The Theory of Photographic Processes, Part II: On the Chemical Dynamics of Development, including the Microscopy of the Image.

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[PLATE 4.]

The investigation of development described in a previous communication[*] was extended by the application of microscopic methods. The fact that both the silver haloid and the resulting silver are distributed through the film in the form of particles of minute but measurable size, allows us in this way to detect finer qualitative differences in, and to draw independent deductions on the processes of exposure and development. The size of the grain is important, both from the practical point of view and from the theoretical : in the one case as bearing on spectroscopical and astronomical photography, in the other on account of the great importance of the degree of surface-extension for heterogeneous systems.[†]

The method has been used previously by Abney, Abegg, Kaiserling, Ebert, and others,[‡] but by far the most systematic and important inquiry is that of K. Schaum and V. Bellach.[§]

The work subsequently described had been carried out in part before Bellach's monograph came to our notice. The investigation was then extended beyond the limits of exposure and development given by Bellach,[||] and arranged to compare both with his results and those of our former paper. As much of the detail is of chiefly photo-technical interest, only the chief results are given here ; a fuller account will be published in the 'Photographic Journal.'

Experimental.

Beck objective $\frac{1}{4}$-inch and Reichart No. 8 $\frac{1}{10}$-inch, both dry systems, and for some work Zeiss $\frac{1}{12}$-inch cedar-oil immersion, kindly lent by Professor

[*] 'Roy. Soc. Proc.,' vol. 74, pp. 447 to 473.

[†] Ostwald, 'Lehrbuch,' vol. 3 ('Chem. Kinetik') ; Bredig, 'Arch. f. wiss. Phot.,' 1900 ; 'Eder's Jahrbuch,' 1899, p. 357.

[‡] H. Ebert, 'Eder's Jahrbuch,' 1894, p. 14 ; Kaiserling, 'Phot. Mit.,' 1898 (I and II) ; Abney, 'Phot. Journal,' 1898 ; R. Abegg, 'Arch. f. wiss. Phot.,' 1899, vol. 1, p. 109.

[§] K. Schaum and V. Bellach, 'Physik. Zeitschrift,' 1901—02, and especially "Die Struktur der Phot. Negative," by V. Bellach (W. Knapp, Halle, 1903). This admirable monograph contains a very complete bibliography on all points.

[||] Except in region of solarisation.

A. W. Porter, B.Sc.   The micrometers were a stage-micrometer in $\frac{1}{100}$ mm., an ocular calibrated on this, and an ocular in squares similarly calibrated.

Emulsion Tests.—As the study of ripening was deferred for further work, only the points bearing on the theory of development were considered. Preparations were made by dissolving a small piece of film in warm water and flattening under a cover-glass, then sealing with Canada balsam. The grains of a very thin layer thus obtained could be examined separately Long exposure had no apparent effect.

The grain in fast plates varied somewhat in size, there being, *e.g.*, in an Imperial special rapid, two species (*a*) 0·0011 mm. and (*β*) 0·0034 mm. The latter were flattened polyhedra, of triangular section; in the slow plates, the emulsion was practically homogeneous, the size of grain in Wratten ordinary being in mean 0·0017 mm. It could not be ascertained with certainty whether the grain was crystalline or amorphous.

The Physical Nature of Silver Haloid Emulsions.—Bellach found that in many cases the mean size of the grain diminished with careful drying.* Thus, after several days' desiccation, a contraction from $0·67 \times 10^{-5}$ mm.^{2} to $0·57 \times 10^{-5}$ mm.^{2} was noticed in an Eder emulsion. This points to the grain itself possessing structure, and agrees with Quincke's views as to the nature of silver haloid emulsions.† He considers that the AgBr "grains" are not pure AgBr, but contain gelatine. An emulsion in which the colloidal particles have flocked together forms a "spume." Liquid or jellified colloids consist of "spume" masses with liquid or solid spume-walls, enclosing very minute or invisible chambers. In haloid emulsions there is a stiff jelly containing a totally or partially solidified solution of AgBr in gelatine, in which a phase rich in AgBr has separated from a second phase poorer in AgBr, but richer in gelatine.‡ In the spume-walls and cells, spheres and crystals of haloid, much smaller than the measured grain, have separated.

The "adsorption" of gelatine to the AgBr agrees with Eder's researches on the separation of pure AgBr from emulsions by centrifugalising.§

Structure of Developed Negative.

By focussing on the top layer of particles, then down on to the lowest observable particles, the thickness of the reduced silver layer can be measured. This apparent thickness, recorded by the micrometer head of the fine adjust-

* Bellach, *loc. cit.*, p. 34.
† G. Quincke, 'Ann. d. Phys.,' 4te Flge., vol. 2, p. 1000, *et seq.*
‡ Hardy, 'Zeit. f. Phys. Chem.,' vol. 30.
§ Eder and Valenta, 'Beiträge zur Photochemie,' etc., sec. 3, p. 19.

ment, and multiplied by n_1/n_2, these being respectively the refractive indices of the gelatine and objective systems, gives the real thickness.*

With Wratten ordinary emulsion, exposed and developed as described, the negative-layer was somewhat as described by Bellach :—

(*a*) Surface-area, particles not very numerous.

