

“The Theory of Photographic Processes: On the Chemical Dynamics of Development.” By S. E. SHEPPARD, B.Sc., and C. E. K. MEES, B.Sc. Communicated by SIR WILLIAM RAMSAY, K.C.B., F.R.S. Received December 20, 1904,—Read February 2, 1905.

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*Historical and Introductory.*—The following work was undertaken with the view of applying physico-chemical methods to the study of photographic development. Although, as has been pointed out by Ostwald, the problem falls in the province of chemical dynamics, but little systematic work has been done from this point of view. The increasing use of gelatino-bromide films in connection with radiation phenomena make a greater knowledge of the laws describing development and exposure very desirable, while the importance of the photographic industry needs no comment. The following brief historical introduction is necessary in order to sum up the progress made and the terminology in use:—

In 1878, Sir W. Abney\* showed that the black reduction product in development was metallic silver. He introduced the measurement of the transparency of the deposits by means of a photometer, and proposed as the relation between the mass of silver reduced and the transparency a form of the law of error. In 1890, Messrs. F. Hurter and V. C. Driffeld† made a systematic survey of exposure and development in which a new terminology was introduced and several very important conceptions and results. These were extended in 1898 in a second paper dealing largely with development.‡ They considered that the ordinary exponential law§ for the absorption of light in homogeneous media held for the photographic image and confirmed this view experimentally. They gave the following terminology, which has been generally accepted:—

$$\text{Transparency ... } T = \frac{I}{I_0} = \frac{\text{Intensity transmitted}}{\text{Intensity incident}},$$

$$\text{Opacity ..... } O = \frac{I_0}{I} = \frac{1}{T},$$

$$\text{Density ..... } D = -\log_e T = \log_e O.$$

D, the density, is for convenience usually taken as  $-\log_{10} T$ , and

\* ‘Phil. Mag.,’ 1878; also ‘E. B.,’ 10th edit., art. “Photography.”

† ‘Journ. of Soc. of Chem. Industry,’ May, 1890.

‡ ‘Photographic Journal,’ 1898; Eder’s ‘Jahrbuch f. Phot.,’ 1899.

§ Bunsen and Roscoe ‘Pogg. Ann.,’ vols. 95 to 100.

according to Hurter and Driffield is directly proportional to the mass of silver per unit area.\*

References to the work on exposure and development will be made in the course of the present work. Many of their conclusions have been controverted† chiefly from isolated experiments. Nevertheless, their method of sensitometry has been nominally adopted for commercial purposes in England. It has, however, been attacked by Dr. Eder‡ in the course of his important researches on sensitometry.

The authors have dealt elsewhere with the question of sensitometry, with the result of confirming in general the results of Hurter and Driffield.

Applications of physico-chemical doctrine to photographic phenomena may be found in the short-lived 'Archiv f. wiss. Phot. § and, in especial, Abegg's "silver-germ" theory of exposure and development. This is dealt with later.

All developers are, chemically speaking, reducing agents, but the converse does not hold. In connection with this, Bredig|| has pointed out the importance of the "reduction potential"¶ as a function of the developer. However, as there is no strict proportionality between "potential" and reaction velocity,\*\* other conceptions are necessary, if the "efficiency" of developers is to be measured. The relation, as has been pointed out, may be conceived as analogous to Ohm's law, velocity =  $\frac{\text{potential}}{\text{resistance}}$ , †† and this "resistance" in chemical reactions is a term difficult to define or measure.

The chemistry of organic developing agents has been extensively investigated by Messrs. Lumière and Dr. Andresen, ‡‡ to whom we owe the following rule:—All organic developers are substituted aromatic derivatives, containing two of the groups OH and NH<sub>2</sub>, joined by an ortho- or para- linking, the meta- bodies not acting as developers. Andresen§§ has pointed out the analogy between these bodies and the simple inorganic types, O<sub>2</sub>H<sub>2</sub>, hydrogen peroxide, N<sub>2</sub>H<sub>4</sub>,

\* Cf. Eder: 'Beiträge zur Photochemie u. Spectral-analyse,' 1904; Luther, 'Zeit. f. Phys. Chem.,' 1900 (*Ref.*) recommends the term "Extinction," instead of the anomalous "density," as this quantity is the same as the "Extinction coefficient" introduced by Vierordt in absorption-photometry.

† For a bibliography of this controversy, see C. E. K. Mees and S. E. Sheppard, "Instruments for Sensitometry," 'Phot. Journ.,' vol. 44, No. 7, p. 222; and "On Sensitometry," *ibid.*, No. 9.

‡ *Loc. cit. supra*, or 'Sitzber. d. Wien. Akad.,' vol. 113, 1899, sect. A.

§ 'Archiv f. Wiss. Phot.,' 1899 to 1900.

|| Eder's Jahrbuch, 1895.

¶ Bancroft and Neumann, 'Zeit. f. Physik. Chem.,' 10, 357. Nernst, 'Theoret. Chem.,' 4te Auflage, p. 710.

\*\* Ostwald, 'Lehrbuch,' 2te Bd., 2te Tl. (2te Auflage).

†† Nernst, 'Theoret. Chemie.,' 4te Auflage, p. 656.

‡‡ 'Photo. Bulletin,' 1895, *et seq.* Eder's Jahrbuch, 1899 (pp. 140 to 147).

§§ 'Phot. Corr.,' 1899, p. 212. Eder's Jahrbuch, 1899 (pp. 140 to 147).

hydrazine, and  $\text{NH}_2\cdot\text{OH}$ , hydroxylamine, all of which function as developers.\* It seems possible that the quantitative investigation of development might throw light on the affinities of a large group of organic bodies.

Owing to the complications present in organic developing solutions,† the reaction was first studied with ferrous salts, those employed being ferrous oxalate, citrate, and fluoride. These can be easily estimated analytically, and disturbing side reactions do not occur to any extent. The methods and conclusions arrived at can then be applied to the study of other developing agents.

*Apparatus and Method of Enquiry.*—The apparatus used by the authors and other investigators for the investigation of sensitometry and development have been very fully described elsewhere,‡ so that only a brief description with an account of the errors in working is here necessary.

The progress of the reaction was studied by measuring the density, varying amounts of light action being obtained by means of a special sensitometer.

(a) The sensitometer impressed a known gradation of exposure on the plate by means of an accurately calibrated sector-wheel, exposed to a constant pressure acetylene burner.§

(b) A special thermostat was employed, so that all the chemical reactions involved took place under constant conditions, temperature to  $0.1^\circ \text{C}$ .

(c) The absorption photometer used was a Hüfner spectrophotometer.|| The silver deposit had no spectral absorption, but measurements were made in the bright green, the region of maximum luminosity in the visual curve.¶ The instrument uses two Nicol prisms for polarising the light, and so darkening the comparison field. If  $\theta$  be the angle of rotation of the analyser, T, the transparency =  $I/I_0$  is equal to  $\cos^2\theta$ , and D, the density (after Hurter and Driffeld) is equal to  $-\log_{10} \cos^2\theta$ . The estimation of the probable error for a single density—the scatter—gave the following result:—The mean probable error from 3.0 to 0.100 was approximately constant at 0.007.\*\* As

\* Le Roy., 'Bull. Soc. Franç. Phot.,' 1894, vol. 23. Andresen, 'Phot. Corr.,' vol. 36, p. 260.

† Mees and Sheppard, 'Zeit. f. Wiss. Phot.,' Bd. II, H. 1, 1904.

‡ 'Phot. Journ.,' "Instruments for Sensitometric Investigation," vol. 44, 1904, No. 7.

§ *Loc. cit.*

|| *Loc. cit.* and 'Zeit. f. Physik. Chem.,' 3.

¶ Further, the region for maximum sensitiveness for small differences in intensity, Unterschieds-empfindlichkeit, lies, according to Pflüger, between  $\lambda$  495 and  $\lambda$  525. 'Ann. d. Phys.,' 4te Flge., Bd. 9, p. 207.

