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A Quantum Theory of the Latent Photographic Image

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An explanation of the process of photographic exposure on the basis of a true photochemical reaction is offered. It is pointed out that the apparent failure of the Einstein equivalence law in the case of photographic exposure for short intervals is not real, and an equation is derived on the basis of the assumption that the *absorption* of one quantum by a sensitivity center of the grain produces an activated, but unstable state which renders the grain as a whole developable. The assumption that an activated grain may revert to an undevelopable state is an important part of the present theory, and evidence in favor of this assumption is cited. The theory that the photographic process is auto-

catalytic is criticized on the basis that the point of inflection of the H and D curve indicated by this theory is much higher than the point found experimentally. A preliminary treatment of the Herschel effect is given on the basis of the proposed theory, and an equation holding under special conditions is derived. The explanation of the intermittency effect as put forward by Blair and Hylan is still valid in the light of the present theory. Data taken from reliable sources are given to show that the general equation holds over wave-lengths ranging from red light to x-rays, and emulsions from Azo to Eastman Portrait.

THE quantum theory of photographic exposure, as proposed by Svedberg, Silberstein and others, has met with marked success neither in affording an equation thoroughly applicable to known exposure-density data, now in explaining such phenomena as the Herschel and intermittency effects. It is clear that a satisfactory theory, in addition to supplying an equation for the time rate of growth of density with exposure, must as well offer an explanation for the phenomena mentioned above, and for the influence of wave-length upon the maximum developable density; e.g., red light produces a much lower maximum than does blue light. Moreover, it must explain why, in the case of certain emulsions, notably the slower ones, the maximum developable density even with blue light is very definitely less than 100 percent.

The theory which, in the opinion of the present author, most closely approaches known facts is that proposed by Blair and Leighton¹ based upon the assumption that during exposure there exists an opposing tendency acting to revert exposed grains to an undevelopable condition. This assumption, in a modified form, will be retained in the present development. Evidence for the actual existence of the "reverse reaction" is furnished both by the success of Blair and his

students in explaining qualitatively the Herschel and intermittency effects on this basis, and by the chemical investigations of James, Germann and Blair.²

PRELIMINARY STATEMENT OF THEORY

A photographically active silver halide grain contains one or more sensitivity centers, haphazardly distributed throughout the grain. The necessary and sufficient condition in order that the grain become developable is that one center *absorb* one quantum. Analogy with the photoelectric effect suggests that only a definite fraction of the quanta which strike the grain become absorbed, and that fraction rapidly decreases with the frequency until at the threshold value of ν_0 , it becomes zero. The experimental work of Eggert and Noddack³ has indicated that, of the total light absorption by the *emulsion*, a large fraction (becoming unity for long wave-lengths) is absorbed by the gelatin. It is an interesting fact that the efficiency curve of the photoelectric effect with the alkali metals is of precisely the same general nature as the corresponding curve for photographic exposure.

² James, Germann and Blair, Reported to Colorado-Wyoming Academy of Science, Dec. 1, 1933.

³ Eggert and Noddack, *Zeits. f. Physik* **20**, 299 (1923); **21**, 264 (1924); **31**, 922 (1925).

¹ Blair and Leighton, *J. Phys. Chem.* **36**, 1649 (1932).

A grain which has absorbed a light quantum exists in an activated, and hence developable, albeit an *unstable* state.⁴ There exists, accordingly, a tendency which may, either spontaneously or under the influence of some agent (quanta of smaller $h\nu$ are not excluded) act to revert the grain to an undevelopable condition. Moreover, the activated state of the exposed grain is smaller for smaller $h\nu$, and the probability that the grain revert to an undevelopable state is correspondingly greater. It does not necessarily follow, however, that the "undevelopable state" referred to is that of the original unexposed grain. It may be a state activated by an excess energy content smaller than a certain minimum necessary for developability. This concept may offer an explanation of the observed shift of sensitivity towards the red during exposure.

MATHEMATICAL STATEMENT OF THE THEORY

Silberstein,⁵ by assuming random distribution of sensitivity centers, deduced a relation between the exposure and the number of developable grains. His formula, with alterations required by the present theory, is:

$$k/N = 1 - e^{\bar{\kappa}(e^{-\epsilon n \omega} - 1)} \quad (1)$$

where k = number of developable grains, N is the total number of sensitive grains in the emulsion, $\bar{\kappa}$ is the average number of sensitivity spots, ω is the average area of a sensitivity spot, n is the number of quanta falling upon the emulsion, and ϵ is a constant (only, however, for a given wave-length). Eq. (1) is valid as the expression for the forward reaction in the light of the present theory.