(*b*) Mean-layer, with characteristic forms.

(*c*) Lower zone of smaller particles, diminishing the lower they lie. This Bellach attributes to the penetration of developer, but we shall show later that a more potent factor is that *the most exposed grains start development first.* On ultimate development these grains reach the same size as the others.

Table I.—N/10 Ferrous Oxalate.

2·0 mins. at 20° C.			10 mins. at 20° C.		
No.	Exposure.	Thickness.	No.	Exposure.	Thickness.
	C.M.S.	mm.		C.M.S.	mm.
2	2·04	0·0226	1	0·101	0·0115
3	4·66	0·0223	2	0·204	0·0116
4	7·75	0·0221	3	0·466	0·0118
5	12·9	0·0223	4	0·775	0·0139
6	27·9	0·0230	5	1·290	0·0195
7	54·5	0·0255	6	2·790	0·0232
8	113·0	0·0241			

Table II.—N/10 Ferrous Oxalate. Time of Development and Thickness.
Exp. = 1·38 C.M.S.

Time.	Density, D.	Thickness.
mins.		mm.
2·0	0·130	0·0200
6·0	0·280	0·0207
8·0	0·349	0·0206
10·0	0·542	0·0203
∞	0·586	0·0203

For the thickness, the following facts were ascertained :—

(*a*) With constant development for a short time the depth of the image is independent of the exposure.

* Bellach, *loc. cit.*, p. 56.

(*b*) With increased time of development the depth increases rapidly to a maximum for each exposure, after which it is constant.

(*c*) With long development the depth increases somewhat with the exposure, a limit naturally being fixed by the thickness of the film.

Every measurement is the mean of 10, each focussing being repeated, and for various portions of the film.

On the Size of the Grain.

Many discordant observations as to the influence of exposure and development on the size of the grain have been published.*   Our observations agree with Schaum and Bellach's, for the early stages of development, but on prolonging the development, the conclusions are modified.   They may be expressed as follows :—

When γ, the degree of development, is low, the size of grain increases with the exposure.

As the time of development increases, the size of the grain does also, until at γ_∞, *it is independent of the exposure.*

In addition to micrometric measurement of the diameter, the mean size was obtained by drawing the outline of the grains on squared paper by means of a reflecting system,† and then measuring the surface-extension.   This method could not be applied to the smallest grains, for which the micrometric measurements are only approximate.   The mean diameter of the " area " method is the mean between greatest and least, and is given to compare with the micrometric diameter.   The results are the means of 20 observations, and of 10 for the area method.

Influence of Exposure.

Table III.—Developed 2·0 mins. in N/10.   Ferrous Oxalate at 20° C.

No.	Exposure.	Micro-diameter.	Area.	Mean diameter.
	C.M.S.	mm.	mm.^{2}	mm.
1	1·03	0·00114	$1·23 \times 10^{-6}$	0·00101
2	1·87	0·00112	1·45	0·00121
3	3·10	0·00124	1·35	0·00123
4	5·17	0·00135	1·82	0·00130
5	11·8	0·00140	1·90	0·00152
6	22·0	0·00162	2·10	0·00182

Mg = C. 920.   Mg = C. 1360.

* Bellach, *loc. cit.*, p. 72.
† *Ibid.*, p. 76.

For the exposure an intensity-scale was used with constant time. Similar results were obtained by varying the time with intensity constant.

Influence of Development.

Table IV.—Exposure 1·38 C.M.S. Developed in N/10. Ferrous Oxalate at 20° C.

Time.	Density.	Micro-diameter (a).	Diameter (b).
mins.		mm.	mm.
2·0	0·150	0·00103	0·0008
6·0	0·280	0·00124	0·0010
8·0	0·349	0·00157	0·0014
16·0	0·542	0·00160	0·0016
∞	0·586	0·00167	0·0017

(a) For mean layer. (b) For lower zone.

Size of Grain on Infinite Development.

For moderately high exposures and prolonged development measurements could not be made on the plate direct, so preparations were made and the grain measured and photographed.

Table V.—Developed to γ_∞ in N/12·5 Ferrous Oxalate.

Exposure.	Density.	Micro-diameter.	Area.	Diameter.
C.M.S.		mm.	mm.²	mm.
2·04	0·277	0·00145	$1·94 \times 10^{-6}$	0·00135
4·66	0·966	0·00150	2·17	0·00165
7·75	1·496	0·00137	1·90	0·00152
12·90	2·400	0·00156	2·14	0·00171
27·90	3·400	0·00149	1·90	0·00159
54·30	4·39	0·00151	2·18	0·00165
209·0	—	0·00140	2·03	0·00156

Hence, generally, $G = \phi(\gamma, E)$, but at γ_∞ G is independent of E, the exposure. (See Plate 4, figs. I and II.)

Effect of Bromide.

Table VI.