\*\* Cf. Martens: "Modified König. Spectrophotometer," 'Ann. d. Phys.,' 4te Flge., Bd. 12, 1903. "As long as  $\alpha_0$  does not lie near  $0^\circ$  or  $90^\circ$ ,  $p$ , the just perceptible difference of brightness of the comparison fields, is constant."

six readings were taken, from 3·000 to 0·100, the figures are trustworthy to three units on the third decimal place.

The next consideration is as to how far  $D$  represents the mass of silver per unit area. In treating the image as obeying the absorption law, no account is taken of the light diffusely scattered.\* It is true that so long as all densities are measured at the same distance, the scattered light lost is probably proportional to the scattering surface, *i.e.*, to the density. In this case the result does not affect the form of the curve, for  $D = \phi(T) = \phi'$  (mass of silver), but only the slope, *i.e.*, the photometer-constant. But the error due to this cause with the Hüfner instrument is, for negatives, inappreciable. If proper precautions with regard to obstruction of light by the absorption stand are taken, and adjustment made so that the zero does not alter, it is found that the measured density does not alter on changing the distance of the light source. Further, if a diffusing medium, such as milk-glass, be interposed, the density readings are not altered beyond the probable error. On the other hand, if this be done with an undeveloped plate, quite different readings are obtained. When measuring highly diffusing media, such as haloid or silver emulsions, *it is necessary to use a highly diffusing light source, and also to utilise only a narrow strip of the transmitted bundle of rays.* This may be accomplished by means of the carriers described in our former paper.

*The Photometric Constant.*—As was stated above, Hurter and Driffeld showed that the amount of silver per unit area was directly proportional to the density  $D = -\log T$  where  $T$  is the photometric transparency. This was found for densities from 0·525 to 2·0, the mean value of  $P$  being 0·0121,  $P$  is the mass of silver in grammes per 100 cms.<sup>2</sup>, corresponding to a density of 1·0, and is henceforth referred to as the photometric constant. A redetermination of  $P$  in 1898 gave  $P = 0·0131$  for ferrous oxalate. The photometric constant varies slightly with the developer, especially if organic stain be deposited. Dr. Eder also confirmed this ratio for densities from 0·5 to 2·0, and obtained the value 0·0103 for  $P$  (ferrous oxalate). As this relation is of great importance in the theory of development and sensitometry, we made a redetermination, extending the range of densities to 3·5, as it seemed possible divergencies might occur at higher densities. The photometric constant allows quantities of silver to be estimated much below analytical measurement.

Hurter and Driffeld, after the necessary density-measurements, removed the film from the plate and dissolved the silver in nitric acid: it was then precipitated as  $AgCl$ , and weighed. Dr. Eder converted the silver directly by means of bichromate and  $HCl$  into  $AgCl$ .

These gravimetric methods are somewhat disadvantageous in dealing with the small quantities of silver present. If plates of small area are

\* Abney, 'Phil. Mag.,' 1875. C. Jones, 'Phot. Journal,' 1898 to 1899, p. 99.

used, the ultimate analytical error for so small a quantity of AgCl may seriously affect the results, while with larger plates the irregularity in the developed density, primarily due to coating, causes errors which are only partially compensated by taking many readings over the plate. It would be preferable, moreover, to precipitate the silver as AgBr, both owing to its slighter solubility and the greater weight of precipitate obtained.

A preliminary gravimetric determination was made, in order to check the volumetric method subsequently employed. The densities ranged from 2·4 to 3·25 and the value of P obtained was 0·01035.

The volumetric method adopted was Volhard's,\* with thiocyanate sometimes controlled by the precipitation with KBr. The standard silver solution was N/100 AgNO<sub>3</sub>, prepared by dissolving 1·6997 grammes pure AgNO<sub>3</sub> in water with excess of HNO<sub>3</sub> and made up to 1000 c.c. at 15° C. This was checked by analysis, and two concordant determinations gave the factor 1·001. The standard KCNS, N/100 had the factor 1·017.

*Details of the Estimation on Plates.*—Half-plates and whole-plates were exposed at 2 to 3 metres, carefully developed, fixed and washed. Very careful washing was necessary in order to extract all soluble salts. They were dried at the standard temperature. The density was measured in 20 to 30 places,† and the area; after this the film was removed by dilute HF and soaked in many changes of distilled water, with frequent pressure between filter paper, to remove all soluble salts which might interfere.‡ The film was then dissolved in slight excess of pure HNO<sub>3</sub>, SG 1·49 and the gelatine completely destroyed by heating, as otherwise it interferes with the subsequent titration by forming a pseudo-solution of the precipitate and retarding its aggregation.§ The solution was made up to 25 c.c. at 15° C. and titrated with N/100 KCNS, using 2 c.c. of 10-per-cent. ferric-am. sulphate as indicator.

The following series is exemplary. Four series of measurements were made in this way, the density ranging from 0·50 to 3·5, and the curve shows that there is no bias throughout the range.

Series IV.

Plate.	Area.	Density.	Titre.	P.
1.....	87·2 cms. <sup>2</sup>	1·438	11·8 c.c.	0·01033
3.....	86·7 „	2·392	18·7 „	0·01019
4.....	87·2 „	2·067	16·5 „	0·01032
5.....	87·2 „	1·809	14·95 „	0·01040
6.....	87·2 „	1·618	13·1 „	0·01022

\* Cf. Mohr's 'Titrimethode.'

† This was necessary, as variations in the developed density up to 10 per cent. occurred, chiefly due to coating errors.

‡ Cf. Lumière and Seyewetz "On Retention of Hypo," Ref. in 'P. J.,' 1902.

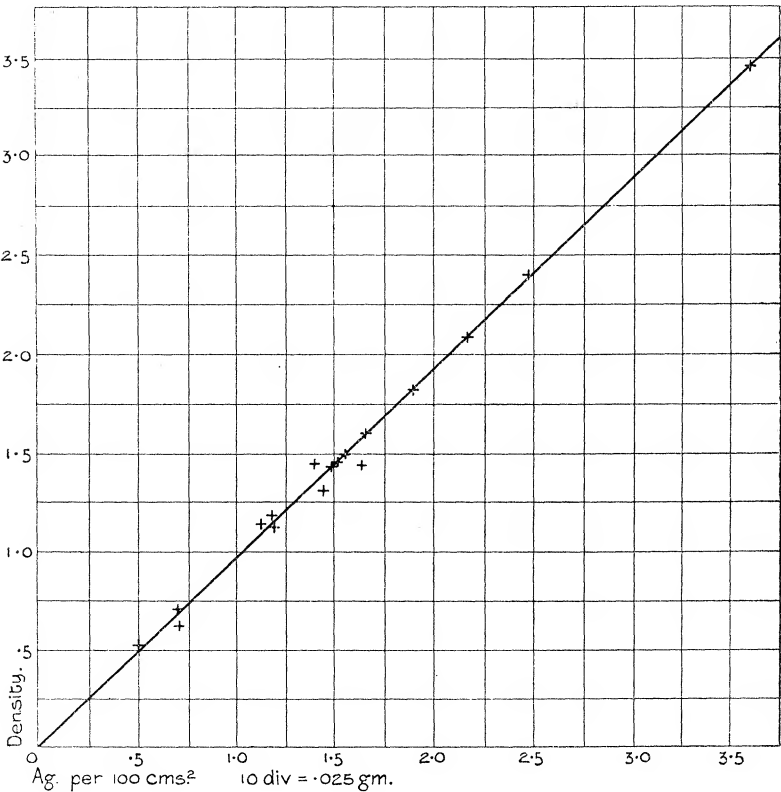
§ Lobry de Bruyn 'Ber.,' 1902, vol. 35, pp. 3079 to 3082.

The means of all series are as follows :—

I.....	0·01035	Gravimetric.
II.....	0·01012	Volumetric.
III.....	0·01037	„
IV.....	0·01029	„
V.....	0·01040	„

Total mean..... 0·01031 = P for plates employed.

