# Phenomenological Theory of Intermediate Intensity Reciprocity-Law Failure at and near the Optimum in Photographic Exposure

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## Introduction

One of the most important problems in the latent image formation in photographic process is the phenomenon known as the reciprocity-law failure corresponding to the breakdown of Bunsen-Roscoe's law for a photo-chemical reaction. As is well known, the developed density of a photographic emulsion does not depend only upon the exposure of light, namely the product of the intensity and time factors. In most cases, there exists an optimal intensity at which the photographic process proceeds most efficiently.

This phenomenon is in general represented graphically by a reciprocity-failure curve. The curve A in Fig. 1 shows a typical case of it, in which the log exposure ($It$) required to produce a constant developed density is plotted against the log intensity ($I$).

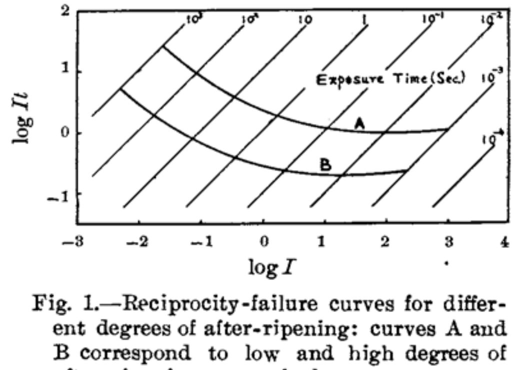


Fig. 1.—Reciprocity-failure curves for different degrees of after-ripening: curves A and B correspond to low and high degrees of after-ripening respectively.

The drop in photographic efficiency at intensities higher than the optimum, which is termed as the high intensity failure, is caused by the relative sluggishness of the inonic process compared with the high rate of the production of the photo-electrons and the limited electric capacity of the electron traps.[1] On the other hand, the failure of reciprocity-law at intensities lower than the optimum arises from the fact that the thermal agitation impedes the creation of the silver specks in the initial stages of the latent image formation.[1, 2]

These interpretations are qualitatively acceptable, but lt is highly desired from both theoretical and practical standpoints to develop this theory, especially so as to interpret quantitatively the shape of the reciprocity-failure curve. This is the reason why the problem in this field has received so much discussion in recent years. Katz[3] and Webb,[4] for instance, have succeeded independently in deriving the theoretical curves in the region of very low intensities. Their methods are based upon the following considerations : (1) the assumed existence of the stable speck in the initial stages of latent image formation and (2) the statistical fluctuation of the number of light quanta absorbed by a grain. Their separate treatments arrived at the same conclusion that the shape of the curve at very low intensities is a straight line, and this is in good agreement with the experimental results.

In the above treatments by Katz and Webb, they attempt to extend their treatments so as to include the region of intermediate intensities below the optimum. However, it seems[5] that in their extensions they do not fully appreciate the interplay of ionic and electronic processes at intermediate intensities below the optimum.

In such a region of exposure intensities special attention must be given to what becomes of the photo-electrons after they have been captured by the electron traps. In some cases, some of such trapped electrons may not be neutralized by ionic process, but, due to thermal motion, escape from the trapping states. Thus these two possibilities may act competitively on the trapped electrons (hereafter referred to as the competitive action).

It is the purpose of this paper, therefore, to point out that there is a more appropriate treatment in the region of intermediate intensities at and near the optimum. The present authors emphasize that in such a region the competitive action should be taken into account.

Moreover, by assuming the accumulation of the trapped electrons in an electron trap throughout exposure, the present authors have phenomenologically formulated a dynamical equation for the rate of increase in the number of the trapped electrons. On the basis of this, analytic expression for the log exposure required to produce the developable image has been derived. Finally, by means of adjustable parameters, comparison has been made to see how this theoretical curve is compatible with the experimental data.

A phenomenon which produces strong evidence for our viewpoint is that the reciprocity-failure curve is shifted as a whole in a definite way in accordance with the changes in various factors such as the degree of the after-ripening, the ionic conductivity, the temperature, etc.

For instance, as the after-ripening is prolonged in its earlier stages, the reciprocity-failure curve at intermediate intensities is in most cases shifted as a whole toward lower intensity along the direction of lines of constant exposure times (hereafter referred to as the diagonal shift).[6] The experimental reciprocity-failure curves at different degrees of after-ripening are shown in Fig. 1, where the curve B refers to the emulsion subjected to a longer after-ripening than that of the curve A. This diagonal shift seen here which is composed of the vertical descent component as well as the traverse shift component would be inexplicable by any idea, unless the competitive action were taken into account.

