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TABLE I.

$\frac{\rho_2}{\rho_1}$	$\frac{p_2}{p_1}$	$\frac{T_2}{T_1}$	Thickness (free paths)	$\frac{p^{(1)}}{p^{(0)}}$
1.0000	1.0000	1.0000	∞	0.0000
2.6661	4.4981	1.6871	3.98	0.3460
3.7899	9.8365	2.5954	3.08	0.7198
4.6382	19.700 ₃	4.2474	2.25	1.0967
5.2931	43.387 ₆	8.1998	1.98	1.4854
6.0000	∞	∞	1.74	2.5000

where, from Burnett's formulae, (9)–(12),

$$p^{(2)}/p^{(1)} \approx p^{(1)}/p^{(0)},$$

and

$$q^{(2)}/q^{(1)} \approx 10p^{(1)}/p^{(0)}.$$

We see that, while there is no guarantee of convergence, the general effect of the third-order terms is to make the front thicker.

Lastly, in the notation of kinetic theory, the Boltzmann equation, the solutions of which we are approximating, is

$$u \frac{\partial f}{\partial x} = \int \int \int \int (f'f'_1 - ff_1) g b d b d \epsilon d v_1 d u_1$$

to determine $f(x, u, v)$ and, if the method of Chapman and Enskog fails to converge, this may be rewritten

$$u \frac{\partial f}{\partial x} + f \int \int \int \int f_1 g b d b d \epsilon d v_1 d u_1 = \int \int \int \int f' f'_1 g b d b d \epsilon d v_1 d u_1$$

and may be approximated by iteration using an already determined approximation both on the right-hand side and in the integral on the left, in the manner used in astrophysics for the transport of radiation in a stellar photosphere.^{10 11}

CONCLUSIONS

All shock waves in air but the weakest are a few free paths thick. If the shock is strong the approximation process of the theory of non-uniform gases probably does not converge, because the distribution function of molecular velocities within the front departs too far from the Maxwellian. There is, however, no reason to doubt that the Boltzmann equation possesses a suitable solution.

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The Charge Effect in Photographic Development: Role of the Gelatin*

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The approach of negatively charged developer ions to the surface of a silver bromide grain is opposed by charge barriers originating both with the gelatin and with the adsorbed bromide ions. It is shown that the effect of neutral salt upon the rate of development by negative ions results primarily from a depression of the gelatin charge barrier. The effect of salt upon the bromide barrier is relatively unimportant. On the other hand, a change in the bromide barrier is mainly responsible for certain other kinetic effects, such as the induction period in development and the accelerating action of phenosafranin.

A COLLOIDAL particle of silver bromide, suspended in a solution containing excess soluble bromide, is negatively charged by the adsorption of excess bromide ions to the surface. This charge acts to concentrate positive ions in the solution near the surface and to oppose the approach of other negative ions to the surface.

* Communication No. 994 from the Kodak Research Laboratories.

The resulting electric double layer consists on the one hand of the adsorbed bromide-ion layer, together with a more or less firmly held water shell, and on the other hand a diffuse ionic atmosphere in which positive ions predominate near the solid surface but decrease in predominance as the distance from the surface increases.

If the system is placed in an electric field, the

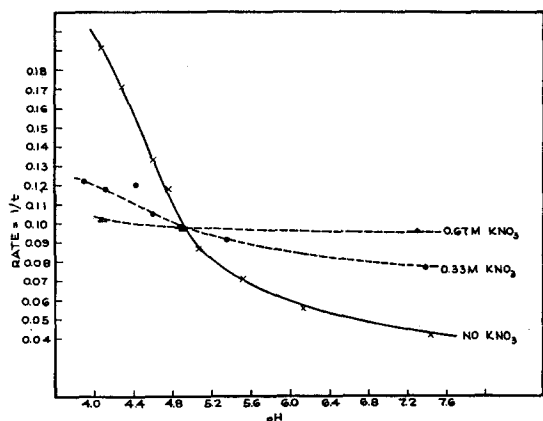


FIG. 1. Effect of KNO_3 on development by $\text{Fe}(\text{C}_2\text{O}_4)_2^-$. $\Delta = 0.67 M \text{KNO}_3$; $\circ = 0.33 M \text{KNO}_3$; $\times = \text{No } \text{KNO}_3$.

particle moves through the solution. The mobility of the particle is determined by the potential at the surface of shear between the particle and the bulk solution, i.e., the zeta-potential. For a given concentration of bromide ions in the adsorbed layer, the potential at any point in the solution near the adsorbed layer depends markedly upon the ion concentration in the solution. The higher the ion concentration, the greater will be the crowding of positive ions near the solid surface, and hence the lower the potential in this region or at the shear surface itself.

