	e.g., $f(i) = Be^{-ki}$	S	$D = Bs\displaystyle\int e^{-ki}di$
			$= Bs\displaystyle\int e^{-kE}dE$
			$= \dfrac{D_m}{k}\left(1 - e^{-kE}\right)$

NOTE.—A uniform rate of reaction, combined with an exponential inertia-distribution, gives the same type of density function (for constant grain size) as the " monomolecular " rate combined with uniform inertia-distribution. If the size of grain s varies, integration must be extended over $f(s)\,ds$ for the corresponding limits as $f(i)\,di$—which are not given unless the relation of i to s is explicit.

EQUATION TYPE B.

Fundamental reaction.	Variation function of inertias.	Size Condition.	Integral, or Exposure function.
I. $\dfrac{dx}{dE} = k(a-x)$	k constant	S same size	$D = D_m(1 - e^{-k'E})$
II. $\dfrac{dD}{dE} = k'(D_m - D)$			
$\dfrac{dD}{(D_m - D)} = k'\,dE$	$k' = f(i)$ $k'\,dE = f(i)\,di$	S	$\displaystyle\int \dfrac{dD}{D_m - D} = \int f(i)\,di$
			$\dfrac{1}{D_m}\,ln\,\dfrac{D_m}{D_m - D} = (1 - e^{-ki})$
			$\dfrac{D_m}{D_m - D} = e^{\frac{D_m}{k'}(1 - e^{-k'E})}$
			$D = D_m(1 - e^{-u})$

NOTE.—This expression, $D = D_m(1 - e^{-u})$ which may be written

$$D = D_m\left[1 - e^{-D_m\int_0^h e^{-k'E}dE}\right]$$

has considerable similarity to that obtained by Ross (*J. Opt. Soc. Amer.*, **4**, 255 (1920)), *viz.*,

$$D = D_m \left[1 - \frac{1}{n} \sum_{p=0}^{p=n-1} e^{-kr^p E} \right]$$

where n is the finite number of classes of grains of different sensitivities supposed arranged in geometrical progression, p the sensitivity factor, r the ratio of sensitivities of different groups.

Relation of Size of Grain to Inertia.

On the " quantum " theory, as developed by Dr. L. Silberstein, the relation of " size of grain " to " inertia of grain " is apparently quite explicit. The projective-area of the grain, say s, is the measure of its chance of being hit by a quantum, hence, is the effective sensitiveness, statistically. On the other hand, the " size

FIG. 4.
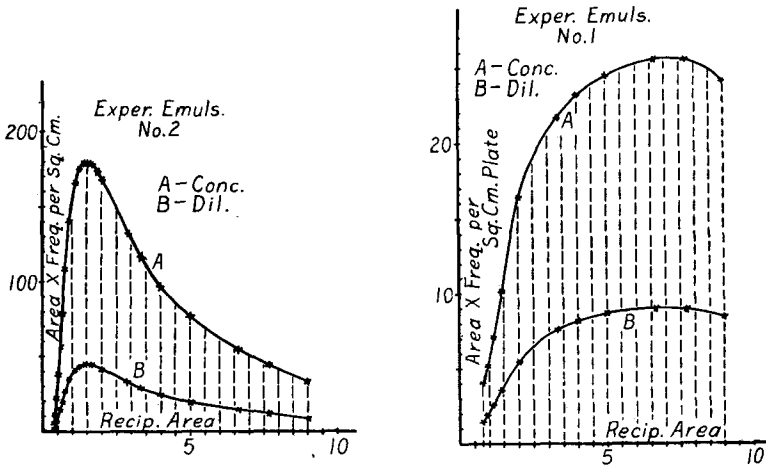
of grain " considered in this is not necessarily the " size " as found by the direct measurements of frequency, nor is the distribution function of sizes thus found directly available for the quantum theory, but requires some corrections for reasons noted later. We may, without immediate recourse to this theory, test empirically the hypothesis that the effective sensitivity of a grain is its " size "—to a first approximation, its " area." Then, the value of $f(i)$ in the foregoing synopses will be given by the distribution of *reciprocals* of the areas of the grains. On this

assumption, the relation of size of grain to inertia is explicit; if the reciprocal area-frequency (= inertia-frequency) per sq. cm. of plate be multiplied at each point by the area itself, the resultant curve should give, to a first approximation, the first derivative of the density-exposure function, when expressed in suitable units. Such curves are given in Fig. 1, as constructed from the original " frequency curve " for the two types of emulsion in question. They are each plotted for two cases,

