Contribution to the understanding of latent image formation in photography

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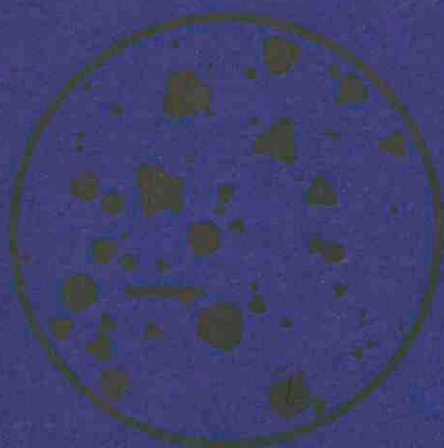# CONTRIBUTION TO THE UNDERSTANDING OF LATENT IMAGE FORMATION IN PHOTOGRAPHY

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LATENT IMAGE FORMATION IN PHOTOGRAPHY

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PROEFSCHRIFT

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Aan mijn Ouders.
Aan mijn Vrouw.

CHAPTER I.

SOME PROBLEMS OF LATENT IMAGE FORMATION.

§ 1. Introduction.

At one time a drawing had to fulfil a twofold purpose: it represented a true image of an object and it showed an artistic treatment. The artist and the "picturer" were identical to a large degree and their work was an entity.

Between 1816 and 1839 NIEPCE and DAGUERRE invented a method of photography in the sense of producing a true and fixed image, registered by the light itself. Photodecomposition of silver salts had been observed before, but these investigators utilized this process for the first time for this purpose technically on a large scale [1]).

Innumerable "true images" devoid of any artistic quality have been produced since; on the other hand art produces pictures deviating strongly from "reality". "L'art pour l'art" appeared parallel with a trend towards "photography for true images". This is one of the many ways by which the principle of division of labour has divided mankind during the past century into two species: the artist and the scientist. Will they ever reunite?

Though photography has rendered great services in all branches of science for the documentation, measurement, and understanding of many phenomena, and though the photographic technique has been developed to a high level, no clear understanding has yet been attained of the physical and physico-chemical processes occurring in a photographic plate when a picture is taken. Of course certain groups of phenomena have been investigated carefully. Theories have been advanced by several schools. But the large

number of theories for several essential parts of the photographic process proves that a general and satisfactory viewpoint has not been reached yet.

Usually the difficulties are not essential, but arise mainly from the complexity of the problems. The extensive researches, performed to elucidate the mechanism of the photographic process are justified by the wide field of practical applications of the plate or film in science, industry and daily life. Also the plate, with its fine grains of silverhalogenide, shows some photochemical or photophysical properties — e.g. latent image formation — which could not be studied so easily with other objects. So their study may well enrich photo-physics and -chemistry. Finally the photographic plate has several essential features in common with many systems in radiobiology, which is due to the smallness of its photosensitive grains. It is more easily accessible to research though, and may thus also contribute indirectly to progress in the latter field.

The physical and physico-chemical problems directly connected with photographic emulsions may roughly be divided into four groups, concerning:

a. preparation and constitution of photographic material;

b. effect of light or other agents (heat, other rays, pressure etc.) upon the photographic material (latent image formation);

c. development and fixing of the latent image;

d. quantitative description of the results (densitometry, etc.) and their relation to the parameters of a, b and c (sensitometry, etc.).

This thesis deals mainly with a few aspects of latent image formation (cf. § 5). For the sake of orientation of the reader we shall outline in the first chapter a number of fundamental concepts or problems and some work of other authors which has led us to the investigations presented in this thesis.

§ 2. Fundamental facts and concepts in photography.

The purpose of this section is, to resume a few basic facts and concepts. It is necessarily incomplete; for extensive information we refer to handbooks.

1. Preparation and constitution of photographic material*).

The principle of preparation of photographic emulsions is: addition of silvernitrate to a moderately heated aqueous solution of gelatin and potassium halogenide (mostly bromide) in excess. Under suitable conditions a yellowish emulsion of very fine crystals or grains of silver halogenide is formed which solidifies after cooling to room temperature. Special after-treatments (ripening processes) increase the average grain size of the emulsion and its sensitivity to light. The rôle of gelatin is in the first place stabilisation of the emulsion both in a mechanical and colloidal sense. Also certain sulphuric impurities occurring at remarkably low concentrations in gelatin are essential for good light sensitivity of the emulsion [4]).

A photographic plate consists of a glass plate covered at one side with a layer of ca. 20 μ of such an emulsion. It is often coated at the back side with a dark substance to avoid false reflections. Its sensitivity can be extended to colours of longer wave length than blue by adsorbing suitable substances to the grains. In general these will sensitize the plate only for radiations which they are able to absorb, but an other mechanism is also known (shift of AgBr absorption, due to adsorbed ions).

The sensitive layer of the plate contains ca. 10^9 grains per cm^2; their shape is mostly like a flat disk; they are oriented preferably parallel to the plate. The average size of the grains usually lies between 0.3 and 2 μ. The grain size distribution in one emulsion has a rather flat maximum.

The absorption coefficient of the grains is very large for light of wave lengths below 4500 Å. For unsensitized grains the absorption for wave lengths above 4800 Å is negligible. In sensitized plates the adsorbed dye molecules absorb the light and transmit some action to the grains (cf. § 4).

An ordinary photographic emulsion is susceptible to many influences. Among these are mainly light, containing radiation

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*) For an extensive description of this subject cf. e.g. [2]) or [3]).

of wave lengths below 4500 Å (blue and violet); ultraviolet-, X-, γ-, β-, α-, atomic- and cosmic radiation, heat, mechanical pressure, etc.

The action of light has been studied most extensively. We shall not discuss other agents, though in some cases their action is more easily understandable.

2. Quantic nature of photographic processes.

In order that light can act on a photographic plate, it is necessary that it is absorbed. In the beginning of this century the quantic nature of all processes of emission and absorption of radiation was well established. Of course the photographic process should be understood in one line with all other absorption processes. In 1922 [5]) and again in 1931 [6]) SILBERSTEIN deemed it necessary to introduce this idea into photographic literature.

It is rather amazing that at present authors are still found who do not yet take this into account [7]) [8]).

3. Print-out effect.

If a sufficient quantity of light acts on a plate, it becomes darker, and black after long exposures. This phenomenon is called direct blackening or print-out effect. The light, absorbed by the grains, decomposes silverbromide (AgBr) into silver (Ag) and bromine (Br). The Br is bound to gelatin, the Ag is responsible for the blackening.

It is generally known [3]) from microscopic observations that the silver is deposited, concentrated or coagulated at discrete spots both at the surface and in the interior of the grains, for ordinary plates as well as for sensitized ones [3]). Also general evidence indicates that such coagulation occurs only at places in the grain where traces of Ag_2S or Ag are present (due to the ripening process [3]) [9])).

The effect of an exposure is measured either by determining chemically the amount A of Ag (or Br) formed per cm^2, or by determining the change in density d of the print-out effect. This quantity d is defined as the logarithm (base 10) of the ratio of the

intensity I_0 of light, incident on the plate for the measurement of d, and the intensity I transmitted by the plate: $d = \log (I_0 / I)$. The result is somewhat dependent on the colour of the measuring light, on its angular distribution and on the aperture of the measuring device. However these dependences are often of minor importance since they consist mainly of proportional changes of different densities.

The lower limit, down to which the first method has been applied, lies at exposures of about 10^{15} quanta/cm² absorbed or ca. $10^{5, 5}$ quanta per grain absorbed [3]). The quantum efficiency (atoms Ag per quantum absorbed) is ca. 1 in these experiments.

The lower limit down to which the second method has been applied (JURRIENS 1938 [10])) lies at exposures of about 10^{12} absorbed quanta/cm² or ca. 400 quanta absorbed per grain.

The region of photographic exposures for practice lies between about 10^{8-9} and 10^{10-12} absorbed quanta/cm² or 1 to 100 or 1000 quanta absorbed per grain.

The results of measurements of the amount of silver A or the density d can be collected in an (A; I; t) or (d; I; t) surface, (I = intensity of irradiation; t = time of exposure), or in sets of curves in plots of either A or d against one of the independent variables I or t, with the other one as a parameter.

(A; t) lines for constant intensity of blue irradiation start linearly from the origin within the limits of error; for increasing time they increase less rapidly [3]) [11]).

(d; t) lines for constant I have a similar shape for blue irradiation according to JURRIENS [10]), but this author reports that upon intense red irradiation non sensitized plates yield curves with a remarkable S-shape or threshold.

Plots against I for constant t have the same shape qualitatively.

4. Latent image and developed density.

If a quantity of light, about 100 times smaller than would be required to produce a detectable print-out effect, acts on a plate, something changes in the grains. A number of grains, dependent on the conditions of exposure, becomes developable; i.e. certain reducing substances (developers), which leave unexposed grains

unaltered, will be able to reduce these grains to Ag. Normally, if a grain is affected by a developer, it is reduced entirely and becomes a black grain of silver.

After solving unreduced AgBr grains (fixing), washing and drying the plate we can measure its (developed) density, which we shall denote by D in contrast to the direct density d. The result is again somewhat dependent on the conditions of measurement.

If we adopt any standard method for development, fixing, density measurement etc., the developed density D is determined by the state of the latent image. In this connection we shall introduce the term "developable density" of a latent image, this being the density that would be obtained if this latent image should be developed etc. according to this standard method. The developable density is not sufficient to characterize the latent image.

Many arguments point to the assumption that the latent image consists of a minute quantity of silver. In other words the latent image and the print-out effect are essentially the same. We shall adhere to this view, in agreement with the general trend in present-day literature.

Owing to the fact that no other method than development can show the presence of the latent image after normal exposures, all evidence that it consists of Ag necessarily is of an indirect nature. To obtain such indirect evidence two ways have mainly been followed.

Firstly large AgBr crystals have been investigated, and their Ag-production was detectable after exposures well within the region of development of AgBr emulsions. Also a very small Ag content of unexposed AgBr emulsions was observed by SHEPPARD e.a. [4]).

Secondly the behaviour of the latent image towards various chemical influences has been investigated. Extensive studies on Ag-AgBr adsorbates by REINDERS, LÜPPO-CRAMER e.a., proved that adsorbed Ag can behave just like the latent image does.

A peculiar feature of the latent image is its distribution through the grains. Microscopic observations of slightly developed grains show that the latent image is concentrated at certain centres (sensitivity specks), just as in the case of print-out silver. In fact, a grain is developable only if at least one speck at its surface has become sufficiently large (cf. also § 10.2). These

centres are, according to extensive researches of SHEPPARD, TRIVELLI, e.a., specks of Ag_2S; also other irregularities in the AgBr grain such as Ag atoms act as such to a lesser extent. A very convincing argument for this view is that if AgBr emulsions are made with gelatin containing a relatively small amount of sulphur their sensitivity is very low, but is restored on addition of certain sulphur compounds.

The mechanism of this concentration of silver has not been understood, till recently the theory of GURNEY and MOTT on latent-image formation succeeded in explaining it satisfactorily (§ 4).

§ 3. The developed density as a function of wave length, intensity and time of exposure.

In this section we continue the general remarks of § 2, pertaining more to the quantitative side of density production.

1. Transformation law.

The transformation law (named thus by VAN KREVELD [13]) expresses that equality of densities is independent of the method of development etc. This law is valid only in first approximation. It is clear that it cannot be valid strictly. For instance: one developer reduces all grains in which n or more quanta have been "effective", and another one already acts on grains with $(n—1)$ effective quanta. The grain size distributions for the two emulsions may differ, so that equality in the former case will cause a slight difference in the latter one.

2. General character of density-exposure curves.

For normally developed plates the density is in first approximation only a function of the energy, i.e. the product of intensity and time of irradiation, called exposure (cf. § 3. 3). We shall first neglect deviations from this "reciprocity-law".

Considering a developed-density-log exposure curve of a general type, we distinguish three parts (fig. 1a).

The first part of the curve, for low exposures has been replotted

in fig. 1b against the exposure itself. It shows a typical S-shape, usually starting quadratically from the origin. The inflection tangent meets the abscissa at an exposure value which we shall call threshold and the ordinate at a negatieve density value which we shall call density-defect. The middle part is more or less straight; its slope is called contrast. This is the most important region for photography. The produced straight part meets the log exposure axis at an energy value called inertia. In the upper part we notice saturation and then again a decrease of density with increasing exposure (solarization, first order reversal) followed by several reversals of a higher order [12] [14]).
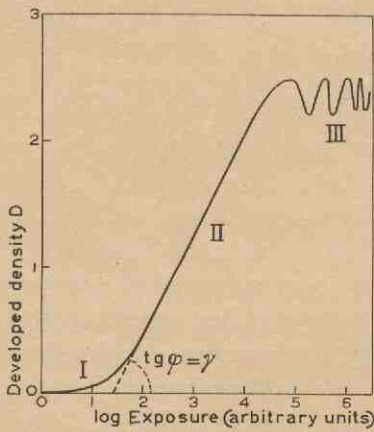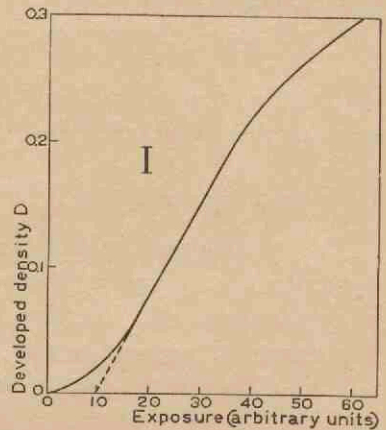

Fig. 1a.   Fig. 1b.

Schematical representation of density as a function of exposure.

a. plotted against log exposure, with   b. enlarged lower part I, plotted against
   contrast γ and inertia.   exposure itself.

Within the mentioned approximation (reciprocity law) density-exposure curves for the different colours coincide in the first part if the exposure is expressed in absorbed quanta per unit area. Consequently, in plots against incident energy the density-defect is independent of the colour.

The exact dependence of saturation density, contrast, inertia, threshold and density-defect on conditions of exposure and development is rather complicated. We restrict ourselves to the following remarks:

The contrast is different in $(D; \log t)$ or $(D; \log I)$ plots. It also depends weakly on the value of the parameter (other variable); for parameter values of the same order of magnitude the $(D; \log I)$ curves are practically parallel.

The same is true for (D; log t) curves. Also the contrast is a function of the conditions of development, especially of the time of development, but for sufficiently long times the kind of developer has hardly any influence. Moreover the contrast depends on the composition of the incident radiation (cf. Ch. V). Usually it is higher for wave lengths for which the plate has been sensitized, than for those absorbed directly in AgBr. This dependence and the fact that the shape of the curves in the lower part (I) somewhat depends on wave length cause (D; log t) or (D; log I) curves for various colours to be in general distinctly non-parallel.

3. Reciprocity law failure.

The reciprocity law states that the developed density D is only a function of the product of intensity I and time t, so only of the energy E absorbed. It only holds with good approximation for relatively small intervals of I and t; deviations are called reciprocity law failure (r.l.f.).
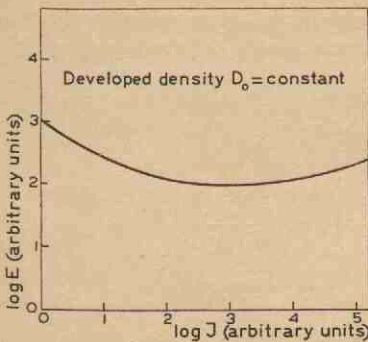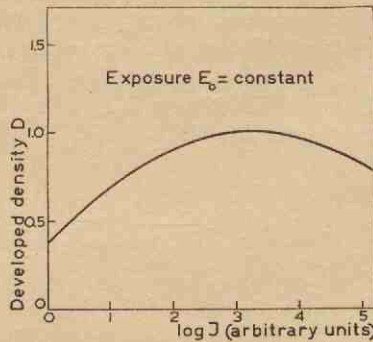
Fig. 2a. Fig. 2b.

Reciprocity law failure diagrams.

a. log energy, required to produce a given density D_0, against log intensity applied.

b. density, produced by a given amount of energy E_0, against log intensity applied.

The situation is usually shown in a r.l.f. diagram, in which $\log E = \log I.t$, required to produce a given density D_0 is plotted against log I (fig. 2a) or against log t; in literature plots of the density D, produced by a given energy E_0, as a function of log I (fig. 2b) or log t are also found. The reciprocity law would in all cases yield a horizontal line, but the curves have a more or

less hyperbolic shape. Extensive investigations on questions concerning the r.l.f. were performed e.g. by JONES e.a. [15].

The minimum or maximum in a plot with constant D_0 or E_0 corresponds to optimal efficiency; it is obtained for optimal intensity I_0 and optimal time t_0. The optimal intensity is of the order of magnitude of 100 quanta/sec. absorbed per grain.

The diagrams for D_0 = constant and for E_0 = constant appear to have almost similar shapes. This can be related to other properties of the (D; I; t) surface in the following way:

Often (D; log t) curves are practically parallel for large I-intervals, so the quantity γ_I, defined as

$$\left(\frac{\partial D}{\partial \log E}\right)_I = \left(\frac{\partial D}{\partial \log t}\right)_I \equiv \gamma_I$$

is independent of I for large regions of this variable, especially near and above the optimal intensity (cf. JONES e.a., l.c.). Since the vertical distance between neighboring r.l.f. curves for constant density is inversely proportional to γ_I, the independence of γ_I of I is equivalent to parallelism of these r.l.f. curves. Considering D as a function of log E and log I we have in one point (log E; log I):

$$\left(\frac{\partial D}{\partial \log E}\right)_I = \left(\frac{\partial D}{\partial \log I}\right)_E \bigg/ \left(\frac{\partial \log E}{\partial \log I}\right)_D$$

In words: the ratio of the slopes of the r.l.f. curves in corresponding points of (D; log I)$_E$ and (log E; log I)$_D$ plots is $-\gamma_I$ Hence, as far as γ_I is independent of I, we have, in connection with the mentioned parallelism, that the r.l.f. curves for D = constant and for E = constant are similar, i.e. related by an affine transformation in the ordinate direction.

The dependence of r.l.f. on wave length was investigated by WEBB [16], who found that (log E; log t)$_D$ lines are congruent for different colours. They differ only by a translation in the log E direction, the magnitude of which depends on the value of D and on the wave length λ (WEBB's relation). The r.l.f. for one wave length can be interpreted as an effect, connected with the mean time interval $\overline{\theta}$ between successive absorptions in the grains. It is highly probable, especially owing to the validity of WEBB's

relation, that intensities of different wave lengths, which produce a given density D in the same time, (corresponding intensities with respect to D) have the same average time interval $\overline{\theta}$ between successive absorptions per grain. Thus the influence of λ on the efficiency with which a given density is formed, is reduced to the influence of the average interval between successive absorptions in the grains.

Innumerable attempts have been made to describe the shape of the r.l.f. curves empirically.

If the relation between density, intensity and time of exposure is written in the form $D = D(I.t^p)$, p is only a slowly changing function of I and D. For corresponding intensities p does not depend on λ, on account of WEBB's relation. The slowly changing character of $p(I, D)$ is apparent from the fact that the slope in the $(\log E; \log I)_D$ plot is 1—p (fig. 2a), and constitutes the basis for the SCHWARZSCHILD approximation with p = constant. This is equivalent with a straight line in an r.l.f. diagram for constant density, which shows the extent to which this approximation is applicable.

Also we mention the KRON-HALM-WEBB formula, which is essentially

$$D = D\left(\frac{I\,t}{\alpha\,I^A + \beta\,I^{-B}}\right)$$

with A = ca. 0.2 and B = ca. 0.3 to 0.6 as experimentally determined values.

A quantitative theoretical discussion of the r.l.f. is one of the most fundamental problems of latent image formation. The decrease of efficiency at each side of the optimal point has to be treated separately. The decrease for lower intensities indicates that the formation of a Ag atom is not merely a single-quantic process. For higher intensities the curve exhibits the existence of processes which are less effective if the mean interval between absorptions of successive quanta is too small; hence some factor limits the rate of utilization of quanta.

§ 4. The Gurney-Mott theory of latent-image formation.

Until 1938 most photographic theories covered a rather narrow

field of observations more or less successfully. Then GURNEY and
MOTT [17]) and MOTT [18]) presented a theory which had the great
advantage of visualizing, from one standpoint, many important
phenomena connected with latent-image formation and development,
and moreover linked these phenomena to electric properties of
large crystals of AgBr, studied in recent times. Of course the
theory incorporates also many features of various previous theories.

The authors start from the following basis:

1. The absorption of light is a quantic process.

2. The latent image consists of silver, which is concentrated at
discrete sensitivity specks.

3. All halogenides of alkali-like elements, e.g. of silver are semi-
conductors that show electronic photoconductivity and cationic
electrolytic conductivity in the crystalline state.

4. The efficiency for the production of a measurable direct
density is of the order of 1 absorbed quantum per atom Ag.

The last point indicates that practically all quanta, absorbed by
the AgBr lead to the formation of a Ag atom. The first two
points indicate that this Ag atom is deposited at definite specks.
Since the absorption of quanta is not restricted to these specks,
a mechanism of transport for the energy has to be visualized,
between its absorption and the final Ag precipitation.

It is known that the energy levels of the stationary states of
excited electrons in photoconductive crystals form "energy bands".
If an electron is in such a state it may travel through the crystal
without requiring supply of energy, and is thus able to increase
the conductivity of the crystal. The energy band concerned is called
a conduction band. Light absorption is known to raise a Br-electron
of the lattice (fig. 3) from the ground state, in which it is bound
to its Br atom, into the conduction band, thus causing photo-
conductivity.

On the other hand the study of the electrolytic conductivity of
crystals of the type of AgBr showed that this property has to be
explained by assuming that the Ag^+ ions in the lattice are bound
relatively losely to their equilibrium positions. The thermal agitation
will dislocate a silver ion relatively frequently from a lattice place

into an interlattice place (fig. 3), leaving a "hole" in the lattice. Eventually an equilibrium will be established between the formation of the interlattice ions and their reunion with holes. The energy required to move such an ion to a neighboring interlattice position is relatively small so that electric fields will draw such ions to the cathode.
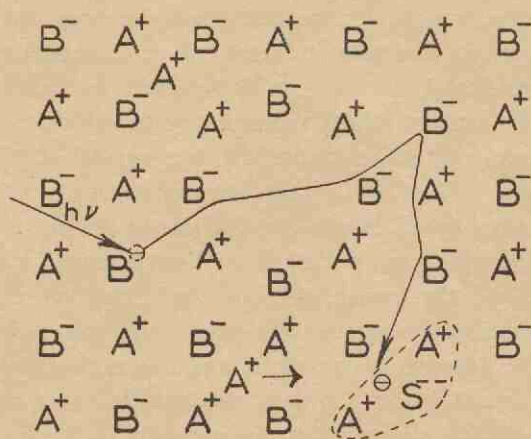

Fig. 3.

Schematical representation of a silverbromide crystal lattice with bromine ions (B⁻) and silver ions (A⁺), two of which are in interlattice positions, and one silver sulphide sensitivity speck. After absorbing a quantum of light a bromine electron is raised into a conduction band and moves about, eventually reaching the speck, where it contributes to the formation of the latent image by attracting an interlattice ion.

