ON THE ADSORPTION THEORY OF PHOTO-GRAPHIC DEVELOPMENT.

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1.

The process of photographic development has been investigated from various points of view. We shall discuss here only those investigations which were concerned with the physico-chemical aspect. Two main lines may be followed in this direction : one tends to give a quantitative description of this process and to state the laws governing it, the other attempts to explain the underlying mechanism.

2.

To the first group belongs the *electrochemical theory* of development. Based on the assumption that the reduction of silver ions into silver atoms in development proceeds along the same lines as in an electrolytic cell, this theory gives a fundamental equation, connecting the progress of development with the oxidation-reduction potentials of two systems : silver/silver ion and organic reducer/its oxidised form, depending on p_H, temperature, etc. This theory appeared long ago but during several decades it remained practically fruitless, which caused a certain disappointment expressed by one of its authors, Luther [1] at the Faraday Society Discussion in 1923.

In fact, this purely thermodynamical theory remains correct when applied to strictly reversible systems. Serious doubts may arise as to the reversibility of complicated processes involved in photographic development. But even if they were fully reversible, thermodynamics, concerned only with the initial and final states of the system, could give no information on the process at intermediate stages nor could it explain its intrinsic mechanism.

This theory has made considerable progress during recent years, especially through the work of Reinders [2] and Faerman.[3] Conclusions drawn from it permitted a rational description of many phenomena observed in development : the influence of alkali, the action of various bases, the part played by sulphite, the importance of redox potentials, the influence of the concentration of the developing agent, etc.

Convincing evidence of the applicability of the electrochemical theory to the development by ferrous oxalate developer has been given in the paper by Reinders [2] who showed that the direction of the process of development is determined by the potential difference $\Delta E = E_{Ag^+/Ag} - E_{Ox/Red}$. It can only commence when this difference shows a certain positive value and it proceeds the farther, the larger this difference. If the sensitive layer has been exposed and predeveloped, development can proceed only at positive values of ΔE ; at negative values it is reversed, *i.e.* silver which has been formed previously is oxidised. Analogous results were obtained later by Evans and Hanson [4] for an organic developing agent—amidol.

It would be wrong, however, to ask from this theory more than it can give. Some adepts of this theory tried to apply it to the solution of kinetic

[1] R. Luther, *Trans. Faraday Soc.*, 1923, **19**, 322.
[2] W. Reinders, IXe *Congrés International de Photogr.*, Paris, 1935, p. 345.
[3] G. Faerman, *ibid.*, 198.
[4] R. M. Evans and W. T. Hanson, Jr., *J. Physic. Chem.*, 1937, **41**, 509.

questions.   Reinders, De Langhe, Faerman assume a simple relationship
or even direct proportionality between the rate of development and the
potential difference ΔE.   De Langhe [5] deduced an approximate equation :
$dx/dt = m = \alpha k'(Ag)R_t . \Delta E$, where α and k' are constants, R_t the total
concentration of the developing agent, (Ag) the concentration of silver.
We were unable, however, to find experimental data in support of this
relationship.   De Langhe and Reinders [2] use for this purpose data by
Reinders and Beukers who studied the change of optical density D with
changing ΔE.   These measurements give equilibrium values of D, ob-
tained after twenty hours' agitation in the respective developing solution,
and are obviously unsuitable for testing a relationship concerning dD/dt.

If there were a simple relationship connecting dD/dt with ΔE one
would expect that at equal ΔE-values various developers would act at
the same rate.   Experiments by Reinders have shown that this is not so :
the following values of D have been attained at ΔE approximately equal
to 240 mV. for eight minutes' development : in metol 2·80, in ferrous oxalate
1·65, in ferrous malonate 0·10, in ferrous citrate $-$ 0.   Analogous diver-
gence was found by Faerman,[3] whose Fig. 3 shows that sixteen minutes'
physical development at $\Delta E = 51$ mV. gave at various concentrations of
$AgNO_3$ optical densities 0·75 and 1·4.   Kahn-Kohan [6] showed that the
doubling of the metol concentration decreased the rate constant (for
sixteen minutes) from $1·29 \times 10^{-3}$ to $0·89 \times 10^{-3}$.

All these data point to the absence of a general relationship between
development rate and potential difference ΔE.   De Langhe himself as-
cribes to it only a limited range of applicability near the equilibrium point
($\Delta E = 0$), where it may hold for the same developing agent at constant
conditions.

3.

The electrochemical theory of development however, being purely
thermodynamical, cannot pass the limits of thermodynamical argument and
explain the mechanism of the process.