In the presence of gelatin, the silver bromide particle becomes coated with an adsorbed layer of gelatin which is tenaciously held to the surface.¹ It is not known to what extent the gelatin displaces the adsorbed bromide and water layer, and to what extent it simply forms an additional outer coating. However, the behavior of the particle in an electric field is now determined by the gelatin and not the bromide layer. On the positive side of the gelatin isoelectric point, the particle moves as a positively charged body; on the negative side, it moves as a negatively charged body.² The surface of shear is between the gelatin layer and the solution.

The sensitive layer of the normal photographic material consists fundamentally of tiny crystals of silver halide (the grains) embedded in a layer of gelatin. These crystals are prepared and aged in the presence of excess halide and gelatin, so

¹ S. E. Sheppard, R. H. Lambert, and R. L. Keenan, *J. Phys. Chem.* **36**, 174 (1932).

² Cf. L. F. Tice and W. G. Batt, *Am. J. Pharmacy* **109**, 29 (1937).

that adsorbed layers of each should form as in the case of the colloidal silver bromide particle just discussed. The adsorbed gelatin layer is now surrounded, however, by bulk gelatin instead of by solution.

In normal "chemical," or contact development of the photographic layer, the reaction takes place at the interface between the silver halide and silver (either from latent image or previous development). The developing agent accordingly must penetrate to the grain surface before reaction can take place. Many of the developing agents are active only in the form of negatively charged ions. In such cases, it has already been shown³ that the potential in the vicinity of the grain surface exerts a pronounced influence upon the kinetics of development.

In previous investigations of this charge effect, development was always carried out in alkaline solution at a pH well above the isoelectric point of the gelatin. Accordingly, both the bromide layer and the gelatin could contribute to a charge barrier resisting the approach of the developer ions to the surface of the silver bromide grain. The existing data on the effect consisted largely of measurements of the change in rates of development produced by the addition of bromide, various dyes, and neutral salts to the developer solution. Certain other development characteristics, particularly the existence and magnitude of the induction period, were also shown to depend upon the charge of the developer ion rather than upon the chemical nature of the agent. These data seemed to be largely explicable on the basis of the bromide charge

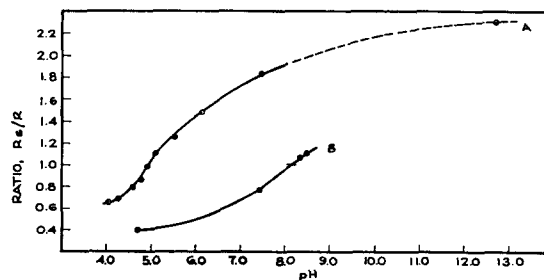


FIG. 2. Salt effect in terms of ratio of rates in presence and absence of $0.33 M \text{KNO}_3$. Curve A is for film with a gelatin of isoelectric point = 4.9; curve B is for film with a gelatin of isoelectric point = 8.

³ T. H. James, *J. Phys. Chem.* **43**, 701 (1939).

alone,^{3,4} but a hint of some action of the gelatin was contained in observations on the behavior of the ferro-oxalate developer in acid solution.³ Recently, however, it has been shown⁵ that negatively charged gelatin layers exert a definite restraining action on the penetration of negatively charged dye ions, and hence might be expected to exert a similar action upon the penetration of developer ions. The resistance to the penetration of the dye ions was largely removed by the addition of large amounts of neutral salt, and Sheppard has suggested⁶ that a similar action can account, at least in part, for the increase in rate of development produced by adding neutral salts to solutions of ionic developing agents.⁷

In the present paper, it will be shown that a change in the electric barrier of the gelatin is almost entirely responsible for the acceleration produced by neutral salt. The slight effect of salt upon the bromide barrier can be measured by working at the isoelectric point of the gelatin. By following this procedure further, it can be shown that the bromide barrier is primarily responsible for the induction period and for certain other kinetic effects, such as the accelerating action of phenosafranin.

MATERIALS AND PROCEDURE

Two distinct photographic materials were employed. The first (A) was a normal motion-picture positive film prepared from gelatin which had an isoelectric point at about 4.9. The second (B) was a positive-type film prepared from an acid-process gelatin which had its isoelectric point at about 8. The light-sensitive material in each case was silver bromide.