    A. For the total thickness of original plates;

    B. For a one-grain layer.

FIG. 5.
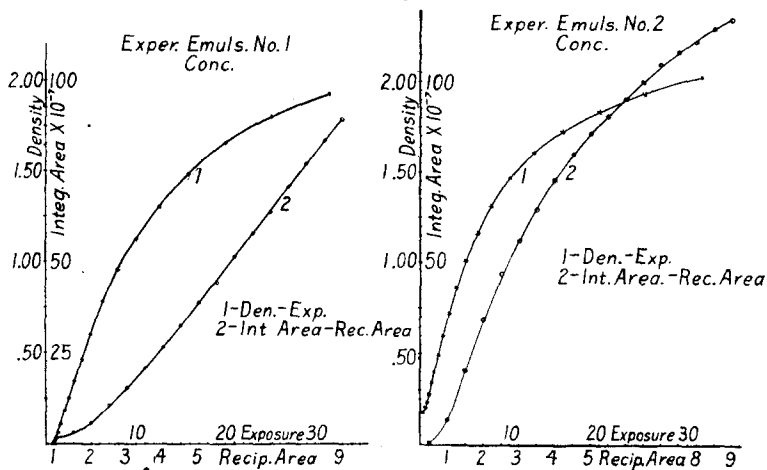
If now the curve No. 1, A and B, and No. 2, A and B (Fig. 4), are integrated graphically, the resulting curves should be comparable with the D-E curves. This has been done for both concentrated and dilute experimental emulsions and the results are shown in Figs. 5 and 6. It is obvious that for adequate comparison both abscissæ and ordinates should be expressed in the same units in both cases. The scale for the exposures is obtained from the condition that the maximum density must be reached with exhaustion of all classes of grains. For the density ordinates, the values 2 and 2′ in Figs. 5 and 6 should be multiplied by a factor for conversion of silver halide of a given grain to density, at same gamma as in Figs. 11 and 12. This correction will be applied when present work on the photometric constant is completed.

It will be seen that the " synthetic " curves give a " cut," as found by Renwick, but a very prolonged under-exposed region, and do not show very satisfactory correspondence with the actual sensitometric curves. The very prolonged " under-exposed " effect corresponds, however, to the fact that no allowance has been made for reduction of available light energy in the thickness of the film. With this correction it appears possible that the comparison may be improved.

Ideally, it would seem that the one-grain layer would be the

FIG. 6.
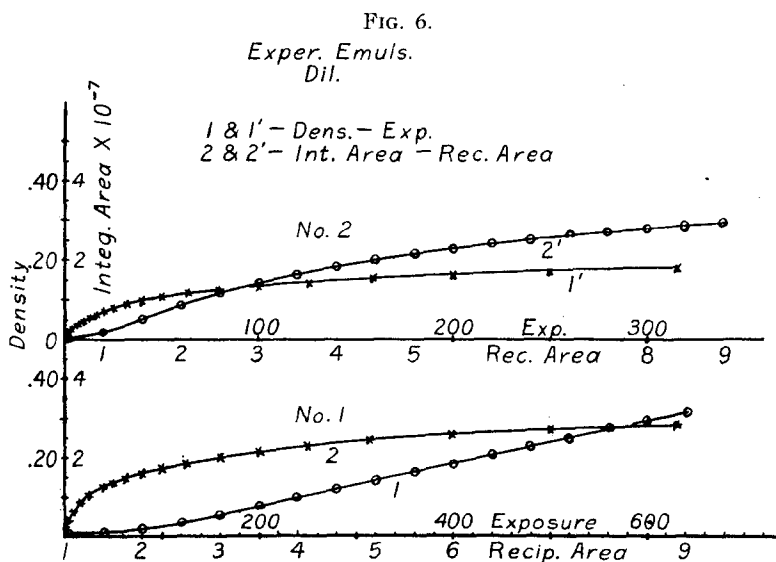
most satisfactory for comparison. The difficulty lies in the measurement of very small " densities "—of the order .002 to .20, with sufficient precision. Work on this is in progress, and a more satisfactory comparison will then be possible.

Experimental Data in Size-Frequency.

To determine size-frequency of grains in large amounts of emulsions we have developed methods of sedimentation and centrifugal fractionation.

For small amounts of emulsion, such as may conveniently be removed from a coated plate or film, we have developed a direct micrometric method. A " one-grain " layer of convenient distri-

bution is produced. Then by means of a high-power microscope, the particles are either photographed, or their outline drawn with a camera lucida. This stage is further enlarged by projection to a total of some 10,000 diameters, and the areas measured directly. For grains sufficiently circular, this is done by measurement of diameters, while larger polygonal grains are planimetered. The data are classified, and the size-frequency curves plotted. Eleven emulsions have already been analyzed in this way. They are enumerated below in Tables I and II.

Most of Table I is self-explanatory; the columns y_0, k and α have the following significance: It is found that the size-frequency curves of all emulsions can be represented by probability equations of two types:

$$\text{Exponential } f(s) = y = y_0 e^{-ks} \tag{5}$$

$$\text{Gaussian } f(s) = y = y_0 e^{-k(s-a)^2} \tag{6}$$
(modified)

and the values given refer to the parameters of the corresponding equations.

It is worth noting here that previous estimates of the thickness of the grains of the silver halide in photographic emulsions have been in many cases too low. If, from the weight of silver halide and the number of grains per sq. cm. of plate, we determine the equivalent volume of the average particle, assuming the density to be that of pure silver bromide (the error in doing this is not greater than 3 or 4 per cent. even with fairly large amounts of iodide present), it is then easy to get the approximate thickness of the average grain (1) where the grains are spherical by determining their diameter

$$d = \sqrt[3]{\frac{6V}{\pi}}$$

and (2) where they are flat by dividing the average volume by the average projective area.

In two of the process emulsions studied which have almost entirely spherical grains this calculated diameter corresponds very closely to the average diameter determined statistically by the microscopic method. The third process emulsion (Process C), which is seen by examination of the photomicrographs to have a number of angular grains (usually indicating flatness) has a cal-

TABLE I.