The GURNEY-MOTT theory assumes for the latent image formation that the above mentioned photoelectron wanders through the crystal until it becomes trapped at a certain sensitivity spot (potential hole) which is to be expected at irregularities of the lattice, e.g. at the edges or at places where Ag or Ag_2S has been formed. The sensitivity speck is thereby negatively charged and neutralizes itself then by attracting a positive interlattice Ag ion. This Ag ion is transformed into a Ag atom upon arrival at the speck. The latter then becomes ready to accept a following electron, etc..

This explains the silver concentration and energy transport. The theory can explain many other phenomena qualitatively or

almost quantitatively. For instance: it requires that latent image formation is almost totally inhibited at liquid air temperatures because ion diffusion is then practically absent. Experiments of WEBB and EVANS [19]) on latent-image formation at low temperatures were in very good qualitative agreement with theoretical expectations deduced from inhibition of ionic conduction.

Since a trapped electron must be neutralized before its successor can be effective, too high intensities will increase the possibility of the loss of an electron; qualitatively this explains the r.l.f. for high intensities.

The authors assume that a sensitivity speck has a tendency (probability) to emit an electron into the crystal, due to thermal agitation.

The remaining speck is positively charged on the average and will attract the electron so that it will preferently remain in the neighborhood of the speck, which gives rise to a cloud like probability distribution around the latter. As long as a speck is positive on the average it cannot attract other interlattice Ag ions to produce a latent image. As soon as photoelectrons are produced in the crystal the dissociation is accordingly reduced to the new equilibrium. If the number of photoelectrons (pressure of the electron gas) is sufficiently high, the speck will, on the average, become negative and will start to grow by attracting Ag ions. For low light intensities the electron concentration will slowly if at all reach this critical value, whereas for higher light intensities the specks will sooner start to grow.

This should explain why low light intensities are less efficient in producing trapped electrons than higher ones (low intensity r.l.f.).

The action of developers is explained by taking into account that these reducing substances have a tendency to give off electrons. These electrons are deposited on Ag specks produced by the action of the light at the surface of the grain, and are then neutralized by Ag-ion diffusion until the entire grain is reduced in a similar way as has been assumed for direct photolysis.

The sensitization by dyes is explained by assuming that a suitable adsorbed dye molecule can, after absorption of a quantum of light, bring one of its own electrons into the conduction levels of the AgBr grain. The electron is trapped and attracts Ag^+ to form

Ag as discussed before; the positive dye ion is neutralized by the charge of a Br⁻ ion which becomes superfluous as soon as an Ag^+ ion is reduced to Ag.

The HERSCHEL effect of latent image erasure by infrared radiation is explained by remarking that these quanta are absorbed by Ag but not by AgBr. Their absorption in small Ag aggregates causes a photoelectric effect, i.e. sends away an electron into the crystal which may become lost. The remaining positive Ag aggregate is neutralized by sending away an Ag^+ ion into the lattice; repetition of this process reduces the latent image to zero.

Finally we remark that the explanation of the WEIGERT-effect of photo adaptation, given by CAMERON and TAYLOR [20]) in 1934 as a result of investigations on Ag-AgCl systems runs practically along the same lines as the GURNEY-MOTT theory for the HERSCHEL effect.

Though its versatility renders the theory most valuable, much remains to be done before a quantitative explanation of these phenomena will be possible.

§ 5. The scope of this thesis.

The work to be presented in this thesis consists of several more or less independent parts that are partly of an experimental and partly of a theoretical nature.

E x p e r i m e n t a l   P a r t.

The work of JURRIENS [10]) on the production of direct density, for exposures just above the region of ordinary exposures for development, with the aid of sensitive absorption measurements, had revealed a few points which we wished to investigate more closely.

This author reports, that with blue light the $(d; t)_I$ curves are straight lines for low exposures; for higher exposures they can be described by a (1 — exponential) saturation formula with the remarkably low saturation density of ca. 0.1. The reciprocity law failure decreases for low values of the exposure so that it is probably absent for direct densities, corresponding to

latent images of exposures that would yield intermediate densities after development. It is of course still present for the developed densities themselves.

The $(d; t)_I$ curves for weakly absorbed radiations (e.g. red) show a marked S-shape, qualitatively resembling developed density-time curves.

Our purpose was to investigate:

1. to what extent the mentioned resemblance is inherent or accidental.

2. the causes for the S-shape of the $(d; t)$ curves and its wavelength dependence.

3. the causes, responsible for the low saturation value.

In the course of the investigation a few related questions presented themselves.

The experimental arrangement and method is described in Ch. II. The measurements, results and discussions are to be found in Ch. III.

Theoretical Part.

In the first place we shall discuss the GURNEY-MOTT theory somewhat more closely. In view of certain quantitative experimental results in literature we shall propose a modification of this theory. (Ch. IV).

In the second place we shall discuss the effect of a mixture of colours on a photographic plate in relation to the effects of the separate components (addition law). We shall see that the empirical VAN KREVELD addition law [13]) must be an approximation. From the GURNEY-MOTT theory we deduce a theoretical addition law which, however, appears to differ not much from VAN KREVELD's law for many practical applications and may thus be considered as its theoretical basis (Ch. V).

In the third place we shall discuss the "intermittency effect". It is well known that the density produced by intermittently irradiated energy generally depends on the conditions of the irradiation (frequency, dark to light ratio, average intensity etc.). For high and for low frequencies of intermittency WEBB linked this effect to the reciprocity law failure. Moreover the discussion

of the experiments, given by WEBB [21]) and by SILBERSTEIN and WEBB [22]) showed that the photographic unit of action, that is the region within which the absorption of a quantum can lead to the production of the same final Ag speck, is of the order of magnitude of one grain. We shall quantitatively extend the theory of this effect to the region of the intermediate frequencies, showing that WEBB's experimental results can be understood entirely in this region on principally the same basis as for high and low frequencies (Ch. VI).

Finally we shall give a comparative discussion of some problems and methods, common to photography and radiobiology (Ch. VII).

CHAPTER II.

APPARATUS AND METHOD FOR THE MEASUREMENT OF DIRECT DENSITY.

§ 6. Apparatus.

We carried out our investigation with the apparatus of JURRIENS, for the measurement of direct density, which we improved in several respects. We arrived after some trials at the arrangement represented schematically in fig. 4. The light source LS, a 125 V 500 W tungsten filament lamp, was connected with the laboratory's constant tension 130 V batteries (constancy $1^0/_{00}$). It was placed in front of the lens L (f = 16 cm) at a distance of 20 cm at such an inclination that the illumination of the lens was as homogeneous as possible. The light passed through a 2 cm water filter W and a set of filters F1 (SCHOTT & Gen. BG17, 3 mm and OG2, 2 mm, transmitting about 10 % at 9000 Å, 60 % at 8000 Å, 100 % between 7000 Å and 5800 Å and 0 % for wave lengths below 5500 Å cf. fig. 5) and a shutter S. An image of the filament was formed at a distance of 70 cm on the lens L2 (f = 26 cm) which in turn focussed L via the mirror M and the diaphragm D2 on the photographic plate P.

The intensity of this light could be varied with the aid of different diaphragms D1.

The light, transmitted by the plate falls through a diaphragm D3 and a filter F4 on a Weston barrier layer cell Ph1. In general F4 was an RG2 filter (2 mm), transmitting $\lambda > 6300$ Å. So the "measuring" light and the "acting" light are obtained from the same beam with different filters.

The cell Ph1 was contained in a hermetically closed glassbox

with some $CaCl_2$, which improved its constancy. It was connected with a similar cell Ph2, and with a MOLL-galvanometer G. The second cell received its light from the same lamp LS through a red filter F2 and some milk glass weakeners; its distance to LS could be adjusted accurately so that it almost compensated the action of the first cell.
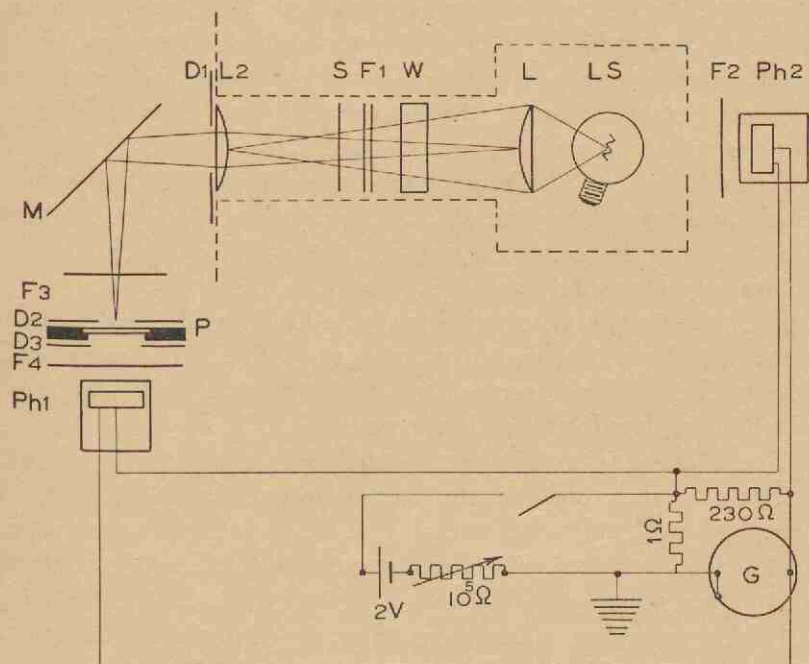
Fig. 4.

Schematical diagram of the apparatus for the production and measurement of direct density. LS = light source; L = lens (f = 16 cm); W = 2 cm water filter; Fl = SCHOTT filter BG17 (3 mm) + OG2 (2 mm); S = shutter; L2 = lens (f = 26 cm); D1 = diaphragm for intensity control; M = mirror; F3 = orange OG3 (2 mm) or red RG1 (2 mm) filter; P = photographic plate; D2 and D3 are diaphragms to avoid spurious light; Ph1 and Ph2 are Weston barrier layer cells; F4 = red RG2 (2 mm) filter; G = galvanometer. The optical part of the figure is a projection on a vertical plane.

The deflection of the galvanometer could either be registered on a drum with photographic paper driven by a synchronous motor

or read off at a scale, both at ca. 4 meters distance. A suitable shunt made the deflection aperiodic.

A strip of 1.5 × 22 cm cut out of a photographic plate of 10 × 25 cm or 18 × 24 cm lay on a carriage which could move perpendicularly to the plane of drawing; by moving the carriage we could expose various parts of the plate to the light, incident through D2. At the end of the carriage a vacuum thermoelement was placed which was in the center of the light spot when the carriage was at an end stop. It was connected with an other MOLL-galvanometer, adapted to its small resistance, and served for accurate determination of the intensity of the "acting" light at the spot of the plate ("measuring spot").

At the other end of the carriage a milkglas was fixed, adjoining to the photographic plate. It had been chosen so as to have practically the same transmission of light to Ph1 as the plate.

Stray light was duly shielded.

If exposed strips were to be developed this was done with metol borax developer [23]), during 6 min. at 18° C. The strip was developed in a large sort of test tube containing the developer which was placed into a thermostate.

The developed density of such strips was measured (after fixing, washing and drying) in the same arrangement as the direct densities. Incidentally we remark that the densities of such strips up to ca. 2, measured with our apparatus and with a MOLL microphotometer, are proportional within ± 3 %, their ratio being 1.40.

In the sequel we indicate the three types of acting light that were mostly used by yellow, orange and red. The meaning of these terms will be:

yellow = light transmitted by BG17 + OG2 without F3
          (cutt off at ca. 5650 Å).
orange = light transmitted by BG17 + OG2 and OG3 at F3
          (cutt off at ca. 5800 Å).
red   = light transmitted by BG17 + OG2 and RG1 at F3
          (cut off at ca. 6050 Å).

The intensity of the acting light, incident on P, will be expressed in relative units. In order to convert these units into absolute ones we have determined one intensity with the aid of an absolutely

standardized thermopile too. In this way we obtained: 1 relative unit $= 1.3 \times 10^3$ erg/cm². sec.

The relative spectral intensities of the various types of acting light used were determined by comparing them through a double monochromator with the radiation of a standardized tungsten band filament lamp. The results are shown in fig. 5. We emphasize that the plates show such a steep gradient of absorption in the wave length region concerned that practically only the shortest wave lengths present in the beam are active in density production.
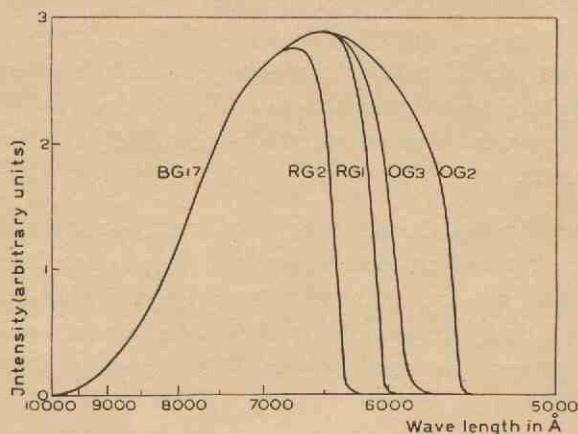
Fig. 5.

Relative spectral intensities of the measuring light and of various colours of the acting light. The filters indicated cause the gradients near which their symbols are placed.

§ 7. Production and measurement of direct density.

After a number of check experiments (see § 8) the following procedure for the production and measurement of (d; t) curves was adopted as being most satisfactory.

1. One hour previous to the beginning of a measurement the light source LS was switched on, the shutter S was open, the light went through the diaphragm D1, the filters of the right colour and through the milk glass. The current through LS was adjusted to 3.90 Amp. and checked from time to time. The filter F2 and

the position of the cell Ph2 were adjusted in such a way that small changes in intensity of LS caused no galvanometer deflection. Since the spectral transmission of F2 was not the same as that of W + F1 + F3 + F4, the required point where compensation of intensity variations is achieved is not quite the same as the point where the entire deflection is compensated. An additional electrical compensation (see fig. 4) brought the galvanometer image back to the desired region of the scale or registration drum if necessary.

2. The position of the galvanometer image was observed from time to time and when it had become very well constant (after ca. 1 hour) its deflection on shutting S was measured, then the carriage was moved to the other end, so that the thermoelement received light after opening S again. The deflection of the other galvanometer was a proportional measure of the intensity in arbitrary units.

3. Meanwhile a plate strip was freed from backing, the shutter S closed, the strip laid on the carriage and the carriage moved to the milk glass end, whereupon S was opened again. Points 2 and 3 were handled as quickly as possible, to obtain a stationary galvanometer deflection as soon as possible (see § 8, properties of the barrier layer cell).

4. After about 10 min. the image was well stationary and was registered. The carriage was moved so as to expose a first spot on the plate which was not registered; the transmission of the milk glass and the plate were practically equal, but for adaptation of the cell after the small differences we waited one minute and moved then to the next spot, which was registered.

At the end of a period of about 30 min. the milk glass was again registered and then the same procedure of adaptation and registration of a following spot was repeated, as many times as the length of a strip allowed.

5. At the end again milk glass, dark and thermoelement intensity measurements as in 2 and 3 were performed.

6. The registration drum rotated once in 2 h. 30 m. so that one paper contained four deflection-time curves, each one enclosed

between two milk glass registrations, which were afterwards connected by a straight line (of small slope) in order to take into account the drift of the entire device. The correctness of such a linear interpolation was checked by the continuity of successive lines. An eventual error, introduced by this procedure was much smaller than the scattering of the individual curves; moreover it was usually cancelled by the averaging of several observations (see § 9).

The registration was then converted into a density-time curve by correcting for this drift and taking into account the value of the entire deflection deduced from 2 and 5.

In a few cases the registration was replaced by scale readings; if the exposure had to be followed longer than $\frac{1}{2}$ hour the latter procedure was always applied and the drift of the device was followed by intercepting the beam once in 10 minutes between P and Ph1.

§ 8. Experimental details.

For the sake of completeness we present here a list of experimental details, checks and difficulties connected with the measurements.

1. Constancy of light.

During the exposures the current of LS was checked from time to time. A few registrations for which the measurement of intensity with the thermoelement at the beginning and at the end of a set of about 8 registrations differed more than 2 % were discarded.

2. Homogenity of light spot.

The vacuum thermoelement was mounted on the carriage in such a way that it could be placed in any part of the light spot. The image of L at P had a diameter of ca. 35 mm; D2 was placed so as to transmit the best 8 mm, which did nowhere differ more than 1 % from the mean value. The entire 35 mm spot showed largest deviations of $\pm$ 7 %, due to the inhomogeneous emission of LS in different directions (inhomogeneous illumination of L). The position and inclination of LS had been adjusted so as to reduce these inhomogenities as much as possible.

3. Constancy of velocity of registration drum.

The gears of the slowly rotating drum were revised to make it go as

3

regularly as possible. This was checked with registration of flashes of known intervals.

4. Leak currents and spurious E.M.F.'s.

The galvanometer house and circuit was grounded. All resistances etc. stood on grounded plates. The number of wire connections was minimal. They were insulated thermically with cotton-wool. Later the galvanometer was placed under a glass box filled up with cotton-wool and containing a cup with $CaCl_2$ to insure still better freedom from thermal influences and humidity, which might cause thermo- or chemo-E.M.F.'s. The blank registration, without illumination of the cells, was under these circumstances very satisfactory, showing fluctuations of ca. 0,3 mm.

5. The barrier layer cells.

Several Weston "photronic cells" at our disposal were tested for constancy. The two best ones were used, after the experience of JURRIENS in hermetically closed dry glass boxes containing $CaCl_2$. During their use their constancy decreased, so that they showed disagreeable sensitivity fluctuations on the registration of about 0.001 % later up to 0.01 % of the deflection with the unexposed plates. This percentage was almost independent of the intensity. The fluctuations were rather annoying for our compensation measurements.

An a.c. photoelectric-cell amplifier after MILATZ [24]) would have been the other alternative for the measurements. After this author the device shows an inconstancy of the same order of magnitude, (10^{-5}) for a light intensity of 1 erg/sec.cm². Preliminary experiments with higher intensities yielded a relative inconstancy of the same order of magnitude, the nature of which we have not traced.

Though the use of the amplifier would have had the additional advantage of weaker intensities of the measuring light, we sticked to the Weston cells, since they were at that time just as constant, and their use was less complicated.

Both compensating cells were connected parallelly with the galvanometer as indicated in fig. 4. This way yields larger deflections and better constancy of the cells than if they are connected in series [25]). The time of indication of a cell depends on the intensity change it undergoes. It is largest for large changes. It took sometimes many minutes before the deflection became constant. Therefore we have always taken care to make intensity changes small (see § 7, 4). For small or slow changes the time of indication is about 5 seconds.

The long times of adaptation before every set of experiments were necessitated entirely by these cells. It may be mentioned that if the cells suffered large intensity changes, they became constant sooner if they were at the same intensity level before and suffered the large changes only for a short time of the order of 10 minutes (see § 7, 5). The galvanometer deflection, after becoming constant, is well proportional to the intensity, determined by the thermoelement. However it shows a temperature dependence of $+ 1.5$ %/°C. In our cellar room the

temperature varied during one day never more than 2°; the drift caused thereby was small since it was for the greater part compensated by the other cell.

6. The diaphragm D1.

This diaphragm served to vary the intensity of the light without changing its relative spectral composition. In connection with the shape of the filament of LS, which consisted of six vertical wire spirals, the shape of D1 was a horizontal rectangular slit. With the aid of the vacuum thermoelement (cf. no. 2) we found that its interposition did not decrease the homogenity. Round or other diaphragms, wire gauze, etc. appeared to cause a large inhomogenity of the light spot on the plate.

7. Comparison with JURRIENS' method of measurement.

In contrast to the method, employed by this author we preferred to let the plate stand still, so that both the measuring and the acting light went continuously through the same part of a plate, allowing a much more economical use of plates. On the other hand local irregularities of the plate sensitivity became much more evident (see § 9).

Our measuring light was many times more intense than in JURRIENS' case, so that it served also as acting light, and increased the sensitivity. The heat production of our larger light source does not allow to place it immediately below the plate, as was done by JURRIENS, but necessitates a large distance between it and the plate and cell. In order to avoid convection near the plate and still have a large intensity we intercalated the system of lenses L1—L2 into the beam. The convenience of working with the plate horizontally, combined with the requirement for stability of the entire arrangement, led to the introduction of the mirror M.

For experiments with blue acting light (necessarily of much smaller intensity than red light) the mirror M could be replaced by a glass plate which reduced the red light and allowed the blue light from an auxiliary light source to reach the plate from above, but this device has not yet been used up to the present.

In connection with the higher light intensities applied, the sensitivity of our arrangement was 3 to 10 times that of JURRIENS, depending on circumstances. Due to the mentioned proportionality of the cell current and its fluctuations, this gain did not result in an increased accuracy. However, by using a smaller diaphragm D2, this state of affairs allowed a much more economical use of the plates.

We did not use the milk glass amplification, in order to reduce as much as possible complications arising from the multiple scattering of the light, especially for the interpretation of the higher densities. The cell Ph1 was placed below the plate in such a way as to cover a solid angle of about 1 steradian, which we deemed sufficient to measure a density, mainly due to absorption of the Ag.

§ 9. Reproducibility of the material for measurements with red light.

Jurriens' results with blue light showed a remarkable reproducibility (within ± 3 %) notwithstanding great variations in coating thickness (± 20 %) on various plates or on various spots of one plate. This reproducibility was, according to this author, probably due to the large absorption of the plate for blue light, which restricts the principal part of the density production to a thin superficial layer of the emulsion.
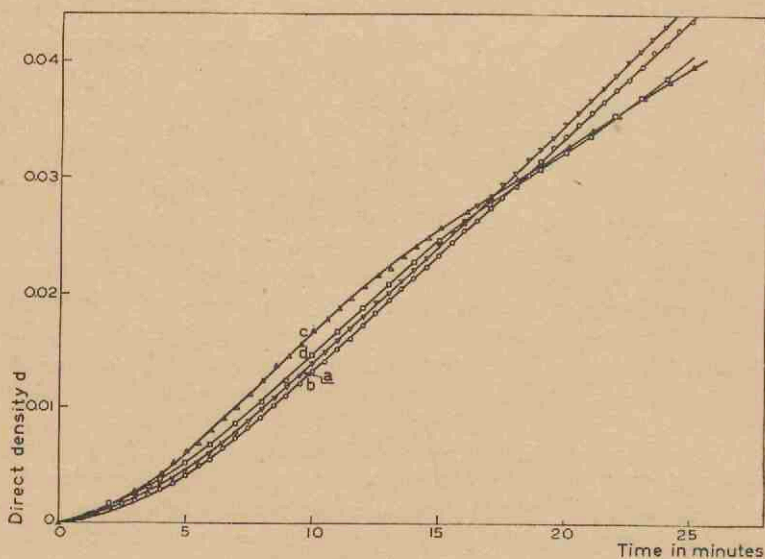
Fig. 6.

Direct density-time curves with equal intensities of red light on neighboring spots of one plate (a, b, c) and on another plate of the same package (d).

A great disadvantage of the measurements with red light was a remarkable irreproducibility, due to the relatively small absorption, combined with variations in coating thickness and probably also other factors (see below). This means that (d; t) curves can be obtained safely by this method, but (d; I) curves have to be considered with reserve, because in the former case only one spot

is illuminated, whereas in the latter one we have to use as many spots as intensities.

To illustrate this dispersion we represent in fig. 6 a number of (d; t) curves obtained with red light (RG1). The curves a, b, c were obtained at various spots of one plate, curve d belongs to another plate of the same package. The figure is characteristic for the dispersion of the results and for the general type of the curves.

