

cussions, I am especially indebted for assistance and advice. I also wish to thank Mr. C. N. Fenner, who kindly undertook the optical examination of the products.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., JUNE, 1913.

THE PHYSICAL CHEMISTRY OF PHOTOGRAPHIC DEVELOPMENT.¹

By C. E. KENNETH MEES.

Received September 9, 1913.

If a precipitate of silver bromide be formed in a gelatin solution in a room lighted only by red light, and a solution of a moderately strong reducing agent be added to it, no reaction will occur for some time, whereas, if the precipitate is exposed for a very brief time to ordinary light, the reducing agent will reduce it rapidly to metallic silver. This reaction is the basis of the process which has made the whole of modern photography possible, namely, the selective action of some reducing agents upon a silver halide which has been exposed to light. The explanation of the reducibility of exposed silver bromide, while unexposed silver bromide is either reduced not at all or with much greater difficulty, has always had a great fascination for the chemist.

There are 3 factors in development:

- (1) The constitution of the emulsion.
- (2) The effect of light upon that emulsion.
- (3) The chemical nature of the reducing agent employed.

(1) *The Emulsion.*—A photographic emulsion is not an emulsion at all in the sense in which that word is used in colloid chemistry. It is a solution of gelatin, containing suspended in it a large number of extremely small crystallin grains of silver bromide which usually hold in solution a small quantity of silver iodide. What may be the exact nature of the relation between the bromide and iodide in ordinary photographic emulsions is not known, but in all probability the iodide is in solution in the bromide, in just the same way as the separate metals are in solution in each other in some alloys, and there would seem to be a possibility of the existence of one or more, probably two, bromo-iodides. The grains in a high-speed emulsion are from 1 to 2 μ in diameter, but there seems reason to believe that the grains themselves are agglomerates of small crystals forming a spongy network. Emulsions are made by the addition of silver nitrate, usually as a concentrated solution, to a gelatin solution containing potassium bromide and iodide. Under certain conditions the crystals, when precipitated, may be ultra microscopic, but

¹ Read at the Rochester meeting of the American Chemical Society, September 9, 1913.

under the influence of heat, they rapidly grow in size until the grain attains the dimensions indicated above. According to Quincke's theory, the gelatin in which these grains are enclosed has a spongy structure; the gelatin, when set consisting of a two-phase system, the one phase, strong in gelatin, forming the walls of the cells or channels, while the other phase, a weak solution of gelatin in water, forms the liquid filling the channels and the cells. Through the channels in the gelatin, ions and molecules can travel with ease at a velocity comparable with their diffusion rate in water, while penetration through the cell walls is a much slower and more difficult process. Diffusion into gelatin, and especially the diffusion of the developing solution into the emulsion film, may therefore be divided into two processes:

(a) Macro-diffusion, or the penetration of the solution through the channels of the gelatin, and

(b) Micro-diffusion, or the penetration through the cellwalls, which is usually necessary to some extent before the developer can reach the silver-halide grains.

(2) *The Exposed Silver Bromide.*—The photographic image before development differs from the non-exposed silver bromide in some way, but the only means by which we can recognize this difference is by treating it with a developer, whereupon the exposed silver bromide is reduced, while the unexposed silver bromide is not. The difference between the two can be lessened and finally destroyed by the action of oxidizing substances, such as chromic acid. These are almost the only facts which we have to guide us in our decision as to the nature of the latent image, that is, as to what happens to silver bromide when it is exposed to extremely small quantities of light energy. If the exposure is to large quantities of light energy, there is no doubt as to what happens. Bromine is given off, and the residue must consist either of silver subbromide or of a mixture of silver bromide and silver. The following statement, for which I am indebted to Dr. P. G. Nutting, as to the energy involved in the exposure of a high-speed photographic emulsion, would seem to suggest that, from a physical point of view at any rate, and therefore from the chemical, it is quite definit what happens when the latent image is produced by a minimum exposure to light, and that the change is really the unit change that can be suffered by any substance when acted on by energy.

Consider the exposure to light which is sufficient after full development to produce a deposit of unit density, that is, one which will transmit one-tenth of the incident light.