Grain Characteristics—Average Size Grain.

Type of Film or Plate.	No. Grains per sq. cm. =N	Gms. Ag-halide per sq. cm. of film of plate.	Per cent. Conc. Ag-halide per sq. cm. Emul. on plate or film.	Equiv. Diam. in μ.	Projective Area in μ².	Equiv. Vol. in μ³.	Wt. in Gms. x 10¹²	Thickness in μ.	Ratio Thick:Diam.	Max. Grain Size Obs. in μ²=M.	y_0	k	α
Process A (Lantern Slide)	4.30 x 10⁹	0.000840	31.4	0.383	0.115	0.0301	0.195	0.386†	1:1	1.2	4000.0	5.81	—
Process B	0.668 x 10⁹	0.001366	33.6	0.844	0.560	0.317	2.05	0.846†	1:1	1.6	340.4	8.95	0.555
Process C*	3.08 x 10⁹	0.001422	35.4	0.874	0.60	0.0711	0.46	0.710†	1:1.2	3.2	286.7	4.72	0.630
Positive Emulsion	1.853 x 10⁹	0.000870	36.8	0.704	0.389	0.0726	0.47	0.187	1:3.8	2.2	573.5	2.52	—
Medium Speed A	2.11 x 10⁹	0.001213	33.4	0.757	0.450	0.0889	0.575	0.198	1:3.8	6.2	1068.0	2.98	—
Medium Speed B	0.941 x 10⁹	0.001300	32.5	0.799	0.502	0.213	1.38	0.124	1:1.9	6.2	276.9	4.27	0.533
Medium Speed C	1.50 x 10⁹	0.001677	33.9	1.41	1.567	0.173	1.12	0.110	1:12.8	8.4	{221.6 / 32.2 / 110.2}	{4.27 / 12.20 / 0.953}	{0.790 / 1.860}
High Speed A	0.656 x 10⁹	0.001350	37.1	0.966	0.732	0.318	2.06	0.435	1:2.2	8.6	{110.9 / 200.0 / 30.3}	{3.36 / 2.78 / 6.45}	{0.758 / 2.046}
High Speed B	0.478 x 10⁹	0.001470	33.7	1.67	2.198	0.467	3.08	0.216	1:7.7	12.6	2375.3	4.75	
Experimental Emulsion No.1	5.690 x 10⁹			0.	0.167					1.4			
Experimental Emulsion No.2	1.660 x 10⁹			0.	0.710					2.8	235.2	3.06	0.575

*This is a panchromatic emulsion.
†Volumes assumed to be spherical.

TABLE II.

Sensitometric Characteristics.

Type of Film or Plate.	K	$\gamma\infty$	Approx. D_{max}.	a	b	Relative H. & D. Speed.			Latitude.		
						1 min.	3 min.	10 min.	1 min.	3 min.	10 min.
Process A (Lantern Slide)	0.354	4.05	7.5	0 to 0.05	0 to -0.27	6	6	7	7	9	3
Process B	0.429	4.95	6.2	$\bar{1}$.90	-0.35	6	7	8	2.3	3.6	2.0
Process C*	0.262	4.87	7.3	$\bar{2}$.91 to $\bar{1}$.05	-0.25 to -0.31	27	47	76	9	3.0	3.0
Positive Emulsion	0.384	4.82	5.1	$\bar{1}$.82 to $\bar{1}$.92	0 to -0.18	8	9	10	4	7	3.2
Medium Speed A	0.398	1.39	5.5	$\bar{3}$.63	-0.32	366	729	918	316	316	316
Medium Speed B	0.352	1.23	4.2	$\bar{3}$.78	-0.15	439	763	856	282	200	200
Medium Speed C	0.323	1.62	5.7	$\bar{2}$.00	0	680	680	680	251	100	45
High Speed A	0.421	1.09	5.2	$\bar{3}$.58 to $\bar{3}$.82	-0.03 to -0.06	1236	1488	1560	178	159	71
High Speed B	0.321	0.932	3.7	$\bar{3}$.15	-0.05	2585	3820	4278	2510	794	398
Experimental Emulsion No. 1	0.254	2.42									
Experimental Emulsion No. 2	0.152	2.81									

*This is a panchromatic emulsion.

