

Quantum Theory of the Latent Photographic Image

T. Howard James and J. J. Coleman

Citation: [The Journal of Chemical Physics](#) **2**, 483 (1934); doi: 10.1063/1.1749516

View online: <http://dx.doi.org/10.1063/1.1749516>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/2/8?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Physics of the Photographic Latent Image](#)

Phys. Today **42**, 36 (1989); 10.1063/1.881181

[The Photographic Latent Image. III. Dimensional Changes in Silver Bromide Following Exposure](#)

J. Chem. Phys. **22**, 1389 (1954); 10.1063/1.1740403

[The Photographic Latent Image II. Outline of the Theory](#)

J. Chem. Phys. **11**, 419 (1943); 10.1063/1.1723867

[Theory of the Photographic Latent Image Formation](#)

J. Appl. Phys. **11**, 18 (1940); 10.1063/1.1712703

[A Quantum Theory of the Latent Photographic Image](#)

J. Chem. Phys. **2**, 132 (1934); 10.1063/1.1749434



Quantum Theory of the Latent Photographic Image

T. HOWARD JAMES AND J. J. COLEMAN, *University of Colorado, Boulder, Colorado*

(Received March 22, 1934)

A general formulation involving quantum ideas is given for the relation between the amount of photolytic action in latent image formation and the amount of light producing it. A method of deducing the number of "effective" quanta per grain necessary to produce developability is given. Slow process emulsions require, in general, the absorption of from 3 to 4 "effective" quanta. This number agrees with that found for physical development by Reinders and Hamburger. Faster emulsions require a

smaller number (1 to 2), showing presumably the presence of more highly developed sensitivity centers. The number for any emulsion should depend to some extent upon the developer used. Parametric equations are given which relate the amount of photolytic product to the number of developable grains. These equations lead to a characteristic curve which has a point of inflection when the number of "effective" quanta required per grain is greater than one but none when the number is equal to one.

I

IT has been proposed¹ that during the period of light-action upon a photographic emulsion, the building up of a developable density is accompanied by a reverse reaction. It was suggested² that this conception must be incorporated with a quantum theory of latent image formation in order to obtain a satisfactory relation between the net amount of photolytic action and the amount of light producing it. On this basis, a modified form of Elder's equation was derived.

In the original formulation of the theory² the true state of affairs was approximated by assuming that the absorption of one quantum by a sensitized area, i.e., a more or less restricted area containing a pro-nucleus, rendered a grain developable and that in considering the effect of the reverse reaction we could ignore the grains in which that area had absorbed more than one quantum. The theory was further marred by the use of the notion of a "time lag." It is the purpose of this paper to develop the theory in a more rigorous fashion and to consider some of the consequences of this formulation. The

assumption that one quantum alone suffices to produce a developable grain is valid only in special cases. In general, however, the assumption is untenable³ and a method will be given for determining (approximately) the number of *effective* quanta required to produce a developable center on a grain. However, the gain in elegance and precision is somewhat at the expense of serviceableness, for we cannot apply the modified theory to density measurements unless we are dealing with emulsions with a uniform grain size and we have given the "maximum ideal developable density" (i.e., the density which would be produced if all of the grains were developable).

Fundamentally, the theory is of great simplicity. We assume: (1) When a quantum of sufficient energy is absorbed by a given grain, one ion or perhaps a group of ions are modified in such a way that, when a sufficient number of modifications are produced within a more or less restricted area, a development center results and the grain as a whole becomes developable by the developer concerned. We shall for convenience term the product of one absorbed quantum in an "effective" area of grain an "active center," emphasizing that one of them alone does not, in general, constitute a development center. The "effective" area refers to that

¹ Svedberg and Anderson, *Phot. J.* **48**, 272 (1924); Lüppo-Cramer, *Proceedings of the 7th Int. Cong. Phot.*, p. 45 (1928) (General references are given.); Kieser, *Zeits. f. wiss. Phot.* **26**, 275 (1929); Sheppard, *Ind. Eng. Chem.* **22**, 555 (1930); Blair and Leighton, *J. Phys. Chem.* **36**, 1649 (1932).