Written ordinary emulsion and ferrous oxalate. Curve I shows the directly proportional ratio between the density  $D = \log_{10} O$  and the mass of silver per 100 cms.<sup>2</sup>. The mean value differs materially from that found by Hurter and Driffeld, but this may be due (a) to a constant error in their photometer ; (b) to the plates used, as it seems probable that the emulsification of the silver haloid has considerable influence on the “covering power” of the silver subsequently deposited. This “covering power” is, of course, the quantity P or photometric constant.



The extent to which the exponential law holds for gelatine emulsions is of great practical importance, as it provides a rapid and easy method of measuring the amount of substance present. The following experiments indicate that it holds within certain limits.

Table calculated from Hurter and Driffield.

Plate.	AgBr per 100 cms. <sup>2</sup>	Density.
1.....	0·016 gramme	0·240
2.....	0·031    ,,	0·520
3.....	0·062    ,,	1·000
4.....	0·124    ,,	2·900*

The writers converted silver into AgBr and measured the density in each case. Considering how high the figures are, the results are satisfactory.

## Series I.

Density of silver.....	2·023	} P, for AgBr = 0·0364.
„ AgBr.....	4·020	

## Series II.

Density of silver.....	1·009	} P, for AgBr = 0·0393.
„ AgBr.....	2·026	

Comparing these with Hurter and Driffield's numbers, it is obvious that the physical state of the haloid has tremendous influence on the opacity. Considering the importance of this quantity for sensitometry, the constant P seems worthy of investigation in connection with emulsification.

The investigation shows that the density can be accepted as a measure of the mass of silver reduced.

*Errors due to Plates.*—Unevenness in the coating of the plates introduces a large source of errors. In these researches, Wratten ordinary emulsion specially coated on patent plate glass was used, the edges being rejected. We have to thank Mr. Wratten for the care taken and his readiness in coating experimental plates. Nevertheless, as the following figures show, the error from this source is considerable. Plates similarly exposed and developed, resulted as below:—

	a.	b.	c.
1 .....	1·364	1·336	1·403
2 .....	1·329	1·342	1·354
3 .....	1·289	1·321	1·247
4 .....	1·287	1·349	1·280
5 .....	1·337	1·375	1·340
Mean	1·3212	1·345	1·325

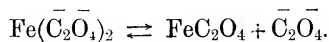
Greatest dev. 3·2 per cent.    2·2 per cent.    6·0 per cent.

\* Probably due to "scatter" error.

From these and other measurements it was calculated that from this cause alone the probable error on a single developed density is 1 per cent.\* The authors have since constructed an instrument for the more exact coating of plates.

*Method of Development and Developer.*—The thermostat and plate-holders have already been described. Previous to development, the plates were soaked for 2 to 3 minutes in a tube of distilled water in the thermostat. Development was stopped by plunging the plates in cold water, they were washed, fixed in pure hypo, washed, cleared in dilute HCl, rinsed, wiped with cotton wool, and dried at a uniform temperature.

The developer first used was ferrous oxalate. A physico-chemical investigation had shown that the iron was present as a complex anion†  $\text{Fe}(\text{C}_2\text{O}_4)_2$ , which is stable in the presence of excess of free oxalate ions, according to the equilibrium



When the ferrous oxalate is present in solid form, the constant for the above equilibrium is 0.8 at 20° C. The standard solutions employed were

A. $\text{FeSO}_4$ .....	278 grammes per litre, molecular,
B. $\text{K}_2\text{C}_2\text{O}_4$ .....	184                   "                   "

checked by titration with standard  $\text{KMnO}_4$ .

The developer was always slightly acidified with pure  $\text{H}_2\text{SO}_4$ .

*The Velocity of Development.*—This was studied by measuring the growth of the density, *i.e.*, the mass of silver, with the time of reaction, in full analogy with other kinetic investigations. The following facts were experimentally proved:—

(a) The silver deposited increases rapidly at first, then more slowly, and finally tends to a limit.

(b) This limit depends only on the exposure.‡

(c) The velocity depends upon the concentration of the reducer.

(d) A soluble bromide reduces the velocity, but the "slowing off" with time is not so pronounced.

Temperature was always 20° 0 C., unless otherwise stated.

Table I for *a*, *b*, and *c*.

Developer A.....	5 c.c. $\text{FeSO}_4$ , M/1.	Exposure 10 CMS.
	45 ,, $\text{K}_2\text{C}_2\text{O}_4$ , M/1.	
"    B.....	2 ,, $\text{FeSO}_4$ , M/1.	Exposure 50 CMS.
	48 ,, $\text{K}_2\text{C}_2\text{O}_4$ , M/1.	

\* *Loc. cit.*, "Instruments for Sensitometry," 'P. J.', 1904, No. 7.

† 'Proc. of Chem. Soc.,' vol. 21, No. 288, p. 10.

‡ Apparent exceptions to this law will be discussed in subsequent work.



Table I.

A. Time.	Density.	B. Time.	Density.
5.0 mins.	1.052	5.0 mins.	0.628
10.0 "	1.230	10.0 "	0.987
20.0 "	1.296	15.0 "	1.323
45.0 "	1.444	20.0 "	1.376
90.0 "	1.591	30.0 "	1.528
120.0 "	1.623	90.0 "	2.429

and confirming *a*, *b*, *d*.

Developer, 4.0 c.c.  $\text{FeSO}_4$ , M/1.  
 40.0 "  $\text{K}_2\text{C}_2\text{O}_4$ , M/1.  
 1.0 "  $\text{KBr}$ , N/10.  
 to 50.0 " with  $\text{H}_2\text{O}$ .

Table II.

$D_6 = 50$ CMS.		$D_9 = 10$ CMS.	
Time.	Density.	Time.	Density.
5.0 mins.	0.256	10.0 mins.	0.522
11.0 "	0.759	15.0 "	0.741
15.0 "	1.001	20.0 "	0.838
20.5 "	1.375	30.0 "	0.939
25.0 "	1.435	40.0 "	1.050
31.0 "	1.541	50.0 "	1.185
40.0 "	1.847	60.0 "	1.212
50.0 "	2.119	75.0 "	1.360
60.0 "	2.148	90.0 "	1.409
70.0 "	2.333	105.0 "	1.574
90.0 "	2.398	135.0 "	1.641
120.0 "	2.398	12 hours	1.641

These facts are in agreement with Hurter and Driffeld's statement that development tends to a limit depending upon the exposure. They considered that their results were represented by the formula  $D = D_\infty(1 - a^t)^*$  where  $D$  = density at time  $t$ ,  $D_\infty$  = ultimate density, and  $a$  is a constant. They stated that this was arrived at "on the idea that the number of silver bromide particles affected by light is greatest in the front layer of the film and decreases in geometrical progression as each successive layer is reached," and "that the developer reduced the particles as it penetrated the film." Apart from the inherent improbability of this process taking place so regularly, it would, as was pointed out by Luggin,† give results in contradiction to the law of constant-density

\* 'J. Soc. of Chem. Ind.,' May, 1890.

† 'Zeit. f. Phys. Chem.,' 23, p. 622.

ratios demonstrated later. A conclusive experimental disproof of the hypothesis is given by the fact that a plate exposed from the glass-side develops normally, although in this case the layer containing fewest reduced particles is reached by the developer first.

Table III.

Time.	Density.	K.
11·0 mins.	0·477	0·0210
15·0 „	0·612	0·0217
20·0 „	0·681	0·0193
33·0 „	0·897	0·0197
75·0 „	1·156	
120·0 „	1·156	For meaning of K, see later.

The mass-time curve is quite normal.

Another theory of development-velocity was proposed by Dr. Abegg,\* based on his "silver-germ" theory of the latent image. According to this, the velocity of development, *i.e.*, the number of silver germs deposited in unit time is proportional to the number present at any time. This may be expressed by  $v = \frac{dx}{dt} = k(a + b + x)$ , where  $a$  and  $b$  are constant numbers of germs due to exposure and ripening respectively, and  $x$  is the number due to development. It is evident that as  $x$  increases the velocity should increase, and a steady acceleration should be noticed till the whole film was developed through; in this unmodified form the expression is in obvious disagreement with the facts of development.