It seems to be also the case with the similar shift caused by the temperature changes, although Katz[3] and Webb[4] have some remarks on this point without being aware of the importance of the competitive action at intermediate intensities.

It is to be noted, therefore, that the treatment given in this paper is especially suitable for interpreting the bodily shifts of the whole curves at intermediate intensities.

## Derivation of the Equation Representing the High Intensity Failure Component

Exposure of silver halide grains of the photographic emulsion releases electrons from the bromide ions or the local absorption centers and raises them up to the conduction levels of the crystal lattice. Such electrons move through the lattice and then may be captured by the electron traps (sensitivity specks) distributed haphazardly on the grains.

Let us consider first the process of electron

(1) R. W. Gurney and N. F. Mott, *Proc. Roy. Soc.*, A **164**, 151 (1938).
(2) J. H. Webb and C. H. Evans, *J. Opt. Soc. Am.*, **28**, 431 (1938).
(3) E. Katz, *J. Chem. Phys*,, **17**, 1132 (1949).
(4) J. H. Webb, *J. Opt. Soc. Am.*, **40**, 3 (1950).
(5) S. Fujisawa and E. Mizuki, to appear in *J. Opt. Soc. Am.*, (L).

(6) E. Mizuki, *Kagaku Butsuri* (in Japanese), **1**, 49 (1949); E. Mizuki and S. Fujisawa, to be published.

trapping. We assume that the electron trap responsible for the latent image formation may be capable of capturing several electrons simultaneously. In this case, however, owing to their electrostatic repulsion against subsequent electrons, the capture cross section $\sigma$ of an electron trap diminishes with increasing the number $n$ of the electrons already captured, in accordance with the relation

$$\sigma=\beta n^{-\gamma}, \qquad (1)$$

where $\beta$ and $\gamma$ are the numerical constants, the former being one of parameters determing the position of the reciprocity-failure curve and the latter one of adjustable parameters which serve to fit the shape of the theoretical curve to the experimental one. It is on this account that the present treatment is to be considered as essentially phenomenological.

Secondly, we now suppose the existence of the competitive action on the trapped electrons. The electrons staying in the electron trap may be either neutralized by the ionic migration (mobile silver ions or vacant anion sites) owing to their negative charge, or ejected on to the conduction band by the thermal motion (leading to inefficiency). These two possibilities should be considered as competing (simultaneously existing) so long as the lifetime of a trapped electron is of the same order as the time of neutralization by ionic migration. Under the existence of such competitive action, the rate of increase in the number of trapped electrons during exposure with intensity $I$ is given by the equation,

$$\mathrm{d}n/\mathrm{d}t = P\beta n^{-\gamma}I-(Q+R)n. \qquad (2)$$

Herein $P$ is the constant proportional to the product of the grain area and the light absorption factor of the grain; the factor $\beta n^{-\gamma}$ is given by Eq. (1): $Q$ is the constant proportional to ionic conductivity for the ionic process playing a role in the neutralization of trapped electron; $R$ is the probability of an electron escaping from an electron trap, or the reciprocal of average lifetime of a trapped electron, having the relationship,

$$R = \nu \exp(-\varDelta E/kT). \qquad (3)$$

In this relation $\varDelta E$ is the thermal depth of the electron trap, and $\nu$ the frequency with which a trapped electron collides with the potential walls of the electron trap, $k$ the Boltzmann constant and $T$ the temperature.

It should be remarked about Eq. (2) that the present authors deal only with the case where the magnitude of the first term $P\beta n^{-\gamma}I$ is larger than that of the second term $(Q+R)n$. If, however, the ionic migration is so rapid that the second term surpasses the first term even when the magnitude of the factor $R$ is very small, the accumulation of trapped electrons in an electron trap will not occur. Accordingly, Eq. (2), therefore the present treatment will be meaningless, but the extensions attempted by Katz and Webb will be found the good approximations in such a case.