culated equivalent diameter somewhat smaller than the average projective diameter. For all the medium and high-speed emul-
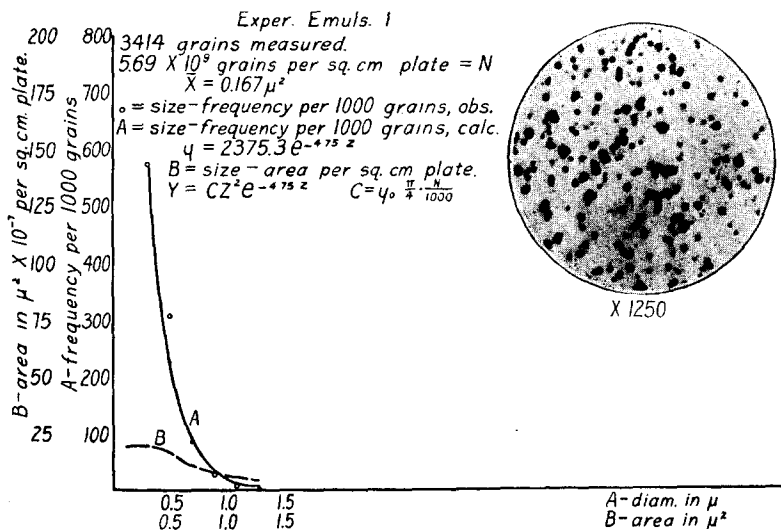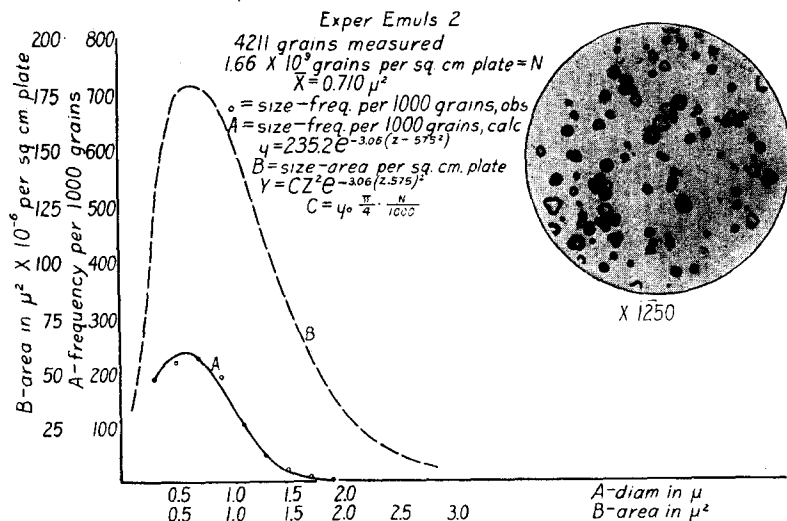
FIG. 7.

Exper. Emuls. 1

3414 grains measured.
5.69 X 10⁹ grains per sq. cm plate = N
$\bar{X} = 0.167 \mu^2$
○ = size-frequency per 1000 grains, obs.
A = size-frequency per 1000 grains, calc.
$y = 2375.3 e^{-4.75 z}$
B = size - area per sq. cm plate.
$Y = CZ^2 e^{-4.75 z}$ $C = y_0 \frac{\pi}{4} \cdot \frac{N}{1000}$

X 1250

A- diam. in μ
B- area in μ²

FIG. 8.

Exper Emuls 2

4211 grains measured
1.66 X 10⁹ grains per sq. cm plate = N
$\bar{X} = 0.710 \mu^2$
○ = size-freq. per 1000 grains, obs
A = size-freq. per 1000 grains, calc
$y = 235.2 e^{-3.06(z - 575^2)}$
B = size-area per sq. cm. plate
$Y = CZ^2 e^{-3.06(z.575)^2}$
$C = y_0 \frac{\pi}{4} \cdot \frac{N}{1000}$

X 1250

A- diam in μ
B- area in μ²

sions the calculations were made assuming the grains to be flat. The ratios of thickness to projective diameter are given in Table I.

Experimental Data on the Sensitometry.

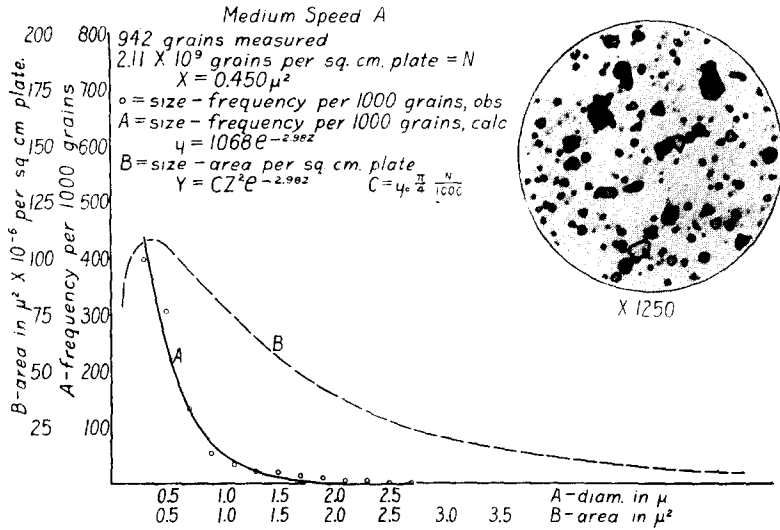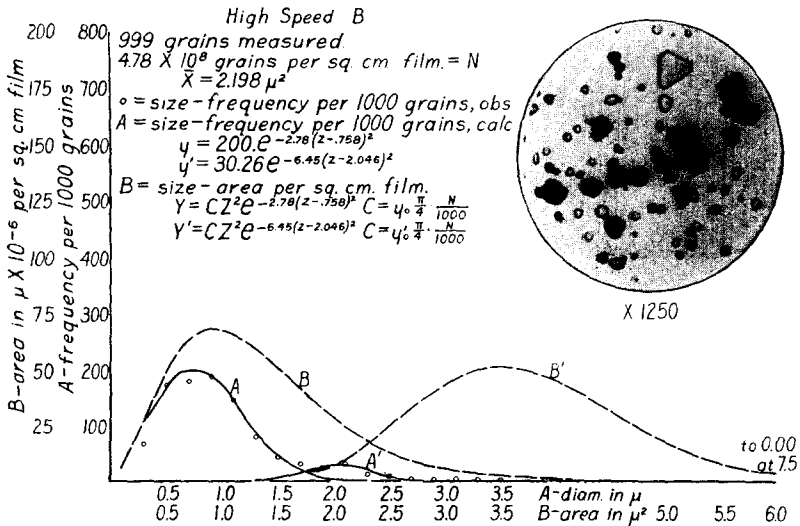The characteristic curves for the emulsions examined were determined in two ways:

FIG. 9.