The deviations between the curves are much larger than the dispersion of the points along any one of the curves. So the former ones are due to variations of the plate rather than to inaccuracies of the method of measurement.

The deviations were not correlated with the extinction of the unexposed plate which consists mainly of scattering. We have also checked the dependence on temperature roughly by performing two experiments, one after another on neighboring spots of one plate. In the first experiment the density curve was taken with a föhn blowing air of room temperature towards the illuminated spot. In the second experiment the föhn blew air of 40° C. The latter curve showed a more pronounced S-shape and the sensitivity increased about 20 %. Roughly this indicates that the temperature sensitivity for this intensity is of the order of 1 %/° C.

However the temperature deviations of the experiments represented in fig. 6 were less than 2° so that this cannot account for the deviations observed between the curves.

Another factor which might possibly cause systematic errors is the humidity. We have performed similar experiments on days when our room was very dry and on other days when it was very humid, but could not observe any correlation herewith. See however for the effect of water § 16.

We have spent much time on checks for all sorts of possible systematic errors, but we have not succeeded to make the reported dispersion disappear.

Since the shortest wave lengths that are present in our beam are the most active ones in the production of direct density, owing to the rapid decrease of AgBr absorption with increasing wave length, we remark tentatively that variations of the absorption spectra of the grains at various regions of the plate, which may eventually be due to adsorbed ions or ion-groups (see e.g. [3]) p. 96) or a

sensitization by traces of some substance, which are not distributed homogeneously, may be the main cause for the observed lack of reproducibility.

We mention in this connection that red exposures taken with the purpose of detecting changes of the latent image between exposure and development, showed a similar unexplained large scattering.

Finally we adopted the procedure to average always 7 to 9 curves obtained from one strip. But still these averages showed considerable variations from strip to strip (cut out of one plate), much more than could be expected from the dispersion of the 7 or 9 individual curves of one strip. Of course the first and last strip of a plate were discarded; they showed still larger deviations. Also the first and last place of each strip were never used to avoid effects of inhomogenity near the edges of a plate.

MEASUREMENTS OF DIRECT DENSITY. *)

§ 10. On the similarity between direct and developed density-exposure curves.

Developed-density-exposure curves (cf. § 3, fig. 1) and direct-density-exposure curves especially for red light show a striking resemblance. The latter ones start with a more or less pronounced S-shape (fig. 8), followed by a straight part, with a tendency towards saturation for still higher densities (fig. 13 or JURRIENS [10] fig. 19). We wish to see to what extent this similarity is accidental. This will be discussed in three parts, corresponding to the division of the curves (fig. 1) into regions of low densities, of intermediate ones and of saturation. Experiments to be described below show that exposures to red light, producing equal direct and developed densities, differ much. We shall reverse the order in which we shall consider these regions because we mainly investigated experimentally the region of low densities.

1. The region of saturation.

Saturation for developed density would be expected when all grains can be developed chemically and for print-out density when all grains are entirely photolysed. For the latter case more exposure would be needed, but finally the same density would be reached, since in both cases the total amount of AgBr contained in the plate is reduced to Ag. But things are not so simple.

The solarization and high order reversals, of which up to eight have been observed [14], are complications which set in at densities often far below the theoretical maximum. Several theories exist

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about solarization [3]). We believe that experiments have shown sufficiently clearly that it is a complication which is due to the development. The number of developed grains, plotted against log exposure, do not or hardly show this peculiarity [3]) fig. 118, p. 179; neither does the print-out density-exposure relation show remarkable features in this region of exposures [10]). Moreover several authors report that the effect disappears if development is prolonged appreciably [26] [27]).

For high exposures the print-out density tends towards saturation without reversal (see e.g § 15 and [3]) p. 141). The saturation density is much lower than for developed densities. So we conclude that the saturation effects are due to different causes.

2. The region of intermediate densities.

A related behaviour of print-out and developed density in this region can hardly be expected, if the entirely different ways are considered in which the two types of density are produced.

For the direct effect all grains take part in producing density. In each grain the silver coagulates at the sensitivity spots which are distributed throughout its volume [3]) p. 141. With increasing exposure these specks grow; soon their number remains almost constant (ca. 1000 cf. § 11).

In the case of the developed density the grains, on the surface of which at least one sufficiently large speck of Ag has been produced by the exposure, will be developed entirely, and the other grains are not developed at all. So with increasing exposure the number of developable grains increases, the average size of the developable grain on the contrary does not change much [3]) p. 233 and 267.

So if we should expose a plate of identical grains to light in such a way that all grains absorbed quanta simultaneously, the direct density would gradually increase with exposure, but the developable density would show the abrupt course of line 1 in fig. 7.

The reason why the developable-density-exposure relation has in reality a similar shape as the direct one, is that the former is a superposition of many such abrupt curves with scattered values of the parameters that determine the value of the threshold in each

grain, which superposition yields a curve of type 2 fig. 7. The causes which are most likely responsible for this effect are:

1. variations in the number of quanta absorbed in each grain, due to:

    a. essential statistic fluctuations in this number,

    b. non-homogenity of the light intensity throughout the plate,

    c. variations of grain size,

    d. possible variations of the absorption coefficient for different grains;

2. variations in the number of absorbed quanta required to produce developability, due to:

    a. variations in the effect of the ripening process, (e.g. in the number of sensitivity specks per grain and their location with respect to the surface),

    b. variations in grain size,

    c. variations in the statistics of intervals between absorptions (see Ch. VI).
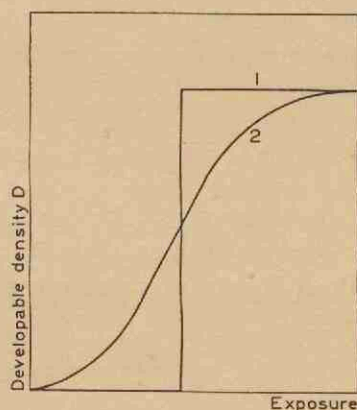
Fig. 7.

Schematical representation of the developable density as a function of exposure; curve 1 for simultaneous effective absorptions in each grain; curve 2 for absorptions that fluctuate from grain to grain, which corresponds to a superposition of curves of the first type with some distribution of threshold values.

Several efforts to explain the entire shape of the density-exposure relation only on the basis of 1b and 1c or 2a may be found in literature, and especially the treatment of the influence of 1b and 1c by SILBERSTEIN and TRIVELLI [28]) indicates that these factors are important, though on the other hand WEBB [29]) showed convincingly that the influence of 2a may not be neglected. Mainly these causes make a quantitative understanding of the developed density-exposure relation difficult. However they all lead to

the conclusion that an essential similarity between direct and developed density production can hardly be expected in this region.

3. The region of low densities.

If the thresholds for direct and developed density are mainly due to the same causes, they should lie at the same exposure. JURRIENS' direct density-exposure curves showed a slight indication of a non-
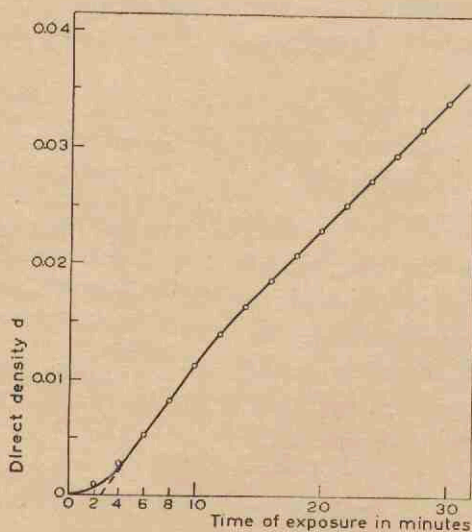
Fig. 8.

Direct density as a function of time of exposure, with red light (same intensity as in fig. 9).

linear course near the origin for blue light, but quantitative comparison of the two thresholds was not possible from his measurements. However, for red light the direct threshold becomes pronounced, so that an investigation of a possible analogy between the thresholds seemed promising.

Experimental difficulties prevented a comparison of the

thresholds for blue light. Though we succeeded to increase the sensitivity of the method of JURRIENS for the measurement of direct density several times, an increase by a factor 100 could not be achieved. This would have been required to measure direct densities in the reigon of exposures corresponding to developed densities not far above the threshold for blue light. So we had to content ourselves with experiments on exposures with red light. Here both thresholds were well within the region of measurement.

The experiments were performed with the arrangement, described in Ch. II. We used Ilford Special Rapid plates (extra sensitive H. & D. 400). Both the acting light and the measuring light were "red RG1." (see § 7).

On one strip a number of identical exposures were performed and the direct density as a function of time was recorded. The average result and its mean error is represented in fig. 8. The well pronounced S-shape in this direct-density-time curve has its threshold at an exposure of $I = 27$ (arb. units cf. Ch. 2) and $t = 2.3$ min.

On each one of three similar strips exposures were made at the same intensity but with various times of exposure. The strips were developed (see Ch. II), fixed, washed and dried. The concentration of the developer was different for these three strips namely: the normal concentration = 1, 0.1, and 0.03.

The results indicate that for this intensity an exposure of 2.3 min. produces almost saturation density after development, hence we may conclude that a common basis of the thresholds does not exist.

The direct threshold will be discussed somewhat more closely in § 17. The conclusion that the thresholds are not linked was probable a priori, owing to the well known experiments of REINDERS and BEUKERS, who showed that the developed threshold is probably an effect of development. These authors proved that physical development of a glass plate on which minute quantities of silver had been condensed, was possible only if the silver occurred in aggregates of several atoms. The transposition of this conclusion

to a photographic emulsion introduces some uncertainty which justified the attack of this question from an other side.

Additionally we exposed similar strips during shorter times and to lower intensities, in order to see how much the direct and developed thresholds differed. The lower intensities were obtained both with the aid of diaphragms (see Ch. II) and with a neutral glass NG3 (SCHOTT and Gen.) of ca. 12 % transmission for the wave length region concerned. Thus we observed that the developed threshold was situated:

in a (D; t) plot for I = 6 at t = 8.5 sec.

in a (D; t) plot for I = 12 at t = 4.5 sec. (see fig. 9).

in a (D; I) plot for t = 5 sec. at I = 11.

Fig. 9.

Developable density as a function of time of exposure, with red light (same intensity as in fig. 8).

The results confirm the well known fact that the threshold does hardly depend on I or t separately, but lies at an almost constant exposure of I×t = ca. 55. Moreover they show that the developed inertia is about 1/600th of the direct one. This figure may be dependent on circumstances, but shows the order of magnitude. We wished to see, whether there is an indication, that the two thresholds would come closer together if the degree of development approaches zero. If this should be the case, it would indicate that the difference in threshold is caused, at least partly, by the development. In order to keep all other conditions constant we decreased development by applying smaller concentrations of the developer, each one during the same time of development. For this purpose we exposed each one of four strips to a given intensity during various times, so that the results would allow a determination of
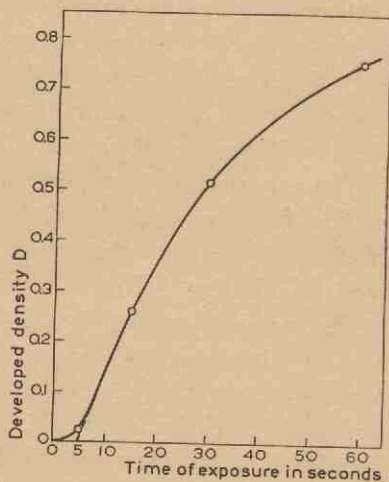
the developed threshold. The strips were developed in concentrations 1, 0.33, 0.067 and 0.033, during 6 min.

The results confirmed the general expectation that the developed threshold is almost independent of the degree of development. A slight tendency was observed in the sense of a decrease of the threshold for lower concentrations of the developer.

We conclude herefrom that both thresholds are not merely quantitatively but also qualitatively different phenomena.

The fact that the difference between the thresholds remains, if development is extrapolated to concentration zero, is probably due to the fixing process, the influence of which upon directly blackened plates is to erase completely densities up to more than 0.05 as was shown by the following experiments. We "fixed" a number of strips with direct densities of 0.007 and 0.05 in fixing solutions of $NaHSO_3$ to which suitable amounts of $NaOH$ were added. The pH of the solutions was determined with a COLEMAN pH-meter and varied between 5.7 and 9. In all cases the direct density decreased so much that not a trace of it could be seen nor measured.

For fully developed plates this effect is not present to a comparable extent, which is probably due to the much larger size of developed Ag grains as compared with the Ag specks of direct blackening.

§ 11. On the relation between direct density and amount of silver (latent image).

An interpretation of the shape of direct-density-exposure curves in terms of photo-silver requires, that the relation between the direct density d and the amount of silver A shall be known.

It is not our purpose to determine the relation between d and A in a strictly quantitative sense e.g. by entering into a detailed discussion of the absorption and sattering of Ag-AgBr-gelatin systems such as the photographic plate; our problem is merely to what extent these quantities are more or less proportional, so that an S-shaped (d; t) curve corresponds to a similar (A; t) curve.

Several arguments suggest that for not too high direct densities the two quantities are proportional. We mention the remarkably

simple relation, found by JURRIENS, for blue light between direct density and exposure. Also we refer to EGGERT and NODDACK [3]) p. 133, who proved chemically that for higher print-out exposures each quantum yields one Ag atom approximately.

The same authors [3]) p. 145, performed experiments which proved that, though the developable latent image of a rather large exposure is erased by a $FeCl_3$ treatment which reoxidizes the Ag at the surface of the grains, 99 % of the photolytic Ag remained unchanged by this treatment. In other words only 1 % was destroyed by $FeCl_3$, or only 1 % was present at the surface of the grains. On the other hand experiments of TOY, SVEDBERG e.a. with microscopic observations of partially developed grains, indicated that the number of spots where the Ag is coagulated or concentrated at the surface is of the order of 10. So the number of specks throughout the volume is ca. 1000. JURRIENS applied exposures in the region considered of the order of $10^{12} - 10^{15}$ quanta/cm². After EGGERT and NODDACK [3]) p. 100, the grains absorb 1/5 th of the light. Since the number of grains/cm² is ca. 10^9, these exposures correspond to ca. $200 - 2.10^5$ quanta absorbed per grain, which means on the average a few — ca. 200 atoms per silver speck (linear dimensions up to ca. 6 atoms). This is still quite small compared with the wave length of light, so that linearity of amount of silver and absorption may be assumed.

On the other hand the straightness of JURRIENS' curves shows that the absorption of the silver per atom is independent of the size of the silver specks, even if it consists of a few atoms only.

We must be aware, however, of two indications which warn for too easy acceptance of this proportionality.

Firstly we know from experiments of WEBB, performed in connection with investigations of reciprocity law failure for developed density, that for very low exposures the efficiency of latent-image formation depends largely on the intensity or rate at which a number of quanta is admitted. In this region of exposures, which cause direct densities far too low to be measurable at present, simple proportionality of exposure and direct density can hardly be expected, so that the arguments fail there.

In the second place the results of JURRIENS show small but systematic deviations from proportionality, in the sense that his straight density-time curves pass above the origin (see § 12). Experiments and discussions to be presented below will sustain the conclusion that both the density and the silver production deviate from proportionality with exposure in this region.

These remarks all tend to show that the amount of silver A and the direct density d are proportional or almost proportional in the region concerned, which is of importance as soon as we have to discuss density time curves, e.g. produced by red radiation, which show a marked S-shape. From what has been said it is likely that such an S-shape is also present in the corresponding (A; t) relation.

The S-shape is not caused by the colour of the measuring light: a plate was exposed by JURRIENS to blue light, which yielded straight (d; t) lines, and to red light, which yielded S-shaped ones but the density was always measured with the same red light.

We have performed similar check experiments by registering one (d; t) curve, with yellow acting and measuring light, one with yellow acting and red measuring light, and one with red acting and red measuring light (see Ch. II). The first and second curve were similar; their difference amounted to a small constant percentage in the density direction. The second and third curve were entirely different (for a closer description of the qualitatively different shapes of (d; t) curves produced by yellow and red light see § 12). From these experiments it follows that, within the wave-length region in which the shape of the (d; t) curves changes considerably, its shape does not depend on the wave length of the measuring light. In other words the S-shapes are not due to a special wave-length dependence of the absorption of the Ag specks for the measuring light, but indicate S-shaped (A; t) relations.

For higher densities the (A; d) relation naturally becomes more complicated than simple proportionality but there is no reason to expect serious disturbance of the analogous behaviour of (A; t) and (d; t) curves, until for still larger specks, the magnitude of which becomes comparable with the wave length of light in AgBr, special resonance absorptions may become important (CAMERON and TAYLOR [20]).

§ 12. Direct density-time curves at low densities for various colours.

Fig. 10 represents a few (d; t) curves, for low densities. The curves "red", "orange" and "yellow" were obtained following the normal procedure described in Ch. II. The curve marked "blue" is taken from the work of JURRIENS for comparison.

We notice, that with increasing wave length the S-shape becomes more pronounced, at first in the upper part and then in the lower part. Furthermore a remarkably straight part appears for higher exposures, also for those colours which show a pronounced S-shape for low exposures. Its produced part passes above the origin.
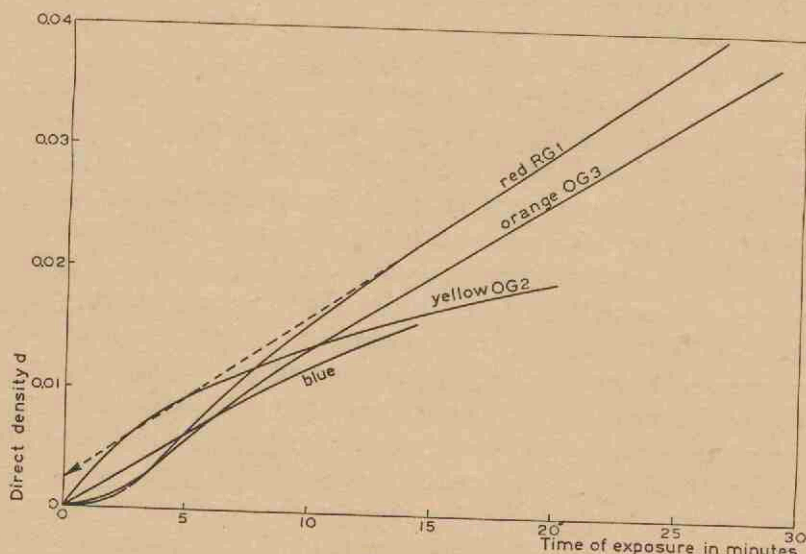
Fig. 10.

Direct density as a function of time of exposure for various colours.

These observations suggest that the straight part of the curves is extended towards the origin with decreasing wave length. Indeed, upon closer consideration the "straight" lines, observed by JURRIENS for blue light, show distinct remnants of the S-shape, which is present so distinctly for red light, in the neighborhood of the origin. We refer in this connection to fig. 11 (blue light), and to table I of the thesis of this author, which indicate that straight lines fitting best the experimental points, systematically pass above the origin.

This makes doubtful the extrapolation of JURRIENS' conclusion that the latent image is proportional to the exposure, into the region of ordinary exposures for development. On the other hand, it suggests that for a study of the direct density in the latter region,

one has either to improve greatly the accuracy of the method, or one may study this matter for red irradiation, and see to what extent the phenomena observed there can be expected to appear on a smaller scale for blue irradiation.

Since we have not succeeded sufficiently in the first way we have chosen the second one.

§ 13. Experiments with various kinds of plates.

We have performed a few qualitative experiments with Ilford plates with orthochromatic and panachromatic sensitization. The results indicate that the S-shape is slightly connected with the rate of absorption of the considered wave lengths; for the ortho-chromatic plates somewhat longer wave lengths were required to produce an S-shape, than with ordinary "Ilford special rapid plates", and this effect was also present with panchromatic plates. However, the differences appeared to be not so pronounced as would cor-respond to the shift of the limit of active wave lengths due to the sensitisation.

The longer wave lengths were obtained with the aid of Schott-glasses RG2, 5, 8, 10 with cut-off wave lengths 6300, 6750, 7000, 7800 Å respectively.

§ 14. Experiments at various intensities of red and orange irradiation.

Notwithstanding the difficulties mentioned in § 8 we deemed a comparison of (d; t) curves at various intensities worth while. The results show a large dispersion. We give in the figures, presented in this section, averages of 7 or 9 individual observations taken immediately one after another on one strip of a plate. The error of this mean as determined by the deviations of the individual observations amounts to about $\varDelta D = 0.0007$. For some reason which is so far not understood, observations on different strips of the same plate deviate much more than this amount (cf. § 9).

We have represented (d; t) curves without measuring points, because they were continuously registered; so the mean error in the curves is not shown in the figures.

4
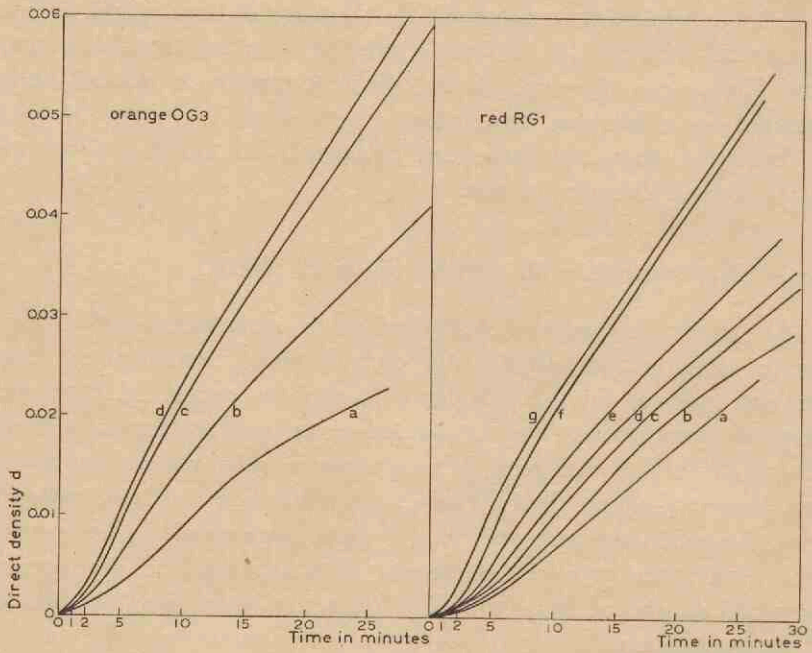
Fig. 11.

Direct density as a function of time of exposure for various intensities.