For this purpose a combination of the thermodynamical theory with
some molecular-kinetic theory is needed which makes definite assumptions
as to the mechanism of the process in question.   As such, the oldest theory
of development, the supersaturation theory, has been chosen by Reinders,
assuming that the main part of the process takes place in the solution.
Proposed at the end of the past century by Ostwald,[7] Abegg [8] and Schaum,[9]
this still remains the most widespread theory of development, although
many other theories have been published since, especially during recent
years.

This theory assumes that the silver bromide of a light-sensitive emulsion
is dissolved in the developing solution, where it is reduced into silver,
forming a supersaturated solution.   From the latter, silver is deposited on
crystallisation centres represented by the silver nuclei of the latent image.
Several serious objections have been raised against this theory.[10]   On close
examination these objections proved, however, not quite convincing.
So far experimental data directly refuting or proving its validity is lacking.
Some considerations, however, form strong evidence against the theory of
supersaturation :

1. It requires a very *high degree of supersaturation* of silver in solution
(thousand-fold), which is not impossible, according to Volmer, though
rather improbable.

[5] J. E. de Langhe, *Physica*, 1936, **3**, 398.
[6] A. Kahn-Kohan, *Photochemical Industry (russ.)*, 1934, **3**, 35.
[7] Wi. Ostwald, *Lehrb. d. allg. Chemie, B, II, T.* 1, 1078, 1893.
[8] R Abegg, *Wied. Ann. Physik*, 1897, **62, 425.**
[9] K. Schaum, *Arch. wiss. Photogr.*, 1899, **1**, 139.
[10] M. Volmer, *Photogr. Korresp.*, 1921, 226 ; W. Meidinger, *Die theoretischen Grundlagen der photographischen Prozesse*, Jul. Springer, Wien, 1932, 244 *et seq.*

2. It requires a very *high solution velocity* of AgBr. For developing a 9 × 12 plate to an average optical density of 1·0, 20 mg. AgBr ought to go into solution during a few minutes. This seems somewhat improbable for a substance whose solubility does not exceed $1·10^{-5}$ g./100 c.c. Even if we assume a layer of saturated solution in contact with the surface of a AgBr crystal, the concentration gradient along a line perpendicular to this plane would be very small and could not lead to a high dissolution velocity.

3. Substances tending to *raise the solubility* of AgBr ought to increase the rate of development. Sodium hyposulphite, however, slows down the development by typical organic developers.[11]

4. *Physical development* after fixing which can be explained only along the lines of the supersaturation theory (except the first step : AgBr solution) is qualitatively different from the usual *chemical development*. The former is very slow, gives low densities, requires frequent change of developing solution and final intensifying. Therefore it is natural to suggest another mechanism in the case of chemical development.

The supersaturation theory of development appeared at the time when the opinion prevailed that substances may react only in solution, according to the rule of mediæval alchemy : *Corpora non agunt nisi soluta.* But the times of alchemy are over ; in the twentieth century more and more experimental material has been gathered showing that chemical reactions in solid phase are rather common, and usually follow the autocatalytic rate law. This has been shown by the work of Larson, Okajama, Taylor, Centnerszwer, Hinshelwood, Frankenburger, von Antropoff, Adhikari, Schenk [12] and many others. Thus the psychological basis of the supersaturation theory collapsed and the way lay open for new theories of development.

4.

As development takes place on the interface between the solid phase (AgBr) and liquid phase (developing solution), it was natural to treat this process as a heterogeneous reaction and to apply to it modern conceptions of heterogeneous catalysis and adsorption from solutions. The former was done in the *catalytic theory* of development (Volmer), the latter—in the adsorption theories of development discussed below.

Volmer [13] considered development as the reduction of AgBr by the developing solution and the simultaneous oxidation of the latter, catalysed by the highly-dispersed silver of the nuclei of the latent image. This was proved by indirect experiments : the presence of dispersed (colloidal) silver accelerates the oxidation of developing substances in solution, through which air is bubbled ; other colloidally dispersed metals act in the same way. This theory presents an important advance over the supersaturation hypothesis : it localises the process of development on the ternary interface AgBr/Ag/solution, where it must occur in reality ; the reduction of AgBr is considered in the solid phase instead of in the solution, where its amount is obviously deficient to give the observed velocities of development ; the *selectivity* of development (reduction of illuminated emulsion grains preferably to those which have not been illuminated) finds its simple and elegant explanation in the catalytic action of silver nuclei absent in the non-illuminated grains. The one serious defect of the catalytic theory is the somewhat broad sense of the term " catalysis " which is applied, without specifying which of the several known types of catalytic action is efficient in this case.