Medium Speed A

942 grains measured
2.11×10^9 grains per sq. cm. plate $= N$
$X = 0.450\mu^2$
$o = $ size $-$ frequency per 1000 grains, obs
$A = $ size $-$ frequency per 1000 grains, calc
$y = 1068 e^{-2.982}$
$B = $ size $-$ area per sq. cm. plate
$Y = CZ^2 e^{-2.982} \quad C = y_o \frac{\pi}{4} \frac{N}{1000}$

X 1250

FIG. 10.

High Speed B

999 grains measured.
4.78×10^8 grains per sq. cm. film. $= N$
$\bar{X} = 2.198 \mu^2$
$o = $ size $-$ frequency per 1000 grains, obs
$A = $ size $-$ frequency per 1000 grains, calc
$y = 200 e^{-2.78(z-.758)^2}$
$y' = 30.26 e^{-6.45(z-2.046)^2}$
$B = $ size $-$ area per sq. cm. film.
$Y = CZ^2 e^{-2.78(z-.758)^2} \quad C = y_o \frac{\pi}{4} \cdot \frac{N}{1000}$
$Y' = CZ^2 e^{-6.45(z-2.046)^2} \quad C = y_o \frac{\pi}{4} \cdot \frac{N}{1000}$
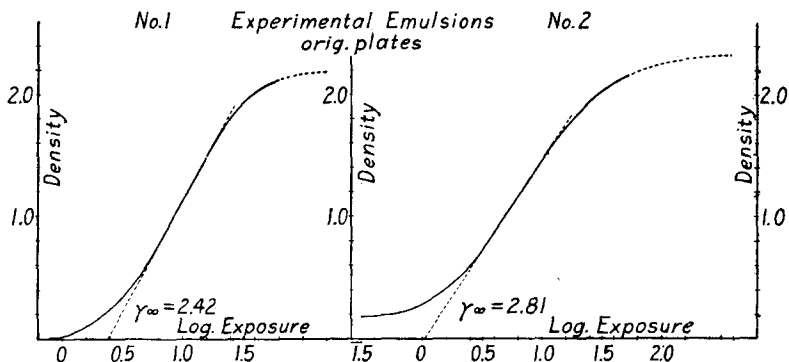
X 1250

1. By intensity scales, using a Goldberg wedge and Higson's modification of Luther's crossed-wedge method. Curves for each

time of development were assembled, and the " family of curves " taken as giving the sensitometric data. (See Figs. 13 and 14.)

2. By time scale, using a Jones non-intermittent sensitometer,
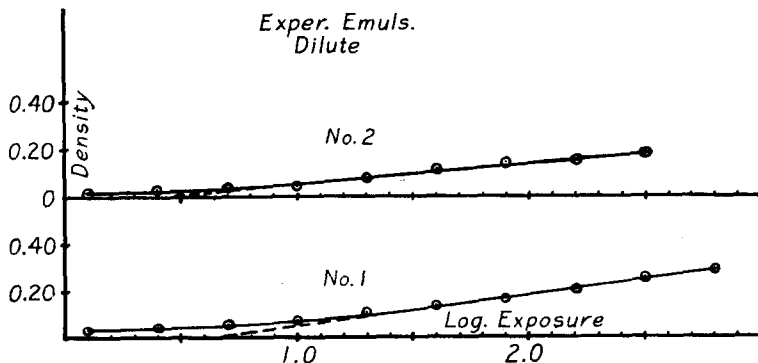
FIG. 11.

measuring the densities, and plotting the curves. (See Figs. 11 and 12.)

The sensitometric curves reproduced correspond to the frequency curves illustrated in Figs. 7, 8, 9, and 10.

FIG. 12.

III. NATURE OF SENSITIVITY AND RELATION TO GRAIN SIZE.

The data summarized in the second section of this paper show, as between different emulsions (mostly of the same fundamental type), a steady progression of " speed " with grain size. This