Integrating Eq. (2), we have

$$n^{1+\gamma}=\{\beta PI/(Q+R)\}[1-\exp\{(1+\gamma)(Q+R)\}t]. \qquad (4)$$

When the factor $(1+\gamma)(Q+R)$ is large enough, Eq. (4) shows that the value of $n$ approaches the saturation value $n_s(I)$ given by,

$$n_s(I) = \{\beta PI/(Q+R)\}^{1/1+\gamma}, \qquad (5)$$

as soon as the grain is exposed. Then we can tentatively assume that the number of the trapped electrons in an electron trap remains constant throughout the whole exposure time, but increases slowly with increasing the exposure intensity $I$ in accordance with the relation (5). On this assumption, the number $N$ of the silver atoms produced by the neutralization process during exposure time $t$ can be calculated by the following equation

$$N = \int_0^t Qn_s(I)\mathrm{d}t. \qquad (6)$$

Substituting for $n_s(I)$ from Eq. (5) and then integrating, we obtain the following equation after a slight rearrangement,

$$\log It = \frac{\gamma}{1+\gamma}\log I-\log\frac{Q}{N} -\frac{1}{1+\gamma}\log\frac{\beta P}{Q+R}. \qquad (7)$$

Eq. (7) expresses the log exposure required to produce the $N$ silver atoms. Eq. (7) plotted on the $\log It$ *versus* $\log I$ type of diagram gives a straight line having a positive slope, and thus represents only the component of the high intensity failure.

## Consideration of the Low Intensity Failure Component

It is believed that the cause of the low intensity failure is found in the initial stages of latent image formation. Thermal vibration of the crystal lattice impedes the creation of the silver specks in the initial stages of latent image formation.

We now assume that the silver speck will begin to form only when the number of the trapped electrons in an electron trap at which the silver speck will be formed exceeds a critical value $n_c$, and that the silver speck so formed is stable to thermal agitation (the stable speck). Such interpretation is very similar to, but slightly different from that proposed by Gurney and Mott.[1]

Since the silver speck can not be formed under the condition that the intensity of exposure is so low that the value of $n_s(I)$ is less than a critical value $n_c$ ($n_s(I)<n_c$), where $n_s(I)$ is the average number of trapped electrons given by Eq. (5), the slope of the reciprocity-failure curve should become suddenly infinite at a critical intensity in the lower intensity side of the curve. Most experimental results, however, do not show such an abrupt upturn in the curve. It seems quite reasonable that the fluctuation of light quanta absorbed by a grain should be taken into account to interpret the non-existence of such an abrupt upturn in the lower intensity failure curve. This step has been already taken by many workers.[7]

Even if the average intensity of light is sufficiently low, its momentary value may be raised up because of the fluctuation phenomenon. Accordingly, it may be assumed[8] that the momentary number of trapped electrons may become larger than $n_c$, although its average number can not exceed $n_c$. Therefore, it is expected that even at such low intensities there exists the possibility of formation of a stable speck, and this possibility will decrease as the average intensity of light is lowered.

Let us now calculate the exposure required to produce the stable speck at intermediate intensities with considering the low and high intensity failure component simultaneously. We believe that Eq. (6) can answer our purpose if such modification is made on it as is based on the afore-said considerations. This modification is made in the following way: When the average number of trapped electons existing in an electron trap is $n_s(I)$, the probability $P(n)$ of $n$ electrons existing in an electron trap can be represented by the use of the Poisson equation,

$$P(n)=\exp\{-n_s(I)\}\{n_s(I)^n/n!\}. \qquad (8)$$

By summing this expression for all $n$ values from $n_c$ to infinity, we can obtain a factor $F\{n_s(I)\}$ corresponding to the probability of at least $n_c$ electrons existing in an electron trap

$$F\{n_s(I)\}=\exp\{n_s(I)\}\sum_{n=n_c}^{\infty}\{n_s(I)^n/n!\}. \qquad (9)$$

The above mentioned modification will be made when $n_s(I)$ in Eq. (6) is multiplied by the factor $F$ so obtained. Thus we can calculate approximately the exposure required to produce the stable speck (the number of silver atoms in it is $N_s$) by means of the equation

$$N_s=\int_0^{t_s} QF\{n_s(I)\}n_s(I)\mathrm{d}t. \qquad (10)$$

Substituting for $n_s(I)$ from Eq. (5) and then integrating, we obtain the following equation after a slight rearrangement,

$$\log It_s=\frac{\gamma}{1+\gamma}\log I-\log\frac{QF\{n_s(I)\}}{n_s}-\frac{1}{1+\gamma}\log\frac{\beta P}{Q+R}. \qquad (11)$$