² James, *J. Chem. Phys.* **2**, 132 (1934).

³ Cf. Sheppard, Trivelli and Loveland, *J. Frank. Inst.* **200**, 51 (1925); Reinders and Hamburger, *Zeits. f. wiss. Phot.* **31**, 265 (1933).

region from which the "active center" may act with a pro-nucleus, by itself or with other similar centers within the region, or with other centers alone, to produce a development center. (2) These centers have a tendency to change either spontaneously or under the influence of various agents (light quanta, chemicals, etc.) to a non-active state which cannot contribute to developability of the grain. (3) If β is the number of ions (or groups of ions) which are available in N grains for the production of active centers and s the number of active centers present at any time, then the speed of the "forward reaction" is proportional to $(\beta - s)$. (4) The speed of the "reverse reaction" is proportional to s itself.

The equation for the rate of formation of the active centers is then

$$ds/dt = K_1(\beta - s) - K_2s \quad (1)$$

in which K_1 and K_2 depend upon the intensity and wave-length of the incident light, the nature of the emulsion and other factors. The equation yields upon integration and evaluation of the constants of integration (we take $t=0$ when $s=0$)

$$s = s_m(1 - e^{-Kt}) \quad (2)$$

$$\text{or} \quad \ln(1 - s/s_m) = -Kt \quad (2a)$$

in which

$$s_m = \beta / (1 + K_2/K_1), \quad (3)$$

$$K = K_1 + K_2. \quad (4)$$

By Eq. (2) it is evident that s_m is the maximum number of centers producible by light of a given wave-length and intensity, i.e., the number present at equilibrium.

There is at present no way of counting the active centers and therefore Eq. (2) cannot be tested directly. The value of s must be determined either from counts of the number of developable grains or from density measurements. As we have already stated, density data can only be used with uniform grain emulsions and when the value of the maximum ideal developable density, b , is known. This information is, unfortunately, lacking in the majority of the published data. If we know b , then since the density is proportional to the number of developable grains, we shall have

$$k/N = D/b \quad (5)$$

in which k is the number of developable grains, N the total number of grains and D the density. The ratio s/s_m , required by Eq. (2a), can be calculated from k/N as follows:

Silberstein⁴ has presented an equation which expresses s/N in terms of k/N ⁵ and since we can put

$$s/s_m = (s/N)/(s_m/N) = (s/N)/(s/N)_m \quad (6)$$

in which $(s/N)_m$ is the maximum value of s/N , we can thus obtain the ratio s/s_m . Silberstein's equation is

$$k/N = 1 - e^{-s/N} \sum_{i=0}^{r-1} \frac{1}{i!} (s/N)^i, \quad (7)$$

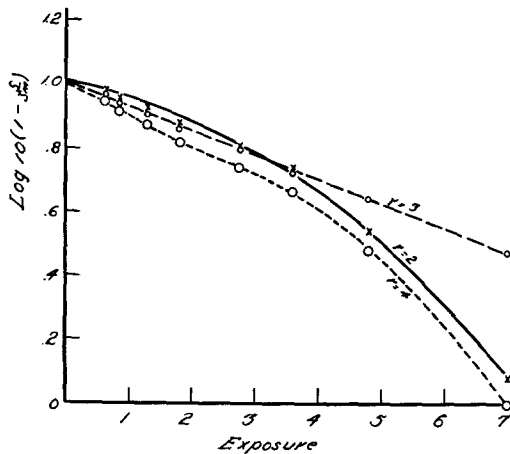
where r is the number of active centers necessary to produce a developable grain. A derivation of this equation will be given in the next section. Eq. (2a) shows that a straight line should be obtained by plotting $\ln(1 - s/s_m)$ against t . Hence such plots made for various values of r , if a straight line can be obtained, both confirm the validity of Eq. (2a) and give us the correct value of r . Such straight lines were obtained in all of the sets of data tried. In Figs. 1 and 2 we give two illustrations.