A deposit which has this density contains 10 milligrams of metallic silver per square decimeter, or one-tenth milligram per square centimeter, which represents roughly 10^{19} molecules of silver, or 10^7 grains 3μ in diameter. Now the energy of the amount of violet light required to give an

exposure necessary to make an emulsion film developable to this density, is of the order of 10^{-7} ergs per sq. cm. Therefore each grain (which contains on the average 10^{16} molecules) receives 10^{-14} ergs to make it developable. Now we know that in order to detach one electron from a molecule, 5×10^{-12} ergs are required in a gas; but this is a maximum amount and it is possible that in the exposure of a photographic plate 10^{-14} ergs are sufficient to detach one electron. Clearly then, the energy incident on a grain during exposure may be sufficient to affect only one molecule in that grain, and the latent image may be composed of grains in each of which, on the average, only one molecule has lost an electron by the action of light.

(3) *Reducing Agent*.—The reducing agents which act as photographic developers are nearly all derivatives of benzene, and are characterized by the fact that they contain either two or more hydroxy groups, or two or more amino groups, or a hydroxy and an amino group.

Indeed, compounds containing these groups without the benzene nucleus can also act as developers, both hydrazine and hydroxylamine being able to develop on exposed photographic plate.

Of other reducing agents than the aromatic derivatives, however, only one has ever come into wide use. This is potassium ferro-oxalate, the complex salt produced by dissolving ferrous oxalate in potassium oxalate solution.

A photographic developer based on an aromatic phenol or amine contains three components in some form or other:

- (1) The reducer.
- (2) An alkali.
- (3) A preservative.

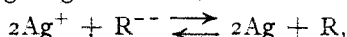
Only a very few reducing agents are able to develop in the entire absence of an alkali, the most notable exception being diaminophenol; normally the presence of a weak alkali is essential to liberate sufficient anions of the reducing molecule. In the absence of a preservative (which is always a sulfite) aerial oxidation of the developer proceeds very rapidly and also the oxidation of the reducer in development proceeds beyond the usual stage, strongly colored oxidation products being formed which stain the image. The behavior of sulfite in the developer is still but little understood; it diminishes air oxidation and limits the production of secondary oxidation products, while the sulfite itself is less attacked by aerial oxidation when organic reducers are present in the solution.

The behavior of sulfite differs greatly with different reducing agents, with hydroquinone, for instance, it appears to form a weak compound existing only at low concentrations of sulfite, but having a very great tendency to reduce unexposed silver bromide.

In order that a reducing agent may act as a photographic developer, it

is necessary that it should be a sufficiently strong reducer to develop exposed silver bromide, but not sufficiently strong to develop unexposed silver bromide.

In order to understand the conditions which determine the occurrence of development, let us consider the equilibrium at a single grain of silver bromide in an emulsion which is being attacked by a solution of a reducing agent, which we may take as a dibasic ion R^{--} tending to oxidize to R . Now the silver bromide goes into solution to the extent represented by its solubility product, giving silver ions, and we have



the silver ions losing their charge and producing silver molecules in solution.

This will then produce equilibrium unless the silver can precipitate, in which case more silver bromide will dissolve, which will precipitate as metallic silver in turn and the reaction will proceed until the whole grain is dissolved.

Now, if we consider the free energy at equilibrium, we can represent it by the expression:

$$F = RT \log \frac{(R^{--})(Ag^+)}{(R)(Ag)}.$$

Now if the free energy of the developer is not such that R^{--}/R will naturally reach a limit forcing Ag^+/Ag past a certain value, such that metallic silver is precipitated, reaction will not occur.

The free energy of the developer will depend on:

- (1) A property of the reducing agent which we may call the reduction potential.
- (2) The concentration of the reducing ion compared with its oxidation product.
- (3) The concentration of silver ions.

Now the limit, past which the value of Ag^+/Ag must be forced to produce precipitation, will be very greatly lowered if a nucleus be present and the production of this nucleus is the function of the latent image. We thus see why a change in one molecule per grain is sufficient to make the whole grain developable and why the grain is the unit of all development. The low solubility of silver bromide is sufficient explanation of the localization of development in the individual grain. If a solvent of silver bromide is added this localization no longer persists and the silver is deposited over a wide area, generally as colored fog.

A nucleus can be produced by other means than exposure to light, *e. g.*, by treatment of the film with auric chloride solution, which produces a nucleus of gold.