This equation expresses the log exposure ($It_s$) required to produce the stable speck in the initial stages of latent image formation. The value of $F\{n_s(I)\}$ for a given value $n_c$ (say two), which can be calculated by the graphical method, begins to decrease less than unity as $n_s(I)$ is lowered. In addition, $n_s(I)$ varies with the intensity $I$ in accordance with Eq. (5), and thus following relation will be given,

$$\Delta\log n_s(I)=\left(\frac{1}{1+\gamma}\right)\Delta\log I. \qquad (5')$$

Using this relation we can easily get an idea of how the factor $F\{n_s(I)\}$ varies with the intensity $I$. It follows that the curve of Eq.

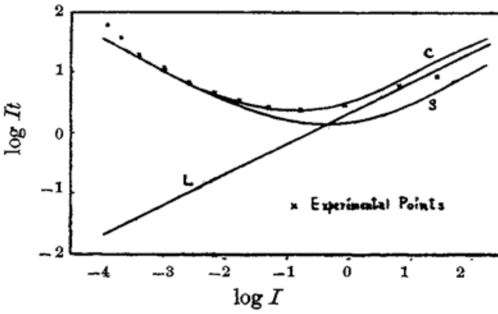


Fig. 2.—Theoretical reciprocity-failure curves for: (S), initial stages; (L), later stages; (C) total stages. Comparison of theoretical composite curve C with experimental curve.

(7) L. Silberstein, *J. Opt. Soc. Am.*, **29**, 432 (1939); P. C. Burton and W. F. Berg, *Phot. J.*, **86B**, 2 (1946); references (3) and (4)

(8) As has been stated, it is assumed that the saturation of the electron concentration in an electron trap is achieved as soon as the grain is exposed.

(11) plotted on $\log It$ *versus* $\log I$ type of diagram has its optimum point (the optimal intensity). Its schematic curve is shown by the curve S in Fig. 2. It has been derived, therefore, that the reciprocity-failure curve for the initial stages of formation of the latent image (the stable speck formation) has the optimal intensity.

### Composite Reciprocity Failure Curve

In order that the stable speck may be brought up to the developable size, there are still repuired some additional silver atoms $N_a$. Then, we assume that this process takes place in that later stages of the latent image formation in which there is no influence of the low intensity failure component, but of the high intensity failure component. Therefore, in order to calculate the further exposure ($It_a$) required to produce $N_a$ addtional silver atmos, Eq. (7) can be directly applicable. Thus we obtain the equation,

$$\log It_a = \frac{\gamma}{1+\gamma}\log I - \log\frac{Q}{N_a} - \frac{1}{1+\gamma}\log\frac{\beta P}{Q+R}. \qquad (12)$$

Since Eq. (12) does not contain the factor $F$, the shape of its reciprocity-failure characteristic is a straight line having a slope $\gamma/(1+\gamma)$ as shown by the line L in Fig. 2.

Finally, the log total exposures ($It$) required to produce the developable latent image from unexposed state will be

$$\log It = \log(It_s + It_a), \qquad (13)$$

where $It_s$ and $It_a$ are given by Eqs. (11) and and (12) respectively. Summation in Eq. (13) can be easily carried out by the graphical method. A composite reciprocity-failure curve so obtained is schematically shown by the curve C in Fig. 2. Using adjustable parameters $\gamma$, $n_c$, and $N_a/N_s$, we can fit the shape of the theoretiacl curve to that of experimental curve at and near the optimal intensity. The other parameters $\beta$, $N_s$, $N_a$, $P$, $Q$ and $R$ determine the position of the curve C in Fig. 2. The theoretical curve having $\gamma = 1$, $n_c = 2$ and $N_a/N_s = 2$ is shown here together with the measured points of the experimental reciprocity-failure curve.