No.	Exposure.	Diameter A.	Diameter B.
	C.M.S.	mm.	mm.
1	1·01	0·0009	Absent
2	2·04	0·00094	Points
3	4·66	0·00105	Points
4	7·75	0·00114	0·0008
5	12·90	—	0·00085
6	27·9	0·0143*	0·00103
7	54·5	—	0·00123
8	113·0	0·0165*	0·00145

* From preparations.

These were developed 1·0 minutes in N/10 ferrous oxalate, A, no bromide, B, N/200 K.Br.

This confirms Bellach's statement that bromide lowers the size of the grain. In addition, it should be noticed that the effect is greater the less the exposure. Also, it was found that the size of the grain diminished as the concentration of the bromide increased.

Bromide at Infinite Development.

Table VII.—Developed to γ_∞ in N/10 Ferrous Oxalate, N/200 KBr.

No.	Exposure.	Micro-diameter.	Area.	Mean diameter.
	C.M.S.	mm.	mm.²	mm.
1	2·04	0·00142	$1·7 \times 10^{-6}$	0·00135
5	27·9	0·00137	1·9	0·00142
8	209·0	0·00172	2·0	0·00139

Mg = 920.   Mg = 1300.

On comparing this table with Table V, it will be seen that on infinite development the grain attains the same size in a bromided as in a non-bromided developer. (See Plate 4, figs. III and IV.)

On the Number of Grains and Exposure.

In the Surface Area.—For this, photo-micrographs were taken at 500 diameters, and the grains counted in a given area on the negative. The values are the means of 20 observations.

Table VIII.—Developed 10 mins. in N/10 Ferrous Oxalate.

No.	Exposure.	No. per visual area.	No. per 1 mm.^{2} film.
	C.M.S.		
2	0·187	17·1	192×10^2
3	0·310	16·2	181
4	0·517	18·8	211
5	1·18	17·8	199

Hence for moderately long development, the number of grains on the surface is constant.

In the Thickness.—These were counted directly under the microscope, with a micrometer in squares. The values are for 25 to 30 squares, readings being taken in different portions of the film. The unit volume is a prism of area 1 mm.^{2} and height equal to thickness of film. It was found that the *number of grains increased with the exposure, and for moderately long development was nearly proportional to the density.* As this is contrary to Bellach's results, several sets of experiments were made, with as wide a range as practicable of exposure and development, which fully bore this out. The conclusion was further tested by making sections through the film. The best results were obtained by removing the developed film from the plate and rolling it up in gum mucilage. A small portion was then frozen on an ether spray microtome and sections cut. These gave a spiral embracing several tones, and it was easily seen that the number of grains increased with the exposure, the depth of the image but slightly. The appearance agreed with Abney's description :[*] " With small exposure the grains are congregated chiefly near the surface. As the exposure increases, the film behind fills up with particles and they crowd together."

Table IX.—Developed 6·0 mins. in N/10 Ferrous Oxalate.

No.	Exposure.	No. per 100 mm.^{2} visual.	Per unit vol.
	C.M.S.		
1	0·04	2·90	$27·3 \times 10^3$
2	0·081	2·46	23·4
3	0·184	3·21	30·2
4	0·312	6·10	57·5
5	0·52	7·58	71·0
6	1·12	8·34	78·5

Mg = C. 1000.

[*] Abney, ' Phot. Journal,' 1898.

1 and 2 were below the "Schwellenwerth." Obviously the number increases with the exposure. This was confirmed for other experiments, as far as the density permitted. Above 0·3 to 0·4 measurements could not be made ; but it can be seen that on extreme development (Table V) the size of the grain is constant. Yet the density has increased from 0·277 to 4·39 or about sixteen times. Since no commensurate increase in the size of the grain has occurred, the number must have increased.
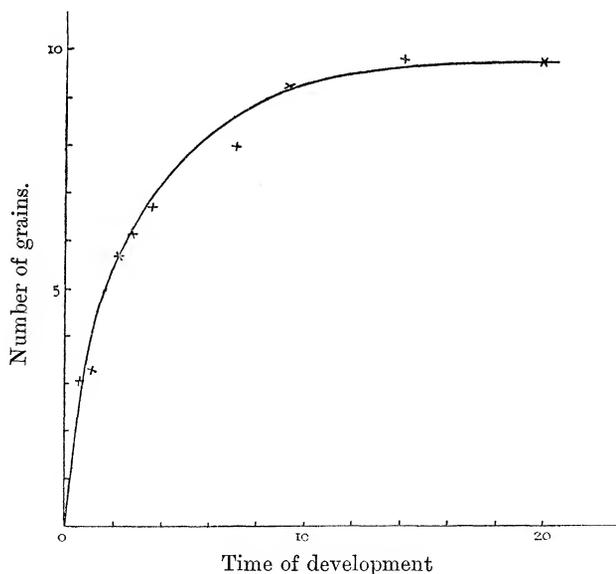
Influence of Development.

Table X.—Wratten Ordinary Plate Exposed for 0·25 C.M.S. developed in N/10 Ferrous Oxalate at 20° C.