progression becomes more evident if the relative " speeds " are tabulated against maximum grain sizes.
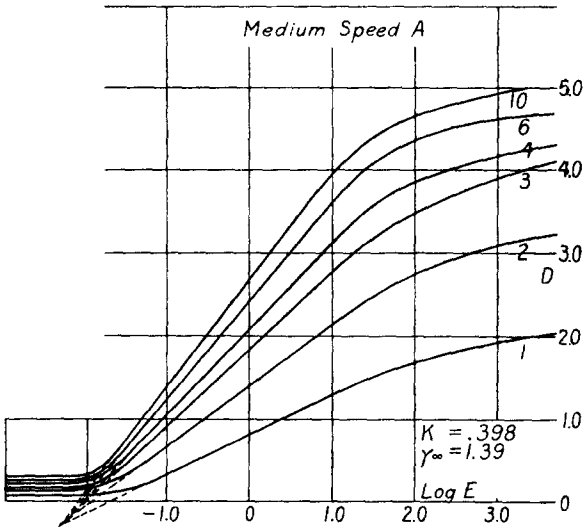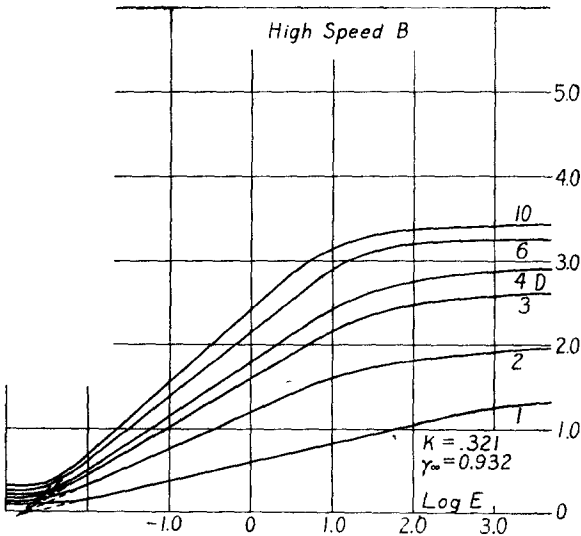
FIG. 13.

FIG. 14.

Since " speed " is obtained from a characteristic curve integrating the effects of grains of various sizes and sensitivities, in

several layers, we cannot, from this, obtain any idea of the quantitative relation of size to sensitivity. The hypothesis was used in the foregoing section, that the *inertia* of a grain was inversely as its projective area, that is, its probability of development directly as its area, to deduce the density-exposure curve. The lack of agreement with the measured curves cannot be taken at present as refuting this hypothesis, for reasons explained. A more direct attack consists in determining microscopically the relation

TABLE III.

Emulsion.	Rel. Speed (Maximum).	Maximum grain area in μ^2.
Process A (lantern slide)	7	1.2
Process B	8	1.6
Positive	10	2.2
Medium Speed A	918	6.2
Medium Speed B	856	6.2
Medium Speed C	680	8.4
High Speed A	1560	8.6
High Speed B	4278	12.6

of developability to projective area for the same exposure in one-grain layers.[28] This has been done by A. P. H. Trivelli and F. L. Righter.[29] They extended their counts and area measurements to clumps of from one to as many as 33 grains; well-confirmed observations showing that with the type of emulsion used, and the technic followed in preparing the one-grain layers, if one grain of a clump was affected, the whole clump is developable.[30] The results, noted immediately, were in striking agreement with those calculated from a quantum theory of the exposure function proposed by Dr. L. Silberstein.[31] This formula he obtained, to a first approximation, as follows: Let the necessary and sufficient condition for a grain to become developable be absorption of at least one quantum of sufficient frequency, above a critical value, as known in photoelectricity. Consider equal-sized grains. Let there be N grains upon an area A and let S be the projective area of each divided by A, and let $n-$ light-

[28] Cf. The. Svedberg and H. Anderson: *Zeit. wiss. Phot.*, 1920, p. 36; *Phot. J.*, 1921, p. 325.

[29] *Phil. Mag.*, 44, 252 (1922).

[30] Contrary to recent results of Svedberg.

[31] In the original paper a more rigorous deduction is given.

quanta impinge upon A—corrected for reflection, etc. To find q, the number of grains hit, the problem can be roughly treated as if N and q were continuous quantities.[31] At any stage the grains unaffected are $N - q$, the available fraction of area $S(N - q)$. Then for an increment dn of quanta

$$dq = S(N-q)dn$$

which gives

$$q = N(1 - e^{-nS}).$$

(It will be noted that this makes $\dfrac{dq}{dn}$, the " sensitivity," directly proportional to S, the projective area, as assumed in section II.)

This simple formula implies that the cross-section of a light-quantum is small compared with a grain. If it be further assumed that only full incidence of a light quantum [32] is effective, and let r be the average equivalent radius of a grain, such that $S = \pi r^2$ and let ρ be the radius of the light quantum. Then the effective area of the grain [33] will be

$$S^1 \cdot \pi (r-\rho)^2 = S (1 - \frac{\rho}{r})^2$$

so that the formula becomes

$$\frac{q}{N} = (1 - e^{-\mu})$$

where

$$\mu = n S_1 = n S (1 - \frac{\rho}{r})^2$$

or if $\delta = \pi \rho^2$ be average area of cross-section of a quantum

$$\log (1 - \frac{q}{N}) = -n S \left[1 - \sqrt{\frac{\delta}{r}}\right]^2.$$

In Table IV the first column gives the number of grains in a clump, the second the average area s of a clump in square microns,

---

[32] The effect of wave-length is discussed in Dr. Silberstein's original paper.

[33] It should be noted that if instead of the total projective areas of the grains as the targets for the light quanta, we assume that the effective targets are silver nuclei in the grains then the quantum hypothesis can still be applied, provided that the areas of the nuclei are distributed in a constant ratio to the total grain area. But, of course, the effective energy acting in a given time per square cm. of plate would be quite different in this case as compared with Dr. Silberstein's original assumption. Energy measurements are being made in this Laboratory which should help to clear up this point.

the third the percentage of clumps affected out of all (N) clumps of each kind originally present, *i.e.,*

$$y = \frac{100\,q}{N}.$$

TABLE IV.