Orange OG3.		Red RG1.	
curve	intensity (arb. units)	curve	intensity (arb. units)
a	6.1	a	11.4
		b	16.8
b	13.4	c	21.7
		d	24.8
c	19.7	e	32.6
		f	39.5
d	25.3	g	49.9

Certain main lines can be deduced from these results though. In fig. 11 we present sets of (d; t) curves for various values of the intensity I, of orange OG3 and red RG1 radiation respectively. The curves show an S-shape, but are not similar, neither by multiplication in the d nor in the t direction. For high intensities their difference becomes relatively small. In order to characterize the curves we introduce four parameters namely: the steepest

gradient γ_m; the gradient in the straight part after the S-shape is passed γ; the density at which the inflection tangent reaches the ordinate axis δ_m, and the density at which the extension of the straight part reaches the ordinate axis δ. We have tabulated these quantities for all comparable data available in table I.
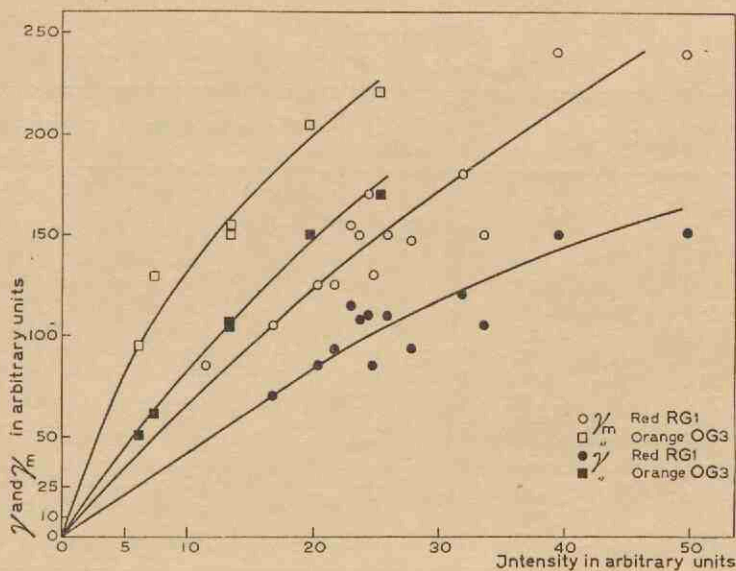
Fig. 12.

Slope of the inflection tangent γ_m and of the straight part γ of direct density-exposure curves as a function of intensity of orange and of red light.

We conclude herefrom that both δ_m and δ do not depend systematically on the intensity; probably their dependence on the wave length is very weak in this region; γ_m and γ are more or less proportional to each other and to I for low intensities, they appear to approach saturation for higher I values.

The dependence of γ and γ_m on I is illustrated in fig. 12. The fact that γ, which is d' for higher densities than 0.02 or 0.03, is only proportional to I for low values of the intensity, means that for higher intensities we have a definite reciprocity law failure. Namely the reciprocity law would require $d = d (I \times t)$ or $d' = I\varphi(d)$. Another way to express the same facts is, that the

density time curves cannot be made congruent by multiplying their scales with a constant factor. The SCHWARZSCHILD exponent p amounts for our intensity region to about 1.4. We have not checked p for these intensities and developed density. General evidence indicates that our intensity was below the optimum, so $p < 1$ for the developed density.

TABLE I.
Characteristics of (d: t) curves.

Intensity (arb. units)	γ_m (arb. units)	γ (arb. units)	$\delta_m \times 1000$	$\delta \times 1000$
A: Red RG 1				
11.4	85	—	4.3	—
16.8	105	70	4.8	3^s
20.4	125	85	4.3	3
21.7	125	95	4.8	2$^-$
23.0	155	115	5.2	1
23.7	150	108	4.8	2
24.4	170	110	6.5	3$^+$
24.8	130	85	4.3	3$^+$
25.9	150	110	5.4	1
27.8	147	94	4.5	5
31.9	180	120	4.3	4$^-$
32.6	150	105	4.8	3$^+$
39.5	240	150	4.8	2
49.9	240	150	3.6	3
		Average	4.8	3$^-$
B: Orange OG 3				
6.1	95	50	3.3	6.5
7.4	(130)	(60)	(6.5)	(6.5)
13.4	155	105	3.0	4.0
13.5	150	105	3.5	4.0
19.7	205	150	4.2	4.6
25.3	220	170	3.3	2.5
		Average	4.0	4.5

§ 15. Experiments on the course of (d: t) curves for higher densities.

The fact that JURRIENS' exponential formula implies a remarkably low maximum of density for blue irradiation (ca. 0.1) and that preliminary observations on (d: t) curves in red light showed a

similar behaviour in this respect, made it seem worth while to perform a few experiments in that direction. These experiments were performed with Ilford Special Rapid plates. The galvanometer deflections were not registered but read off at the scale. The zero was frequently checked without interrupting the exposure (§ 7). Fig. 13 shows a curve taken with yellow light and two curves with red light of high and of low intensity. A maximum density at some low value of d is not present, but a low rate of density production sets in at the region of densities near d = 0.3. The first part of the curve can be represented as the difference

Fig. 13.
Direct density as a function of (long) times of exposure.

of a slowly ascending linear function and an exponential part. To represent these experiments, the time scale had to be reduced by a factor 25 as compared with previous figures so that not much can be seen of the S-shape near the origin.

§ 16. Experiments on the influence of water.

We mentioned, that the humidity of the air is probably not responsible for the lack of reproducibility reported in § 8. These experiments led us into a side line, worth to be reported briefly, because the results are somewhat unexpected and not yet understood.

In a first set of experiments we compared the (d; t) curves of plates that were soaked in water and those of ordinary plates (Ilford Special Rapid, red light RG1). Of course the soaked plates were still wet during the exposure, and the gelatin was still swollen. The water changed the colour of the plates from yellow to greenish

so that the absorption of the wet plates was larger for the red light.

In accordance herewith the (d; t) curves rise steeper, almost proportionally by a factor of about 2. The effect was independent of the time during which the plate was soaked in the water, if this time was varied from 2 minutes to 25 minutes. Also after such plates had dried again, the green colour and the increased sensitivity for direct density production by red remained unaltered. Even after drying 4 days in a $CaCl_2$ exsiccator the results were the same, so that we have here an effect which is difficult to reverse. Incidentally we remark that the density at which the rate of density production becomes small, as exposed in § 15, is not altered.

However, this water treatment caused a strong desensitization for developed density production by the red light. So the direct density and the developed one are influenced by water in opposite ways.

§ 17. Discussion.

We are not able to give a definite interpretation of the experiments presented, but we wish to advance a few tentative remarks from the standpoint of the GURNEY-MOTT picture.

1. The S-shape of (d; t) curves for red light.

In § 11 we made plausible that the S-shape occurs both in (d; t) and (A; t) curves.

The HERSCHEL effect is known to occur in this wave-length region. This effect is present for latent images in the region suited for development, so if the Ag specks are relatively small and the direct density is below the region of our measurements. It has not or hardly been observed for higher direct densities, far above the region where the S-shape occurs [3] p. 322. The effect can be understood by the GURNEY-MOTT theory (see Ch. I and IV). Is the occurrence of the HERSCHEL effect perhaps related to that of the S-shape?

This question led us to consider the course of d', the time derivative of d. Fig. 14 and 15 represent d' against t and d respectively, pertaining to an exposure to orange light (OG3). We notice: d' rises from a very low value, probably almost zero, proportionally with time, corresponding to a quadratic rise of d

with t, then passes over a maximum and reaches an almost constant level with a slight decrease. If the HERSCHEL effect is connected with these effects, we have to consider d' as the difference of two functions, one for Ag production (I) and one for Ag destruction (II).

For low densities the rate of destruction d'_{II} of the HERSCHEL effect will be proportional to the direct density, that is to the number of absorptions in the Ag. The relative rate of destruction d'_{II}/d must then

Fig. 14.

Direct density d as function of time of exposure for orange OG3 (I = 13.4) (a) and its time derivative d' (b).

be constant for low densities and approach zero for higher densities; if we assume that d'_{II} has a course, similar to the dotted line II in fig. 15, we obtain for the total rate of production the sum of the ordinates of the original curve and of II which yields the ordinates of curve I. Possibly the shape of curve I is connected with changes in the absorption spectrum of the grain during the exposure (BECQUEREL effect). It lies at hand to interpret this effect as being due to the production of silver on the surface of the grains. It is known that the absorption of Ag^+ ions to AgBr causes a large shift of the limit of absorption towards

Fig. 15.

Schematical representation of constructive (I) and destructive (II) components of the rate of direct-density production.

the infrared, but we do not know of experiments concerning the effect of adsorbed Ag atoms on the absorption of AgBr. Whatever the precise cause may be, apparently the sensitivity does increase with density.

If these considerations are correct we may conclude that the simple (d; t) curves for blue light, where we have to do neither with a HERSCHEL effect nor with a BECQUEREL effect, are the most general ones and the S-shapes for red are due to additional complications which are essentially connected with the HERSCHEL effect and with the BECQUEREL effect.

2. The effect of water.

It is known [3]) p. 93, that adsorption of OH-ions shifts the absorption limit of AgBr towards the infrared. It is plausible that the change in colour of the emulsion and its i n c r e a s e d sensitivity for direct blackening after the water treatment is due to such an adsorption of OH-ions. The d e c r e a s e d sensitivity for developed-density formation, reported in § 16 possibly means that the OH-ions are adsorbed mainly in the neighborhood of (superficial) sensitivity specks. Owing to their negative charge photo-electrons will then preferably settle at specks in the interior of the grain, thus becoming inaccessible for the developer.

THEORETICAL PART.

CHAPTER IV.

DISCUSSION OF SOME FEATURES OF THE GURNEY-MOTT THEORY.

§ 18. Quantitative difficulties and uncertainties of the theory.

We mentioned in Ch. I that the GURNEY-MOTT theory explains many phenomena connected with photography from one viewpoint. This renders the theory most valuable. However, in view of certain quantitative features we deem a slight modification necessary. We shall consider these features here in some detail.

1. The reciprocity law failure for high intensities.

In § 4 we briefly mentioned the explanation of this part of the r.l.f. in which it is assumed that a negatively charged speck needs some time for its neutralization; subsequent electrons, that arrive too soon, are repelled and thus a decrease in efficiency results.

We shall see that the time required for neutralization is of the order of 10^{-6} sec. so that the intensities at which this type of r.l.f. should become observable corresponds to rates of absorption, comparable with one quantum per 10^{-6} sec. per grain. In reality these effects become markedly observable at intensities of the order of 1 quantum in 10^{-3} sec., per grain.

This discrepancy indicates that, though the effect proposed by the authors may appear at much higher intensities, the observed deviations from reciprocity law at high intensities require an other explanation.

An estimate of the average time of neutralization of captured electrons can be obtained in the following way.

Suppose the number of the interlattice silver ions per cm³ is N, their average spacing l, with $l^3N \sim 1$, the specific conductivity of AgBr is σ e.s.u. and the charge of the ion or electron $\pm$ e e.s.u. Then the current density J in a field of F e.s.u./cm, with ions moving at average speed v in the direction of the field, is:

$$J = N \cdot v \cdot e = \sigma F$$

or

$$v = \frac{\sigma \cdot F}{N \cdot e}$$

The field, caused by an electron at distance l, is $F = e/l^2$, so that the time required to neutralize a trapped electron by a silver ion is of the order:

$$t = \frac{l}{v} = \frac{l^3 N e}{\sigma e} = \frac{1}{\sigma} \sim 2.10^{-6} \text{ sec.}$$

at room temperature. The value $\sigma = 0.5 \times 10^{-6}$ Ohm^{-1} cm^{-1} was taken from TUBANDT *) 30).

2. The reciprocity law failure for low intensities.

Here GURNEY and MOTT assume that a sensitivity speck has a tendency to dissociate into an electron and a positive speck owing to the thermal agitation. An arriving photoelectron has to overcome this tendency, if the speck is to be charged negatively. At higher light intensities the higher outer electron vapour pressure reduces the dissociation and succeeds in charging the speck negatively, which is followed by attraction of interlattice silver ions etc. and leads to the formation of the latent image, as described in § 4.

The maximal concentration of electrons that can be reached at

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*) Additionally we mention that, according to measurements of ARZYBY-SCHEW 31), the mobility of similar ions in similar lattices is of the order of magnitude of 1 cm²/sec.Volt at room temperatures. Assuming a similar value for the mobility of Ag+ ions in an AgBr lattice, this would correspond to a value for l of the order of 2.10^{-6} cm or ca. 10^6 interlattice ions per grain.

a given light intensity depends on the factors determining the mean life time of the free electrons. The authors assume that an electron may fall into a hole from one of the 6 adjacent halogen ions in a time of the order of 10^{-8} sec., and that it will spend about 6.10^{-12} of its life on these ions, the grain consisting of 10^{-12} ion pairs. So the mean life time of an electron with respect to one hole is of the order of 2.10^3 sec.; the life time is n times as small if n electrons (hence n holes) are present in the grain. This is a characteristic time for the grain. If a critical electron concentration has to be established to start the process of latent image formation, it follows that the intensity must exceed a given critical value of the order of at least 1 quantum per 2.10^3 sec.. For emulsions with fine grains ($0.2\ \mu$ or 10^9 ion pairs) the corresponding figure would be 2 seconds.

Several points give rise to difficulties if this explanation is considered more closely.

In the first place it seems doubtful that a neutral Ag_2S speck should have an appreciable tendency to emit electrons into the conduction levels of AgBr, much larger than the AgBr itself, if it has a conduction band, lying somewhat below that of AgBr (which is necessary to make it trap electrons at higher concentrations) since the dissociation electron has to be released from a ground level.

In the second place the estimate of the electron-life time would suggest that plates with fine grains cannot be made developable by intensities of one quantum in 2 sec. or longer, whereas we know that such intensities have an efficiency below optimal but by no means negligible. Moreover it should be mentioned that if the attraction between an electron and its hole is taken into account this discrepancy becomes still more pronounced.

WEBB [32]) advanced a somewhat different explanation for the r.l.f. at low intensities. This author performed experiments, similar to those of WEINLAND [33]), concerning the effect of a given exposure which is partly admitted at the optimal intensity and partly at a much lower one. It was found that the density D_1 of an entire low intensity exposure is almost equal to that of an exposure consisting of low intensity for the first half and of optimal intensity for the second half of the energy; on the other hand the

density D_2 produced by exposing entirely to the optimal intensity is almost equal to that of an exposure consisting of optimal intensity for the first half and of low intensity for the second half of the energy. In other words the efficiency of the intensity of the second half of the exposure is almost equal to that of the intensity of the first half. These results led this author to the hypothesis that a Ag speck is unstable against thermal agitation, as long as it has not yet surpassed a critical size, which is about half of the size required for developability. The disintegration of such a small Ag speck is assumed to proceed in the same way as proposed by GURNEY and MOTT for the HERSCHEL effect, namely by the emission of an electron, followed by the expulsion of a Ag^+ ion. The latter authors have pointed out that this type of neutralization is to be expected preferably for small Ag aggregates, consisting of a few atoms. According to WEBB the instability of small Ag specks is responsible for the lower efficiency of low intensities for building developable Ag specks, i.e. the low-intensity r.l.f.

The essential difference of the latter type of explanation with respect to the former one is firstly that the ionization of the Ag_2S speck needs no longer to be assumed for the special purpose of explaining the r.l.f., and secondly that the ionization of Ag specks is combined with the expulsion of Ag^+ ions, an effect which is known to exist from the HERSCHEL effect.

3. The developability of an appreciable number of grains after absorption of about 10 quanta.

As has been discussed in Ch. III the sensitivity specks where electrons may stick are distributed throughout the volume of the grain; at the surface we find about 1 %, so that grains which need only one quantum to be developable should be relatively rare from this standpoint. Even grains that are developable by a few quanta should be very improbable, whereas we know that a large fraction of the grains do belong to this group.

In fact, the probability to find 3 electrons at the same speck if 10 electrons are distributed at random over 1000 specks is ca. 10^{-4}.

Though the GURNEY-MOTT theory does not take into account

the large number of sensitivity specks in one grain it is possible to extend this picture so as to cover also these facts. The dissociation of sensitivity specks depends very strongly on the depth of their potential hole, so that if we assume a relatively small dispersion in these depths, already a great preference has to be expected for the deepest holes, which determine the maximum electron vapour pressure in the grain. It seems not implausible that holes at the surface should be slightly deeper on the average than in the volume. It was pointed out also by the mentioned authors that lack of room in the interior of the grain may be responsible for this. However, in order to maintain the validity of the explanation for the low intensity r.l.f. the deepest hole may on the other hand not be too deep.

In § 19 we shall show that another explanation, covering also the high intensity r.l.f., is more probable.

§ 19. Proposed modification of the theory.

From the preceding section it has become plausible that some minor changes of the theory are necessary to make it applicable also to the cases mentioned, which caused some quantitative difficulties to the theory in its original form. These difficulties can be overcome by pushing WEBB's idea one step further, and discussing what happens to electrons and ions that are produced by disintegration of unstable Ag aggregates.

Two factors are of importance in this connection: the probability of the emission of an electron from a Ag speck and the probability that an emitted electron shall reach another sensitivity speck. The essential assumptions in our discussion are:

1. the probability for the emission of an electron from a Ag aggregate, followed by the expulsion of Ag^+ ion, decreases gradually as the aggregates become larger.

2. the probability for an electron to reach an other potential hole (sensitivity speck) is almost unity.

These two circumstances cause an electron to travel hither and thither in te grain, being captured, neutralized, and released at intervals, until it finally arrives at such a large Ag speck that it is bound and neutralized stably, or unites with a positive hole and

is lost for latent-image production. In other words the mean life time for the electrons is considerably increased on one hand, by the fact that they spend part of their life at the sensitivity specks; on the other hand it is decreased, especially at low concentrations of electrons, due to the greater chance to be trapped at sensitivity specks, so that an a priori estimate of its magnitude can hardly be given. Moreover this picture ensures automatically that the electrons are concentrated to those few specks which happen to be the first ones to reach the stability size.

The fact that small Ag specks are unstable against thermal agitation as assumed by Webb (see above), that somewhat larger specks are stable, that still larger ones are developable (bind electrons of the developer) and are destroyed by infrared quanta (ca. 1.5 e.V) as observed with the Herschel effect, indicates that the depth of a silver potential hole increases gradually with its size, probably reaching asymptotically the value for large Ag bulks. Also the fact that the developability of a Ag speck depends on the reducing power (oxydo-reduction potential) of the developer points towards this conclusion.

The smallness of the probability of electron loss during one journey follows from several experiences. Firstly the quantum efficiency for the production of a detectable amount of Ag is almost 1, which indicates that then most electrons reach a sensitivity speck. This experience suggests that also under other circumstances the capturing-probability per single journey of an electron will be negligible. Secondly the conservation of the amount of Ag upon red irradiation of directly blackened plates in the experiments of Cameron and Taylor [20]) on the photoadaptation effect indicate that this sort of electron transport occurs with very small losses.

§ 20. Application of the modified theory.

We shall show to what extent the modified theory is able to describe experimental facts.

We have seen already that it automatically ensures Ag coagulation at a few specks which are situated preferably on the surface of the grain, or in general at initial sensitivity specks with deepest potential holes.

The low intensity reciprocity law failure is interpreted as the loss of the first electron if the second one arrives much later than the mean life time of the first one, so that the chance to reach the stability size with a given number of electrons becomes smaller.

The high intensity reciprocity law failure is interpreted as an increased probability to find the electrons wandering simultaneously through the crystal, if they are excited at intervals that are much smaller than the mean life times of their predecessors. This state of affairs will then favour the formation of more small Ag specks above one large one.

Let us assume for example that a speck of two Ag atoms is stable and one of four atoms is developable. Then we consider four successive photoelectrons of which the first and second one have formed a stable speck (1; 2). If the time between the third and fourth electron is shorter (higher intensities) the chance that both will stabilize each other at a place (3; 4) different from (1; 2) is larger, which is a non developable configuration. If, however, the third electron has enough time (optimal intensity), it will have an increased chance to form (1; 2; 3), leading finally to the developable (1; 2; 3; 4) configuration.

It is probable in that case, that there is also a relatively larger chance for electron loss, since the latter must be expected to depend quadratically on the electron concentration, namely on the product of the concentrations of electrons and holes.

Both causes cooperate in decreasing the chances for the formation of developable specks. The optimal intensity (at room temperature: interval between successive quanta ca. 10^{-2} sec.) so corresponds more or less to the mean life time of the first electrons. An additional feature of this modified view is that it automatically explains why the region of optimal intensity is so short.

Concerning the experiments of WEBB, mentioned in § 18. 2 we remark:

As soon as stable Ag specks are formed an electron will not have to wait for the next one in order to be bound stably, so its efficiency becomes independent of the intensity and equal to that of the optimal intensity; the low intensity r.l.f. for exposures following optimal intensity disappears, but we expect that the high intensity r.l.f. remains for corresponding cases.

Concerning low temperature experiments (cf. WEBB) this picture

makes us expect that if the speed of warming up a film after exposures at low temperatures, is varied within wide limits, an optimal (rather low) speed should exist with respect to the obtained developed density. For, at low temperatures the electrons are trapped stably also in shallow potential holes, from which they are released during the warming up period by the increasing thermal agitation. If all of them are released almost simultaneously we obtain an efficiency corresponding to very high light intensities, on the other hand very slow warming up corresponds to low light intensities. In both cases the effect will be independent of the intensity at which the electrons were produced originally. So this explains the absence of reciprocity law failure for low temperature exposures as observed by WEBB. Moreover, if the electrons are released and neutralized one by one, a much higher efficiency in the production of developable density has to be expected.

In one case the sensitivity at liquid air temperature was found to be even greater than at moderately low temperatures (—78°) for quite high intensities (cf. WEBB l.c.), which is in qualitative agreement with our explanation.

An additional feature of the proposed theory is, that it yields a basis for a qualitative explanation of the changes of developable density as a function of the time that elapses between exposure and development (BRUSH effect). A more or less quantitative elaboration of these ideas lies beyond our present purpose.

CHAPTER V.

THE ADDITION LAW.

§ 21. Van Kreveld's empirical addition law.

In 1933 van Kreveld [13]) published the results of an investigation, concerning the developed density, produced by simultaneous irradiation with various wave lengths on photographic emulsions. Briefly this author found, that the photographic plate "adds different radiations correctly". For instance if an intensity I_a of colour *) a, admitted during time t produced the density D, and an intensity I_b of colour b produced the same density D in the same time t, then D was also produced in t by the mixture of both colours with components $\frac{1}{2} I_a$ and $\frac{1}{2} I_b$ or αI_a and $(1 - \alpha) I_b$.

This addition law has been confirmed for various types of emulsions, intensity ratios of components of the mixture, compositions of components, number of components, densities, times of exposure, conditions of development and finally for various methods of density measurement. More or less systematic errors of the order of 5 % occurred.

Under certain extreme conditions, especially if D approached its saturation value, large systematic deviations of this simple law were established definitely.

Various attempts to generalize the addition law failed, (see § 28), except one, which is due to Webb. Besides extensive verifications of van Kreveld's law for simultaneous colour addition, this author presents experiments that indicate correct successive addition of corresponding intensities of various colours.

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*) In this connection the word colour indicates a radiation of given relative spectral composition.

The remarkable simplicity of the addition law has lead VAN KREVELD to propose to use this law as the basis for the standardization of colour sensitivity of photographic emulsions.

The aim of our discussion is to investigate to what extent the addition law can be justified theoretically and to what extent it has to be considered as an approximation. For this purpose we shall theoretically deduce a new addition law which can be interpreted more easily in terms of the underlying physical processes; from this law we shall be able to derive VAN KREVELD's law under certain circumstances.

The formulation, which we shall use in dealing with the empirical law, is: Let E_a be the energy required to produce a density D in time t by irradiation with the colour a, let E_b be the same for colour b, then a mixture E_m, composed of an energy $_aE_m = \lambda \times E_a$ of the colour a and $_bE_m = \mu \times E_b$ of the colour b, will also cause D in t, provided that:

$$\lambda + \mu = 1$$

or
$$\left\{ \frac{_aE_m}{E_a} + \frac{_bE_m}{E_b} = 1 \right\}_{D,\ t} . \tag{1}$$

For mixtures of more than two colours this becomes

$$\sum{}^i \lambda_i = \sum{}^i \frac{_iE_m}{E_i} = 1.$$

Because of the equality of t for E_a, E_b and E_m the energies may be replaced by the corresponding intensities. The ratio of E_a and E_b depends in general on D; it does not depend on t on account of WEBB's relation (see § 3 or 12).