No.	Time.	No. of grains per 100 mm.² visual.	Per unit vol.
	mins.		
1	0·5	3·35	$31·5 \times 10^3$
2	1·0	3·54	33·3
3	2·0	6·10	57·5
4	2·5	6·45	62·5
5	3·5	7·20	67·8
6	7·0	8·58	80·8
7	9·0	10·03	94·5
8	14·0	10·50	99·0
9	20·0	10·40	98·9

See Curve I.

Curve I.

Time of development

The number of grains increases rapidly at first, then more gradually till a maximum is attained.   This agrees with Bellach's results.

Exposure Through the Glass-side.

Two plates were given identical exposures behind the sector-wheel, and developed for 10 minutes in $N/10$ ferrous oxalate at 15°.   One was exposed through the glass-side, the other from film-side but with a glass plate in front.   On fixing, etc., although both showed 5 tones, the densities of the glass-side plate were considerably less than that of the other.   This agrees with Abegg[*] and Bellach.[†]

Thickness of Negative-Layer.

No.	Exposure.	Thickness (a).	Da.	Thickness (b).	Db.
	C.M.S.	mm.		mm.	
1	10	0·0204	—	0·0192	—
2	5	0·0199	0·110	0·0180	0·257
3	2·5	0·0188	0·042	0·0153	0·098
4	1·25	0·0181	—	0·0152	0·027
5	0·62	0·0148	—	0·0152	—

(a) Glass-side.   (b) Air-side.

The depth is much the same for both plates.   According to Abegg, all the grains in back exposed plate appeared equally developed, whereas Bellach describes his preparations as similar to front exposed plates, *i.e.*, uppermost zone with few and small particles, mean characteristic layer, and lowest with very small particles.   In our plates the appearance agreed with Abegg's description, the increase in size of grain being in the opposite sense to that of a film-side exposed plate.   The apparent divergence in description is probably due to the fact that Bellach used short development, 110 seconds, with a strong developer, while Abegg used prolonged stand development, more comparable with the author's conditions.   The result shows, that other things being equal, *the grain receiving most exposure is most reactive and starts development first.*

Thus, for 1·25 C.M.S. exposure,

	Micro-diameter. mm.	Focus. div.
Film-side plate .... {	0·00135	76·0
	0·0008	74·6
Glass-side plate .. .. {	0·00106	79·5
	0·00140	77·0

* R. Abegg u. Cl. Immerwahr, 'Sitz. ber. d. Wien. Akad.,' vol. 114, abt. 2A, 1900.
† *Loc. cit.*, p. 61.

The number of grains was greater in the plate exposed from air-side. For 1 mm.^{2} of film,

$$\text{Air-side} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 132 \times 10^3,$$
$$\text{Glass-side} \ldots\ldots\ldots\ldots\ldots\ldots \quad 71 \times 10^3,$$

while Abegg and Immerwahr give $41 \cdot 0 \times 10^3$ and $32 \cdot 5 \times 10^3$. Both the densities and the number of grains are greater for the air-side plate. Abegg attributes this to the prevention of halogen diffusion. Braun's[*] observation on the part played by oxygen in the formation of latent images may also account for it however. Possibly connected with this is the statement of Wulf,[†] that for the so-called photo-electric effect the sensitiveness to light increases as the potential fall of electrode to surrounding gas increases.

The general results of the microscopic survey are in agreement with the theory of development proposed before. Each grain develops as a more or less isolated system, only uniting to form "aggregates" with other grains at high exposures, when the packing is closer. The thickness of the reaction-layer is from 0·02 to 0·04 mm., a value similar to that found by Brunner for many heterogeneous reactions. But in this case *the solid phase lies entirely in the layer.* The diffusion of the developer may be divided into two parts :—
(a) through the total thickness, δ, (b) through the micro-layer, δ', of the order 0·0005 mm. surrounding the grain. This is the true reaction-layer, and the reaction is somewhat like to the catalysis of H_2O_2 by colloidal metals, save that there is no convection. As the diffusion has to take place through gelatine, the structure and state of this may influence the velocity. This will be dealt with later. The fact that the size of the grain with low time of development—or better—low development-factor varies with the exposure, indicates that the "reactivity" of the individual haloid grain is a steady function of the exposure. Hence at low development-factors departures from the law of constant density-ratios are possible, but difficult to confirm. *Such departures will be the more marked whenever the chemical-velocity approaches that of the diffusion process.*

The conclusions given here were confirmed for other developers, and we hope to publish them later in connection with the general survey of these ; since this work was finished, Messrs. Lumière[‡] and Wallace[§] have published short studies on the size of the grain. Their results do not contradict ours, but they do not seem to have considered sufficiently the effect of the degree of development, γ, on all observations.

* Braun, 'Zeitschrift f. wiss. Phot.,' vol. 2, Heft 8.
† Th. Wulf, 'Ann. d. Phys.,' 4te Flge., vol. 9, p. 946.
‡ Lumière, 'Zeit. f. wiss. Phot.,' vol. 2, p. 256.
§ Wallace, 'Astrophysical Journ.,' 1905.