As a developer, the bivalent ferro-oxalate is well suited to the purpose of the investigation. The oxidation product produces no complicating

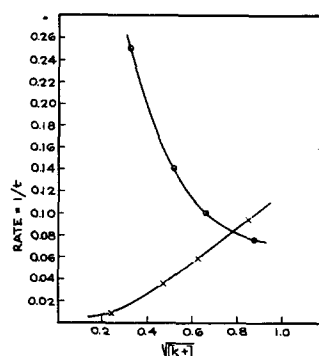


FIG. 3. Salt effect on film with gelatin isoelectric point of approximately 8. —○—○=pH=4.7; log E =1.45; —×—×=pH=12.7; log E =1.75.

kinetic effects under the experimental conditions employed. The developer can be used in acid, neutral, and slightly alkaline solution. Thus, development can be carried out on either side of the isoelectric point of the gelatin. The bivalent iso-ascorbic acid ion was used as developer in the highly alkaline region, since in this case also the oxidation product does not complicate the development kinetics.⁸

The ferro-oxalate developer contained 0.005 M ferro-oxalate and 0.04 M excess potassium oxalate. The pH of the solution was adjusted by adding the required amount of sulfuric acid for pH values of less than 7.5, and borax for higher values. The concentration of iso-ascorbic acid was 0.005 M in a solution containing 0.04 M potassium hydroxide. The developers were prepared from oxygen-free component solutions, and all development operations were carried out in an atmosphere of tank nitrogen which had been freed of oxygen. The apparatus and procedure were essentially those previously described.³ Development rates were determined in terms of $1/t$ and R , where t is the time required to obtain a fixed, small optical density at a given exposure, and R is the slope of the curve obtained by plotting density against time of development. All values are corrected for fog. Unless otherwise specified, the data recorded here apply to an exposure of log E =1.45, where E is expressed in meter-candle-seconds, t is measured at a density of 0.20, and R at a density of 0.80. Similar results were obtained for other exposure values in the normal exposure range.

⁴ F. Urbach, IX^e Congrès International de Photographie (Paris, 1935), p. 432. J. E. de Langhe, Zeits. f. wiss. Phot. 35, 201 (1936). A. Lottermoser and R. Steudel, Kolloid Zeits. 82, 319; 83, 37 (1938). T. H. James, J. Phot. Soc. Am. 9, 62 (1943).

⁵ S. E. Sheppard, R. C. Houck, and C. Dittmar, J. Phys. Chem. 46, 158 (1942).

⁶ S. E. Sheppard, "Colloid chemical aspects of photographic development," in *Colloid Chemistry*, edited by J. Alexander (Reinhold Publishing Corporation, New York, 1944), p. 472.

⁷ H. Lüppo-Cramer, Kolloid Zeits. 15, 164 (1914).

⁸ T. H. James, J. Am. Chem. Soc. 66, 91 (1944).

TABLE I. Salt effect in development at the isoelectric point. Ferro-oxalate developer, $pH=4.9$, film *A*.

KBr	KNO ₃	1/ <i>t</i>	<i>R</i>
0.0	0.0	0.099	0.0485
	.33	.098	.048
	.67	.097	.046
.00067	.0	.034	.036
	.67	.036	.041
.0020	.0	.022	.029
	.67	.025	.033

RESULTS AND DISCUSSION

The rate of development of film *A* in ferro-oxalate decreased with increasing pH , as indicated by the solid curve of Fig. 1. The addition of neutral salt changed the rate of development in most cases, but produced no change at the pH corresponding to the isoelectric point of the gelatin (4.9). The broken curves in Fig. 1 illustrate the effect of potassium nitrate upon the development rate. On the positive side of the isoelectric point, the salt produces a *decrease* in the rate of development; on the negative side, the salt produces the more conventional increase. The three curves, corresponding to no added salt, 0.33 *M* potassium nitrate, and 0.67 *M* potassium nitrate, cross at the isoelectric point. Quite similar results were obtained when *R* was plotted instead of 1/*t*.

The absolute rate of development also can be related to the charge of the gelatin. In the absence of salt, increase in the positive charge of the gelatin increases the rate of development, and increase in the negative charge decreases the rate of development. At high salt concentrations, the charge effect of the gelatin is practically eliminated,⁵ and the rate of development becomes almost independent of the pH .

As a check on the results obtained with film *A*, the effect of salt on development of film *B* was measured. Figure 2 illustrates the results obtained. In this figure, the *ratio* of development rate in the presence of 0.33 *M* potassium nitrate to that in the absence of added salt is plotted against pH (curve *B*). The ratio is unity (no salt effect) at a pH of about 8.1. This corresponds well with the isoelectric point of the gelatin used in the preparation of this film. For comparison, results obtained with film *A* are plotted in the

same way (curve *A*). The point on this curve corresponding to $pH=12.7$ is for iso-ascorbic acid instead of ferro-oxalate, but the extension of the curve follows the general shape indicated by the ferro-oxalate points. Thus, the specific properties of the individual developing agents do not appear to be involved in determining the magnitude of the salt effect in these two cases. Only the charge is important.