The "reduction potential" of a developer cannot be measured by the velocity of development, which is mainly conditioned by diffusion processes; nor is it related to the number of molecules of silver which can be

reduced by a molecule of the reducer, while attempts to determine electrically the reduction potentials of organic reducers have given no reliable results because of the complicated side-reactions which occur.

A measurement of the reduction potential can, however, be obtained by taking advantage of the fact that the addition of free halides to the developer will lower the value of Ag^+ , so that the concentration of free bromide ions necessary to produce a given lowering of the amount of silver produced at a given stage of development will be a measure of the reduction potential of the reducing agent employed.

By this method it has been found that the reduction potential of para-amino-phenol is about $3^{1/2}$ times that of ferrous oxalate and about 5 times that of hydroquinone. Much further work is required to be done upon this subject and it should be a most fruitful field for investigation; the effect of the substitution of various groups in the molecule of an organic reducer, for instance, should lead to results of great interest.

Equilibrium in Development.—With most reducers the chemical reaction of photographic development is reversible to some extent, but with the more complex organic developers the first oxidation product of the reducer is further oxidized either by air or by the silver bromide, and the reaction is not then reversible. With hydroxylamine, again, one of the products of the reaction is a gas, either nitrogen or nitrous oxide being formed according to the concentration, and the reaction is irreversible. But with ferrous oxalate the reaction of development is a typically reversible one, potassium ferric oxalate and potassium bromide acting on a developed plate to regenerate silver bromide from the metallic silver, and the extent to which development can proceed is governed by the usual equation of equilibrium, the position of equilibrium being, however, very far in the direction of development.

When we consider the development of the film as a whole, we must deal with the velocity of change of exposed silver bromide into metallic silver. It can be shown that if \bar{I} be the light incident on an exposed and developed photographic plate, and \bar{I}' be the light transmitted, then $\log I/\bar{I}'$, is very nearly proportional to the mass of silver deposited in a given area of film. This value, $\log I/\bar{I}'$, is termed D , the density of the deposit, and is taken as proportional to the mass of metallic silver produced. The velocity of development is therefore dD/dt .

Now the rate of development is proportional to the diffusion rate of the developer to the grain, to the diffusion of the reaction products away, to the concentration of the reducer and of the silver bromide in solution, and to the surface attacked. Since all these factors, except the last, are constant during development we have $dD/dt = KS$.

Now S represents the number of grains, or parts of grains, which are unchanged, but are changeable (that is, exposed) at the time T . If we

write a for the number of grains which were affected by light and express D_t as the number of developed grains at time T , then

$$\frac{dD}{dt} = K(a - D_t).$$

If we continue development for an infinitely long time we shall develop all the exposed grains and therefore we may write $a = D_\infty$ and

$$\frac{dD}{dt} = K(D_\infty - D_t)$$

which integrates into

$$K = \frac{1}{t} \log \left(\frac{D_\infty}{D_\infty - D_t} \right)$$

which is the familiar equation for a reaction of the first order.

Now the relation between the density obtained on development and the exposure which was given to the plate is given by a complicated expression which for the greater portion of the range of exposures simplifies to the expression $D = \gamma (\log E - \log i)$.

For a given exposure $\log E - \log i$ is a constant and D is therefore strictly proportional to γ , so that we may write the equation we have just obtained as

$$K = \frac{1}{t} \log \left(\frac{\gamma_\infty}{\gamma_\infty - \gamma_t} \right).$$

In this equation γ represents the contrast shown by the developed plate and γ_∞ is therefore the maximum contrast which can be obtained on any plate with the most prolonged development. This value, γ_∞ , is independent of the developer employed and is a natural constant of the plate, of great importance as conditioning its behavior and property.

In concluding this brief review of the physical chemistry of development, I should like to call attention to the many interesting problems presented by the subject and to hope that this paper may induce some workers to turn to photographic chemistry as a field for their investigations.

EASTMAN KODAK CO.,
ROCHESTER, N. Y.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 96.]

THE ISOLATION AND THE PROPERTIES OF SOME ELECTRO-POSITIVE GROUPS AND THEIR BEARING ON THE PROBLEM OF THE METALLIC STATE.

BY CHARLES A. KRAUS.

Received September 6, 1913.

The results set forth in this paper were obtained some ten years ago, being one of a number of investigations directed toward furnishing evidence as to the molecular constitution of metallic substances. At the