The early stages of development.—Considerable information concerning the velocity of development can be obtained from the " time of appearance " of the image, which is a function of it. In 1893 Mr. Watkins announced that for any given reducer the time of appearance gave an accurate indication of the speed of working, and that any variation in the alkali, temperature, or strength affected the time necessary to reach a given density or development-factor in the same proportion that it affected the time of appearance. Generally stated, $T_D = WT_A$, where T_D is time for density, D. T_A is time of appearance, and W is a constant.

This rule has been usefully applied in practice for timing development, but the above statement is too wide, both experiment and theory showing that such a simple relation does not hold for many complex developing solutions. The following considerations from the theory of the order of reactions* explain both the rule and the deviations from it.

If two analogous reactions continue to equal fractions of the total change, then the times necessary for this are inversely as the velocity-factors.

Of course, it is assumed that the same function of the variables still represents the course of the reaction. If experiments with different concentrations are carried to the same fraction of these, the following relations hold :— For reactions of the first order the factors are directly, the times inversely as the concentrations, of the second order as the squares, and so on. We may apply this to development as follows :—The density which is first visible, *i.e.*, first distinction between exposed and unexposed, is a physiological constant and a fixed density, θ, say (Schwellenwerth).† Hence for same exposure, *i.e.*, same final density, θ *is always an equal fraction of the total density ;* so ϑ, the time of appearance, *i.e.*, for density, θ, is inversely as the velocity-coefficient, and is similarly modified by concentration, etc.

With different final densities and constant developer, the values of ϑ are inversely as the final densities, D_1, D_2, etc. Here, of course, θ measures an equal fraction of the total oxidation of reducer.

Let D_1 and D_2 be any two final densities, and λ a fixed density, where D_1, $D_2 = $ or $> \lambda$, and let ϑ_1 and ϑ_2 be their respective times of appearance, and t_1, t_2 corresponding times to reach λ. Then we have

$$t_1/\vartheta_1 = t_2/\vartheta_2 = t_n/\vartheta_n = \text{constant W,}$$

whose numerical measure is proportional to the Watkins multiple, and is independent of concentration and only dependent on velocity function.

* Ostwald, 'Lehrbuch,' 2te Auflge., vol. 2, p. 236.

† This fact rests on the existence of a " Schwellenwerth " or " threshold " value of perception of contrast by the eye.

The general theorem is only true for simple reactions, and does not hold for "graded," "catalysed," and so forth. *The same limitations hold for development,* and the occurrence of initial disturbances, varying in the specific developers, probably account for the wide variation of the Watkins multiple for various developers, and also its variation with the same reducer. *Only for developers* in which the balance between reduction-potential and diffusivity is within certain limits will W be constant, since deviations will easily occur for such a small fraction of the total change, and yet the development-function remain much the same.

The writers have extensively developed the use of the "time of appearance" for investigation of development-kinetics. The most similar use of such a method of inquiry in chemical dynamics is A. von Oettingen's* research on the decomposition of thio-sulphate by acids, in which the "time of appearance" of the sulphur-cloud was observed. The limiting conditions for experimental accuracy discussed there hold also for development. The time must not be so short that the limiting error of measurement seriously affects the result, nor so long as to cause doubt as to the exact moment. The observations are made in a dark-room, but using as much of a steady reddish light as possible, since subsequent fogging is in general immaterial.

The timing was done with a stop-watch marking $\frac{1}{5}$ of a second; several observations of each time were made, and the mean used, and all measurements for comparison made at one period. The method is accurate within the limits employed to about 2 per cent.

Effect of Concentration with Ferrous Oxalate.

Table XI.—Plate, Wratten Ordinary, exposed 8 C.M.M.

Concentration.	T_A in secs.	Mean T_A.	C = Product.
0·2 N.	22·0, 19·0, 19·0, 18·8	19·7	3·94
0·1 N.	40·4, 40·0, 40·2	40·1	4·01
0·05 N.	81·0, 79·8, 80·5	80·4	4·02
0·025 N.	160·2, 158·2, 157·0	158·4	3·96
			Mean 3·98

This shows from N/5 to N/40 the velocity is directly proportional to the concentration, even at this early stage of development.

* 'Zeit. f. Phys. Chem.,' vol. 30 ; *cf.* also H. Landolt, ' Ber.,' vol. 19, p. 1317, 1886.

Temperature and Development-Velocity.

Experiment showed that the variation of temperature did not influence the density-ratios. The effect of temperature on the velocity-constant $K = \frac{1}{t} \log \frac{\gamma_\infty}{\gamma_\infty - \gamma}$ was measured, and also on $V = 1/T_A$. In this case four series of measurements were made, embracing the range $0°$ C. to $30°$ C. By interpolation the reduced results gave the following table.

Table XII.—Developed in N/12·5 Ferrous Oxalate.