Clumps of		s in μ^2	y obs.	y calc.		Δy
1	grain	0.754	16.5	16.2	+	.03
2	"	1.925	44.9	48.4	—	3.5 ·
3	"	2.03	76.6	68.9	+	8.3
4	"	4.88	87.1	87.3	—	0.2
5	"	6.18	96.0	93.3	—	2.7
6	"	7.42	98.2	96.4	—	1.8
7	"	(8.6)	100.0	98.0		2.0
8	"	(9.8)	100.0	99.6		0.4
9	"	(11.0)	100.0	99.8		0.2
10–31	"	(12.0)	100.0	100.0		0.0
32 " >		24.	100.0	100.0		0.0
33 " >		25.	100.0	100.0		0.0

The data are represented graphically in Fig. 15.

FIG. 15.
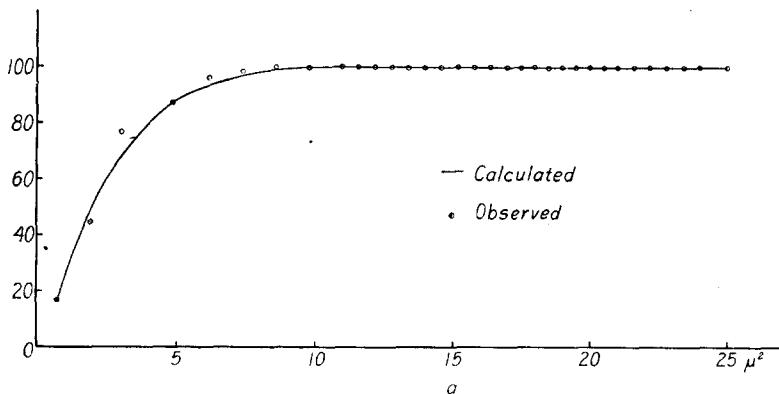
As stated earlier, this theory makes " sensitivity " entirely a matter of " effective projective area," *i.e.,* area of grain not shielded by other grains, and probability of being hit by at least one light quantum. A recent paper by The. Svedberg,[34] which has appeared since the investigations noted here were concluded, requires discussion in this connection. Svedberg has followed up the obser-

[34] *Phot. J.,* 1922, p. 186.

vation by M. B. Hodgson, of this Laboratory,[35] that development starts at one or more points of a grain. By interrupting development of grains exposed in a one-grain layer, he was able to count the number of " nuclei " thus revealed per grain for a larger number of grains of two size-classes (diameter $>$ 1.18μ and $<$1.18μ). " Assuming that the product of light action, *i.e.*, the substance of the latent image, consists of small centres distributed through the grain, or through the light-affected part of the grain according to the laws of chance," a certain grain will become developed if it contains one or more than one developable centre. Now according to the laws of chance the percentage probability for the occurrence of n centres in a grain is

$$P_n = 100 . \frac{e^{-\nu} v^n}{n!}$$

where ν is the average number of centres per grain. Thus the percentage probability that the grain will contain at least one centre is $P = 100(1 - e^{-\nu})$.

Svedberg's results confirm this formula and thereby the hypothesis of a chance distribution of centres. Now it is apparent that this result is in good agreement with the quantum theory just discussed. It is, however, equally accounted for by the alternative hypothesis of a photocatalyst formed in emulsification, and located in the grains according to chance. As regards the relation to size of grain, Svedberg's data only confirm the rapid increase of sensitivity with grain size. They are insufficient in range to correlate the sensitivity factor ν absolutely with either volume or cross-section, although it is pointed out that the results obtained differ, so far as they go, for light and X-rays, a *volume* relation being indicated in the latter case. This result would be more probable on the emulsification-nucleus theory than on the quantum theory, and therefore confirmation is important. Trivelli and Righter's results [36] indicate that the proportion of. developable grains in a one-grain layer increases more rapidly, with increasing area, than provided by the simple formula

$$q/N = 1 - e^{-nS}$$

where S is the projective area, and using nearly monochromatic blue light of $\lambda = 480\mu\mu$. This might be interpreted in terms of an

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[35] J. FRANK. INST., 1917, p. 705, **184**.
[36] *Loc. cit.*

increase in number of centres more nearly proportional to the *volume;* on Silberstein's quantum theory, as already noted, it is accounted for by allowing a finite cross-section to the quantum of dimensions comparable to the area of the grain.