[11] W. Meidinger, *loc. cit.* [10], p. 222
[12] References in : M. Volmer, *Z. Elektrochem.*, 1929, **35**, 555.
[13] M. Volmer, *Z. wiss. Photogr.*, 1921, **20**, 189.

5.

The *adsorption theory* of development was proposed by Bancroft [14] in a somewhat indefinite form : the developing agent is adsorbed on illuminated grains of AgBr in preference to the non-illuminated ones, which leads to accelerated reduction of the former. Bancroft proposed some indirect experiments in support of his hypothesis, but the results of these experiments have not been published. Another statement of this author, namely that the selective adsorption must be reversed in cases where the development gives a reversed image, also was not proved by him.

In another, more definite form of the adsorption theory Sheppard [15] assumes the adsorption of developing agents on the surface of AgBr, formation of complex compounds of the type AgBr*Red* and their subsequent decomposition into metallic silver and the oxidised form of developer. In this form the adsorption theory admits direct experimental checking ; but the main feature of photographic development, the selective action of illuminated AgBr grains, remains unexplained. An attempt to prove the validity of this theory was undertaken by Wulff and Seidl ; [16] however they could not overcome considerable technical difficulties and had to content themselves with an indirect evidence of the adsorption on silver bromide of *resorcinol*, an isomer of hydroquinone which is devoid of developing properties. Later direct measurements in our laboratory have shown that hydroquinone is not adsorbed by AgBr, contrary to the assumption of Sheppard.

6.

An adsorption theory of development was published by the present author in 1931, [17] and has been supported since by a series of experimental investigations carried out in the Karpov Research Institute of Physical Chemistry.

It can be briefly formulated in a few statements :

Organic developers (reducers with definite values of redox-potential) are not adsorbed on the surface of AgBr-grains.

They are considerably adsorbed from solutions on colloidal silver particles forming the nuclei of the latent image (development centres).

The increase of concentration of the developing agent on the interface Ag/AgBr, caused by adsorption, greatly increases the velocity of the process of reduction which takes place in the silver bromide of the grain in direct contact with the silver nucleus of the latent image.

On the interface Ag/AgBr new quantities of silver are formed which adsorb new portions of developing substance, and the process spreads autocatalytically over the whole silver bromide grain.

Results of previous investigations published in collaboration with S. S. Peissachovitch [18] may be briefly mentioned here as they strongly support the adsorption theory of the present author :

Complete absence of adsorption of typical developing substances on dispersed silver bromide (colloidal solution and suspension) in neutral and acid medium has been shown, which confirms the first thesis of our theory and contradicts the theory of Sheppard.

[14] W. D. Bancroft, *Trans. Faraday Soc.*, 1923, **19**, 252.

[15] S. E. Sheppard, *Photogr. Korresp.*, 1922, 76.

[16] P. Wulff and K. Seidl, *Z. wiss. Photogr.*, 1930, **28**, 239.

[17] A. J. Rabinovitsch, S. Peissachovitch and L. Minaev, *Bericht üb. d. VIII Internat. Kongress f. wiss. und angew. Photogr.*, Dresden, 1931, p. 186; A. J. Rabinovitsch, *Z. wiss. Photogr.*, 1934, **33**, 57.

[18] A. J. Rabinovitsch and S. S. Peissachovitch, *Z. wiss. Photogr.*, 1934, **33**, 94 ; *Acta physicochimica U.R.S.S.*, 1936, **4**, 705.

It has been shown that a typical developing substance (hydroquinone) is strongly adsorbed on colloidal silver analogous to the substance of the nuclei of the latent image. More hydroquinone is adsorbed than is required to form a monomolecular layer on the surface of silver.

A simple model of the process of development has been constructed, which may be used as a demonstration experiment and as a means to study various factors influencing this process (concentration and size of nuclei, p_H, action of sulphite, etc.). A small quantity of colloidal silver added to a mixture of colloidal AgBr, developing substance and alkali causes its rapid darkening (reduction to metallic Ag) in the dark room or in weak light.

Colloidal silver can be successfully replaced in this model by other colloidal metals (Pt, Au, Cu) which are able to adsorb hydroquinone. Other colloids (Bi, Al_2O_3, Fe_2O_3, TiO_2) and activated charcoal, which do not adsorb hydrochinone, are unable to cause the darkening of the model.