*Theory of Development.*—The investigations of Boguski,† Noyes and Whitney,‡ and especially of M. Wilderman,§ E. Bruner, and Nernst,|| have led to a better understanding of the reaction-velocity in heterogeneous systems, among which the development of silver-bromide naturally stands. When a solid dissolves, the rate is proportional to its surface and to the difference between the saturation-concentration and that at the given moment. At the boundary between the phases saturation exists, so that the rate of solution depends on the diffusion velocity. When a chemical action is superposed, Nernst assumes that in most cases the equilibrium in the reaction-layer is adjusted with practically infinite velocity compared with the diffusion process. If the length of the diffusion path and the diffusion coefficients are known, in many cases the velocity may be calculated in absolute measure.

\* R. Abegg, 'Archiv f. Wiss. Phot.,' 1899, vol. 1.

† v. Ostwald, 'Lehrbuch,' 2te Auflage, 2te Bd., 2te Fl. 'Chem. Kinetik.'

‡ 'Zeit. f. Phys. Chem.,' 23.

§ M. Wilderman, 'Phil. Mag.,' October, 1902; 'Zeits. Physik. Chem.,' vol. 30, 1899, p. 341.

|| 'Zeit. f. Phys. Chem.,' 47, 1904, p. 56.

Now, the chemical equation for development with ferrous oxalate is probably  $\overset{+}{\text{Ag}} + \overset{-}{\text{Fe}} (\text{C}_2\text{O}_4)_2 = \underset{(\text{met.})}{\text{Ag}} + \overset{-}{\text{Fe}} (\text{C}_2\text{O}_4)_2$ , *i.e.*, one silver ion is converted into metallic silver. The velocity equation will then be  $dx/dt = K C_{\text{Ag}}^+ C_{\text{FeOx}}^-$ .

$C_{\text{Ag}}$  may be reckoned as constant on the above view of the instantaneous adjustment of the equilibrium, as solid AgBr is present. If we assume a layer of constant thickness,  $\delta$ , in which diffusion takes place, then there will diffuse into the reaction-layer  $S \frac{\Delta}{\delta} (a - x) dt$  of reducer in the time  $dt$ , where  $\Delta$  is the diffusion coefficient of the reducer,  $a$  its initial concentration, and  $x$  equivalents of AgBr have been reduced. If  $x$  be very small compared with  $a$ , the total concentration, this becomes  $S \frac{\Delta}{\delta} a dt$ , and the velocity of development is given by  $dx/dt = KS$ , where  $S$  is the surface of the solid phase, and  $K = \Delta a / \delta$ . Now the existence of a maximum and fixed quantity of developable AgBr is proven by the experiments detailed above. We shall distinguish the amount of this by  $(\text{AgBr})$  and in the course of the reaction it varies from  $(\text{AgBr})$  to 0. The surface  $S$ , therefore, also varies from  $\phi (\text{AgBr})$  to 0. Now, the microscopic examination of the photo-film shows that it consists of a number of very fine AgBr grains embedded in gelatine. This, and the fact that the emulsion absorbs light, according to the law  $I/I_0 = e^{-m}$  where  $m$  is the mass of haloid, allow us to substitute for  $S = \phi (\text{AgBr})$ ,  $S = p (\text{AgBr})$ , *i.e.*, the surface is directly proportional to the mass of AgBr at any time, and therefore to its optical density. The optical density  $D_0$  of the latent image  $(\text{AgBr})$  must equal  $D_\infty$ , the density reached on ultimate development, while, obviously, the density of the  $(\text{AgBr})$  at any time,  $t$ , equals  $D_\infty - D$ , where  $D$  is the density of reduced silver at the time,  $t$ . Hence  $dD/dt = KS = K (D_\infty - D)$ , which gives on integration

$$\frac{1}{t} \log \frac{D_\infty}{D_\infty - D} = K.$$

If this formula be written  $D = D_\infty (1 - e^{-Kt})$ , it will be seen to be the same as Hurter and Driffeld's, when  $e^{-K} = a$ , but it has been obtained on quite general grounds, free from hypothesis, as to the nature or distribution of the developable haloid.

\* A fine-grained heterogeneity may be treated formally as a solution, *cf.* Bredig, "Anorganische Fermente," Leipzig, and Bodenstein, 'Zeit. f. Physik. Chem.,' 49, p. 42, 1904.

Tested experimentally, the first series gave a decreasing value for K. It was found that this was due to the accumulation of bromide, which lowered the velocity. This was avoided by adding excess of free bromide in such quantity that the amount due to development was negligible.

The following series give some of the results :—

Table IV.

$$K = \frac{1}{t} \log_{10} \frac{D_{\infty}}{D_{\infty} - D}$$

Series I.			Series II.		
Time.	Density.	K.	Time.	Density.	K.
5.0 mins.	0.294	0.0144	5.0 mins.	0.370	0.0182
10.0 „	0.742	0.0212	10.0 „	0.683	0.0186
15.0 „	0.973	0.0205	15.0 „	0.999	0.0206
20.0 „	1.178	0.0207	20.0 „	1.203	0.0206
25.0 „	1.276	0.0190	25.0 „	1.270	0.0181
30.0 „	1.448	0.0203	30.0 „	1.479	0.0203
40.0 „	1.547	0.0180	160.0 „	1.962	
95.0 „	1.828	0.0195	∞	1.962	
135.0 „	1.899	0.0199			
∞	1.919				

Mean... K = 0.01995.

Mean... K = 0.0194.

Series III.			Series IV.		
Time.	Density.	K.	Time.	Density.	K.
5.0 mins.	0.311	0.0149	5.0 mins.	0.283	0.0190
10.0 „	0.838	0.0229	10.0 „	0.547	0.0208
15.0 „	1.000	0.0193	15.0 „	0.759	0.0217
20.0 „	1.266	0.0208	20.5 „	0.919	0.0214
25.0 „	1.401	0.0199	25.0 „	0.990	0.0203
∞	2.053		30.0 „	1.114	0.0217
			45.5 „	1.276	0.0209
			∞	1.437	

Mean... K = 0.01992.

Mean... K = 0.0208.

Total mean of four series ..... K = 0.0203

The developer was—

4.00 c.c. FeSO <sub>4</sub> mol.	} Fe = N/25. Br = N/500.
2.00 „ KBr, N/10	
40.00 „ K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> mol.	

To 100.0 c.c. with H<sub>2</sub>O.

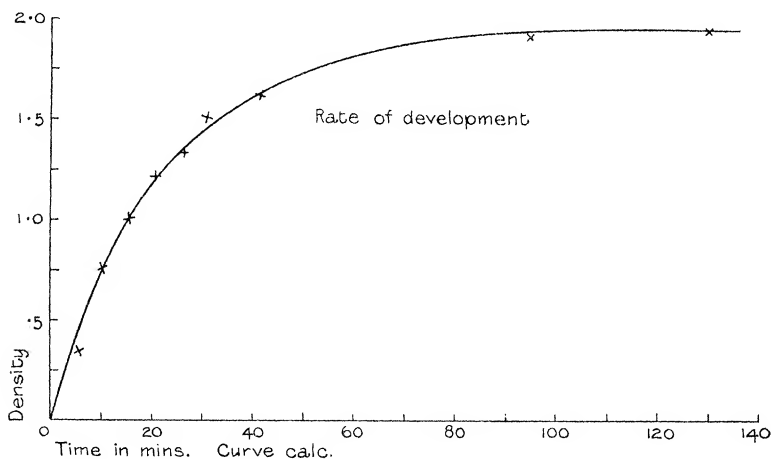
Another batch of the same emulsion gave—

Series I.....	K = 0.0191,	Series III.....	0.0217,
„ II.....	K = 0.0201,	„ IV.....	0.0204.
Total mean .....			0.0204,
Total mean of four series...	K = 0.0203.		

The following table and curve show that the expression is satisfactory over a wide range of development, considering the experimental difficulties. All the series,  $D_1$ ,  $D_2$ , and  $D_3$ , were reduced by common proportion to the same value :—

Table V.—Curve for N/500 Br and N/25 Ferrous Oxalate.