Another way to state this law is: the efficiency with which the energy of a certain colour, irradiated at constant intensity, contributes to the formation of a latent image of developable density D (see Ch. I) depends only on D and t. It does not depend explicitly on the blending ratio of simultaneously acting colours.

This law would allow a simple interpretation in the (hypothetical)

case that $(D; t)$ curves for corresponding intensities of different colours were congruent. Then illumination with intensities I_a of colour a and I_b of colour b, that would cause equal densities for one value of t, would do so for all values of t, in other words the ratio $I_a : I_b$ had the meaning of relative colour sensitivity, which could then easily be interpreted as ratio of absorption of quanta. Also in that case the relation of WEBB would be almost self-evident, since the processes in the grains are determined by the number of absorbed quanta; this number would be equal for all grains if the same density was produced in the same time and so the reciprocity law failure should be equal also.

However in reality the situation is more complicated. The ratio $I_a : I_b$ depends on D, or as we, mentioned before, the contrast γ of an emulsion depends on the colour of the light, so that a constant colour sensitivity is not present. If the gradual production of density during exposure is considered for two colours separately and mixed (see fig. 16) it is hardly possible to predict on theoretical grounds how the ratio of the intensities should be chosen in relation to the time of termination of the exposure.

This suggests that the empirical addition law is an approximation, be it a very good one. Especially the fact that the empirical addition law does not allow to establish a differential law sustains this idea, since one may well expect that the addition of the effects of the mixture components obeys some differential law. We will start our discussion therefore from the differential point of view.

§ 22. A new theoretical addition law.

We consider a plate which consists of grains of uniform size. Its sensitive layer is assumed to be so thin that, if a beam of light passes through the plate, practically no decrease of light intensity results. If this plate is irradiated with a constant intensity I of colour a, both the developable density D and the rate of increase of the developable density D' are determined by a, I and t; we prefer to express D' as a function of the independent variables I and D, and of the colour a, which is possible by excluding from our discussion the region of solarization

$$D_a' = D_a' (I; D).$$ (2)

If this plate is irradiated with an intensity $I(t)$, varying with time, of colour a, the value of D' at each instant will in general not be given by (2), since the efficiency also depends somewhat on the way in which the density D was produced. If $I(t)$ can be expanded in a TAYLOR power series in t we may express this dependence analytically in the form:

$$D_a' = \mathbf{D}_a' (I, D; I', I'' \ldots).$$

The dependence on I' etc. is weak and for constant illumination we have:

$$D_a' (I, D) = \mathbf{D}_a' (I, D; 0, 0, 0 \ldots).$$

Then also for a sufficiently slowly changing intensity ("adiabatic variation") we may assume that the relation (2) remains valid. In other words we assume that, within certain limits, the rate of density increase at a given density and intensity does not depend sensitively on the way in which this density was produced.

So far we have considered the irradiation with one colour; let us now consider a mixture of two (or more) colours. It follows then from most pictures about latent image formation, and especially clearly from the GURNEY-MOTT theory that, as soon as a grain has absorbed a quantum of either colour, some rather involved process or chain of processes starts to proceed, ultimately leading to the formation of a Ag atom with an efficiency, in general dependent on the state of the grain and on the colour (energy) of the quantum.

For simplicity we shall consider the GURNEY-MOTT picture here. The absorbed quanta yield a photoelectron which is subsequently neutralized by a Ag+ ion. The efficiency of the processes after the absorption is in general determined by the number of Ag atoms, the rate of their formation and the colour of the light.

The influence of the rate of formation of Ag atoms on the efficiency becomes evident in the reciprocity law failure (see Ch. I and Ch. IV). Its influence may for example be pictured as the distribution of Ag atoms over the sensitivity spots and the number of electrons that have not yet been neutralized stably, which may in turn be characterized by D and D'.

The influence of the wave length is required by the non-congruence of $(D; \log t)_I$ curves for different wave lengths, their slope being usually higher for wave lengths for which the plate has been sensitized. Various causes may be responsible for this fact. It is theoretically possible to ascribe it to a difference in number of grains that are sensitive to different colours (both contrast and maximum density dependent on colour, as assumed by VAN KREVELD). We deem this improbable since this would mean that usually more grains of a panchromatic emulsion are sensitive to red than to blue. We agree with the mentioned author that also the grain size is not the selective factor. But besides these two possibilities we wish to point out that other factors may be responsible; for instance the efficiency of transfer of photoelectrons from a sensitizer to the AgBr conduction levels may have less dispersion about its mean value than the corresponding efficiency for the transfer of excited Br electrons to these levels.

Other theories which take into account the quantic nature of light absorption may correspond to other pictures, but will lead to essentially the same conclusion, namely that the efficiency of a quantum after its absorption depends on the state of the grain and so is practically determined by D, D′ and the colour of the acting light.

The differential addition law which may then be expected states: Let I_a be the intensity of the colour a required to produce D′ at a density D (which was produced with almost the same I_a just before), correspondingly I_b for the colour b, and correspondingly for a mixture of a and b containing $_aI_m = \lambda\, I_a$ of the colour a and $_bI_m = \mu\, I_b$ of the colour b. Then these quantities satisfy the condition:

$$\lambda + \mu = 1$$

or

$$\left\{ \frac{_aI_m}{I_a} + \frac{_bI_m}{I_b} = 1 \right\}_{D, D'} \qquad (3)$$

For mixtures of more than two colours this becomes:

$$\sum{}^i \lambda_i = \sum{}^i \frac{_iI_m}{I_i} = 1$$

The form of this addition law is almost the same as that of the empirical one, but the subscripts D,t are changed into D,D′. As was mentioned before, this law does not follow from van Kreveld's law by differentiation. It is not possible to deduce a differential law from this empirical law at all, on account of the dependence of γ on λ. The theoretical law merely follows from the general picture of Gurney and Mott and others. The part of the law placed between parentheses, which requires that D was produced just before with almost the same intensity, may in most practical questions be omitted, since the influence of I′ and higher derivatives, or more generally the history of D, for which it stands, is usually very small.

§ 23. The integrated differential addition law.

In order to be able to compare the differential law with van Kreveld's law we will bring it into an integral form.

We consider a (D, t) plot (see fig. 16), containing three lines which connect the origin with the point $P(D, t)$, namely one for the constant intensity I_{aP} of the colour a, one correspondingly for I_{bP} and one for the constant mixture intensity $_aI_m + {_b}I_m$. The lines will in general run rather closely together and the third line will usually lie between the first and the second one.

Now the mixture line can also be described by type a radiation of suitable intensity as a function of time $I_a(t)$ and correspondingly $I_b(t)$. In practice both functions will closely fulfil the requirement of adiabatic change of I.
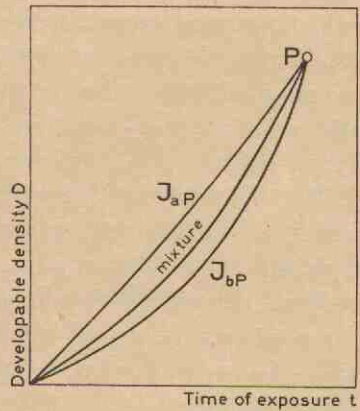
Fig. 16.

Schematical representation of the developable density as a function of time of exposure, for corresponding intensities with respect to P, of two colours a and b and their mixture.

Integration of the differential law then yields:

$$_aI_m \int\limits_{t_1}^{t_2} \frac{dt}{I_a(t)} + {}_bI_m \int\limits_{t_1}^{t_2} \frac{dt}{I_b(t)} = t_2 - t_1$$

or
$$\left\{ \frac{_aI_m}{I_a{}^\star} + \frac{_bI_m}{I_b{}^\star} = 1 \right\}_{D(t),\, t_1,\, t_2.} \tag{4}$$

with $\dfrac{1}{I_a{}^\star} = \dfrac{1}{t_2 - t_1} \int\limits_{t_1}^{t_2} \dfrac{dt}{I_a(t)}$ and $\dfrac{1}{I_b{}^\star} = \dfrac{1}{t_2 - t_1} \int\limits_{t_1}^{t_2} \dfrac{dt}{I_b(t)}$.

The formal similarity with VAN KREVELD's law is obvious, but there is a distinct difference in the meaning of the coefficients of $_aI_m$ and $_bI_m$.

§ 24. Conditions for agreement between both integral laws.

Though the discussion of § 23 has given rise to an addition law which is somewhat different from VAN KREVELD's law, it is not necessary that one of them excludes the other one.

We ask for the conditions that the two integral laws shall be valid simultaneously. There are three possibilities for an answer to this question.

In the first place it is obvious that the two laws will agree if $I_a(t)$ is constant throughout time, thus identical with I_{aP}, and also $I_b(t) \equiv I_{bP}$. This would mean that the sets of density-time curves for constant intensity for the colours a and b are congruent. (An arbitrary relation between the parameters I_a and I_b of congruent curves may still exist). We know that in practice this condition is not fulfilled; the situation is in general more like that in fig. 16.

The second possibility for the simultaneous validity of both laws is that $I_{aP} = I_a{}^\star$ and $I_{bP} = I_b{}^\star$ (term by term agreement).

The condition for this case is that:

$$1/I^\star = (1/(t_2 - t_1)) \int\limits_{t_1}^{t_2} dt/I(t)$$

shall be independent of the path of integration in the (D; t) plane,

for each colour separately, or at least, since only a narrow group of ∞^1 paths is considered between I_{aP} and I_{bP}, corresponding to different mixing ratios $\lambda : \mu$ of a and b, the first variation of the integral (with fixed boundary points) shall be zero. If we recall that $1/I_a(t) = F_a(D(t), D'(t))$, variation calculus requires for first order independence of path:

$$L_a \equiv \frac{\partial F_a}{\partial D} - \frac{d}{dt} \frac{\partial F_a}{\partial D'} = 0. \tag{5}$$

We require this for the I_{aP} curve along which F does not depend on t so that, omitting the subscripts a, we have:

$$\frac{\partial F}{\partial D} = \frac{\partial^2 F}{\partial D \partial D'} \cdot D' + \frac{\partial^2 F}{\partial D'^2} D'' \tag{6}$$

and

$$\frac{dF}{dt} = 0 = \frac{\partial F}{\partial D} D' + \frac{\partial F}{\partial D'} D'' . \tag{7}$$

We call:

$$\frac{\partial F}{\partial D} \Big/ \frac{\partial F}{\partial D'} = Q(D, D').$$

Substitution of this expression into (7) yields:

$$Q D' + D'' = 0 \tag{7a}$$

Eliminating D'' from (6) and (7), we obtain a differential equation in Q and D' only, which can be solved without difficulties, and leads to:

$$Q = \varphi(D) \cdot D' \tag{8}$$

with an arbitrary function $\varphi(D)$.

Eliminating Q between (7a) and (8) we obtain:

$$D'' = - \varphi(D) \cdot (D')^2. \tag{9}$$

This non-linear differential equation can be integrated by

choosing D instead of t as independent variable. This transformation leads to a linear equation, with solution:

$$D'_{(D)} = D'_{(0)} \; \Psi(D) \tag{10}$$

with an arbitrary function $\Psi(D)$.

Formula (10) is identical with the requirement that the $(D; \log t)_{Ia = const.}$ curves in the neighborhood of I_{aP} are parallel in the log t direction.

Since $D'_{(0)}$ depends only on I_a we may write:

$$D' = X(I) \; \Psi(D) \, {}^{*)} \tag{10a}$$

in a more or less narrow region of intensities at both sides of the I_{aP} curve.

Similarly for the b irradiation the requirement (10a) has to be satisfied, eventually with other functions X and Ψ. Then both addition laws will be concordant.

In practice these requirements are fulfilled very well. $(D; \log t)_I$ curves are not parallel if large ratios of I are considered, but for small ratios often even up to about 2, the curves are very satisfactorily parallel. So our conclusion is that good term by term agreement may be expected between both laws to the first order.

We may inquire whether also the second variation can be made to vanish, insuring a still better agreement. The condition therefore, as developed by variation calculus, is:

$$2 \frac{\partial L}{\partial D} - \frac{d}{dt} \frac{\partial L}{\partial D'} = 0. \tag{11}$$

This leads in a completely analogous way to

$$1/D'_{(D)} = 1/D_{(0)}' + \Psi_1(D). \tag{11a}$$

---

*) A singular solution (without physical applicability) is:
$$1/I = C.(D')^2 + B(D)$$

Both (10a) and (11a) can only be fulfilled if $(D;t)_I$ curves are straight lines. This is a special case of the condition of p. 61 for strict agreement between the two laws. It is generally not the case for photographic plates, so that second order agreement can in general not be expected. Special forms of (10a) may however cause such an agreement, since (11) is derived without making any assumptions about $X(I)$ or $\Psi(D)$.

Special forms of (10a) which satisfy (11) are a.o.:

$$D' = \Phi(D) / \sqrt[3]{}(1/I - C)$$
$$D' = \Phi(D)(1/I - C)$$

which are not in agreement with real density curves.

In the third place we inquire about the conditions which cause agreement between both integral laws, allowing inequality of corresponding terms.

We proved that the path in the $(D;t)$ plane for constant intensity will make the integral under discussion to be extreme (first variation zero). It can be shown easily (see below) that this extremum is a minimum. Hence the integrated differential law will always yield somewhat larger terms than the empirical law, if second order effects are considered (see § 25), there being no chance that the increase of one term will be compensated by the decrease of the other one. So we conclude that in as much as the differential law is strictly valid and both laws do not agree term by term, they will show no overall agreement.

However, it is possible that deviations from the differential law occur on account of the fact that when we describe the mixture line with one colour the intensity changes are not strictly adiabatic. We wish to point out, that in such a case the integrated differential law remains valid, but the term by term agreement may be disturbed, both terms undergoing changes that are equal in first approximation and of opposite sign. If the mixture curve is described e.g. by the colour a, the intensity $I_a(t)$ will decrease with time; for b it will then increase with time. In connection with the experiments of WEBB and of WEINLAND described in Ch. IV we may expect that the efficiency of these intensities will then be somewhat higher or lower respectively than for the adiabatic case (intensities supposed below the optimum). The same will be true for I_a^* and I_b^*, so that the two terms of the integrated addition law change in opposite

directions. This situation can be formulated more precisely in the following way.

Suppose the (small) difference between $1/I_{aP}$ and $1/I_a{}^*$, connected with the fact that the intensity changes are not strictly adiabatic, is given by the parameter μ of the mixing ratio.

Thus
$$\frac{1}{I_a} = \int F_a(D; D'; \mu)\, dt$$

and
$$\frac{1}{I_b} = \int F_b(D; D'; \lambda)\, dt.$$

Here we introduce the plausible first order approximation that the mixture curve divides the distance between the single-colour curves into the ratio $\mu : \lambda$ and that the effect of varying the intensities shall be proportional to these distances with opposite sign. Then the first-term difference is:

$$_aI_m\left(\frac{1}{I_{aP}} - \frac{1}{I_a}\right) = \frac{{}_aI_m}{I_{aP}} \times - c\,\mu = - c\,\frac{{}_aI_m}{I_{aP}} \cdot \frac{{}_bI_m}{I_{bP}}.$$

For the second-term difference we have similarly:

$$_bI_m\left(\frac{1}{I_{bP}} - \frac{1}{I_b}\right) = \frac{{}_bI_m}{I_{bP}} \times + c\,\lambda = + c\,\frac{{}_bI_m}{I_{bP}} \cdot \frac{{}_aI_m}{I_{bP}}.$$

So we conclude that in first approximation deviations from the adiabatic changes of I do not influence the validity of and agreement between both addition laws.

We believe that the considerations given in this section may give some theoretical foundation to the empirical VAN KREVELD addition law and show why this law holds so astonishingly well. The reasons are the parallelism of $(D; \log t)_I$ curves for each colour

separately and the fact that, moreover, the $(D; t)_I$ curves for different colours run not widely differently.

§ 25. Second order effects.

Both the differential addition law and the empirical addition law have so far been considered for simplified conditions. We wish to apply them to real plates, in which not all grains receive the same light intensity, due to the absorption of the incident light, which causes an intensity gradient from superficial layers to deeper ones. Moreover, the effective intensities (rates of absorption of quanta per grain) in one layer differ from grain to grain, on account of a large dispersion of the grain sizes. The construction of the VAN KREVELD law and of the new law, both in differential or integral form, is such, that any more complicated situation will cause only second order devia-

tions, as is also the case for eventual deviations between the VAN KREVELD law and the integrated addition law. Indeed both laws, according to their formulation, refer to the case that the final density D, or the momentaneous density D and the rate of density increase D' respectively, are equal for each colour separately, whatever may be the light gradient, grain size distribution, method of development of the plate, etc.. So D and D' will show maximum (second order) deviations for $\lambda \infty 0.5$ (fig. 17). A general estimation of the order of magnitude of these deviations for various cases is rather difficult. We restrict ourselves to the following remarks.
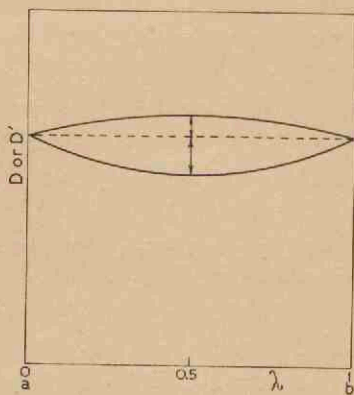
Fig. 17.

Schematical representation of second order deviations in the developable density D or its rate of increase D', for mixtures $\lambda I_a + (1-\lambda) I_b$ of corresponding intensities I_a and I_b of two colours a and b.

1. Integrated differential law and van Kreveld law.

The condition for first order agreement between the two laws was that $\int dt/I(t)$ should be extreme along a $(D; t)_I$ line. It is well satisfied, due to the parallelism of $(D; t)$ curves for various intensities of one colour. The integral is a minimum, as may be seen by chosing part of the corresponding $(D; t)$ path horizontally or vertically. So the integral corresponding to the intensity $I_a(t)$ describing the mixture line should be somewhat larger.

Assuming that the differential law is correct, we expect that VAN KREVELD's law shows small systematic negative deviations $(\lambda + \mu < 1)$. These deviations should be negligible for densities, where D is almost proportional to t, but will increase for higher densities, and also for densities in the neighborhood of the threshold.

VAN KREVELD published data for 27 plates measured at densities between 0.03 and 1.6. These show indeed a systematic error of $- 1.4 \pm 0.3 \%$ which may partly be due to the cause mentioned (cf. also § 25. 2). For higher densities larger systematic errors in the same sense occur. For a given time of exposure the way in which the density reaches its saturation value as a function of the intensity may be different for different colours, especially so for sensitized plates, as is well known. In this saturation region the empirical law breaks down. The colour which tends sooner towards saturation will need extremely high intensities to produce the required density in the given time, so its term in the addition law becomes negligible; however, in the mixture it is more efficient, so that negative deviations result $(\lambda + \mu < 1$; cf. VAN KREVELD l.c. fig. 5). It is difficult at present to estimate what errors (if any) the theoretical addition law will show in this region. Possibly in its differential form it may show some disagreement with experiments for very high densities, but at any rate the integrated form will suffer herefrom much less, being not affected by this effect for the largest part of the path of integration. The possibility to apply this form of the law successfully in a larger region of densities may be considered as a feature of trustworthiness.

2. The effect of the grain size distribution and the light gradient.

The rate of Ag production corresponds to the rate of absorption occuring in one grain. So the effective intensity is proportional to the grain area. The non-uniformity of the grains is from this standpoint similar to a non uniform illumination of equal grains, so its effect will be of the same type as the effect of a light gradient occuring in plates of finite thickness. A difference may be expected with respect to the influence of wave length. The non-uniformity owing to the grain is practically the same for all wave lengths, in as much as the absorption spectra of the grains do not depend on their sizes, but the gradient of light intensity owing to absorption will in general vary with wave length, which gives rise to a somewhat more complicated situation.

Rather special assumptions have to be made to extend the strict validity of the differential addition law to cases of non-uniform illumination or grain size. The difficulty is mainly, that if the intensities I_a, I_b and I_m fulfil the addition law for the entire plate, they will be adapted to some average depth and average grainsize. But higher or deeper layers of the plate and smaller or larger grains will show distinct first order deviations in density production due to I_a and I_b. For the total density of the plate the higher density of higher layers and larger grains compensates the lower density of lower layers and smaller grains to the first order, but the second order effects that remain can hardly be estimated. Even their sign cannot be predicted on general grounds.

§ 26. Extensions of the addition law.

1. Mixture components of unequal duration.

Van Kreveld has tried to extend his addition law to mixtures, the components of which are not of the same duration. For instance this author took for I_a : 10 seconds red, for I_b : 50 seconds violet and for the "mixture": 10 seconds a combination of both immediately followed by 40 seconds of the violet component of

the mixture. From fig. 18 and § 23 it is clear that here large deviations must be expected from the standpoint of the differential law. Its integration for this case yields the same as an ordinary addition law for an exposure from O up to the point P (so along the common path of both components). Instead of putting I_{aP}, I_{bP}, D_P and t_P into his formula, VAN KREVELD used I_{aQ} and I_{bR}, causing a decrease of the first term and an increase of the second one. His intensities were below the optimal one, so that the efficiency increases with increasing intensity. If we assume linear $(D; t)_I$ curves, satisfying the relation $D = I^{1/p} .t$, which is a reasonable approximation for densities of the order of 0.3, and if we assume adiabatic change of

Fig. 18.

Schematical representation of developable density as a function of time of exposure for intensities, connected with VAN KREVELD's addition law for components of unequal duration.

intensity at P, it can be shown simply that the sign of the deviations of $\lambda + \mu$ from 1 is negative or positive if the intensity is above or below the optimal one respectively. So one expects positive deviations in VAN KREVELD's experiments, especially for low densities. Indeed, large positive deviations of the order of 20 % were found. By assuming SCHWARZSCHILD's $p = 0.75$ the assumptions made above lead to $\lambda + \mu = 1.15$, which is of the correct order of magnitude.

VAN KREVELD notices that his extended law would necessarily neglect any difference resulting from the sequence of the mixture components; so e.g. 40 sec. violet followed by 10 sec. red + violet irradiation should yield the same density as 10 sec. red + violet followed by 40 sec. of violet, whereas in practice such differences exist. Also here the integrated differential addition law corresponds better to experimental evidence, since it does predict such differences.

Namely in the first example mentioned, integration yields the addition law, only to be applied between O and P; in the second case it should be applied between P′ and R′ (see fig. 19), so in both cases along the common path of both components, which may involve quite different intensities.

2. The time addition law.

A second extension of the empirical addition law (cf. VAN KREVELD [13]) p. 69), namely the time addition law, has been recognized by this author himself to be in general incorrect. This law would state: If I_a yields D in t_1 and I_b yields D in t_2, then both together yield D in t_3 with $1/t_3 = 1/t_1 + 1/t_2$. We fully agree with his proof, that time- and intensity addition law exclude each other if the reciprocity law does not hold, so if intensities are not approximately optimal.
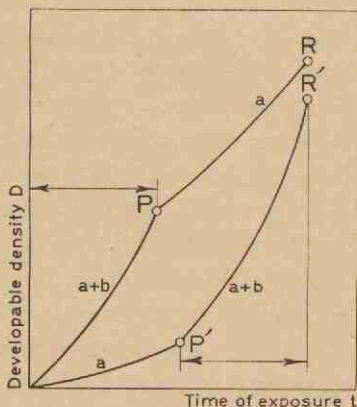
Fig. 19.