The data used to obtain Fig. 1 are by Toy (Table 5, reference 2). The graph in this case very definitely indicates 3 as the proper value of r . Fig. 2 (data by Trivelli and Loveland, Table 4, reference 2) does not yield as pronounced a divergence from a straight line for values of r adjacent to the correct value but the divergence is definitely present, in this case for small values of exposure.⁶ The results obtained for other sets of data are given in Table I. In some cases the graphs allow no choice between two consecutive values of r but definitely exclude all others.

⁴ Silberstein, Phil. Mag. 5, 464 (1928).

⁵ Silberstein's formula expresses ϵan , the average effective number of quanta in each grain, assuming all to have equal area a , in terms of k/N . By the above definition, $s = \epsilon anN$, and hence $\epsilon an = s/N$. We are not, in this paper, considering the effect of the size of the grains and formula (7) is not restricted to emulsions with uniform grain size (see derivation, section II).

⁶ The value of x_m where $x = k/N$ for this emulsion was redetermined by careful extrapolation to be 0.64. The old value, 0.65, yields however the same value of r .

FIG. 1. Graph of $\log 10(1-s/s_m)$ against exposure, E .

Strictly speaking, Eq. (7) is valid only for cases in which the number of active centers required for developability is the same for all of the grains in the emulsion. However, at least a small fraction of the grains undoubtedly require a number of centers different from that found for the plate as a whole.

It is to be expected that the value of r will depend upon the emulsion and to some extent upon the developer used. The theory of Sheppard, Trivelli and Loveland⁷ that the number of quanta required to render a grain developable depends upon the size of the "pro-nuclei" present in the grain before exposure, is of interest in this connection. Reference to Table I

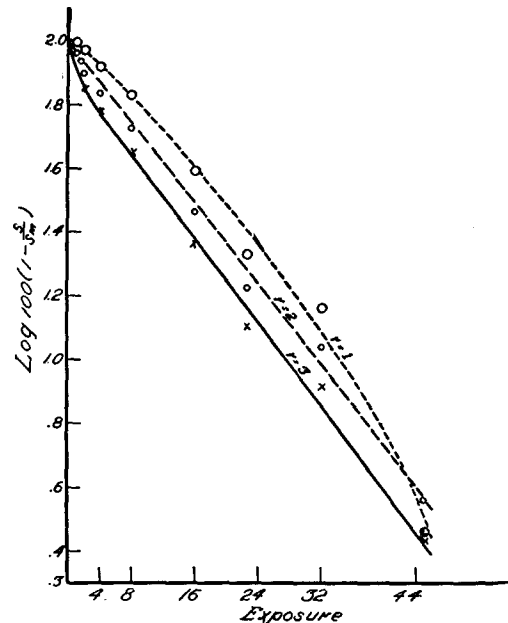
TABLE I. Values of r for various emulsions.

Emulsion	Grain size	s_m/N	r	Investigator
Ilford Process	$0.3\mu^2$	8.5	3	Toy, Phil. Mag. 45 , 719 (1923)
Special. Uniform grain size	—	6.3	3	Toy, Phot. J. 61 , 420 (1921)
Eastman 40	$0.4\mu^2$	2.0	2	Trivelli and Loveland, quoted by Silberstein, Phil. Mag. 45 , 483 (1923)
Eastman Slow Process	$0.115\mu^2$	7.8-9.2	4-5	Trivelli and Loveland, from Fig. 1, Silberstein, Phil. Mag. 5 , 464 (1928)
	$0.7\mu^2$	10-10.6	3-4	
High speed	$0.98\mu^2$	2.6-5.5	1-3*	Toy, Phil. Mag. 44 , 365 (1922)
	$1.75\mu^2$	3.3	1	
	$2.75\mu^2$	3.75	1	
Special Eastman Lantern slides**	—	3.0-4.8	1-2	Lester, quoted by James, J. Chem. Phys. 2 , 135 (1934)

* Correct value uncertain, probably 2.

** Exposure by x-rays.

⁷ Sheppard, Trivelli and Loveland, J. Frank. Inst. **200**, 51 (1925).