A series of measurements of the salt effect at various salt concentrations was made at $pH=4.7$ with ferro-oxalate and 12.7 with iso-ascorbic acid, using film *B* as the photographic material. (Data for film *A* at $pH=12.7$ have been given.⁸) The determinations with the ferro-oxalate developer were made in the absence of added bromide, but addition of 0.00667 *M* potassium bromide to the iso-ascorbic acid developer was necessary to eliminate excessive fog. Results of the determination at the two pH values are given in Fig. 3 as the rate of development, 1/*t*, plotted against the square root of the potassium-ion concentration. The salt effect is large in each case, but is opposite in direction.

All of the preceding experiments with ferro-oxalate were carried out in the absence of added bromide. Only the bromide in excess in the original film was present. Under these conditions, the evidence shows clearly that the salt effect is acting exclusively upon the gelatin charge, within the limits of experimental error. This does not, however, preclude an effect upon the bromide when the latter is in considerable excess. Accordingly, measurements in the presence of added bromide were made at the isoelectric point of the gelatin, where the electric barrier of the latter is eliminated. Some results are given in Table I. At the higher bromide concentrations, a

TABLE II. Effect of bromide on development by ferro-oxalate. Film *A*—no added salt.

pH	KBr	1/ <i>t</i>	<i>R</i>	<i>R</i> / <i>t</i>
4.76	0.0	0.118	0.054	0.45
	.000167	.071	.052	0.73
	.000667	.044	.049	1.11
	.00167	.030	.039	1.30
4.06	.0	.192	.080	0.42
	.000167	.167	.087	0.52
	.000667	.114	.084	0.76
	.00167	.080	.075	0.94

TABLE III. Effect of phenosafranin. Film A; $pH=4.06$; KBr, 0.001667 M .

Phenosafranin	$1/t$	R
0.0	0.080	0.075
.00002	.105	.084
.00005	.132	.099
.00010	.154	.095
.00020	.192	.100
.00050	.455	.126

small increase in development rate is obtained by increasing the salt concentration. However, the effect is very small in comparison with that observed at similar salt concentrations, but in alkaline solution well to the negative side of the isoelectric point. *The neutral salt acceleration of development, therefore, is caused primarily by an action upon the gelatin charge barrier, even when considerable excess bromide is present.*

It was shown previously³ that the induction period in development is caused by a charge effect. The original explanation of this effect associated it with a *change* in the adsorbed bromide layer as development progressed. This explanation remains in agreement with the evidence. The induction period persists even on the positive side of the isoelectric point. Moreover, its characteristic sensitivity to the bromide-ion concentration^{8,9} is maintained on the positive side of the gelatin isoelectric point. This is indicated by the data given in Table II. It will be noticed that the $1/t$ rates, which are measured in the induction period region, decrease much more rapidly with increasing bromide concentration than do the R rates, which apply to the region of development beyond the induction period.

The relative change in $1/t$ with respect to R is indicated by the figures in the last column. The increase in Rt with increasing bromide is not as great at $pH=4.06$ as at 4.76, probably because of the tendency of the *positive* gelatin layer to counteract to some extent the kinetic effects of the negative bromide barrier. Similarly, the absolute decrease in rate of development with increasing bromide is not as great at the lower pH —a fact which can be explained in the same way. However, the induction period persists at $pH=4.06$, and the relative extent of the induction period still increases with increasing bromide-ion concentration.

The action of phenosafranin supplies another indication that the bromide barrier is still actively retarding development well to the positive side of the gelatin isoelectric point. This substance increased the rate of development by all of the doubly-charged agents previously studied, and its action is definitely associated with the charge of the developer.³ In the present investigation, it was observed that phenosafranin accelerates development at the isoelectric point of the gelatin, and indeed well to the positive side of this point. The data in Table III illustrate the effect at $pH=4.06$, and in the presence of 0.001667 M potassium bromide. The acceleration produced by the dye is marked, and comparison with Table II shows that 0.0002 M phenosafranin almost completely erased the retarding action which the bromide exerted on development in the absence of the dye. Thus, under the present conditions, approximately one molecule of phenosafranin offsets the retarding effect of eight bromide ions. Approximately the same relation held over the sixteen-fold range of exposures for which data were tabulated.

⁹ T. H. James, J. Phys. Chem. **44**, 42 (1940).