If $\epsilon n \omega$ (a pure number) is a small fraction, Eq. (1) yields as a first approximation

$$k/N = 1 - e^{-n\alpha} \quad (1a)$$

where $\alpha \propto \epsilon \omega$. Eq. (1a) has ample mathematical accuracy when consideration is taken of the degree of experimental error in determining the

quantities involved, and is indeed the relation which would hold rigorously if the sensitivity centers were uniformly distributed.

Eq. (1a) will be rewritten:

$$x = k/N = 1 - e^{-bt}, \quad (2)$$

where we shall define x as the developability coefficient, b is a constant, and the exposure intensity is assumed to be uniform throughout the time t . Whence, the velocity of the forward reaction tending to produce developable grains becomes:

$$(dx/dt)_f = b(1 - x). \quad (3)$$

The reverse reaction tending to return the grains to an undevelopable state will, in the first approximation, be proportional to the number of grains developable at any time, and hence:

$$(dx/dt)_r = cx. \quad (4)$$

This approximation becomes poorer as x increases (see following section on Herschel effect), a point borne out by the data presented elsewhere in this article.

Combining (3) and (4), we have for the complete equation

$$\begin{aligned} dx/dt &= b(1 - x) - cx \\ &= K_1 - K_2x, \end{aligned} \quad (5)$$

where K_1 and K_2 are constants. Integrating, we obtain:

$$x = (K_1/K_2)[1 - e^{-K_2(t - A/K_1)}]. \quad (6)$$

The coefficient x will assume a maximum value $x_m < 1$ when dx/dt becomes zero. Hence, by Eq. (5) we have

$$x_m = K_1/K_2.$$

Further, when $x = 0$, $t = t_0 \geq 0$,⁶ and, from Eq. (6),

$$A/K_1 = t_0.$$

Hence, we have, substituting the above values in (6)

$$x = x_m[1 - e^{-K_2(t - t_0)}], \quad (7)$$

⁴ More definite assumptions as to the nature of the "activated state" will be made at a later date. The above rather vague statement is sufficient for present purposes.

⁵ Silberstein, Phil. Mag. 45, 1062 (1923).

⁶ There is evidence to support this assumption of a small but finite time lag, and it cannot be considered as introduced *ad hoc*. It must not, however, be assumed that during this period, no action is occurring, but rather that it is a period of incubation.

an equation which, although it resembles superficially that of Silberstein, differs fundamentally from the latter. The values of x_m and t_0 are read directly from the H and D curve, and the only constant to be evaluated is K_2 .

Although Weigert and his co-workers,⁷ studying the action of light on emulsions used in daylight photographic papers, found a point of inflection in the curve obtained by plotting time of illumination against silver which was found, Eggert and Noddack,⁸ working with a similar emulsion, observed no such point. The same state of affairs exists in the data of various workers on ordinary photographic emulsions. When the time lag, t_0 , is very small, the point of inflection has no definite existence. When t_0 is (relatively) large, the evidence favors the existence of an S-shaped curve. It is noteworthy in this connection that the equation of Blair and Leighton, which is based upon the assumption that the photographic process is auto-catalytic, yields as a relation between the point of inflection and the maximum developable density:

$$x_m^{-\frac{1}{2}}(1-x_m) = x_i^{-\frac{1}{2}}(1-3x_i),$$

which, when x_m is of the order of 1, yields the value $\frac{1}{3} > x_i > 0.3$, a value much higher than the usual experimental one.⁹

It is, accordingly, the opinion of the author that the existence of a point of inflection in the H and D curve is an incidental, rather than a fundamental, property of the curve, and is probably in some way associated with the fundamental cause of the lag.

PRELIMINARY CONSIDERATIONS ON THE HERSCHEL EFFECT

Blair and Joehneck¹⁰ have explained the Herschel effect on the basis of the postulated simultaneous forward and reverse reactions. If we assume, on the basis of the present theory, that light of longer wave-length than the initial exposing light, constitutes an agent which

accelerates the reversal of exposed grains, we are faced with a problem presenting much greater difficulties in its quantitative treatment than the problem of initial exposure. For, although in order to make a grain developable, it is sufficient that only one developable center be formed, if the grain is to revert to an undevelopable state, every activated center of the grain must become passive. It has been demonstrated experimentally that the average number of activated centers per grain increases with exposure and when the initial exposure approaches a maximum this number becomes appreciably greater than one. As suggested in the preceding section, this factor would also enter into the expression for the reverse reaction as a correction term in Eq. (5), but its omission does not greatly affect the applicability of Eq. (7). In the present case, however, it is very important. We may write, then, as a more accurate expression,

$$dx/dt = b(1-x) - c(x-x_2), \quad (8)$$

where x_2 is a nonlinear function of x .