Temperature, ° C.	Absolute.	Velocity.	V mean.
− 0·8	272·2	1·00	1·00
0·0	273·0	1·01	1·01
5·2	278·2	1·29	1·29
6·7	279·7	1·33	1·33
9·2	281·2	1·42, 1·56, 1·51	1·50
15·0	288·0	2·126	2·13
20·0	293·0	2·50	2·50
25·0	298·0	3·29	3·29
30·0	303·0	4·35	4·35

Van't Hoff's equation $\frac{d \log K}{dT} = \frac{A}{T^2}$* in the integrated form for A sensibly constant, $\log K = -\frac{A}{T} + C$ was found to represent the results very fairly.

Table XIII.—C found as 7·60.

Temperature.	A.	V obs.	V calc.	Δ per cent.
272·0	1794	1·00	0·982	− 1·8
273·0	1798	1·01	0·991	− 1·9
278·2	1807	1·29	1·290	0·0
279·7	1911	1·33	1·380	+ 4·0
281·2	1806	1·50	1·506	+ 0·4
288·0	1806	2·13	2·133	+ 0·1
293·0	1817	2·50	2·69	+ 8·0
298·0	1813	3·29	3·467	+ 5·0
303·0	1807	4·35	4·361	+ 0·25

Curve calculated from $\log K = -1806/T + 7·60$.

* J. H. van't Hoff, 'Kgl. Svenska Vet. Hdl.,' vol. 21, No. 17, 1885.

Curve II.

Velocity of development.
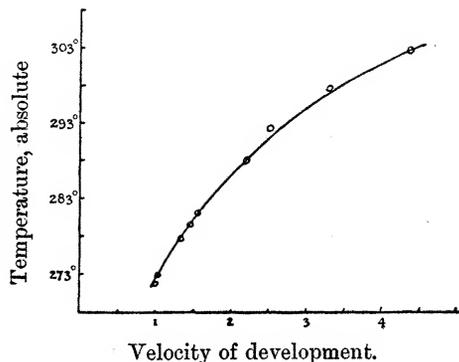
The temperature-coefficient for 10° from 0° to 30° C. is $(K+10°)/K = 1\cdot7$.

The validity of these results is shown by measurements of K, the mean velocity coefficient.

Table XIV.

Temperature, °C.	K found.	K calc.	Δ per cent.
9·6	0·0632	0·0632	—
20·8	0·0870	0·0891	+2·2
30·7	0·1174	0·1210	+2·0

The Temperature-Coefficient.

Bodenstein[*] and Senter[†] have indicated the value of the temperature-coefficient for 10° as a criterion in heterogeneous reactions. For chemical reactions in homogeneous solution the value is generally about 2 to 3,[‡] while Brunner found 1·5 for rate of solution of benzoic acid in water; for diffusion-processes we should expect a value about 1·5, and not varying for different bodies very much.

Now we have found that the expression $K = \dfrac{1}{t} \log \dfrac{\gamma_\infty}{\gamma_\infty - \gamma}$ can be used to measure the development velocity for most developers. A preliminary study of the temperature-coefficient for different emulsions and developers gave the following results:—

[*] 'Zeit. f. Physik. Chem.,' vol. 49, p. 42, 1904.
[†] 'Roy. Soc. Proc.,' vol. 74, p. 214.
[‡] Van't Hoff, 'Vorlesungen,' vol. 1, p. 225.

Table XV.

Reducer.	Emulsion A.	B.	C.
$Fe(C_2O_4)$	1·60	1·90	1·70
FeF	1·52	—	—
Fe Citrate	1·54	—	—
$C_6H_4(OH)_2 p$	—	2·10	—
$C_6H_4(OH)_2 o$	—	2·80	—

The temperature-coefficient frequently passes the value to be expected from the diffusion-theory. But in the case of development, we must be cautious in applying the criterion, as the following consideration will show :—

Beside the increase in diffusivity (mobility of reducing molecule), we must also consider (*a*) alteration of resistance to diffusion in gelatine; (*b*) in complex developing-solutions, alteration of concentration of reducing ion by changing the chemical equilibrium, especially in alkaline developers. Under these conditions *a high temperature-coefficient in development does not necessarily mean that the velocity is that of a chemical reaction.*

In the case of ferrous oxalate, the theoretical formula of Van't Hoff, which is a deduction from the reaction-isochore, was employed. This is not legitimate in the case of diffusion phenomena, and the best formulation would probably be the ordinary parabolic interpolation formula in the form $K_t = K_0(1 + at + bt^2)$; a comparison of the constants a and b for different plates and developers should yield useful information on temperature influences.

Resistance of the Gelatine.

Hardening agents, which raise the melting point of the gelatine, are generally supposed to alter the velocity of development by changing the diffusivity. Many emulsions, however, show no such effect. Thus, with formalin (40-per-cent. formaldehyde) in 4-per-cent. strength and increasing time of immersion, although the film became quite insoluble in boiling water, the development-velocity was not lowered.

The general theory of the action of hardening agents will be discussed later in connection with the destruction of the " latent image."

Table XVI.

No.	Time of immersion.	T_a in secs.	Mean.
	secs.		secs.
1	0	24·0, 23·2, 24·0	23·7
2	30	24·0, 24·2, 23·8	24·0
3	60	24·0, 24·2, 23·4	23·9
4	120	23·6, 24·6, 24·0	24·0
5	240	24·0, 23·0, 23·4	23·4
6	8 per cent 10 mins.	25·2, 23·4	24·3
			T = 23·9

"Penetration" of Developer.