Time in mins.	$D_1$ .	$D_2$ .	$D_3$ .	D obs.	D calc.
5.0	0.330	0.303	0.373	0.335	0.410
10.0	0.773	0.815	0.697	0.762	0.736
15.0	1.013	0.975	1.020	1.003	0.995
20.0	1.227	1.232	1.228	1.229	1.201
25.0	1.330	1.365	1.296	1.330	1.364
30.0	1.510		1.510	1.510	1.495
40.0	1.610			1.610	1.681
95.0	1.904			1.904	1.960
135.0	1.970			1.970	1.980
$\infty$	2.000	2.000		2.000	2.000



It appears that generally the value of  $K$  is constant for a standard emulsion freshly coated. Variations, however, may be caused by different emulsification, and the value varies with different plates.

Thus

Wratten ordinary .....	K = 0·0203
Barnet ordinary .....	K = 0·0260 (0·0249 - 0·0254)

For occasions of space the mean value of K with the extremes are given, except where it seems desirable to show that the course of the reaction is unchanged.

*Influence of Concentration on the Velocity.*—The constant as developed above contains implicitly  $C_{Fe}$ , the total concentration of the iron; it should, therefore, be proportional to this experimentally.

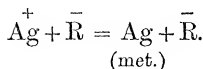
Table VI.

$C_{\text{Ferrous oxalate}}$	K found.	
N/12·5	0·4011	$\bar{Br} = N/500$
N/12·5	0·4061	
N/25	0·203	
N/50	0·100	
N/50	0·102	

The values for N/12·5 showed some tendency to decrease; this is probably due to the rapid accumulation of bromide and other reaction products, which do not diffuse rapidly, and so influence the velocity by remaining in the reaction layer, a fact which is one of the main causes of divergencies and difficulties in heterogeneous reactions.\* A more stringent proof of the proportionality is given later.

On the diffusion theory of the development velocity, this proportionality is simply the expression of the fact that the amount of reducer diffusing into the reaction layer is proportional to the concentration (*vide* p. 457). Nernst† has pointed out that on this theory it is not admissible to draw conclusions as to the order of the reaction in heterogeneous systems, so that the otherwise probable theory, that the reaction is mono-molecular with respect to iron, cannot be regarded as strictly proven by this.

*Influence of Bromide on the Velocity.*—It is well known to photographers that bromide considerably influences the rate of development, for which reason it is used as a restrainer. The influence of bromide must be due to its effect on the purely chemical reaction



The effect on the expression  $K = \frac{1}{t} \log \frac{D_\infty}{D_\infty - D}$  was studied.

It was found that the values of K for low values of  $t$  increased till

\* Ostwald, 'Lehrbuch,' 2te Auflage, 2te Bd., 'Chem. Kinetik.'

† W. Nernst, 'Theoretische Chemie,' 4te Auflage, p. 573.

a fairly constant maximum period was reached. This initial induction was already noticeable in N/500 bromide, and increased as the concentration of the bromide increased. Further, it was modified by the value of  $D_{\infty}$ , *i.e.*, of  $(\overline{\text{AgBr}})$ , being shorter for higher values of this. Values of K were obtained from "maximum" period.

*Results.*

Developer, N/25 Ferrous oxalate.  
N/1000 KBr.

I. *a.* K = 0.0280 (0.023—0.031). Increase due to fog.

*b.* K = 0.0280 (0.030—0.026).

II. KBr = N/100.

III. KBr = N/50.

*a.* K = 0.0145 (0.0142—0.017).

*a.* K = 0.0123 (0.0110—0.0147).

*b.* K = 0.0142 (0.0169—0.0137).

*b.* K = 0.0113 (0.010—0.0130).

And with N/12.5 Ferrous oxalate—

Series I. KBr = N/50.

*a.* K = 0.0181 (0.0166—0.0203).

*b.* K = 0.0182 (0.0195—0.0176).

Tabulating results we get—

Developer N/12.5 Ferrous oxalate.

Concentration of Br.	Velocity constant.
0.002 N	0.0404
0.020 N	0.0181

And for the lower concentration N/25 Ferrous oxalate.

Concentration of KBr.	K.	$K \times \log \text{Br.}$
0.001 N	0.0280	0.0280
0.002 N	0.0203	0.0265
0.010 N	0.0143	0.0285
0.020 N	0.0118	0.0274

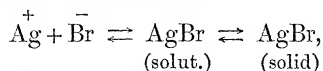
C = 0.0276

It will be seen that the results obtained with bromide are fairly represented by the simple empirical formula  $K \times \log_{10} \overline{\text{Br}} = \text{constant}$ , *i.e.*, as the bromide is increased in geometrical progression, the velocity diminishes in arithmetical.

We may discuss here the theoretical grounds from which the behaviour of bromide might be deduced.

It has been suggested that the action of bromide is due to the reversal of development, silver bromide being re-formed and develop-

ment retarded,\* but the writers found that the addition of small quantities of ferric oxalate, the other reaction-product, had no effect comparable with that due to equimolecular quantities of bromide. Only with very large concentrations of ferric oxalate (above N/25) was an effect perceived. Bromide is therefore shown by this method of "isolation" to have an effect *per se*. A more probable theory is that bromide acts by lowering the concentration of the silver ions in accordance with the reversible ionic equilibrium



when we have  $C_{\text{Ag}} \cdot C_{\text{Br}} = \text{constant}$ .

Now, the chemical equation gives

$$dD/dt = K \cdot C_{\text{Ag}} \cdot C$$

for the reaction velocity, and in consequence, the velocity should be inversely as the concentration of the bromide ions. That it has a smaller effect than this confirms the view that the reaction-velocity is chiefly determined by the diffusion equation. Nevertheless, bromide may so slow the chemical reaction that its velocity begins to affect that of the total reaction.

We may further notice, as was remarked above, that the expression  $\frac{1}{t} \log \frac{D_\infty}{D_\infty - D} = K$  does not hold over so wide a range when bromide is introduced, but that the values of  $K$  rise at first, and then reach a fairly constant period, the induction-period apparently depending both on the concentration of the bromide and on the value of  $D_\infty$ . The phenomena observed are similar to those in "graded" reactions taking place in homogeneous systems.† These initial disturbances are intimately connected with the disturbance of the density ratios by bromide. In order to investigate the action more fully, a series of exposures on the same plate, thus giving different values of  $D_\infty$ , were obtained by means of the previously described sensitometer; the results of this work will be noted later, with an elaborated theory of the mechanism of development.

*Age of Plate.*—In the course of this work, it was found that the velocity of development depends largely on the age of the plate, diminishing with keeping. This change is accelerated by heat and atmospheric conditions. This was discovered when plates of Batch I were used a considerable time after making, and gave quite divergent velocities according as they had been kept. The phenomenon, while the cause was still unsuspected, caused much trouble. The following tables exhibit the divergencies obtained:—

\* Hurter and Driffeld, 'Phot. Journal,' 1898; Luther, 'Chemische Vorgänge in der Photographie,' 1900.

† J. Walker, 'Proc. Roy. Soc., Edinburgh,' December, 1897.



Table VII.—Developer Fe = N/25, KBr = N/500, K = .0203.\*

Time.	Density.	$K = \frac{1}{t} \log \frac{D_{\infty}}{D_{\infty} - D}$
15.0 mins.	0.259	0.0048
20.0 „	0.452	0.0066
30.0 „	0.643	0.0068
40.0 „	0.816	0.0070
50.0 „	0.960	0.0071
60.0 „	1.042	0.0068
70.0 „	1.089	0.0062
80.0 „	1.214	0.0067
90.0 „	1.302	0.0069
100.0 „	1.333	0.0065
120.0 „	1.423	0.0064
12 hrs.	1.713	
14 „	1.712	

Mean, K = .0067, *i.e.*, a reduction to one-third of its former value. This was for an opened box kept in laboratory cupboard.

Table VIII.

Developer Fe = N/25. Br = N/500.