In the simplest case ($x_2=0$) Eq. (8) yields the same expression as before (Eq. (6)). The constants, however, will have different values. When $t=0$, $x=x_a$, and when $t=\infty$, $x=x_0$, the equilibrium density for the light producing the Herschel effect. Substituting these values, Eq. (6) becomes:

$$x = x_0[1 + [(x_a - x_0)/x_0]e^{-K_2 t}]. \quad (9)$$

For low densities, the value of x_2 will be small, and Eq. (9) will be applicable with considerable accuracy, as Table VI shows. The data for this table are taken from Table II of Trivelli's paper on *The Herschel Effect*.¹¹ At much higher densities, the experimental curve is markedly flatter than that indicated by Eq. (9), a condition which is to be expected in the light of the previous discussion.

CORRELATION OF THEORY AND DATA

There can be little discrimination between Eq. (7) and Eq. (2) in cases where x_m is of the order of 1. The obvious test of Eq. (7) is, then, its appli-

⁷ Weigert and co-workers, Sitzb. Preuss. Akad. 641 (1921).

⁸ Eggert and Noddack, Zeits. f. Physik 31, 922, 942 (1925).

⁹ Cf. Silberstein, Phil. Mag. 5, 464 (1928).

¹⁰ Blair and Joehneck, J. O. S. A. 23, 67 (1933).

¹¹ Trivelli, J. Frank. Inst. 207, 781 (1929).

cation to cases where x_m is appreciably less than one. Tables II and IV give data for two such cases.

Tables I–VI included in this article are selected from a wide range of workers and conditions. Each of the tables presented has been abbreviated by omitting (as a rule) every other value. Several additional sets of trustworthy data found in the literature (chiefly by Trivelli and Loveland and Blair) were tested by Eq. (7) and found to be in as good agreement as the data presented here. Further data both with light of longer wave-length and with slow emulsions (e.g., Azo) are greatly to be desired.

In cases when the data are expressed in terms of density rather than in terms of x , D may be

TABLE I. Eastman 40 emulsion. (Trivelli and Loveland.)

x (obs.)	x (calc.)	$E = It$	x (obs.)	x (calc.)	$E = It$
0.02	0	0.05	0.73	0.72	0.3
.07	0.08	.075	.845	.833	.4
.16	.19	.1	.935	.93	.5
.52	.53	.2			
$E_0 = 0.06 \quad x_m = 0.99 \quad K = 5.39$					

TABLE II. Azo special emulsion. Red light. (Blair—unpublished.)

Density (obs.)	Density (calc.)	t (hours)	Density (obs.)	Density (calc.)	t (hours)
0.08	0.09	3	1.44	1.44	70
.23	.21	6	1.60	1.61	92
.71	.72	24	1.76	1.75	120
1.12	1.12	44			
$t_0 = 0.5 \quad D_m = 1.92 \quad K = 0.02 \quad x_m = 0.58$					

TABLE III. Special Eastman lantern slides. X-rays. (J. Lester—unpublished.)

Density (obs.)	Density (calc.)	t	Density (obs.)	Density (calc.)	t
0.23	0.22	0.85	1.05	1.08	5.6
.27	.27	1	1.35	1.37	8.4
.42	.45	1.8	1.51	1.51	10.4
.62	.67	2.9	1.64	1.61	12.1
.80	.84	3.9			
$D_m = 1.94 \quad K = 0.1455 \quad t_0 = 0$					

TABLE IV. Trivelli and Loveland. (Quoted by Silberstein, Phil. Mag. 5, 483.)

x (obs.)	x (calc.)	E	x (obs.)	x (calc.)	E
0.014	0.016	1	0.276	0.274	8
.074	.071	2	.463	.444	16
.155	.153	4	.582	.588	32
$x_m = 0.65 \quad K = 0.075 \quad E_0 = 0.7$					

TABLE V. Toy, Phil. Mag. 45, 719. (Data read from Fig. 4.)

x (obs.)	x (calc.)	E	x (obs.)	x (calc.)	E
0.03	0.025	0.65	0.66	0.66	2.75
.11	.12	.85	.79	.77	3.6
.25	.29	1.3	.92	.87	4.8
.45	.45	1.8	.98	.95	7.0
$x_m = 0.99 \quad E_0 = 0.6 \quad K = 0.503$					

TABLE VI. Herschel effect with infrared (Trivelli).

Density (obs.)	Density (calc.)	t	Density (obs.)	Density (calc.)	t
0.34	0.337	18	0.30	0.303	290
.34	.335	36	.29	.292	410
.33	.329	74	.28	.279	579
.32	.320	145			
$x_0 = 0.23 \quad x_a = 0.34 \quad K = 0.0014$					

directly substituted for x in the equation, since it has been shown¹² that a linear relation exists between the two.

In conclusion, as an indication of the general applicability of the theory presented, it may be pointed out that the data for x-rays and for red light satisfy Eq. (7) as well as that for blue light.

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¹² Sheppard and Mees, *Theory of Photographic Process*, Arens, Eggert and Heisenberg, Veroff. wiss. Agfa 2, 28 (1931).