FIG. 2. Graph of $\log 100(1-s/s_m)$ against exposure, E .

will show that in one set of data by Toy the value of r is one. This emulsion would be, on this theory, one which was approaching the limit beyond which an emulsion cannot be ripened without fog. We should expect that, grain size being constant, the sensitivity of various emulsions would depend both upon their power to absorb light and upon the value of r . Unfortunately no usable data are available with which to test this hypothesis. It is further to be noted that in Toy's data we have three different grain sizes. The differences in sensitivity exhibited by these sets may well be ascribed to differences in the sizes of the grains.

It is interesting to note that the density-exposure data for α -particles fit well within the experimental error the simple equation of reference (2)⁸ without a "time lag," i.e., the equation

$$x = x_m(1 - e^{-Kt}). \quad (8)$$

This relation also holds approximately for x-rays⁹ indicating in each case that r is probably one. This is, perhaps, to be expected in view of

⁸ Svedberg and Andersson, Phot. J. **61**, 325 (1921).

⁹ Svedberg, Phot. J. **62**, 310 (1922).

Trivelli, VIII Int. Cong. Phot., p. 378 (1931).

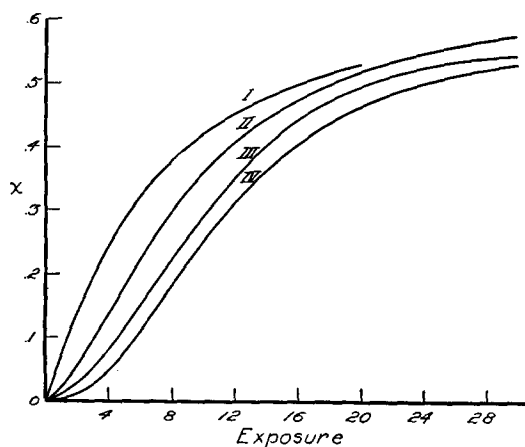
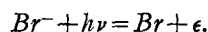


FIG. 3. Characteristic curves determined from the parametric Eqs. (2) and (7).

the large energy of x-ray quanta and of α -particles.

In the foregoing development no definite assumptions were made as to the nature of the active centers. The theory is, insofar as the development of the quantitative formulation is concerned, independent of such assumptions as long as the four fundamental postulates enumerated above remain valid. It is nevertheless desirable to show the application of this formulation to modern theory of the mechanism of latent image formation.

The evidence at present points strongly to the following mechanism for the primary action of an absorbed quantum:



This "... photo-ionization process is essentially virtual. If the electrons are not taken over by silver ions, the halogen atoms by some acceptor, the process must reverse."¹⁰ If the electron is taken over by a silver ion, a silver atom results, which is the manifestation of an "active center."

If this mechanism is correct, then the process of developable center formation is similar to that with which Reinders and Hamburger¹¹ were concerned in their studies of physical development. It is interesting to note that the

¹⁰ Sheppard, *Ind. Eng. Chem.* **22**, 555 (1930) (Nichols Medal Lecture).

¹¹ Reinders and Hamburger, *Zeits. f. wiss. Phot.* **31**, 32 (1932) and **31**, 265 (1933).

value of r is from 3 to 4 for most slow emulsions and that this agrees with the results of Reinders and Hamburger (most probable value, 4).

It is not necessary to assume that the value of r represents the total number of atoms which are produced in the entire grain. It is rather the number produced in the "sensitive" area (used in the sense already indicated rather than referring to any sensitizing action of dyes) of the grain. Only quanta absorbed in this area are *effective* quanta. This area may represent the effective area around a sensitivity speck in the grain; i.e., that area from which the silver atoms could concentrate upon the sensitivity speck and thus tend to produce a developable center. It is conceivable that this area is dependent upon temperature to some extent. Moreover, Silberstein's work indicates that no great error would arise in the calculations if there exist several such areas upon each grain, as will, indeed, usually be the case.

Fig. 3 gives four "characteristic curves" calculated from the parametric Eqs. (2) and (7). The values of r range from 1 to 4, and those of x_m are approximately 0.6. It will be seen that these curves represent adequately the general form of the experimental characteristic curve. The presence or absence of a point of inflection is governed by the value of r and hence is dependent upon the nature of the emulsion. The "time lag" previously assumed to exist in certain cases² appears quite naturally and not as something foreign to the theory.