Time.	Density.	K.
10.0 mins.	0.226	0.0062
15.0 „	0.575	0.0118
25.0 „	0.713	0.0094
30.0 „	0.835	0.0097
40.0 „	1.041	0.0102
50.0 „	1.185	0.0102
60.0 „	1.284	0.0101
70.0 „	1.411	0.0108
80.0 „	1.432	0.0099
190.0 „	1.666	
6 hrs.	1.708	

K = 0.01004

Table VIIIa.

Fe = N/25. Br = N/1000.

Time.	Density.	K.
10.0 mins.	0.552	0.0174
16.5 „	0.744	0.0185
20.0 „	0.891	0.0166
25.0 „	0.900	0.0136
30.0 „	1.040	0.0141
40.0 „	1.277	0.0157
50.0 „	1.375	0.0151
60.0 „	1.403	0.0134
175.0 „	1.646	
$\infty$	1.669	

K = 0.01555

The values obtained six months before were

N/500 Br. K = 0.0203. N/1000. K = 0.0280,

so that in this case the speed has been about halved. This was for a sealed box kept in laboratory cupboard.

Further, for an opened box kept in college locker :—

\* See table, pp. 458—459.

Table IX.

N/500 KBr. K = 0.0203.		
Time.	Density.	K.
10.0 mins.	0.513	0.0156
15.0 „	0.809	0.0195
20.0 „	1.002	0.0200
26.0 „	1.115	0.0185
30.0 „	1.174	0.0180
45.0 „	1.418	0.0184
60.0 „	1.560	0.0190
190.0 „	1.664	
3 hrs.	1.664	

Mean... K' = 0.0189.

Table IXa.

N/200 KBr. K = 0.0170.		
Time.	Density.	K.
10.0 mins.	0.549	0.0149
15.0 „	0.835	0.0168
20.0 „	0.961	0.0163
25.0 „	1.119	0.0155
30.0 „	1.274	0.0161
40.0 „	1.461	0.0160
46.0 „	1.562	0.0164
60.0 „	1.688	0.0162
∞	1.895	

Mean... K' = 0.01603.

In this case a reduction of only 5 per cent. in the velocity has taken place.

These measurements show that the rate at which a plate develops is diminished with time of keeping. Apparently a slow irreversible change takes place in the film, which is accelerated by heat and presence of gases, etc. If we consider the expression for the velocity  $K = \frac{\Delta}{\delta} \cdot a$ , it seems probable that the alteration is due to an effect on  $\Delta$ , the diffusivity coefficient. It is quite different from that produced by so-called "hardening" agents, which do not affect the development velocity.

Only the absolute value of the velocity, and not the velocity-function, is altered.

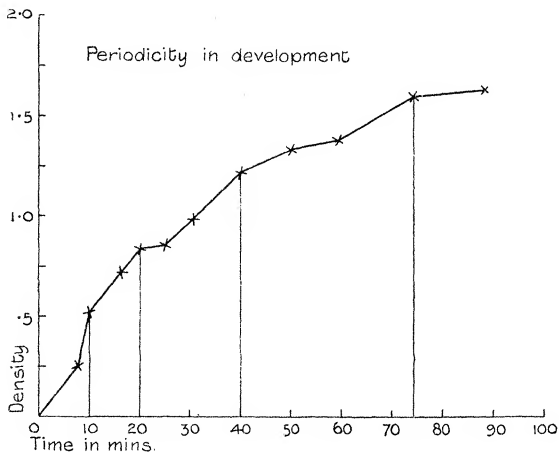
*The Diffusion Path,  $\delta$ .*—In his work on heterogeneous reactions, Bruner measured the thickness of the diffusion layer by electro-chemical reactions, and found, for example, for rate of solution in water of benzoic acid, 0.03 mm. In general, the layer was of this order, but was lessened as the rate of stirring increased.

In the photo film the diffusion path must be equal to the depth of the latent image plus a small layer on the gelatine surface. The former is not alterable by stirring, and the subsequent microscopic measurements show that it is of about the same order as Bruner found, viz., about 0.02 to 0.03 mm. The outer layer is alterable by rotation, but is probably not very large, as increasing the rotation had but a slight effect on the velocity. Unfortunately, very high velocities of stirring increased the fog materially, and also produced uneven marking. A rate of about 30 revolutions per minute was found to ensure homogeneity of the solution on the bounding surface.

It should be noticed that the whole mass and surface of the developable image in the case of development lie in the short diffusion layer in

the gelatine. How far this modifies the Nernst theory for the reaction-velocity will be considered later.

A slight periodicity in the rate of development was sometimes noted, see curve\*.



*Note on Fog.*—It is usual in density measurements to subtract the so called “fog” from the total density. This is the density due to inherent fog in the plate, extraneous light, etc. Usually a separate reading is made of the so-called fog strip, but, owing to the differential nature of our instrument, the “fog” reading was automatically subtracted, and taken from the same portion of emulsion as the exposure.

But the formula  $\frac{1}{t} \log \frac{D_{\infty}}{D_{\infty} - D} = K$  shows that there is a theoretical error in assuming the fog in the unexposed strip is equal to that in the exposed strip.

For let  $A + B = C$  be total mass AgBr,

where  $A = \text{AgBr}$  changed by light,  $B = \text{AgBr}$  unchanged.

Then rate of fogging  $= (dD/dt) C = K(A + B)$  in fog strip, and equals  $(dD/dt) B = KB$  in exposed film.

Obviously, fog increases faster in unexposed film than in the exposed; it is desirable, therefore, for photo-chemical investigations, to have an emulsion which does not give fog-density higher than 0.15 to 0.2, even on infinite development, and in most of this work this was fulfilled.

*Law of Constant Density Ratios.*—Another deduction from the development formula is the law of constant density ratios. If a series of increasing exposures are given to a plate, as every density increases

\* Cf. Ostwald, ‘Vorles. über Naturphil.’ Leipzig, 1902, pp. 274, 315, 362, ‘Zeit. Phys. Chem.’ 35, p. 33, 1900. G. Bredig u. Weinmayer, ‘Z. f. p. Chem.’ 42, p. 600, “Periodic Contact Analysis.”

proportionately, the ratio of the densities due to any two exposures is constant, and independent of the time of development.

Hurter and Driffield showed that if a geometrically increasing series of exposures be given to a plate over a certain range, the density increased arithmetically. Over this period of "correct exposure" the following equation holds:— $D = \gamma \log E/i$ , where  $E$  is the exposure,  $i$  is a characteristic constant of the plate, termed the inertia, and  $\gamma$  is a constant depending upon the development, and called the development factor. The magnitudes  $i$  and  $\gamma$  are obtained graphically as follows: the densities due to nine successive exposures are plotted as ordinates, and the logarithms of the corresponding exposures as abscissæ. A curve is obtained which, for a certain period, is practically a straight line. The point where this cuts the exposure axis gives  $\log i$ , and if  $\theta$  be the angle of inclination,  $\gamma = \tan \theta$ . Analytically, the value of  $\gamma$  may be deduced as follows: for two exposures,  $E_1$  and  $E_2$ , we obtain the densities  $D_1$  and  $D_2$ , the equations being

$$D_1 = \gamma \log E_1/i, \quad D_2 = \gamma \log E_2/i,$$

eliminating  $i$ ,

$$\gamma = \frac{D_2 - D_1}{\log E_2 - \log E_1} = \frac{\Delta D}{\Delta \log E};^*$$

$\gamma$  is therefore independent of the absolute exposure, and only dependent on the  $E_2/E_1$  which is fixed by the sector wheel.†

In order to test the constancy of the density ratios, two plates were exposed simultaneously in the sensitometer to avoid errors due to light inconstancy, and developed for different times. The values of  $\gamma$  were obtained from the curves in the graphic manner described. Each plate was allowed 100 c.c. of developer.

$\text{FeSO}_4$  Mol. 8.0 c.c. +  $\text{K}_2\text{C}_2\text{O}_4$  Mol. to 100 c.c.