## Discussion of Theoretical Results

**Discrepancies at Lower and Higher Intensities.**—As is shown in Fig. 2, the theoretical curve C does not perfectly agree with the experimental points in the region of lower and higher intensities. The discrepancy at lower intensities is probably connected with the fact that in such a region the trapped electron in an electron trap can not be accumulated continually during the entire course of exposure, therefore the fundamental Eq. (2) will lose its meaning. On the other hand, the discrepancy in the region of higher intensities presumably arises from the following fact: The present theoretical curve redresenting the log exposure required to produce only one just-developable speck in a grain is worthy of comparing with the experimental results obtained under the special condition that only the grains having a just-developable speck can initiate the development. In the region of higher intensities, however, the grains having the sub-speck whose size is too small to be developable for a short duration of development are likely to be formed together with the grains having the developable one. This tendency will progressively predominate with increasing the intensity. Thus, it is expected that the development conditions exert strong influence upon the shape of the curve in the region of higher intenisities at and beyond the optimum. Accordingly, the experimental curves would be more compatible with the theoretical curves, if the exposed emulsions were developed for a shorter period by means of a weaker developer.

**Bodily Shift of the Whole Curve.**—It is to be emphasized that the important feature of this theory is the strong dependence of the position of the whole curve in diagram upon the factors such as $\beta$, $P$, $Q$ and $R$. An interesting conclusion theoretically derived on the basis of this is that the position of the reciprocity-failure curve will make a bodily shift if the value of the above factors is changed.

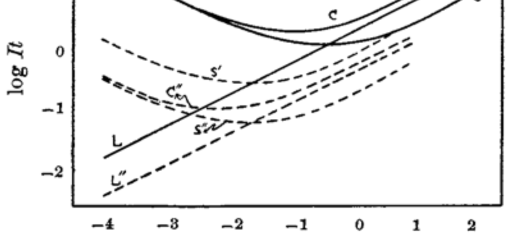


Fig. 3.—Bodily shift of the whole curve caused by the change in the magnitude of the factor $R$.

This conclusion has been reached in the following way: Let us consider, for instance, the case of the factor $R$, which is also applicable to the case of the factors $\beta$, $P$ and $Q$ with slight modifications. When the thermal depth $\Delta E$ of electron trap is increased, the probability $R$ of an electron escaping from the electron trap will be decreased in accordance with the relation (3). This decrease in the $R$ factor exerts an influence upon the factors $n_s(I)$ in accordance with the relation (5). If the value of $\beta P/(Q+R)$ is increased by a factor $\lambda$ due to a decrease in the $R$ factor, it is easily seen that the value of $n_s(I/\lambda)$ after this change equals to that of $n_s(I)$ before this change, and thus leaving the value of the $F$ factor unchanged. In Eq. (11), because of the existence of the term containing the $F$ factor, the position of the minimum point in the curve S will be shifted toward lower intensities along a straight line having a slope $\gamma/(1+\gamma)$ by an amount whose projection on the abscissa is $\log \lambda$ (as shown by the shift S $\rightarrow$ S′ in Fig. 3). It is to be noted here that the curves S and S′ have the same shape. Hence, the magnitude of the vertical descent of the upturn portion of the curve S will be $\{\gamma(1+\gamma)\} \log \lambda$. In addition, the curve S′ will vertically descend as a whole by an amount $\{1/(1+\gamma)\} \log \gamma$ (the shift S′$\rightarrow$ S″), since Eq. (11) has the last term containing the $R$ factor. This shift will change the shape of the composite curve. However, the straight line L will only vertically descend by the same amount originating in the last term in Eq. (12) (the shift L $\rightarrow$ L″), which does not contain the $F$ factor. Accordingly, the shape of the composite curve does not change. The vertical descend of the upturn portion of the composite curve (the shift C $\rightarrow$ C″) will be $\log \lambda$ after all. Thus, the composite curve will be shifted toward lower intensities diagonally (along the direction of 45-degree lines of constant exposure times) as a whole, since the vertical descend equals to the traverse shift in their magnitudes.

The present authors maintain that the above theoretical conclusion is tenable,(5) since it is consistent with the experimental facts concerning the diagonal shifts caused by the prolongation of after-ripening in its earlier stages. The detailed effects of after-ripening upon the position and shape of the reciprocity-failure curves will be discussed in our forthcoming publication.(6) It is to be added here that the measurements(9) of the reciprocity-failure curves of the photographic emulsions having the different ionic conductivities respectively are consistent with the theoretical conclusion derived by means of changing the factor $Q$ in the theory of this paper.

We are indebted to Prof. S. Makishima for helpful discussions concerning several points.

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(9) S. Fujisawa and E. Mizuki, *Bull. Soc. Sci. Phot. Japan*, (in press).