II

Consider a state of exposure which is the result of exactly s quanta, i.e., s quanta have been effective in producing "active centers." Any of the quanta can act upon any of the N different grains and accordingly all of the quanta can act upon all of the grains in N^s different ways.

If, now, it be required that a particular grain be unaffected, the number of possible ways in which the quanta can act upon the remaining grains is $(N-1)^s$. If it be required that this particular grain be affected by one and only one quantum, this condition can be satisfied in exactly the number of ways in which one quantum can be chosen out of a total of s ;

namely, in s different ways. In each case there will be $(N-1)^{s-1}$ ways in which the remaining quanta can act upon the remaining grains. Hence, the total number of ways in which the grains can be exposed under the condition that some particular grain be affected by exactly one quantum is $s(N-1)^{s-1}$. In general, the number of ways of exposing the grains under the condition that a particular grain be acted upon by exactly i quanta is,

$$[s!/(i!(s-i)!)](N-1)^{s-i}$$

in which $s!/(i!(s-i)!)$ is the number of ways of selecting i quanta out of a total of s .

If all of the ways of making the grains developable are equally probable, then the probability that exactly i quanta out of a total of s effective quanta will act upon a particular grain in a given exposure is given by

$$\frac{s!}{i!(s-i)!} \frac{(N-1)^{s-i}}{N^s} = \frac{s!}{i!(s-i)!} \frac{1}{(N-1)^i} \left(\frac{N-1}{N}\right)^s.$$

If P is the probability that a given grain be affected by *at least* r quanta, then

$$P = \sum_{i=r}^s \frac{s!}{i!(s-i)!} \frac{1}{(N-1)^i} \left(\frac{N-1}{N}\right)^s \\ = \left(\frac{N-1}{N}\right)^s \left[\sum_{i=0}^s \frac{s!}{i!(s-i)!} \left(\frac{1}{N-1}\right)^i - \sum_{i=0}^{r-1} \frac{s!}{i!(s-i)!} \left(\frac{1}{N-1}\right)^i \right].$$

The first summation is merely the binomial expansion of

$$(1 + 1/(N-1))^s = (N/(N-1))^s,$$

therefore

$$P = 1 - \left(\frac{N-1}{N}\right)^s \sum_{i=0}^{r-1} \frac{s!}{i!(s-i)!} \left(\frac{1}{N-1}\right)^i.$$

Since both N and s are very large, the fraction of the total number of grains which are acted upon by at least r quanta (where $r \ll s$ and $r \ll N$) will be (approximately) the same in all of a number of exposures of identical plates. Moreover this fraction will be the probability that a particular grain in a given exposure be acted upon by at least r quanta. Hence if k is the number of grains that have been acted upon by *at least* r effective quanta, then

$$\frac{k}{N} = P = 1 - \left(\frac{N-1}{N}\right)^s \\ \times \sum_{i=0}^{r-1} \frac{s!}{i!(s-i)!} \left(\frac{1}{N-1}\right)^i \quad \begin{matrix} r \ll s \\ r \ll N. \end{matrix} \quad (9)$$

This equation is exact but a more convenient approximation will be of sufficient accuracy for the present purposes. We can put

$$((N-1)/N)^s = (1 - 1/N)^{N(s/N)} = e^{-s/N},$$

since $(1 - 1/N)^N$ is asymptotically equal to e^{-1} for large N . Furthermore

$$s!/(s-i)! = s(s-1)(s-2) \cdots (s-i+1)$$

and since $r \ll s$, and hence $i \ll s$ in each term of the summation in (9),

$$s!/(s-1)! = s^i$$

approximately. Finally, 1 can be neglected in comparison to N in the factors $[1/(N-1)]^i$ as long as i is small. (Note that these last two approximations tend to cancel each other.) Eq. (9) can now be written:

$$k/N = x = 1 - e^{-s/N} \sum_{i=0}^{r-1} \frac{1}{i!} (s/N)^i. \quad \begin{matrix} r \ll N \\ r \ll s \end{matrix} \quad (10)$$

This is the equation first presented by Silberstein.⁴