Hydroquinone can be replaced by other developing substances (adurol, p-aminophenol, metol (elon) amidol, eikonogen).

No darkening of the model occurs if silver bromide is protected from contact with particles of colloidal silver by introducing a strong solution of gelatin. Gelatin itself does not prevent darkening. That is shown' by adding the components of the model in another succession (AgBr, developer, colloidal Ag, gelatin, alkali), which is followed by a normal darkening.

After the publication of these data some new results were obtained in our laboratory : V. J. Sheberstov in his thesis extended the former measurements of adsorption of hydroquinone to other developing substances widely differing in their selective power, *e.g.* adurol (highly selective developer) and phenyl-hydrazine (poor selective and developing properties). The adsorptive property of adurol on colloidal silver is of the same order of magnitude as for hydroquinone whereas phenyl-hydrazine is poorly adsorbed on this substrate. This explains its bad selective developing properties from the point of view of our theory. Attempts to measure the adsorption of developers on Ag and AgBr in alkaline medium have been made in collaboration with L. N. Minaev, and preliminary results are available to-day.

An attack of the same problem has been attempted along a new line and using a new method in collaboration with K. M. Steifon. We tried to measure the microkinetics of the development of a single grain of an AgBr emulsion, making a rapid series of photomicrograms during the process of development. Previous work of Meidinger [19] enabled us to carry out this investigation which requires a very slow emulsion with large-sized AgBr crystals (6-8 μ).

Using gelatin deactivated by oxidation and using a formula similar to that of Meidinger, we prepared such an emulsion with uniformly large grains. Some improvements made it possible to follow the whole process of darkening of a single grain by the objective photographic method instead of visual observation, to avoid the use of desensitisers which could introduce serious complications and to prevent the formation of more than one nucleus per grain.

Under suitable conditions (chemical composition and concentration of developing substance, temperature, high concentration of KBr, etc.) the process of development of a single grain proceeds very slowly and quietly (" regular development "), the initial form of the grain being preserved, and allows one to make 5-6 photomicrograms at equal intervals of time.

[19] W. Meidinger, *Physikal. Z.*, 1935, **36**, 310.

The experimental set-up consisted of a Zeiss microscope with apochromatic lenses, a conical camera with an eye-piece, bearing a Leica-camera with a special attachment, allowing the operator to wind up the shutter and to change the film by a single turn of the hand. The emulsion spread on a cover glass as a single-layer preparation was illuminated by a low-voltage lamp through an orange colour-filter, was wetted by a few drops of developing solution and photographed every 4-5 seconds on a panchromatic red-sensitive film, e.g. Dupont's Superior. Negatives were developed in a developer giving high contrasts and magnified up to × 2100. An example of such a series of photographs is given in Fig. 1.

From an invisible nucleus situated mostly on the edge of the grain, darkening spreads over the grain in *circular zones,* in all cases of " regular development." Measuring the radii of these zones at equal time-intervals we obtained the rate-law of their growth. The length of radius increases linearly with time, which is shown graphically in Fig. 2.

This gives the growth of the darkened *area* (and the mass of silver) approximately as the square of time, *i.e.* an *autocatalytic law,* predicted by our adsorption theory. If we accept the mechanism of development
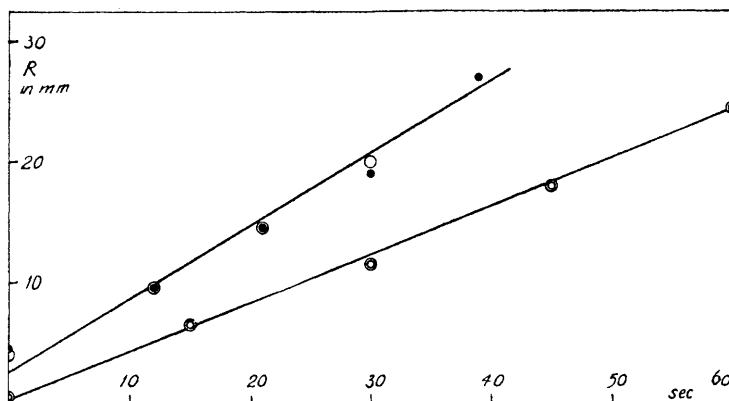

FIG. 2.

traced above, reduction can take place only in the narrow zone where the developing substance is concentrated by absorption to the freshly formed silver, *i.e.* around the perimeter of the silver patch. If the substance of the AgBr grain is uniform, this process must go with equal velocities along all the radii, forming circular rings, independently of the size of the already formed zone. That gives uniform growth of the radius, proportional to the time.