Schematical representation of developable density as a function of time of exposure if the order, in which components of unequal duration are applied, is reversed.

3. Webbs extension of the addition law.

A third extension of the VAN KREVELD addition law has been given by WEBB [34]), for successive illumination with different colours. This law states: Let the intensity I_a of a colour a produce D in t, the same I_b for b, then an exposure of $(t — x)$ to I_a followed by x to I_b will also produce D.

It is clear that this law can be expected to be an approximation which must show second order deviations, since it predicts that the sequence in which the colours are applied is not essential, whereas it is known that reversal of the sequence causes small

changes, be it much smaller than in the first extension, on account of the average equivalence of I_a and I_b. Fig. 20 shows in an exaggerated way what the differential law makes us expect: I_b during $\frac{1}{2}$ t after I_a during $\frac{1}{2}$ t yields $D + \varDelta$; I_a during $\frac{1}{2}$ t after I_b during $\frac{1}{2}$ t yields $D - \varDelta$*). The data published by WEBB [34]) allow an estimation of the difference $\varDelta$ to be expected. In all cases it falls within his experimental accuracy so that a check cannot be obtained from these data.

Herefrom it follows that for many practical purposes WEBB's extension is a satisfactory approximation.

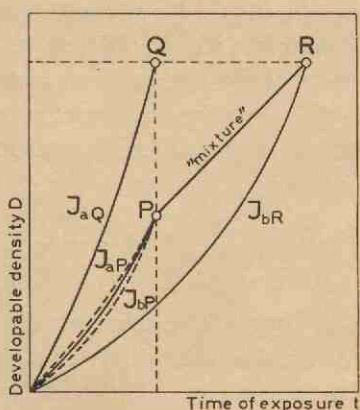Summarizing we see that there are five approximations to describe colour addition of photographic plates.

Fig. 20.

Schematical representation of developable density as a function of time of exposure for intensities, connected with WEBB's law for successive colour addition (comp. text).

1. The (integrated) theoretical differential addition law (errors very small).

2. VAN KREVELD's empirical law (errors small, except for large densities).

3. WEBB's law for successive addition (errors probably somewhat larger).

4. VAN KREVELD's extended law for components of unequal duration (errors large).

5. The time addition law (errors very large except near optimal intensity).

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*) It is possible that the non-adiabatic change of effective intensity at the switch point $\frac{1}{2}$t causes deviations from what would be expected by simple integration. If the effect is analogous to the results of the experiments of WEBB and of WEINLAND mentioned in Ch. IV, a decrease of $\varDelta$ would result.

CHAPTER VI.

THE INTERMITTENCY EFFECT.

§ 27. Density, obtained by an intensity varying with time.

The simplest case of an illumination varying with time is: illumination during a time t_1 followed by darkness during a time t_2, and then succeeded by development etc.. Changes in developable density (comp. § 3) as a function of t_2 for given t_1 appear in various papers; BRUSH [35]) observes an increase for 15 minutes, thereafter a decrease, WEINLAND [36]) finds no effect, MAUZ [37]) observes a decrease, HYLAN and BLAIR [38]) observe a decrease and give more literature, A. A. KRUITHOF (priv. comm.) finds a decrease during the first 15 min. followed by an increase, of several days, approaching to an asymptotic value. We conclude from the discordance between these authors that the conditions of this effect are not yet clear from an experimental point of view.

Another aspect of this question is reported by LONG, GERMANN and BLAIR [39]) who expose a paper to green light, so that development would yield a density of 1.3. Then they wait 40 minutes and thereafter they continue the exposure. The second exposure at first decreases the developable density. Several other observations may be found scattered in literature.

Also WEBB's [32]) experiments on the efficiency of high or low intensities after applying part of the exposure at low or high intensities respectively (see e.g. § 18, 2) should be mentioned in this connection.

But besides this more or less incidental research the question of density as a function of inconstant illumination has been attacked systematically only for the case of periodic intermittency. Up to about 1925 many authors had found that intermittency caused an increase of density and just as many had found a decrease. DAVIS

and also WEINLAND (see MEIDINGER [3]) p. 307) clarified conditions appreciably, showing that the effect depends generally on the intensity of illumination, sector dark to light ratio, and frequency, in a rather complicated way. These authors recognized that the sign of the effect was correlated with the reciprocity law failure.

In 1933 WEBB [21]) pushed the problem two steps forward. Firstly he showed that for frequencies, sufficiently above a critical frequency, the density obtained was independent of the frequency and secondly that it was equal to the density, obtained by a continuous exposure with the same average intensity during the same time. He found that at the critical frequency approximately one quantum per flash was absorbed per grain and interpreted his findings in a simple way on the basis of the quantic nature of light absorption. SILBERSTEIN and WEBB [38]) gave a more complete theory of the phenomena observed. ZIMMERMAN [8]) found deviations for very short flashes, but WEBB [40]), repeating ZIMMERMAN's experiments, found his own theory comfirmed, which was a priori probable already on general grounds.

We believe that the theory given by SILBERSTEIN and WEBB is correct in its main lines but incomplete in a few points, which we endeavour to elaborate in § 28; also we wish to present a more general method for the computation of the intermittency effect.

§ 28. Discussion of the treatment of the intermittency effect by Silberstein and Webb.

In WEBB's experiments plates were exposed to the green Hg radiation in three ways namely: firstly to an intensity Iq, applied continuously during time T_1, secondly to an intensity I, applied continuously during time qT_1, and thirdly to an intensity I, applied during time T_1 through an intermittency sector wheel of transmission q, rotating at a frequency f. The third type of exposures was performed at various frequencies (fig. 21). In all exposures of such a set the plate received the same amount of energy. Denoting the densities obtained by D_∞, D_0, and D_f respectively, WEBB found that:

$$\text{Lim } D_f = D_0 \quad \text{and} \quad \text{Lim } D_f = D_\infty$$
$$f \to 0 \qquad\qquad\qquad f \to \infty$$

Since the difference between $D_0(I,qt)$ and $D_\infty(Iq,t)$ is the reciprocity law failure, these relations link the intermittency effect to the reciprocity law failure.

A plot of D_f against log f yielded curves of the type of fig. 22, and the frequency f_c at which the ascending part "reached" the D_∞ level was interpreted as the frequency at which on the average one quantum was absorbed per flash in one unit of action.
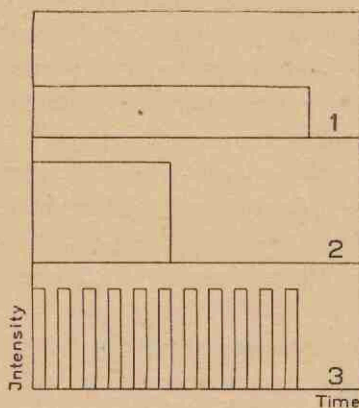
Fig. 21.

The intensity as a function of time:

1. for an exposure during time T_1 to a constant intensity Iq,
2. „ „   „   „   „ qT_1 „ „   „   „   I,
3. „ „   „   „   „ T_1 „ an intensity I, applied through a sector wheel of transmission q, rotating at a frequency f.

The basic idea of this interpretation is, that "continuous" irradiation causes, in fact, a discrete number of absorption acts, due to the quantic nature of the process of light absorption. The statistics of such absorptions will hardly differ from those for "really" intermittent exposures of the same average intensity if the frequency of intermittency is higher than or equal to the frequency of quanta reception. The experiments roughly agree with this theory in as much as f_c and I are proportional.

The intensity of irradiation being known, the receptive area of a unit of action could thus be determined and appeared to be of

the same order of magnitude as the average cross section of a AgBr grain.

In SILBERSTEIN and WEBB's paper both statistics are discussed quantitatively, and the authors point out that the "critical frequency" cannot be defined sharply, due to the assymptotic character of the curve. In its place they define a "fusion frequency" which is the value of f where the curve deviates just observably from its final value.

We believe that the treatment of the authors is qualitatively correct, but is quantitatively subject to the following remarks.
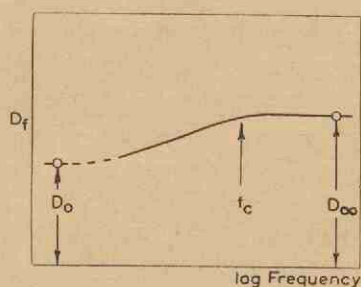
Fig. 22.

Schematical representation of WEBB's results of intermittency experiments. The course of the density, obtained with a given energy, applied at a given mean intensity, as a function of log frequency (fig. 21, type 3). For comparison the figure also contains the densities obtained by exposures with the same energy, applied at the same mean intensity (fig. 21, type 1), and at the same maximal intensity (fig. 21 type 2).

1. For density production the theory should take into account that the statistics of Ag depositing and other links of the process, are in general not equivalent to the statistics of absorption acts, at least if the dispersion (root mean square deviation) in the time that elapses between light absorption and silver production is not negligible, compared with the time intervals between two absorptions in one unit or grain (interquantum time).

2. No account is taken of the decrease of light intensity with the depth of the emulsion. If this would be done by merely taking the average intensity in the plate instead of the incident intensity, the

size of the units would be found about 1.4 times as large as given by the authors.

3. The grain size distribution is not sufficiently taken into account.

4. An experimentally badly defined point is chosen to deduce the critical frequency from, namely the point at the high frequency side of fig. 22 where the intermittency effect becomes "just observable". Moreover it would be desirable to use the whole curve of density against log f, instead of one single point, for the determination of a parameter like the effective receptive area.

5. The quantity, which the authors choose as a (qualitative) measure for the comparison of the intermittency effect of exposures of a given energy and a given average intensity, is the standard deviation (root mean square deviation) of the intervals between successive absorptions. Their derivation of the formulae for this standard deviation can be replaced by a shorter and more general one. However we shall show that this quantity is not suited for a well approximating description of the intermittency effect.

We shall give a theory satisfying the requirements of these remarks without making essentially new assumptions about the mechanism of the intermittency effect. Also we shall discuss the connection, that exists between the intermittency effect for the entire frequency range and the reciprocity law failure, without making assumptions about the details of the mechanisms of both effects.

§ 29. The influence of secondary processes on the critical frequency.

The fact that D_f approaches D_0 as $f \to 0$ is self-evident. For low frequencies the difference $D_f - D_0$ will in general be comparable with those mentioned in § 27. It is usually small compared with the difference between very low and very high frequencies, $D_\infty - D_0$. On the other hand the fact that the density obtained with $f \to \infty$ approaches the effect of a continuous exposure with with the same overall time and the same mean intensity is due to

the circumstance that the statistics of absorptions for both methods of exposure cannot be distinguished (see below). As for these two points we quite agree with WEBB, but the interpretation of the critical frequency as corresponding to approximately one quantum per flash per unit is subject to several restrictions.

In the first place it can be stated that the considerations of WEBB are applicable without restrictions if the statistics of the process of silver depositing are equal to those of quantum absorption. This would be the case e.g. if no time would elapse between the absorption and the formation of silver. However, we know that some time does elapse between the two processes. If this "relaxation" time is constant, the two statistics are still equal. Generally the relaxation time will scatter from absorption to absorption, about a mean value. Its dispersion, measured e.g. by the root mean square deviation, will be of the same order of magnitude as its mean value. In particular this is the case for processes, the occurrence of which has a fixed probability per unit time, independent of previous occurrences. The GURNEY—MOTT theory suggests that the processes, which are responsible for this relaxation time, belong more or less to this type (e.g. the chance for a wandering electron to become stabilized is the same for every journey). In that case the critical frequency, at which the statistics of Ag depositing becomes markedly influenced, will only be proportional to the light intensity, if the latter is sufficiently low. As soon as the mean interval between two successive absorptions ("interquantum time") passes below the relaxation time, the critical frequency will become independent of the intensity and will be determined by the relaxation time only. Indeed, the fluctuations of the latter cause a decrease of the critical frequency because they make the statistics of Ag depositing more irregular than those of quantum absorption.

Hence the reciprocal critical frequency ("critical time") is equal to the largest characteristic time of the process (interquantum time and relaxation time).

In the second place there may be several chain links in the processes, occurring between absorption and Ag precipitation, dealing with unstable intermediate products. So the absorption of a number of quanta, selected by chance, does not lead to Ag production. Eventually this situation may be combined with a dark

reaction, effected by a system of limited capacity. It can be shown that in all these cases the observed critical time will be approximately equal to the largest one of the relaxation times or the interquantum time. The purpose of these general remarks will become clear after the discussion of the special examples given herebelow.

For example we consider the following cases.

1. Suppose we have an unstable intermediate product, which is formed by one quatum and has to wait for the next one to be stabilized. For instance we consider the electrons which have not yet been neutralized stably, and have to wait for a following electron to form together a primary stable silver speck (cf. Ch. IV). In that case, for high light intensities and high frequencies, all electrons will be stabilized in time, so that each electron leads to the production of a Ag atom. If the frequency is lowered, losses will become apparent as soon as the dark intervals become comparable with the mean life time of the intermediate products (electrons), hence the critical time is of the order of the mean life time of the unstable products. For low intensities the efficiency will be much lower. It may readily be seen that the critical time will then be of the order of the interquantum time.

2. Suppose we have an unstable intermediate product in combination with a dark reaction that is effected by a system of limited capacity. For instance we consider the wandering electrons that can be neutralized at a maximum rate, which is determined by the number of sensitivity specks and the mobility of the Ag+ ions (cf. Ch. IV). In that case two relaxation times are to be considered: firstly the mean life time of the intermediate products (electrons), with respect to their instability, and secondly the relaxation time of the dark reaction (neutralization by ion attraction), which may for instance be defined as its reciprocal maximum reaction velocity, or as the average time needed for the neutralization of one electron. If the former is by far the smaller one, the electrons which cannot be utilized immediately by the limiting reaction are lost. For high light intensities, for which the interquantum time is small, compared with the relaxation time of the limiting system, the latter sets the pace of the entire reaction, and an intermittency effect will become observable only, if the dark times are comparable with this relaxation time. On the other hand, for low intensities the incidence of quanta is the pace-setting factor, hence the critical time will be of the order of the interquantum time. If, on the contrary, the life time of the intermediate products (electrons) is much longer than the relaxation time of the dark process with the limited capacity (neutralization time), it may be shown similarly that, in order to obtain an observable intermittency effect, the dark times, hence the critical time, have to be comparable to the larger one of this life time or the interquantum time.

In the third place it is almost self-evident that, if each absorption has a fixed probability to exert no influence on the process of silver formation, the effective intensity in connection with the

critical frequency has to be deduced from the interquantum time of the effective quanta only, as was already remarked by WEBB [41]). However, according to the above considerations concerning the relaxation times, this remark applies only for those statistic losses which are independent of the interquantum time; losses connected with reciprocity law failure are not to be discussed in the way proposed by WEBB, but according to the views developed here, in the way described for relaxation times. The probability for the occurrence of independent statistic losses is small theoretically (cf. GURNEY and MOTT and Ch. IV) and experimentally, especially on account of the observed efficiency of ca. 1 quantum per atom Ag for directly blackening exposures.

In Ch. IV we have seen that the optimal intensity more or less corresponds to such a relaxation time. From the preceding discussion it will be clear that, in order to deduce the receptive area of a unit from the critical frequency it is justified to proceed according to WEBB's method, provided that the intensity is well below the optimum, whereas for intensities above the optimum the receptive area of a unit should be computed as if the intensity should have been optimal.

The experimental results obtained by WEBB indicate distinctly that the grain area computed from experiments with intensities above the optimum is smaller than the analogous result for low intensities (cf. table II). Moreover, this author published one intermittency experiment performed at —75° [41]), with an intensity far above the optimum, which yields an extremely small effective grain area (ca. 2 % of the value at room temperature). Obviously the result of this experiment corresponds to the relaxation time belonging to the optimal intensity, and not to the interquantum time of the intensity actually applied.

§ 30. The statistics of absorption of quanta.

In order to be able to carry out the computations for the determination of the intermittency effect we shall consider the statistics of absorption of quanta in some detail. In the following sections various questions, related with these statistics will occur. In order to avoid there interruption of the discussion by mathematical

derivations we shall collect the main part of the latter ones here.

Consider one AgBr grain with cross-section area a. Let the grain be irradiated with an intensity of $I(t)$ quanta/cm².sec., with $I(t)$ a periodic function of time with period T and frequency $f = 1/T$.

Our purpose is in the first place to find an expression for the distribution of the interquantum times. The probability $W(t)$ that our grain shall absorb a quantum of light in the infinitesimal time interval between t and $t + dt$ is then:

$$W(t)\, dt = I(t)\, a^*\, dt$$

in which the effective receptive area a^* is smaller than or at most equal to 2a. If the grain would be optically opaque, a^* would be equal to 2a; in most practical cases this condition will not be fulfilled, firstly on account of the rather large reflection of the grains and secondly because their transmission is not zero. However, within not too wide limits a^* and a in one emulsion will practically be proportional (For a justification of the factor 2 see p. 93).

The chance $N(t_1, t_2)$ that no absorption takes place during the time interval between t_1 and t_2 is the product of the chances for no absorption during all intervals dt between t_1 and t_2,

or
$$\ln N(t_1, t_2) = \sum_{t_1}^{t_2} \ln (1 - W(t)\, dt).$$

After expanding the logarithm, neglecting terms of higher order than dt and replacing the summation by integration we arrive at:

$$N(t_1, t_2) = e^{-\int_{t_1}^{t_2} W(t)\, dt}.$$

The chance for an absorbtion during the interval dt_1 at t_1, followed by an interval θ of non-absorption and closed by an absorption during the interval $d\theta$ at $t_1 + \theta$ is:

$$C(t_1, \theta)\, dt_1\, d\theta = W(t_1)\, N(t_1, t_1 + \theta)\, W(t_1 + \theta)\, dt_1\, d\theta$$

Denoting by T_1 the total time of the exposure, the probability $P(\theta)\, d\theta$ that an interval between two successive absorptions has a duration between θ and $\theta + d\theta$ is given by:

$$P(\theta) = \int_0^{T_1} dt_1\, C(t_1, \theta) \Big/ \int_0^{\infty} d\theta \int_0^{T_1} dt_1\, C(t_1, \theta).$$

This definition makes $\int_0^{\infty} P(\theta)\, d\theta = 1$; furthermore $P(\theta) = 0$ for $\theta \geq T_1$.

For all practical purposes we may approximate the expression for $P(\theta)$ by

taking ∞ instead of T_1 as the upper limit of the integrals, since T_1, the total time of the experiment, will always be very large compared with the average spacing of absorptions and the periods of intermittency studied. With this approximation we can replace the denominator by:

$$\int_0^{T_1} d\,t_1 \; W\,(t_1) \;.$$

Then we can replace the upper limit of both integrals by T, the period of $I(t)$. Then the denominator becomes $a^*\overline{I}T$ and so:

$$P\,(\theta)\,d\,\theta = \frac{a^*}{\overline{I}\,T}\int_0^T d\,t_1 \; I\,(t_1)\,I\,(t_1 + \theta)\,e^{-a^*\int_{t_1}^{t_1+\theta} I(t)\,d\,t}\,d\,\theta \qquad (1)$$

It is now possible in general to compute $\overline{\theta^n}$ and averages of other functions of θ. We shall first compute $\overline{\theta}$. On physical grounds we see that:

$$\overline{\theta}\,\overline{I}\,a^* = 1$$

or
$$\overline{\theta} = 1/a^*\,\overline{I} \qquad (2)$$

since $a^*\overline{I}$ is the average number of quanta absorbed per second in one grain. Mathematically the same result is easily obtained by substituting (1) into:

$$\overline{\theta} = \int_0^\infty d\,\theta \,.\,\theta\,.\,P\,(\theta)$$

and integrating partially.

For some purposes it is more convenient to use the dimensionless quantities:

$$I/\overline{I} = Y; \; t_1/T = \tau_1; \; t/T = \tau; \; \theta/T = Q; \; \overline{\theta}/T = \overline{Q} = 1/x$$

Formula (1) becomes then:

$$P\,(\theta)\,d\,\theta \equiv P_1\,(f,\,Q)\,d\,Q = \frac{1}{Q}\int_0^1 d\,\tau_1\,Y\,(\tau_1)\,Y\,(\tau_1 + Q)\,e^{-x\int_{\tau_1}^{\tau_1+Q} Y(\tau)\,d\,\tau}\,d\,Q. \qquad (1a)$$

a. For continuous illumination we have:

$$Y = 1; P\,(\theta)\,d\,\theta = e^{-\theta/\overline{\theta}}\,d\,\theta/\overline{\theta}$$

Calling:

$$\Delta = (\theta - \overline{\theta})$$

we compute herewith:

$$\overline{\Delta^n} = \int_0^\infty \Delta^n P(\theta) \, d\theta = \overline{\theta}^n \, n! \, (1/0! - 1/1! + 1/2! \ldots \pm 1/n!) \quad (4)$$

which tends to $\overline{\theta}^n \, n!/e$ for high values of n.
Furthermore:

$$\overline{{}^{10}\log \theta} = \int_0^\infty \log \theta \, P(\theta) \, d\theta = \log \overline{\theta} - 0.250 \quad (5)$$

with $0.250 = {}^{10}\log e \times$ EULER's constant.

b. For an intermittent exposure of frequency f to intensity I through a sector wheel of transmission q we have:

$$Y = 1/q \quad \text{for} \quad n < \tau < n + q$$
$$Y = 0 \quad \text{for} \quad n + q < \tau < n + 1 \quad \text{with} \quad n = 0, 1, 2 \ldots \text{etc.}$$

After putting these expressions into (1a) we obtain for $q \leqq \frac{1}{2}$:

$$P_1(f, Q) = 0 \qquad \text{for} \qquad n + q \leqq Q \leqq n - q + 1 \quad (6)$$
$$P_1(f, Q) = ((q-\delta)/q^2 \overline{Q}) \cdot e^{-(n+\delta/q)/\overline{Q}} \quad \text{for} \qquad n \leqq Q \leqq n + q; Q = n + \delta$$
$$P_1(f, Q) = ((q-\delta)/q^2 Q) \cdot e^{-(n-\delta/q)/\overline{Q}} \quad \text{for} \quad n + 1 - q \leqq Q \leqq n + 1; Q = n - \delta$$

The course of $P_1(f, Q)$ is represented in fig. 23. Herewith we shall compute:

$$\overline{\Delta^2}(f) = \overline{(\theta - \overline{\theta})^2} = \overline{\theta^2}(f) - \overline{\theta}^2,$$

with:

$$\overline{\theta^2}(f) = T^2 \int_0^\infty Q^2 \cdot P_1(f, Q) \, dQ.$$

The integral is evaluated by substituting the above values for the nth segment of Q; an arithmetical series of higher order results; its sum is determined easily. So we obtain in a direct and more general way the result for: $\overline{\Delta^2}(f)$ derived by SILBERSTEIN and WEBB:

$$\overline{\Delta^2}(f) = \overline{\theta}^2 \, ((x \coth x/2 - 2)(1 - q)^2 + 1) \quad (7)$$

We notice that for $f \to 0$ or $x \to \infty$: $\overline{\Delta^2} \to \infty$
and for $f \to \infty$ or $x \to 0$: $\overline{\Delta^2} \to \overline{\theta}^2$.

the latter value being the same as for continuous irradiation with the same average intensity.
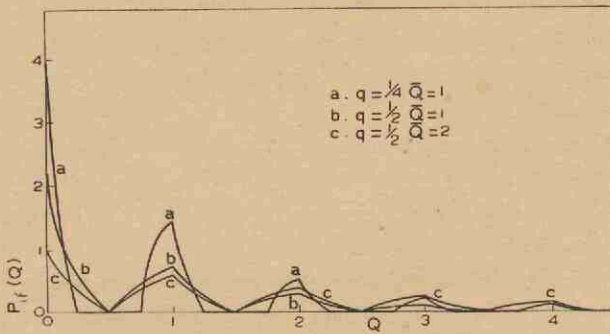
Fig. 23.