By the rate of penetration the time for the reducer to pass through the reaction-layer, δ, is understood. This was studied as follows :—

If plates are exposed through the glass-side, the image will lie nearer the glass, and we may expect it to appear—

(*a*) On front first if the penetration of the developer count most.

(*b*) On back first if the greater reactivity of the more exposed particles be the predominant factor.

A strip of Ilford ordinary film was exposed, cut up, and developed in $N/10$ ferrous oxalate at 15° C.

The values of T_a given are means of four experiments.

Table XVII.

Exposure.	T_a film-side.	T_a glass-side.
Ilford film—		
300 C.M.S.	40·3 secs.	45·3 secs.
60 ,, ...	54·6 ,,	52·6 ,,
10 ,, ...	72·4 ,,	63·0 ,,
Wratten ordinary—		
300 C.M.S.	94·2 ,,	90·4 ,,

Consequently, with low exposures, the back appears before the front, but as the exposure increases, the developer being the same, the two times become equal, and eventually the image appears on front first. This was confirmed on plates exposed in the sensitometer.

Plates given the same exposure from the front always show the image from the front first, the relative difference in time being somewhat greater, the absolute value of T_a always less.

The above phenomena may be explained by the following considerations drawn from the microscopy of the image :—

(*a*) The absolute thickness of the layer of developable particles increases but slightly with the exposure.

(*b*) Reckoning down through the layer from the exposed side, the reactivity of each layer .of grains diminishes through the thickness. *The slope* of this reactivity-gradient then depends upon the exposure.

(*c*) With short time of development the penetration increases rapidly ; further, as the developer reaches the lowest layers, its concentration will be diminished somewhat by diffusion and oxidation by developable AgBr. There will, therefore, be a concentration gradient through the film.

(*d*) Then in the case of exposure from air-side, the two gradients will be in the same direction, and will reinforce each other ; for exposure from the back, the gradients will be opposite in sense, and the front layers or back will appear first according as one factor or the other predominates.

This result is in agreement with the microscopic deduction, that other things being equal, the more exposed grains possess the greater reactivity and start developing first.

With regard to the absolute time required for the developer to penetrate the thickness of the film, an estimate can be obtained as follows :—With an Ilford film, the $\gamma_1 t$ curve of which was known, the *least* time of appearance at the back for any exposure through the back was about 10 seconds with N/10 ferrous oxalate at 15° C. Now, under these conditions, the half-period of development, *i.e.*, for $\gamma_\infty / 2$, was 5·0 minutes. Hence, the error due to incomplete penetration is not of a very large order, and, moreover, reasons will be given later for assuming a chemical-induction generally greater than any diffusion-induction. However, for accurate comparison of velocities, in order to avoid an erroneous time-zero, the form

$$\text{K} = \frac{1}{t_2 - t_1} \log \frac{\gamma_\infty - \gamma_1}{\gamma_\infty - \gamma_2} *$$

is the most suitable.

In development the temperature-coefficient has been found an inadequate criterion for distinguishing diffusion from chemical-velocity. Such a criterion, however, we believe to exist in the action of soluble bromides, and in a discussion of this and the reversibility of development we hope to

* Senter, *loc. cit.*, p. 203 ; see also Ostwald-Luther, 'Physico-chem. Messungen,' p. 455.

show that the development process probably takes place in general in two phases, in the first period the chemical-velocity being slow compared with diffusion, in the second the contrary holding. It is the velocity of the second period which is usually measured.

In conclusion we have much pleasure in expressing our great thanks to Sir William Ramsay, F.R.S., for his interest in the investigation.
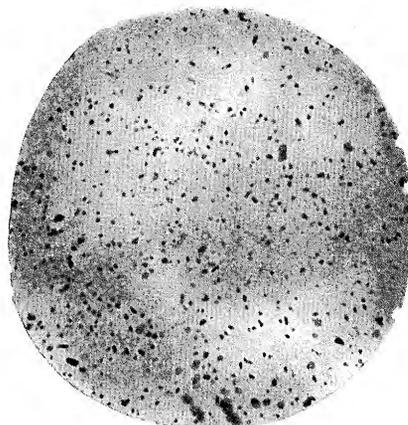
DESCRIPTION OF PLATE.

F gs. I to IV are from preparations as described on p. 217, etc.
Fig. V was photographed directly from the Plate and shows the grains *in situ ;* the large "aggregates" are as much due to superposition of grains as to physical fusion.