If we term E, the exposure, provisionally $= It$, ν the average number of nuclei per grain (due to emulsification plus exposure), then evidently for a one-grain layer

$$q/N = 1 - e^{E\nu f(S)}.$$

Where $f(S)$ expresses the relation between ν and projective area of grain. If, on the simplest correlation discussed by Svedberg (and assumed provisionally by ourselves for " sensitivity," Sect. II) we put $f(S) = S$, we have

$$q/N = 1 - e^{-E\nu S}$$

which is of similar form to the simplest form of the quantum hypothesis

$$q/N = 1 - e^{-nS}.$$

The relations of these expressions to the density-exposure function are again of essentially similar type, initially. Silberstein [37] has pointed out that, assuming the simple formula above, for each class-size of an emulsion of type $\phi(S)$, where $\phi(S)$ is the equation of frequency distribution, the number of grains from s to $s + ds$ affected (at one quantum per grain) by n quanta will be $q_s ds$, where

$$q_s = \phi(S) \left[1 - e^{-nS}\right].$$

The total area of halide made developable will be found by integrating $q_s ds$ over the whole range of sizes, say from S_1 to S_2. Thus taking the exponential type of frequency curve $\phi(S) = Be^{-\mu s}$, from $S = S_1$ to S_2 where B and μ are constants, then the required integral or density value is

$$\Sigma = \frac{\beta}{(n-\mu)^2} \left\{ 1 + (n+\mu)S_1 e^{-(\mu + n)S_1} - [1 + (n+\mu)S_2]e^{-(\mu+n)S_2} \right\}$$

an equation which can be greatly simplified if $S_1 = 0$.

Formally, the same integration would apply to the equation derived from the " nucleus " hypothesis of Svedberg. It appears, however, that the actual range of " grain-areas " effective in the two cases would differ considerably. On the quantum hypothesis, for ordinary plates of several layers and high concentrations, the

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[37] *Loc. cit.*

function $\phi(S)$ will not coincide with the size-frequency curve of that emulsion as determined by the methods discussed here. For, in the first place, if several grains form a contiguous clump, they may behave as *one grain* of class corresponding to their total projective area. Next, either a grain of a lower layer is shielded or not shielded.[38] If not shielded, it belongs to its proper class in one layer; if shielded it is reduced in class size to its unshielded portion. Hence, the effective size-frequency function $\phi(S)$ is not immediately determinable by mere counts, but has to be carefully corrected for the said factors. On the other hand, in the emulsification-nucleus hypothesis, the value S is the actually observed value in size-frequency determinations, and $\phi(S)$ the empirically determined size-frequency function. But, the correlation to n, that is, the exposure quantity (energy available or absorbed), requires in turn correction for diminution in passing through a multigrained layer. (See previous section II.) Hence it does not appear probable that a crucial distinction between the two hypotheses can be made on the ground of the integrated formulæ, since in either case mathematical refinements not immediately susceptible of experimental verification could be introduced making sufficient agreement with the actually measured density-exposure functions.

For physical optics, an experimental proof of the quantum hypothesis, of the discrete structure of light, is the issue. For photographic industry, if the "quantum" hypothesis is correct, the emulsion-maker has only to adjust the size-frequency curve of his precipitated silver halide, and ensure *absence* of inhibiting (desensitizing) substances in his gelatin to secure the maximum possible of speed, density, contrast, latitude, etc. If, however, the "emulsification-nucleus" hypothesis is correct, then the process of "sensitization" is of equal, or greater importance than that of grain-size determination; although at present apparently loosely coördinated with this, the possibility would exist of a more independent control of the two factors. In this connection, and as possibly helping to judge between the two hypotheses discussed, the phenomena of desensitizing are of great importance; particularly where it can be shown that the densensitizer has not been acting by mere destruction of the latent image as formed. In the subsequent paper certain independent evidence for the nucleus

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[38] Cf. L. Silberstein, *loc. cit.*

hypothesis will be considered, as also the problems of densitizing, nucleus activation, and what has been termed by Lüppo-Cramer [39] the topo-chemistry of the silver halide grain.

SUMMARY.

1. The existence and nature of statistical variation of sensitivity among silver halide grains is discussed.

2. The relation of the statistical variation of sensitiveness, or inertia (its reciprocal), to the density exposure function is discussed. It is concluded that under certain conditions the first derivative of the density-exposure function will correspond with the intensity-variation function or curve.

3. The results of experimental determinations of grain-size-frequency curves are noted, and correlated with sensitometric data.

4. The decisive influence of the grain-size distribution and limits on the " speed " and other sensitometric variables is discussed in relation to the " quantum " and the " photocatalytic " theories of grain sensitiveness.

The Solvent Properties of Acetone. R. F. REMLER.—The paper takes up the following industrial consideration regarding acetone as a solvent: Uniformity of the present grade of acetone from calcium acetate, boiling point and volatility, freezing point, inflammability, dehydrating properties, miscibility with other solvents, use as a coupling or bending agent between immiscible solvents, relative test per gallon, physiologic effects and recovery. The solubilities of acetylene, cellulose acetate and cellulose nitrate, rosin and mineral oils, gums, resins, shellacs, animal and vegetable oils, fats and greases, waxes, asphalts, and bitumens, are discussed. Mention is also made of acetone in dry cleaning and leather industry, and as a constituent of paint, varnish, and carbon removers. (A. C. S. Abstract Service.)

Automatic Volumetric Analysis—Carbon Monoxide Recorder. HUGH S. TAYLOR and GUY B. TAYLOR.—An instrument for automatically making chemical analysis and recording the results is described. The instrument can be adapted to any case where two or more fluids can be mixed in regulated volumes, and the result of the obtained reaction of the fluids recorded by electrical conductivity, temperature rise, etc. Specifically the application of the apparatus to the analysis of flue-gas for carbon monoxide is described. (A. C. S. Abstract Service.)

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[39] *Loc. cit.*