Examples of the probability distribution of $Q = \theta/T$

a. for sector transmission $q = \frac{1}{4}$ and freq. $=$ critical freq. $(\overline{Q}=1)$

b. „ „ „ $q = \frac{1}{2}$ „ „ $=$ „ „ $(\overline{Q}=1)$

c. „ „ „ $q = \frac{1}{2}$ „ „ $=$ twice the critical freq. $(\overline{Q}=2)$.

Quite generally one can show for $\overline{\theta^n}$ (f), and for most other functions $\overline{\varphi}$ of θ e.g. $\overline{\log \theta}$, that:

$$\lim_{f \to \infty} \overline{\varphi(\theta)} = \overline{\varphi(\theta)} \text{ for continuous irradiation,}$$

by considering the expression (1) for P (θ) d θ. For $f \to \infty$ we may replace the integrand factors by their mean values, since the length of the time interval of integration T approaches 0, and d θ is considered as a small but finite interval. The relation (1) is thus simplified to:

$$P(\theta) \, d\theta = e^{-\theta/\overline{\theta}} \, d\theta/\overline{\theta} \quad,$$

which is equal to the θ distribution for continuous exposure. This proves that, for sufficiently high frequencies of intermittency, intermittent and continuous θ statistics are entirely indiscernible.

We wish also to point out how $\overline{\log \theta}$ (f) can be computed.

$$\overline{\log \theta}(f) = \log T + \overline{\log Q}(f) = -\log \overline{Q}(f) + \log \overline{\theta} + \overline{\log Q}(f)$$

The third term is:

$$\overline{\log Q}(f) = \int_0^\infty d Q \, \log Q \cdot P_1(f, Q) \quad.$$

This integral can be evaluated by substituting the values for $P_1(f)$ given above for the nth segment of Q, followed for $n = 0$ by series expansion of $P_1(f)$ about $Q = \delta = 0$, whereas the other terms can be integrated. The resulting expressions have to be summed over n. They are suited for the computation of $\overline{\log \theta}(f)$ especially for values of $\overline{Q}(f)$ of the order of magnitude of 1, since then the series converges rapidly with n (frequencies near the critical frequency f_c which we define as $\overline{\theta} = 1/f_c$).

For high frequencies we have, analogous to (5):

$$\lim_{f \to \infty} \overline{\log \theta}(f) = \log \overline{\theta} - 0.250 \quad .$$

For low frequencies (small Q) we use the following approximation for $\overline{\log \theta}(f)$. We assume that in the open parts of the sector the distribution of $\log \theta$ is practically undisturbed, relative to continuous illumination with intensity I (see fig. 24). Denoting by $\overline{\theta'}$ the mean interquantum time within one light period, we have:

$$\overline{\theta'} = 1/Ia^* = \overline{\theta} \cdot q$$

and $\overline{\log \theta'} = \log \overline{\theta'} - 0.250 = \log \overline{\theta} + \log q - 0.250.$

Fig. 24.

Absorption of quanta during light periods of an intermittent exposure for low frequencies. During the light periods the θ distribution is almost equal to that corresponding to continuous irradiation with maximum intensity (comp. text).

The mean number of intervals in one light period qT is $qT/\overline{\theta'} = T/\overline{\theta}$. These intervals together with one large interval $(1 - q)T$ yield

$$\overline{\log \theta}(f) = ((\log \overline{\theta} + \log q - 0,250) \, T/\overline{\theta} + \log(1 - q) \, T)/(1 + T/\overline{\theta}) \quad (8b)$$

For $f \to 0$ we have in contrast to the behaviour of $\overline{\Delta^2}(f)$:

$$\overline{\log \theta}(0) = \log \overline{\theta} + \log q - 0.250.$$

which is the same value as for continuous exposure to intensity $I(8a)$. Finally we notice:

$$\overline{\log \theta}(0) - \overline{\log \theta}(\infty) = \log q. \quad (8c)$$

§ 31. Computation of the intermittency effect.

In Ch. V we deduced the relation connecting the action of colour mixtures with that of their components from general features of the photographic process in a differential form, which could then be integrated, becoming comparable in this way with experimental data.

This was achieved by considering the infinitesimal exposure elements of each colour and of the mixture, required to produce the same rate of density increase, starting from a given density. In the present chapter we shall see, that intermittent light can in a sense be considered as a "mixture" of different constant intensities of the same colour. It is our purpose to show that here too it is possible to deduce a differential relation, at least for light intensities below the optimal one (cf. § 29), by considering the exposure elements of each intensity and of the intermittency "mixture", required to produce the same rate of density increase, starting from a given density. This relation will then after integration connect the intermittency curve (log exposure, required to reach a definite density with intermittent radiation of given mean intensity, as a function of log frequency) and the r.l.f. curve (log exposure, required to reach the same density with radiation of constant intensity, as a function of the intensity at which the light is admitted). The relation found will be compared with the experimental results of WEBB mentioned previously.

We shall first confine our discussion to a thin emulsion with homogeneous light intensity throughout, and with grains of equal size, so with the same effective intensity (rate of absorption of quanta) for each grain. The elimination of these restrictions will be effected thereafter; in contrast to the analogous case for colour addition this does not meet with essential difficulties here.

We assume:

1. For intensities well below the optimum the influence of the $n-2^{nd}$ quantum in one grain on the efficiency for density production of the nth one will be negligible, compared to that of the $n-1^{st}$ quantum on the efficiency of the nth one. In this connection we shall introduce for the entire plate the hypothetical quantity: differential efficiency R of an energy, admitted with interquantum

times θ at a given density $D, R(\theta, D) \equiv \left(\dfrac{dD}{dE}\right)$: here the density increase from D to $D + dD$ is assumed to be effected by equidistant absorptions in each grain at intervals θ, representing together an energy dE.

This assumption is plausible in connection with the finite mean life time of the electrons, excited by the absorption of a quantum.

It is well known that $R(\theta, D)$ depends also weakly on the way in which the density D has been produced previously (history of D); especially the intensity with which this production has taken place is a factor of influence, which means that the density is not determined merely by the amount of latent-image silver. However effects of this type become apparent only for light intensities above the optimum, according to the considerations of Ch. IV, whereas our discussion is restricted to intensities below the optimum (cf. § 29). Moreover, if a number of different ways are compared to produce D with intensities, the time averages of which are equal, the effect in question may be expected to be practically absent.

Therefore we assume:

2. The differential efficiency of an additional exposure, immediately following the production of the density D, does not depend on the way in which D has been produced (history of D), in as much as the mean light intensity for the latter production lies well below the optimum and, moreover, is the same in the cases to be compared.

The efficiency for the production of an increase in developable density from D to $D + \Delta D$, by quanta, admitted in such a way that θ shows a probability distribution $P(\theta)d\theta$, is then given by:

$$R(P(\theta); D) = \int_{0}^{\infty} R(\theta, D) . P(\theta) d\theta, \qquad (9)$$

If we consider an exposure to intermittent light, the frequency of which is not too low [*]), so that for a density increase ΔD for

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[*]) For low frequencies it seems possible to eliminate the effect of the larger changes of R during one flash by averaging over experiments with various phase angles of the initial point with respect to the intermittency cycle.

which R does not yet change much, $P(\theta)$ is the same (several intermittencies during the production of ΔD), formula (9) can be integrated over the energy, from 0 up to the total energy admitted in the exposure in order to obtain a given density D_0. The same is true for a "continuous" exposure, with another $P(\theta)$ distribution (3).

3. We assume that $R(\theta,D)$ can be written as the product of a function of θ and a function of D. This assumption is equivalent to parallelism of $(D; \log t)_I$ curves in the $\log t$ direction or parallelism of $(\log E; \log I)_D$ curves in the $\log E$ direction. In practice these parallelisms are realized in good approximation (compare the condition derived in Ch. V for the agreement between the empirical and the theoretical addition law).

Then formula (9) leads after integration over the energies admitted to produce a given final density D_0, to:

$$1/E\,(P\,(\theta)\,;\,D_0) = \int_0^\infty d\,\theta\; P\,(\theta)/E\,(\theta,\,D_0)\;\;{}^*) \qquad (9a)$$

The overall efficiencies for the entire production of D_0 with a $P(\theta)$ distribution or with equidistant intervals θ respectively are:

$$\mathbf{R}\,(P\,(\theta)\,;\,D_0) = D_0/E\,(P\,(\theta)\,;\,D_0)$$

and
$$\mathbf{R}\,(\theta,\,D_0) = D_0/E\,(\theta,\,D_0)$$

By multiplying both sides of (9a) by D_0 we see that these quantities satisfy a relation of the same form as (9):

$$\mathbf{R}\,(P\,(\theta)\,;\,D_0) = \int_0^\infty \mathbf{R}\,(\theta,\,D_0)\,P\,(\theta)\,d\,\theta \qquad (9b)$$

This formula gives the connection between the efficiency of intermittent light and an "ideal" r.l.f. curve, i.e. a curve representing the efficiencies of exposures with equal interquantum times without

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*) This formula can be verified e.g. by differentiation of $E(P(\theta); D_0)$ towards D_0, taking into account that $E(\theta, D_0) \times R(\theta, D)$ is independent of θ.

statistic fluctuations, both efficiencies still for plates with homogeneous light intensity and grains of equal size. This ideal curve is related to that which would be obtained experimentally with such a plate by a transformation of averaging of neighboring points, similar to that described in § 32 which takes into account the statistic fluctuations that occur necessarily in real exposures. By the inverse transformation the experimental curve may be transformed into the "ideal" curve, which may then be compared with the intermittency curves according to form. (9a), so that in principle the problem is solved.

For practical purposes it is more convenient to compute the shape of the "intermittency curve" by which we mean a curve of

$$\varepsilon\,(f) \equiv (\log E\,(f) - \log E\,(\infty))/(\log E\,(0) - \log E\,(\infty)) \qquad (10)$$

against $\log f$, $E(f)$ being the energy required to produce a given density D_0 with intermittent exposures of frequency f, and with a given average intensity. For the same reasons as mentioned for D in § 29 we have here: $\varepsilon(f) \rightarrow \varepsilon(0) = 1$ for $f \rightarrow 0$ and $\varepsilon(f) \rightarrow \varepsilon(\infty) = 0$ for $f \rightarrow \infty$.

In order to proceed with the computation of $\varepsilon(f)$ the values of E, derived from (9a) have to be substituted into (10). For the present we have followed an approximating method, in view of the limited accuracy of the experimental data (see fig. 25). It appears to be quite satisfactory if a θ-region, covering a factor of e.g. 30 is considered. Within such a region the deviations of the r.l.f. curves from straight lines are small. So we have used the SCHWARZSCHILD approximation:

$$\log E\,(\theta, D_0) = \alpha\,(D) + \beta\,(D) \log \theta \text{ *)} \qquad (11)$$

Since the amplitude of the statistic fluctuations of $\log \theta$ for "continuous" radiation is independent of $\overline{\theta}$, as can be shown by expressing $P(\theta)d\theta$ in terms of $(\log \theta - \log \overline{\theta})$ only, straight parts of the "ideal" r.l.f. curve correspond to straight parts of the real

---

*) The relation between β and the SCHWARZSCHILD exponent p is:
$$\beta = 1/p - 1$$

curve, i.e. the SWARZSCHILD approximation remains valid where it was valid **).

Substituting the expression (11) for log E into (10) we have:

$$\varepsilon(f) = (\overline{\log \vartheta}(f) - \overline{\log \vartheta}(\infty))/(\overline{\log \vartheta}(0) - \overline{\log \vartheta}(\infty)). \tag{12}$$

Formula (12) is independent of the values of α and β in (11). This means that, in so far as this approximation is valid, the "intermittency curves" for a given sector transmission q all have the same shape. They would coincide if we should plot $\varepsilon(f)$ against $\log \overline{Q} = \log \theta/T$, since $\overline{\log \theta}(f) - \overline{\log \theta}(\infty)$ is a function of $\overline{Q}$ only, as can be verified with the aid of form. (6), (8), etc. (§ 30). Substituting the results, obtained there, into (12) we find:

$$\varepsilon(f) = (\overline{\log \vartheta}(f) - \overline{\log \vartheta} + 0.250)/\log q \tag{13}$$

This formula has been used to compare theory and experiments, but before such a comparison will be carried out we shall first dismiss in § 32 the restrictions made, concerning the uniformity of light intensity and grain size.

A (more laborious) possibility to compute $\varepsilon(f)$ rigorously would be a graphical evaluation of the integral expression (9b).

Another suitable method to compute $\varepsilon(f)$ approximately, is to replace $R(\vartheta, D_0)$ bij a sum of two or more exponential functions of ϑ.

If the SCHWARZSCHILD approximation (11) is considered as part of a series expansion of log E in powers of $(\log \vartheta - \overline{\log \vartheta})$, of which quadratic and higher order terms have been omitted, it can be shown by rather laborious calculations, which we shall omit here, that this expansion converges rapidly for functions describing the r.l.f., e.g. WEBB's function: $\log E = \log A\vartheta^{-B} + C\vartheta^{+D}$ (cf. Ch. I). If desired, closer approximations can be calculated with the aid of this expansion.

We wish to emphasize that the evaluation of the integral (9b) cannot be carried out by series expansion of $R(\vartheta, D_0)$ about $\overline{\vartheta}$, of the form:

$$\mathbf{R}(P(\vartheta); D_0) = \mathbf{R}(\overline{\vartheta}, D_0) + \{\mathbf{R}'(\overline{\vartheta}, D_0)\overline{\varDelta}/1! = 0\} + \mathbf{R}''(\overline{\vartheta}, D_0)\overline{\varDelta^2}/2! + \dots$$

with $$\varDelta = \vartheta - \overline{\vartheta}.$$

**) With respect to this transformation β, hence also p is invariant.

It is tempting to break off this formula after the second order term; since $\overline{\theta}$ is independent of f, this expansion seems to be a justification of the method of Silberstein and Webb to characterize the intermittency effect by the quantity $\overline{\Delta^2}$. Closer consideration shows that the opposite is true, since the series diverges, both for the Swarzschild approximation and for Webb's approximation of the r.l.f. for alle values of f, even for $f \rightarrow \infty$, because:

$$\overline{\Delta^n}/n! \sim \overline{\theta}^n/e$$

for $n \rightarrow \infty$. This divergence is not essentially due to the fact that the formulae for $P(\theta)$ (1),(3),(6) have been derived with the approximation that the upper limit of θ is ∞ instead of T_1. We have calculated the behaviour of $\overline{\Delta^n}/n!$ also in this case for $f = \infty$ and have found that the series remains divergent for $T_1 > \overline{\theta}$, which condition is satisfied in all of Webb's experiments where T_1 was of the order of $100.\overline{\theta}$. For all $f < \infty$ it diverges then a fortiori, since:

$$\left| \overline{\Delta^n}(f) \right| > \left| \overline{\Delta^n}(\infty) \right|.$$

Herefrom we conclude that the quantity $\overline{\Delta^2}$ is unsuited to describe the intermittency effect even approximately. This difficulty is avoided by using the rapidly convergent expansions of log E in log θ.

§ 32. The effect of the non-uniformity of grain size and of light intensity.

We shall discuss now the effect of the non-uniformity of grain size and of light intensity throughout the plate, upon the shape of the "intermittency curve" $(\varepsilon(f);\ \log \overline{Q})$. Since $\log \overline{Q} = \log f - \log \overline{I} - \log a^*$, and each of the two last mentioned quantities has its own (assumed independent) dispersion, we have to determine a weighed mean for $\varepsilon(f)$.

If the relative contribution to the total intermittency effect, by grains with log a lying between log a and log a $+$ dlog a and log $\overline{I}$ lying between $\log \overline{I}$ and $\log \overline{I} +$ dlog I is

$$W(\log \overline{I}, \log a).\ d\log \overline{I}.\ d\log a,$$

normalized so that integration over all values of log a and log $\overline{I}$ occurring yields 1, then the weighed mean to be considered is:

$$\varepsilon(f) = \iint \varepsilon(f).\ W.\ d\log \overline{I}.\ d\log a.$$

The assumption of independent dispersion of the two quantities is equivalent with:

$$W = W_1 (\log \overline{I}).\ W_2 (\log a).$$

We assume that a and a* have similar distributions, and that the light intensity can be approximated by an exponential light decrease in the plate, causing a linear decrease of log I, the magnitude of which is directly connected with the absorption of the plate.

We shall expand therefore the resulting function $\overline{\overline{\varepsilon}}$ (f) of the whole plate, averaged over log a* and log $\overline{I}$, after TAYLOR, about the point (log a*, log $\overline{I}$), chosen in such a way that

$$\varDelta \log \overline{I} = \overline{\varDelta \log a^*} = 0 = \overline{\varDelta \log I . \varDelta \log a^*}$$

In this connection $\overline{\log a^*}$ has to be defined as the value of log a* averaged with respect to its contribution to the density. So if N(a)da is the grain size frequency:

$$\overline{\log a^*} = \int_0^\infty \log a^* N(a) . a . d a / \int_0^\infty N(a) . a . d a.$$

Similarly $\overline{\log I}$ has to be defined as the average intensity, weighed with respect to its contribution to the intermittency effect, c.q. to its contribution to the total density of the plate. We shall see below, that the influence of the dispersion of $\overline{I}$ is negligible, compared with that of a.

We shall consider in this expansion of $\overline{\overline{\varepsilon}}(f)$ only terms up to the second order (the first order terms being zero on account of the definitions of the averages of log a* and log $\overline{I}$, and the assumed independence of the dispersions of the two quantities). It is then convenient to replace the expansion by the following form, which does not differ from it within the approximation mentioned:

$$\overline{\overline{\varepsilon}} (f) = \Sigma \, \varepsilon (f) \{ \log \overline{I} \pm \sqrt{\overline{(\varDelta \log \overline{I})^2}} ; \log a^*) \pm \sqrt{\overline{(\varDelta \log a^*)^2}} \} \qquad (14)$$

The sum has to be extended over all (four) combinations of the $+$ and $-$ signs. It yields an easy way to determine $\overline{\overline{\varepsilon}}(f)$ from $\varepsilon(f)$ if $\overline{(\varDelta \log I)^2}$ and $\overline{(\varDelta \log a^*)^2}$ are known. These quantities can be estimated in principle from absorption data and from grain size frequency data respectively (given by WEBB).

We observe that the points near $\varepsilon(f) = \frac{1}{2}$ change hardly by the transformation (14) which smoothens the curves of $\varepsilon(f)$ against log $\overline{Q}$ by "pulling at the ends". However points corresponding to a density which is just discernible from the value for $\overline{Q} \to \infty$ are shifted considerably (cf. fig. 25).

$\overline{\overline{\varepsilon}}(f)$ is again a function of (log f $-$ log a* $-$ log $\overline{I}$) only so that it is now possible to compare the theoretical curves with the experimental data over their entire range.

§ 33. Comparison of the theory with Webb's experiments.

In fig. 25 we have compared the theory with the experimental data of WEBB [21] [41]). We have plotted $\varepsilon(f)$ against $\overline{\log \overline{Q}} = \log f - \overline{\log a}^* - \log \overline{I}$. The thin curves have been computed according to form. (13) for the sector transmissions used. They have been corrected then for inhomogenity of light intensity and grain size according to § 32, which yields the heavy lines. The experimental points of WEBB were then plotted against log f —
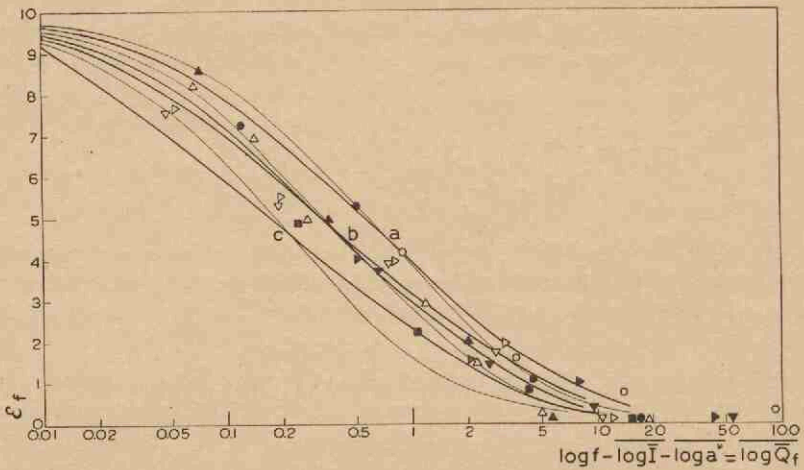
Fig. 25.

Comparison of theoretical intermittency curves with experimental points of WEBB. The quantity ε_f which measures the intermittency effect, is plotted against $\log \overline{Q} = \log f - \log a^* - \overline{\log \overline{I}}$. Each set of experimental points has been adjusted by a horizontal translation, so as to fit the curves best. Since the other variables are known, $\log a^*$ can be derived from these plots. Thin lines for plates with homogeneous light intensity and grains of equal size. Heavy lines corrected for light gradient and grain size distribution occurring in the real plates.

Solid symbols: Intensities above the optimum; open symbols: intensities below the optimum.

Emulsion I 1933	□	(sector transm. q = 1/2)	comp. curve c
„	II	„	△	„	„	1/4	„	„ b
„	III	„	▷	„	„	1/4	„	„ b
„	IV	„	▽	„	„	1/4	„	„ b
„	I 1935	○	„	„	1/16	„	„ a.

$\overline{\log ac} — \overline{\log I}$ in the same figure, choosing c so as to make them fit the theoretical curves best. The adaptation of c means that each set of points can undergo a horizontal translation without changing their relative positions.

We conclude that the agreement between the experimental points and the theoretical curves is quite good (within the experimental error). This agreement allows a relatively accurate estimation of c, using all points of a set.

Though we have stated explicitly that our theory is only applicable to intensities below the optimum, we have seen, on the other hand, in § 29 that intensities above the optimum may be expected in this connection to behave more or less as if the optimal intensity would have been used. Therefore we have also compared those data of WEBB, which pertain to intensities above the optimum, with the shape of the theoretical curve for low intensities. The agreement is better than would be expected.

In table II we collected the data, needed for a quantitative comparison of WEBB's results with the theory developed here and with that of SILBERSTEIN and WEBB.

Columns 1-4 contain WEBB's data. The average values of $\log a$ and $\overline{\log I}$ as occurring in our theory are collected in col. 6 and 8. For $\overline{\log I}$ an exponential light decrease in the plate and absorption of 50 % or 20 % (see MEIDINGER[3]) p. 97 and col. 5) has been assumed. For $\overline{\log a}$ WEBB's grain-size frequency data have been used pertaining to the plates used for these experiments. The dispersions of $\log a$ and $\log I$ about their mean values, needed for the transformations of § 32, are collected in col. 7 and 9. The former ones are deduced again (roughly) from WEBB's grain-size data, the latter ones again from the same assumptions on the light decrease in the plate mentioned above. The influence of the latter is small compared with that of the dispersion in grain size, and both influences cause differences of the order of the experimental error only, according to fig. 25.