I

II

III

IV

V
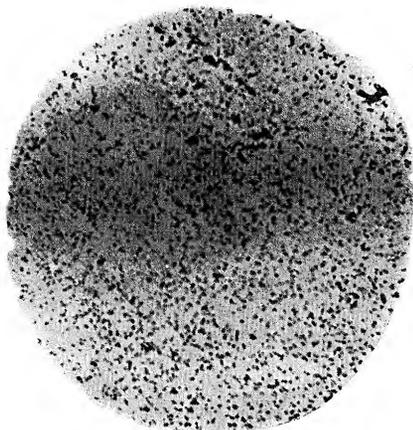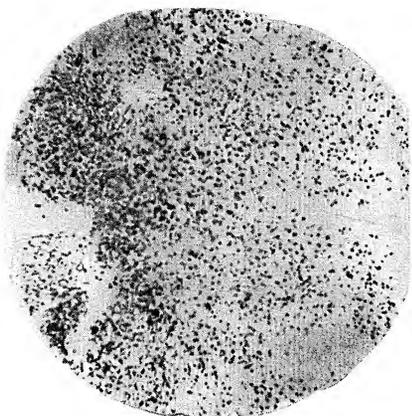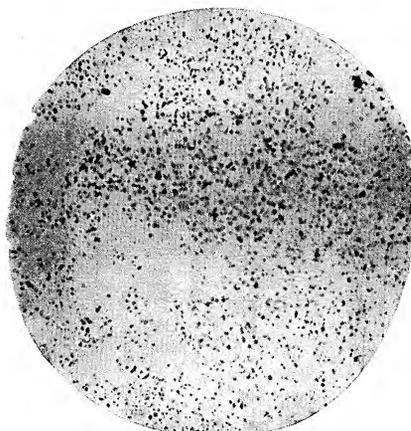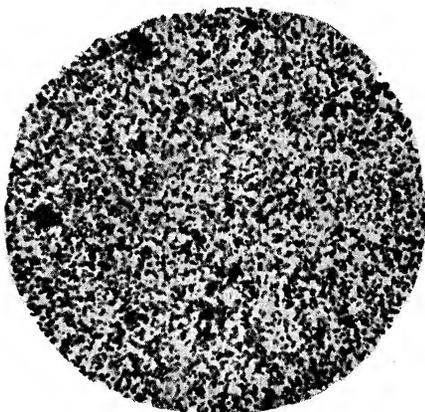
I, II for γ_∞, 209 C.M.S. and 2 C.M.S.
III, IV, ditto   ditto   ditto
in N/200 KBr.
Mg., C. 900.
(See Tables **V** and VII.)
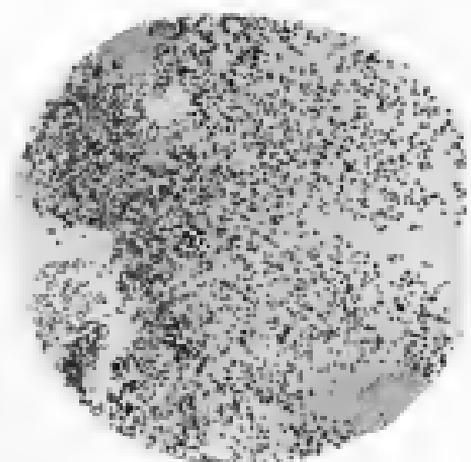
V, 1·38 C.M.S., dev. 10 minutes.
in N/10 FeOx at 20° C.   Mg., C. 900.

I, II for γ_a, 300 C.M.S. and 2 C.M.S.
III, IV, ditto ditto ditto
in N/200 KBr.
Mg., C. 900.
(See Tables V and VII.)

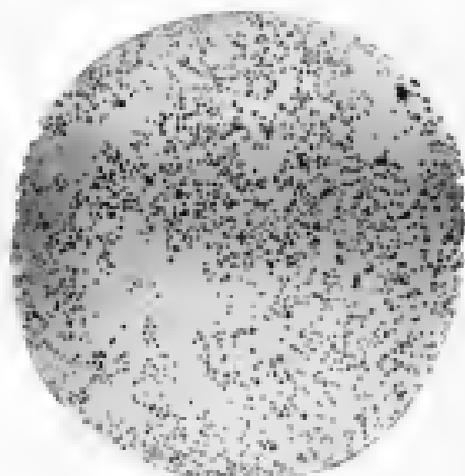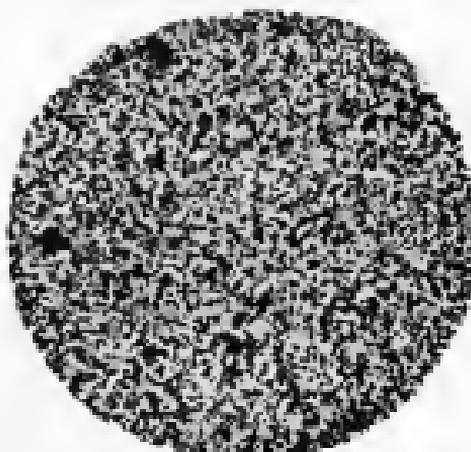V, 1·38 C.M.S., dev. 10 minutes.
in N/10 FeOx at 20° C. Mg., C. 900.

F gs. I to IV are from preparations as described on p. 217, etc.
Fig. V was photographed directly from the Plate and shews the grains *in situ*; the large "aggregates" are as much due to superposition of grains as to physical fusion.