The logarithms of the exposures are given on an arbitrary scale, putting  $\log E_0 = 1.0$ , as the absolute value is unimportant. A typical table is given below:—

Table X.— $T_1 = 2$  mins.,  $T_2 = 6$  mins.

No.	Log E.	Density $T_1$ .	Density $T_2$ .	Ratio $D_1/D_2$ .
1	3.30	—	—	—
2	3.012	0.876	2.563	2.935
3	2.72	0.759	2.230	2.900
4	2.42	0.685	1.995	2.920
5	2.14	0.499	1.491	2.983
6	1.80	0.332	1.096	3.330
7	1.575	0.234	0.716	3.050
8	1.360	0.128	0.329	2.680
			Mean ...	2.957

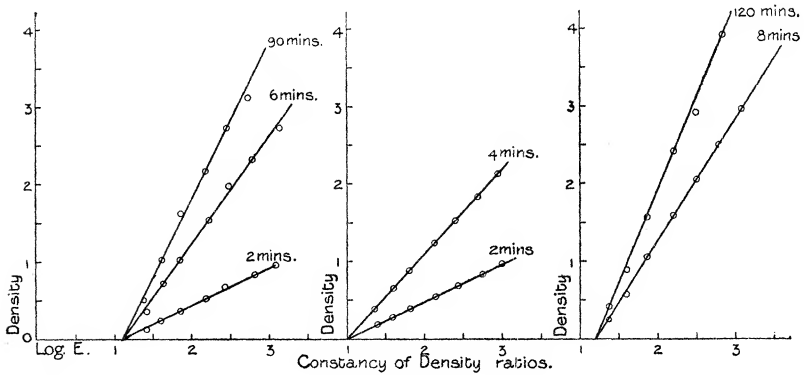
\* Or  $D = \gamma \frac{\log E}{i}$ , hence  $\gamma = \frac{dD}{d \log E}$ .

† For calibration of sector-wheel v. *loc. cit.*, p. 2.

Other results abbreviated :—

Series II ...	R = 1.465.	Mean dev. = $\mp 0.04$ .	T <sub>1</sub> = 6 mins.
			T <sub>2</sub> = 120 "
„ III ...	R = 2.21.	„ = $\mp 0.04$ .	T <sub>1</sub> = 2 "
			T <sub>2</sub> = 4 "
„ IV ...	R = 1.49.	„ = $\mp 0.05$ .	T <sub>1</sub> = 8 "
			T <sub>2</sub> = 120 "
„ V ...	R = 1.353.	„ = $\mp 0.032$ .	T <sub>1</sub> = 5 "
			T <sub>2</sub> = 10 "
„ VI ...	R = 1.48.	„ = $\mp 0.05$ .	T <sub>1</sub> = 10 "
			T <sub>2</sub> = 120 "

Range of exposure ..... 1—250.  
 „ development ..... 2 mins. to 2 hrs.



The ratios of densities due to different exposures are unchanged by time of development in a non-bromided developer.

These tables and the curves show that for variations in the time of development from 2 minutes the density ratios and the values of  $i$  are unaffected. Every density grows proportionately with the time, a fact which finds its rational explanation in the theory of development proposed.

For the straight line portion of exposure the equation  $D = \gamma (\log E - \log i)$  holds, and for a single density the expression in brackets is a constant. The development factor,  $\gamma$ , is, therefore, strictly proportional to  $D$ , and as

$$D = D_{\infty}(1 - e^{-Kt}),$$

so  $\gamma = \gamma_{\infty}(1 - e^{-Kt}),$

where  $\gamma = \gamma$  at time  $t,$

$$\gamma_{\infty} = \gamma \text{ infinite dev.},$$

which gives the relation between  $\gamma$  and the time of development.

The following tables show the validity of the expression for different batches of plates :—

Table XI.

Time.	Development factor $\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
2.0 mins.	0.50	0.0460
2.5 „	0.73	0.0562
4.0 „	1.08	0.0572
5.0 „	1.33	0.0608
6.0 „	1.47	0.0578
8.0 „	1.77	0.0602
10.0 „	1.91	0.0541
15.0 „	2.17	0.0480
$\infty$	2.67	
Mean ...		0.0550

Table XII.

Time.	$\gamma$ .	$K = \frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
2.0 mins.	0.684	0.0495
2.5 „	0.840	0.0500
4.0 „	1.23	0.0500
5.0 „	1.63	0.0470
8.0 „	1.90	0.0470
$\infty$	3.40	
Mean ...		K = 0.0487

This shows that both  $\gamma_{\infty}$  and K vary for different batches ; for the same developer,  $\gamma_{\infty}$  and K are the characteristic development constants of the emulsion.

The factor  $\gamma$  is of considerable importance in practical photography, as it measures the gradation or degree of contrast in a negative.

*Influence of Concentration on  $\gamma$ .*—As might be expected, this is simply, the time taken to reach a given factor is inversely as the concentration of the ferrous oxalate.

Thus for N/12.5 and N/25 ferrous oxalate—

N/25	.....	5.0 mins.	.....	$\gamma = 0.73$
N/12.5	... ..	2.5 „	.....	$\gamma = 0.72$
N/25	.....	5.0 „	.....	$\gamma = 1.54$
N/12.5	.....	10.0 „	.....	$\gamma = 1.59$

Over the range N/5 to N/40—

(A)	N/5	.....	1.5 mins.	(C)	N/20	.....	6.0 mins.
(B)	N/10	.....	3.0 „	(D)	N/40	.....	12.0 „

Table XIII.

E.	Log E.	DA.	DB.	DC.	DD.	Mean D.
304.5	2.48	—	1.358	1.440	1.446	1.414
154.8	2.19	1.302	1.248	1.278	1.270	1.274
78.0	1.89	1.094	1.114	1.104	1.120	1.108
40.6	1.61	0.892	0.892	0.902	0.850	0.884
18.8	1.26	0.604	0.688	0.676	0.608	0.644
11.1	1.05	0.422	0.436	0.428	0.358	0.414
6.72	0.83	—	0.244	—	—	0.244

The velocity of development is proportional to the concentration of the ferrous oxalate.

The magnitude  $\gamma_\infty$ , i.e., the limiting  $\gamma$  of the plate, is of great importance. It expresses numerically the ultimate density-giving powers of plates, and gives a numerical measure of the quality that has hitherto been expressed by such phrases as “contrasty plates,” soft plates, “flaue platten,” and so forth.  $\gamma_\infty$  is proportional to the photometric constant of the reduced silver, and so varies slightly with the developer, but more so with the emulsification of the haloid.

The practical estimation of  $\gamma_\infty$  and  $D_\infty$  is in many cases beset with much experimental difficulty. If  $\gamma_\infty$  is very high, the resultant densities are hard to measure, while many commercial plates, especially rapid ones, give much fog on prolonged development. Since the equilibrium is only theoretically reached after infinite time, only a close approximation is reached by very long development. The method given by Ostwald\* for evaluating the end-result was employed to check the results.

The following method of obtaining  $\gamma_\infty$  and K from simultaneous values of  $\gamma$  and  $t$  was pointed out by Dr. L. N. G. Filon:—

Writing the equation  $\frac{1}{t} \log_e \frac{\gamma_\infty}{\gamma_\infty - \gamma} = K$  in the form  $\gamma = \gamma_\infty (1 - e^{-Kt})$ , and taking  $\gamma_1$  and  $\gamma_2$  so that  $t_2 = 2t_1$ , we get

$$\gamma_1 = \gamma_\infty (1 - e^{-Kt_1}) \dots\dots\dots (a),$$

$$\gamma_2 = \gamma_\infty (1 - e^{-Kt_2}) \dots\dots\dots (b),$$

putting  $e^{-Kt_1} = x$  we have from (a) and (b)

$$\frac{\gamma_1}{\gamma_2} = \frac{1-x}{(1-x^2)} = \frac{1}{1+x} = \frac{1}{1+e^{-Kt_1}},$$

$$\therefore \frac{\gamma_2 - \gamma_1}{\gamma_1} = e^{-Kt_1}, \quad \frac{\gamma_1}{\gamma_2 - \gamma_1} = e^{Kt_1},$$

and  $\frac{1}{t} \log_e \frac{\gamma_1}{\gamma_2 - \gamma_1} = K,$

\* ‘Lehrbuch,’ 2te Auflage, 2 Th., 2 Bd., p. 210.

which gives  $K$ , whence  $\gamma_\infty$  may be obtained by substitution; but it must be noticed that the expression only holds when  $\gamma_2/\gamma_1 = < 0.8$  approximately, *i.e.*, when the tangential part of the curve is past.