The agreement between the experiments and the present theory is shown in col. 11; that with the theory of SILBERSTEIN and WEBB in col. 12, by comparing the grain-size data from microscopic observations with those effective in intermittency experiments. Their ratio c may be ≤ 2, since in the latter case the effective area of the entire grain surface (both sides) is found, the former case referring to the cross section area.

TABLE II †)

Data concerning WEBB's intermittency experiments and their comparison with theory.

	1					2	3	4	5	6	7	8	9	10	11	12
	Experiment					Incident intensity I in 10^{10} qu/sec.cm²	Av. grain area $\bar{a}$ in μ^2	Effective rec. area $\bar{a}^*$ (WEBB) in μ^2 **)	Absorption of plate assumed in %	Eff. av. int. $10^{\overline{\log I}}$ in 10^{10} qu/sec.cm²	$(\varDelta \log \bar{I})^2$	Eff. av. grain area $10^{\overline{\log a}}$	$(\varDelta \log a)^2$	Eff. rec. area $\bar{a}^*$ (new theory) in μ^2	c (new theory) column 10 : 8	c **) (WEBB) column 4 : 3
Emuls.	Publ. J.O.S.A.	Temp.	λ in Å	q												
					below optimal											
II.	1933	room	4360	1/4	0.034	0.7	2.2	50	0.024	0.008	1.4	0.3	1.4	1.0	3.1
III.	1933	"	4360	1/4	0.085	0.5	6	50	0.06	0.008	0.9	0.14	2.0	2.2	12
IV.	1933	"	4360	1/4	0.14	0.1	1.1	50	0.10	0.008	0.23	0.3	0.5	2.2	11
I.	1935	20°	5460	1/16	0.028	0.5	0.57	20	0.025	0.001	0.9	0.14	0.17	0.19	1.1
					above optimal											
I.	1933	room	4360	1/2	8.7	0.7	1.4	50	6.1	0.008	1.4	0.3	8	5.5	2.0
II.	1933	"	4360	1/4	8.7	0.7	1.0	50	6.1	0.008	1.4	0.3	2.7	1.9	1.6
III.	1933	"	4360	1/4	8.7	0.5	1.1	50	6.1	0.008	0.9	0.14	1.6	1.8	2.2
IV.	1933	"	4360	1/4	8.7	0.1	0.27	50	6.1	0.008	0.23	0.3	0.08	0.35	2.7
I.	1935	-75°	5460	1/16	0.11	0.5	0.01	20	0.10	0.001	0.9	0.14	1.7	1.9	0.02

†) Column 1, 2, 3, 4 after WEBB. 8, 9 deduced from WEBB's data on grain-size distributions.

" 5, assumed. (see MEIDINGER ³) p. 97), 7 deduced from 5, 6 deduced from 2 and 5 (comp. text).

**) The figures of columns 4 and 12 should be multiplied by 1,4 (1933) or 1,1 (1935) to take into account the gradient of light intensity in the plate.

Compare especially columns 3, 4, 12 and 8, 10, 11.

Column 10, 11 reinterpretation of WEBB's intermittency results with new theory.

" 12 deduced from WEBB's intermittency results with the theory of SILBERSTEIN and WEBB, for comparison with 11.

The agreement with the present theory (coll. 11) is quite satisfactory for low intensities. Except for one case also for intensities above the optimum the agreement is quite good especially if it is considered that the theory was not deduced for these cases; according to § 29, c has been computed here as if the optimal intensity had been active.

The agreement with WEBB's theory (col. 12) is decidedly less good, since values of c up to 12 occur for low light intensities; this becomes even worse if it is taken into account that the mean light intensity was in most cases lower by a factor of about 1.4. For light intensities above the optimum, where the intensity itself has been used, the disagreement shows up especially clearly in the case of the low temperature experiment, since experiments with the same plate at room temperature with an intensity below the optimum show that no deviating value of c should be expected. The corresponding figure in col. 11 does not show such a discrepancy but fits in well with the other values of this column.

Summarizing we may conclude:

1. WEBB's experiments are described better by the present theory than by that of SILBERSTEIN and WEBB.

2. For light intensities below the optimum the shape of the intermittency curves is understood quantitatively for all frequencies on the basis of the reciprocity law failure and needs no other principles for its explanation.

3. For light intensities above the optimum the same explanation holds with good approximation, provided that the optimal intensity is substituted when the calculation of the effective receptive grain area is carried out.

CHAPTER VII.

SOME PROBLEMS COMMON TO PHOTOGRAPHY AND RADIOBIOLOGY.

§ 34. Introduction.

The wide field of radiobiology is attacked nowadays along several lines. Between its problems and those of the field of photographic research a remarkable similarity appears to exist. This is especially true for biochemical processes which only proceed under absorption of visible or near ultraviolet light and which have proved to be not merely photochemical reactions, but chain processes, the occurrence of which is essentially bound to some cellular structure. The effect of these structures is then often comparable to that of the grains in the photographic emulsion.

We will discuss in this chapter some problems and methods which are common to photography and to radiobiological processes.

We shall deal particularly with examples of methods which have been transposed from one field to the other one and we shall indicate a few cases in which such a transposition may be expected to yield new results. We shall chiefly consider the process of vision occurring in the human eye and the process of photochemical carbon dioxide assimilation in plant cells, for instance in *Chlorella*, both processes having been studied extensively. Many remarks are applicable to other processes as well.

Necessarily this chapter does not aim at completeness. It is restricted to a few, but typical examples which tend to connect the fields in question.

§ 35. Similar problems, methods and effects.

1. P i g m e n t s   a n d   s e n s i t i z a t i o n.

We know that the light has to be absorbed before it can produce

a photochemical effect. In photography the absorbing "pigment" is AgBr. For photochemical CO_2 assimilation it is chlorophyll in green plants; similar compounds are used for this purpose in other photosynthetic organisms; for vision the visual purple plays probably an important rôle. The nature of the pigment(s) of vision is not yet fully known. The effective absorption spectra of the pigment complexes involved in these processes are well established.

Especially for chlorophyll, bacteriochlorophyll and bacterioviridine it is known that in the living cell these pigments are bound to a protein complex. Also for visual purple this idea has been advanced [42]. This bond shifts the absorption spectrum of the pigment towards longer wave lengths [42].

In photography the situation is somewhat different in so far as no (proper) protein is involved. However the adsorptive bond of smaller (colourless) molecules or ions (for instance OH-ions) to AgBr is also known to shift the absorption spectrum to longer wave lengths (MEIDINGER [3]) p. 96, also Ch. III).

The sensitization of photochemical processes by the adsorption of suitable dyes to the original pigment complexes was discovered in photography about 50 years ago by VOGEL. For the assimilation various authors have suggested that the action of chlorophyll amounts to a sensitization of the photosynthetic process [43]. Also it does not seem impossible that carotenoid substances, which are practically always present at the side of chlorophyll, act as sensitizers.

METZNER reports that phototaxis of colourless bacteria could be achieved with visible light after sensitization with eosine and other dyes (cited after WASSINK [44]). This is perhaps a special case of photodynamic sensitization, as studied extensively by JODLBAUER and TAPPEINER [45]).

Neither the sensitization of assimilation nor that of vision to normally inactive wave lengths, by application of solutions of suitable dyes has been reached, as far as we know. On grounds of analogy this might be possible, as was remarked already by ENGELMANN in 1883 [46]).

2. The addition law.

For photography this law has been discussed in Ch. V. The

theoretical remarks about the differential addition law can easily be transformed, so that they are applicable to the corresponding situations in assimilation and vision. We do not know of any experimental checks in the former case, but the law is likely to be valid.

For the eye the siuation is somewhat different, because the reaction product is not accumulated. Here the corresponding rates of the processes involved in vision have to be compared. Many authors assume that the brightness impressions are additive. This is not in agreement with the fact that brightness impressions can not yet be measured by these authors, since they can only define and establish equality of brightness impressions. So an addition law ought to be formulated in such a way as to relate all factors to equal brightness impressions.

Although the conclusions, drawn from experiments on the brightness of colour mixtures were thus not always formulated correctly, the addition law has essentially been verified long ago and has since been used as a basis for heterochromatic photometry in the brightness region of constant relative colour sensitivity. Generally it proved to be in good agreement with experimental evidence; however, when comparing saturated colours with their mixtures, positive deviations ($\lambda + \mu > 1$, see Ch. V) were established. For regions of lower brightness, where the relative colour sensitivity depends on the brightness, the validity of the law is not self-evident. In analogy to photography it was verified there by BOUMA [47]), who found excellent agreement, which constitutes a basis for his new four-dimensional colorimetric system.

3. The reciprocity law and the influence of temperature.

The deviations in the behaviour of a photographic plate from reciprocity law are well known. For photosynthesis a rather large region of intensities I and times t exists, in which the amount of CO_2 assimilated is proportional to $I \times t$.

However, for higher intensities the well-known BLACKMAN saturation appears; for very low intensities theoretical considerations (cf. WOHL [48])) indicate that the efficiency will decrease, since

the rate of assimilation proceeds with I^4. For very short and very long times of illumination initial changes and changes in the cells occur, causing a reciprocity law failure.

In most other radiobiological problems the $I \times t$ law holds within a certain region of I and t, therebeyond deviations are observed (cf. WASSINK [44]). In various cases these will have to be explained probably in different ways.

Though the reciprocity law failure may be due to different causes, two features are of a quite general nature.

In the first place we mean the low intensity failure for more-quantic processes with unstable intermediate products. For photography SILBERSTEIN and TRIVELLI [28] showed in general that for sufficiently low intensities the rate of density production is proportional to I^n if the reaction requires n effective quanta to produce its minimum effect, and if the intermediate products, formed by less than n quanta, are not stable. (For most plates it was found that $n = 2$). Independently WOHL [48] reached the conclusion that the rate of CO_2 assimilation which requires probably 4 quanta for the assimilation of one CO_2 molecule, should be proportional to I^4 for sufficiently low intensities. This principle is valid for all radiobiological reactions and yields a method for the determination of the number of quanta, required for such a process. This method has not sufficiently been utilized up to the present.

Secondly we refer to the GURNEY—MOTT explanation of the high intensity reciprocity law failure in photography [17], and its dependence on temperature. The similarity of the curves of the rate of Ag production against light intensity given there and curves of the rate of CO_2 assimilation by *Chlorella* [49] against light intensity is most striking. Also their temperature dependence is quite similar (see fig. 26).

This type of saturation is explained commonly by the assumption of a chain of (at least) two partial processes. One of these processes is assumed to be photosensitive but rather insensitive to temperature (in photography: electron transport to sensitivity specks), the other one has the reverse properties (in photography: neutralization of trapped electrons by ion conduction) and moreover possesses a limited capacity, which is due for instance to a limited number of

reactive places. Such a system must have just these properties provided that intermediate products are not infinitely stable.

Here radiobiology had given the explanation before it appeared in photography.
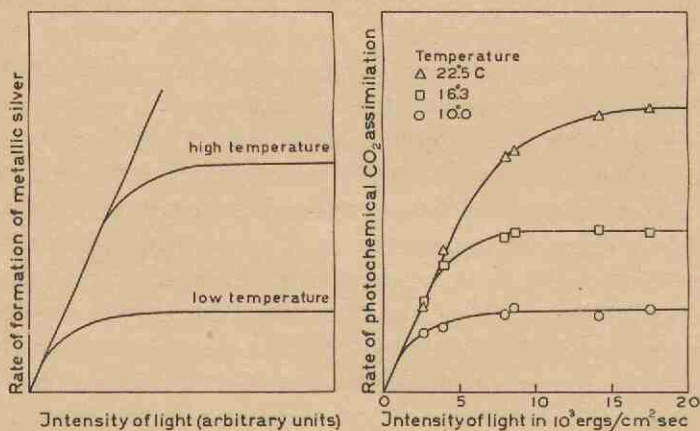

Fig. 26.

Illustration of the similarity of the influence of light intensity and of temperature, left: on the rate of production of metallic Ag, according to the GURNEY-MOTT theory (cf. [17]) fig. 3),
right: on the experimentally determined rate of photochemical CO_2 assimilation in *Chlorella*, according to WASSINK, VERMEULEN, REMAN AND KATZ [49]).

§ 36. The unit of action.

An important item in our discussion is the application of the idea of the unit of action in both fields. We shall discuss this matter somewhat more in detail.

The idea of a unit of action implies that a number of pigment molecules is connected by some mechanism in such a way that, if any molecule of a unit absorbs a quantum of light, this energy is furnished to one definite reactive molecule.

In photography it was known since long that silver is deposited at a few definite "concentration specks" (SHEPPARD e.a.) independent of the place in the AgBr grain where the corresponding quantum was absorbed.

So for this process a unit appears to exist, of the order of magnitude of a grain.

From this example we see quite generally that in a unit of action the energy must be transported over a certain distance, to the place of the final reaction. The development of more specified ideas about the unit of action depends entirely on the possibilities to visualize suitable mechanisms of energy transport.

For photography the GURNEY—MOTT theory proposes for this mechanism photoconduction of an electron from the place of absorption to some structural irregularity as expounded in Ch. I. This is conceivable on the basis of general ideas, developed from the study of photoconduction and semiconduction in crystals.

A few years before the publication of this theory J. H. WEBB [21]) had developed an experimental method to determine the size of a photographic unit of action. This method is based on a study of the intermittency effect, and has been discussed in detail in Ch. VI. The results of WEBB's experiments and their additional discussion in Ch. VI make plausible that the unit of photographic action is of the order of magnitude of an entire AgBr grain (ca. 10^9 molecules).

In the field of photosynthesis the idea of a unit of action of chlorophyll is about 10 years old. It was first introduced by EMERSON and ARNOLD [50]) to explain their observations regarding saturation of CO_2 assimilation by *Chlorella* in flashing light. GAFFRON and WOHL [51]) and WOHL [48]) discussed these experiments more closely and collected all arguments that pointed towards the existence of such a unit. Its magnitude was estimated at about 2000 molecules of chlorophyll. More recent work of EMERSON, GREEN and J. L. WEBB [52]) indicates that this number tends to increase with the age of the cells up to almost ten times this value.

The problem of energy transport is here a very difficult one, since it is not known whether chlorophyll is present in the cell in a state which is comparable with the crystalline one. In grana the chlorophyll is rather densely packed, so that processes similar to photoconduction of electrons might not be impossible, especially since one knows from the work of HANSON [53]) and of KETELAAR [54]) that monomolecular films of chlorophyll on water tend to form very regular tile-like structures. Whether the electrons are con-

ducted through a chlorophyll structure or through a protein complex is an open question.

Another argument for electron transport is the fact that in assimilation the light probably ultimately gives rise to a reducing agent [55]).

We wish to point out that WEBB's method for the determination of the size of the unit is in principle applicable to the process in question. After the discussion of Ch. VI it is clear that the required intermittency experiments should not be performed in the region of light saturation, where the relaxation time of a limiting factor interferes, nor can any result be expected in the region where the rate of assimilation is proportional to the intensity of irradiation. Experiments of this type would only yield an independent estimate of the size of the photosynthetic unit, if one succeeds to perform them at low intensities where the rate of assimilation is proportional to I^4.

Moreover experiments of the same type, performed at intensities a little below light saturation would yield an estimate of the dispersion of the relaxation time (root mean square deviation from the average relaxation time) of the processes of energy transport (BLACKMAN reaction etc.). This question has so far not been attacked at all.

In the study of vision TALBOT's law has since long been known. It states that the brightness impression of intermittent irradiation of so high frequency that a continuous sensation results, is equal to the brightness impression of "really" continuous irradiation with the same average intensity. We now understand this law for very high frequencies from the remarks of WEBB for photography; it is essentially connected with the quantic nature of light absorption.

In this case the critical frequency of WEBB corresponds to the fusion frequency at which the sensation becomes continuous. It has been determined for a wide range of light intensities (cf. S. HECHT e.a. [56])). This frequency is not proportional to the intensity in the region where measurements were performed, but it shows a tendency to become so for still lower intensities. Probably relaxation times of secondary processes interfere; moreover it is conceivable in this case that the absorption or the amount of pigment present, is dependent on the light intensity, which may be an additional complication.

It is likely, however, that for sufficiently low intensities both complications drop out, so that in this region WEBB's method should enable one to determine the size of the unit of vision, if desired for each eye-pigment separately, and for various regions of the retina.

The resulting size of the unit may in principle exceed that of one rod or cone, because by this method the unit for the entire process of vision is determined. But a priori dimensions smaller than one rod or cone seem more probable.

Moreover, for the mentioned low intensity regions the theoretically lowest value of the just observable brightness increment must be expected to vary inversely proportionally with the root of the intensity, that is with the relative statistic variations in the number of quanta absorbed per unit time in one unit of vision.

We terminate here the list of examples, which, though far from complete, intends to support the conviction that an interchange of ideas and methods between the fields of photography and of radiobiology will prove to be highly fruitful.

SUMMARY.

This thesis contains several more or less independent parts, dealing with different aspects of latent-image formation, namely with the formation and measurement of low direct densities, with the GURNEY-MOTT theory, with the addition law for different colours, and with the relation between the reciprocity law failure and the intermittency effect.

Experimental Part.

Accurate compensation measurements were performed in a way more or less similar to that followed by JURRIENS, on the direct-density production of weakly absorbed wave lengths. The apparatus used is described in Ch. II (fig. 4 and 5), the results of the measurements are to be found in Ch. III. The mentioned radiations give rise to direct-density-time curves with a peculair S-shape for densities near 0.01. This shape appeared to be connected in no way with the similar shape of developed-density-time curves. It may be expected similarly in silver-time curves. We mainly investigated the influences of wave length (fig. 10), of light intensity (fig. 11 and table I), and of water-addition on the shape of these curves. The S-shape disappears gradually for decreasing wave lengths. This sustains the view that it has to be considered as the resultant of two components, one of which is connected with the silver production, showing a pronounced BECQUEREL-effect, whereas the other one is connected with a silver destruction, probably related to the HERSCHEL-effect. The effect of water is to sensitize the production of direct density and to desensitize that of developed density, in these wave length regions. This may be due to adsorption of OH^- ions to the sensitivity specks.

Theoretical Part.

A quantitative discussion of the GURNEY—MOTT theory, especially with respect to both parts of the reciprocity law failure,

on the basis of TUBANDT's conductivity measurements in AgBr, lead to a slight modification of the theory (Ch. IV).

On the basis of general views on latent-image formation the photographic action of a mixture of colours, as compared with that of the component colours separately, is discussed (Ch. V). This leads to the formulation of a new theoretical differential addition law, which is, after integration, compared with the empirical VAN KREVELD addition law. The difference between the two laws appears to be negligible for many practical cases, so that the new law may be considered as a theoretical justification of the empirical law, and at the same time the former shows why the empirical law fails under certain extreme conditions.

After a discussion of the treatment of the intermittency effect by SILBERSTEIN and WEBB we proceed to compute the effect, in a way, similar to that followed for the derivation of the addition law, which leads again to a differential relation, connecting the reciprocity law failure with the intermittency effect for all frequencies, provided that the intensities used are well below the optimum. After integration this relation is compared with WEBB's experimental results, with which it is in good agreement, yielding more reliable values of the effective receptive area of the unit of photographic action (Ch. VI).

Finally a brief survey is given of some problems which are common to photography and to radiobiology (Ch. VII).

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    J. O. S. A. **12**, 321, '26,
    J. O. S. A. **13**, 443, '26,
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CONTENTS.

STELLINGEN

I.

Ten onrechte noemt P. J. Bouma die kleuren, die buiten de spectrale kegel liggen, niet reëel.

P. J. Bouma, Phil. Tech. Tijds. **2**, 39, '37.
Proc. Kon. Acad. v. Wet. Amst. **38**, 35, '35.

II.

Het instrument van H. B. G. Casimir en C. A. Crommelin ter demonstratie van interferentie figuren van één-assige kristallen in convergent licht kan constructief vereenvoudigd worden.

H. B. G. Casimir en C. A. Crommelin,
Ned. Tijds. v. Natk. **7**, 38, '40.

III.

Het bewijs, dat in sommige leerboeken voor de middelbare scholen van de „Reststelling" gegeven wordt, is fout.

A. v. Thijn en M. L. Kobus, Algebr. Hoofdst.
P. Wijdenes, Lagere Algebra I.

IV.

Op soortgelijke wijze als Cesaro het sommatie begrip uitbreidt, kan men als volgt het integraal begrip uitbreiden.

Tot dit doel definiëren we de operatoren:

$$O(n) \equiv 1/B_n \int_A^{B_n} dB_{n-1} \cdot , \qquad (n > 0)$$

$$O(0) \equiv 1. ,$$

en beschouwen de rij:

$$I(n) = \operatorname*{Lim}_{B_n \to \infty} O(n) \cdot O(n-1) \dots O(0) \cdot \int_A^{B_0} F(x)\, dx \qquad (n = 0, 1, 2, \dots).$$

Men bewijst gemakkelijk: Indien I(n) bestaat, dan bestaat ook I(n + 1) en heeft dezelfde waarde. Het is dan zinvol I(0) de waarde I(n) toe te kennen, ook al is F(x) niet integreerbaar in gewonen zin, en F(x) Cesaro integreerbaar te noemen.

Op deze wijze komt men tot bevredigende uitkomsten voor oscillerend divergente integralen, zoals de integraal van 0 tot ∞ van sin x (= 1), cos x (= 0), x sin x (= 0).

V.

Het is mogelijk de verhouding van helderheids-*indrukken*, teweeggebracht door twee aan elkaar grenzende vlakjes van ongelijke helderheid, kwantitatief te schatten. Het gebruik van de aldus geschatte verhoudingen als grondslag voor een metriek der kleurenruimte is te verkiezen boven dat van de juist onderscheidbare verschillen.

VI.

Voor experimenteel werk op het gebied der fotografische spectraalphotometrie is het gebruik van de op het intermittentie effect berustende roterende sector volgens EVANS vaak te verkiezen boven het gebruik van trapspleten of trapverzwakkers, vooral wanneer men met lange belichtingstijden te maken heeft.

C. H. EVANS, J. O. S. A. **39**, 18, '40.

VII.

Voor die kleurenfotografische platen, waarbij elementen met verschillende kleurgevoeligheid naast elkaar liggen, kan men betrekkelijk sterke afwijkingen van de somwet verwachten.

VIII.

Meting van het absorptiespectrum van bacteriën en andere microorganismen die kleurstoffen bevatten vormt een snel en doeltreffend hulpmiddel bij de identificatie.

E. C. WASSINK, E. KATZ en R. DORRESTEIN, Enzymologia **7**, 113, '39.
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IX.

De rol, die een waterstof donator speelt bij de photosynthese van purperen zwavel-bacteriën kan niet als secundaire reactie gezien worden met (hypothetische) zuurstof, die uit de primaire photosynthetische reacties zou vrijkomen.

E. A. HANSON, Rec. trav. bot. Néerl. **36**, 183, '39.
H. NAKAMURA, Acta Phytochym. **9**, 189, '37.

X.

De bepaling van het aantal neutronen, dat een bron per sec. uitzendt, met behulp van metingen in een watertank, volgens een methode waarbij in elk punt het aantal thermische neutronen dat van *beide* kanten op een (dunne) detector valt wordt bepaald, verdient de voorkeur boven de methode van FERMI.

E. FERMI, La Ric. Scient. Serie II, Vol. 2, Anno 7.