The velocity of this process is markedly increased with temperature, and also the length of the " induction period " of each grain is shortened with growing temperature. Under usual conditions of development the induction period is very much longer than the time of " visible development " which can be followed by microscopical observation. This can be used to remove the apparent discrepancy between the autocatalytic law of development of a single grain and the usually observed unimolecular law for the layer as a whole. As shown by V. J. Sheberstov in his thesis, if the total duration T of development of a grain is much greater than τ (the length of the " visible development "), the mean velocity of development of the whole layer may be taken as proportional to the number of the yet undeveloped grains and expressed by the same differential equation

$$\frac{dD}{dt} = k(D_\infty - D)$$

33 *

(D, the mass of silver formed during the time t and proportional to the number of developed grains, D_∞ maximal amount of silver, which may be formed by development, proportional to the total number of grains) which is usually assumed in deducing the law of macrokinetics of development and gives, after integration, the well-known equation : [20]

$$D = D_\infty (1 - e^{-kt}).$$

If $T \gg \tau$, microkinetics has no influence upon macrokinetics and the latter obeys the same unimolecular law as other processes depending on a great number of spontaneous elementary acts taking place in various parts of the reacting system.

If the conditions of development are radically changed ("fast developer," much alkali, high temperature, etc.) regular development is disturbed, a "stormy" process sets in with the formation of protuberances or "explosions" shot out from the grain and the well-known "recoil" of this latter. These forms of development are now being studied, and some intermediate forms between the two types of development have been found (see Fig. 3).

The great forces which are developed in these cases and which cause the explosion of the grain are readily explained from our point of view by the formation of a new crystal lattice (Ag) with different parameters (distance between Ag atoms $d = 4.06$ A.) within the initial solid phase (AgBr) (distance between Ag-ions $d = 5.78$ A.).

7.

Thus we have shown the considerable rôle played by adsorption phenomena in the process of photographic development and its autocatalytic course in a single grain of the photographic emulsion. These facts allow us to consider this process as a heterogeneous reaction taking place on the interface of two solid phases (Ag, AgBr) and one liquid phase (developing solution). During quite recent years the theory of adsorption catalysis has made considerable progress. Born and Franck [21] have attempted to explain it from the point of view of quantum mechanics, by assuming a "tunnel effect" through the potential wall for adsorbed molecules whose time of contact, measured by seconds, is enormously longer than the time of contact (10^{-12} to 10^{-13} sec.) of molecules colliding in the gaseous phase. A fruitful method based on classical statistical mechanics has been proposed simultaneously by Eyring [22] and Evans and Polanyi [23] for the calculation of absolute reaction velocities. This method, based on the conception of "transition state" or "activated complex," has been applied by M. Temkin of this Institute to the solution of some problems of adsorption and catalysis.[24] One of these methods will probably prove useful for the quantitative calculation of the microkinetics of development, whereas thermodynamics in the form of the electrochemical theory determines the conditions of equilibrium and the direction of the process of photographic development.

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[20] S. E. Sheppard and C. K. Mees, *Untersuchungen über die Theorie des photographischen Prozesses*, W. Knapp, Halle a.S. 1912, p. 58 *et seq.*
[21] M. Born and J. Franck, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl.*, 1930, 77.
[22] H. Eyring, *J. Chem. Physics*, 1935, **3**, 107.
[23] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.
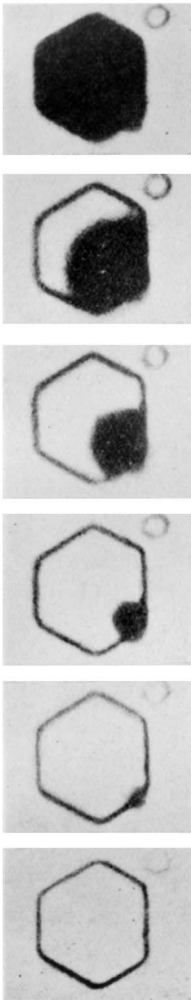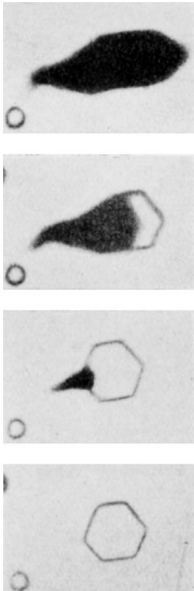[24] M. Temkin, *Acta physicochimica, U.R.S.S.*, 1938, **8**, 171.

FIG. 1.

FIG. 3.

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