*Comparison of Developers.*—By means of the  $\gamma$  formulæ the relative efficiencies for different developers can be compared. The following results give the comparison for ferrous oxalate, fluoride, and citrate:—

*Ferrous Fluoride.*—The use of this salt was suggested by Peters' work on the reduction potential of ferrous salts. Luther explains the fact that ordinary ferrous salts—Fe''R—as  $\text{FeSO}_4$  do not develop as due to the reversal of the reaction by ferric ions. But Peters has shown that the E.M.F. of a ferrous chain is very much increased by the addition of a soluble fluoride, owing to the fact that  $\text{Fe}''\text{Fl}_3$  is but slightly dissociated, and further that a complex ferrid-fluoridion is formed, both causes tending to remove ferric ions. We found that an N/10 solution of  $\text{FeSO}_4$  in excess of KF developed but slowly. Prolonged development removed the film from the plate, so that celluloid films had to be used.

The developer was made by mixing  $\text{FeSO}_4$  and NaF solutions, as the sodium double salt seems more soluble than the potassium one. The solutions were nearly colourless.

Table XIV.—Ferrous Oxalate, N/10.

Temp. 13° C.

Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_\infty}{\gamma_\infty - \gamma}$ .
3.0 mins.	0.64	0.056
6.0 „	1.13	0.060
8.0 „	1.39	0.064
$\infty$	2.00	—

K = 0.060

Temp. 20° C.

Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_\infty}{\gamma_\infty - \gamma}$ .
2.0 mins.	0.49	0.062
4.0 „	1.01	0.076
7.0 „	1.35	0.071
8.0 „	1.49	0.074
$\infty$	2.00	—

K = 0.071

$\gamma_\infty = 2.00$ , mean value found by Filon's expression.

The experiments with ferrous fluoride showed that the law of the constancy of inertia with time of development held here. For brevity, only the  $\gamma$  values are given.



Table XV.—Ferrous Fluoride, N/10.

Temp. 13° C.

Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
45·0 mins.	0·50	0·0028
90·0 „	1·00	0·0033
135·0 „	1·35	0·0036
280·0 „	1·72	0·00303
$\infty$	2·00	—————

K = 0·0032

Temp. 20° C.

Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
15·0 mins.	0·204	0·0030
60·0 „	0·895	0·0043
90·0 „	1·22	0·0045
120·0 „	1·36	0·0041
$\infty$	2·00	—————

K = 0·0043

Hence, comparing results,

Temp.	K Ferrous oxalate.	Ferrous fluoride.	Ratio.
13° C.	0·060	0·0032	18·7
20° C.	0·071	0·0043	16·5

This indicates that ferrous fluoride has a somewhat higher temperature-coefficient than ferrous oxalate.

*Ferrous Citrate.*—This is a good developer for chloride plates, but develops silver bromide very slowly. For the plates employed  $\gamma_{\infty} = 3·40$ , and K for ferrous oxalate at 20° C. = 0·0487.

It was found that here also the density ratios and the inertia were independent of the time of development. For the velocity at 20° C.—

Table XVI.—Ferrous Citrate, N/10.

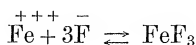
Time.	$\gamma$ .	$\frac{1}{t} \log_{10} \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma}$ .
60·0 mins.	0·474	0·0011
120·0 „	0·720	0·0009
240·0 „	1·40	0·00096
$\infty$	3·40	—————

K = 0·0010

Whence for table of relative efficiencies at 20° C.—

Developer.	Efficiency = K
Ferrous citrate .....	1·00
Ferrous fluoride .....	2·95
Ferrous oxalate.....	48·7

*On the Theory of Development.*—In the ferrous fluoride developer the reducing agent seems most probably the ferrous ion,  $\text{Fe}^{++}$ , the concentration of which is extremely high. With ferrous citrate, a complex ferro-citratanion. Now, on the diffusion theory the great difference in velocity observed is difficult to explain; in particular, the mobile ferrous ion should have proved the most efficient reducer. Possibly we still have to do with the influence of free ferric ions on the reduction velocity, although their original concentration in the ferrous fluoride solutions was extremely small, while those formed by the reaction  $\text{Fe}^{++} + \text{Ag}^+ \rightleftharpoons \text{Fe}^{+++} + \text{Ag}$  (metal), should be immediately removed by the ionic equilibria



and



However, the action of bromides shows that the actual chemical reaction can, under certain circumstances, influence the total reaction velocity. Although, in general, ionic reactions, such as we must conceive development to be, occur with practically immeasurable velocity, yet it is possible to follow some in which the ionic concentration is very low.\* In the development of silver bromide, the concentration cannot pass the solubility product of  $\text{AgBr}$ , so that the maximum concentration of silver ions is very low. Further, the unknown nature and influence on the reaction of the so-called latent image have not been taken into account.

Bodenstein,† in a criticism of the Nernst-Bruner theory, has indicated the presence of a high temperature coefficient as a criterion for distinguishing whether the speed of reactions in heterogeneous systems is conditioned by the diffusion process or the chemical reaction. A study of the temperature-influence, of the influence of soluble bromides, the reversibility of the reaction, and of the microscopy of development and exposure has been made, in continuance of the present work, as well as experiments on the nature and destruction of the "latent image," and it is hoped to publish these shortly.

The work given here shows that development can be studied quantitatively, and brings it in line with general physico-chemical.

*Summary of Results.*—(1) An accurate quantitative method of attacking photographic questions is described, and it is shown that if  $T$  be the optical transparency of the silver deposited in photographic processes, the  $D = -\log T$  is accurately proportional to the mass of silver.

\* Cf. Donnan and Le Rossignol, "Velocity of Reaction between Potassium Ferricyanide and Iodide in Neutral Solution," 'J. C. S. Trans.,' p. 703, 1903.

† M. Bodenstein, 'Zeit. f. Physik. Chem.,' 49, H. 1, p. 42, 1904.

(2) From considerations of the growth of the density during development, and of the theory of heterogeneous reactions, the equation  $\frac{1}{t} \log \frac{D_{\infty}}{D_{\infty} - D} = K$ , a constant, was shown to represent the reaction; this was experimentally confirmed. It is considered that the velocity of development mainly depends upon the rate of diffusion to the affected haloid. In agreement with this (*a*), the velocity as measured by the constant above, is directly proportional to the concentration of the reducer; (*b*) is affected by the age and condition of the plate; (*c*) is reduced by the addition of soluble bromides, but not in the proportion which would occur if the velocity of the chemical reaction  $\text{Ag} + \bar{\text{R}} = \text{Ag}(\text{met.}) + \bar{\text{R}}$  alone were measured.

(3) The law of constant density-ratios due to varying exposures, deduced from the above theory, is experimentally confirmed.

(4) It is shown that the development-factor  $\gamma$  in the sensitometry equation  $D = \gamma \log E/i$  is governed by the same laws as a single density. Methods for calculating and controlling  $\gamma$  are given, by means of the equation  $\frac{1}{t} \log \frac{\gamma_{\infty}}{\gamma_{\infty} - \gamma} = K$ .

(5) By means of this expression the velocities with ferrous oxalate, fluoride, and citrate were compared, the relative values of  $K$  being in N/10 concentration 0.0487, 0.003, 0.001; the anomalies here and the theory of development are discussed.

In conclusion, it is our pleasant duty to express our thanks to Professor Sir William Ramsay, F.R.S., for continual interest and advice throughout the research, and also to Dr. F. G. Donnan, and to Dr. M. W. Travers, F.R.S., for much advice and sympathy.

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