REDUCTION OF SILVER HALIDES AND THE MECHANISM OF PHOTOGRAPHIC DEVELOPMENT[1]

T. H. JAMES AND G. KORNFELD

Kodak Research Laboratories, Rochester, New York

Received September 19, 1941

Exposure of photographic emulsions results in the formation of development centers consisting of latent-image silver; one development center is sufficient to produce the development of a whole silver bromide grain. The amount of latent-image silver is determined by the amount of absorbed energy, but its effectiveness for development depends on its location and distribution,—factors which are greatly influenced by preformed sensitivity centers. The number of quanta required for the developability of a grain is variable, but certain limits can be estimated.

Developers are reducing agents which react with exposed silver bromide at a much greater rate than with the unexposed material. A great number of reducing agents, inorganic as well as organic, possess this property. Hydroxylamine belongs to this group and its oxidation can easily be followed analytically; its rate of oxidation was investigated with silver ion in solution, with silver chloride sols, and with precipitated silver chloride. The catalytic influence of metallic silver was found in all cases; the reaction in solution proved that silver ions are adsorbed at the silver.

Some secondary features of development can be viewed in the light of the oxidation product theory, others in the light of the surface charge theory. The mechanism of development, however, cannot be explained by either of them. The development reaction can be regarded as belonging to a group of reactions which proceed with enhanced activity at an interface. It is discussed in connection with experimental data and theoretical considerations concerning this group.

I. DEVELOPABILITY OF EXPOSED EMULSIONS

Silver halides are not stable in the presence of a reducing agent, but react to form metallic silver. This property of the silver halides, although a necessary condition for photographic development, is not sufficient. A reducing agent cannot be a developer unless its reaction rate with exposed silver halide is of a higher order of magnitude than its reaction rate with the unexposed material. Only a very weak reducing agent will differentiate between exposed and unexposed pure precipitates of silver halide (79), but many developers can be found for silver halide sols. Even more reducing agents act as developers in photographic emulsions.

Photographic emulsions are not true emulsions as defined in colloid chemistry, but consist of silver halide grains of microscopic dimensions embedded in gelatin. In the negative material, the emulsion grains are silver bromide crystals, sometimes containing a small percentage of silver iodide. The diameter of these grains normally lies between 1 and 0.1 μ. In some positive emulsions silver chloride is used. In most emulsions, excess halide ions are adsorbed to the sur-

---

[1] Communication No. 821 from the Kodak Research Laboratories.

face and, in the case of optically sensitized emulsions, dyes are adsorbed to the surface.

After a photographic emulsion has been exposed to light which it can absorb, subsequent treatment with a developer produces silver in an amount which will be a measure of the exposure. In this way, a developed image of the photographed object is obtained. Even though the emulsion does not show any visible change after the usual exposure, it is safe to assume that hidden changes occur which give the shape of the image after development. The term "latent image", which was chosen for the effect of exposure on the photographic emulsion, is thus accounted for. The nature of the latent image has been the object of a long controversy between exponents of widely different opinions. This controversy may be regarded as closed, however, since the identification of the latent image with metallic silver is reasonably well supported by all the available evidence.

A. Photolytic silver

The production of silver by prolonged exposure to light had been established much earlier and was the subject of numerous studies. Eggert and Noddack (20, 21) found that the amount of photolytic silver followed Einstein's law of photochemical equivalence, so that the number of reduced silver atoms is equal to the number of quanta absorbed. This relation can be found only in the presence of a halogen acceptor. For moderate exposures gelatin is sufficient to prevent recombination, but for higher exposures it is necessary to add other acceptors, like sodium nitrite, in order to obtain a quantum efficiency of 1. Eggert and Noddack assumed that their results were valid also for the silver of the normal latent image; their conclusions are supported by the investigation of van Kreveld and Jürriens (55), who developed a very sensitive method of detecting the silver by its absorption in the red region of the spectrum. They showed that the production of silver is proportional to the exposure over a very wide range, extending to exposures which are in the region of the latent image. Moreover, on extrapolation, the straight line obtained by plotting the amount of silver against the exposure goes through the point of origin of the coördinates.

It has been shown that two emulsions of equal absorptive power contain, after equal exposure, equal amounts of latent-image silver. Their photographic sensitivity, however, may differ widely, which means that the amount of silver[2] produced by development will be completely different in the two emulsions. It is clear that the mere formation of photolytic silver is not a sufficient condition for developability.

---

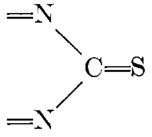
[2] The developed silver is usually measured by the optical density, as originally proposed by Hurter and Driffield (36). This density, the logarithm of the ratio between incident and transmitted light, was supposed to be proportional to the mass of the silver. Later investigations (31, 67, 78, 87, 103) showed that this relation does not always hold, but it is approximately valid over a considerable range if the degree of development is constant and only the exposure is varied.

B. Development centers and sensitivity centers

In their early investigations on photographic development, Sheppard and Mees (92) discovered the important part played by the individual grains. Microscopic investigations revealed that, if development is carried to completion, every grain which starts to develop is reduced throughout. Development in one grain does not affect the neighboring grains, however, unless they are in such close contact that "clumping" occurs (114). Large-sized grains can be expected to produce, therefore, a much greater density than grains of small size, since a much larger area is affected if development is started in a large grain. By microscopic observations on arrested development, Hodgson (34) was able to locate the starting points of development on the grains. He found that the formation of one center was sufficient for the development of the whole grain. The development centers subsequently were made the subject of numerous studies. Svedberg and Andersson (116a) developed a technique for investigating emulsion layers consisting of single-grain layers of one size-class, and Toy (118) succeeded in preparing single-grain layers not only of equal size but also of equal shape. It was always found that the centers were distributed at random over the various grains, the probability of center formation increasing with the projective area of the grains.

Thorough investigations of the effect of grain size on developability were carried out by Sheppard with Wightman and Trivelli (143 to 150). Within the same emulsion, the projective area of the grains was found to be the decisive factor for the formation of development centers, and an attempt was made to interpret the density curve on the basis of the different grain-size classes. However, the difference in the sensitivity of various emulsions could not be explained in the same way, and it became more and more evident in the course of the investigation that some inherent property of the emulsion played an even more important part.

In the subsequent search, it was found that this property was connected with the nature of the gelatin used in the after-ripening process (96). It was assumed that an impurity is responsible for the effect on sensitivity. This impurity, tentatively called gelatin X, was concentrated from the gelatin by various disintegrating operations, using the effect on sensitivity as an indicator. A comparison with the effect of plant seeds led to the discovery of the effectiveness of mustard oil and finally to the grouping of gelatin X with the thiocarbamides. The active group was supposed to have the constitution



which is able to form a complex with silver ion and finally to produce silver sulfide. Thiocarbamide was found to have, indeed, a strong sensitizing effect if it is used under conditions where silver sulfide can be formed. One part in 100,000 to 300,000 parts of silver bromide already gives the optimum effect; much more than this results in fog. This high efficiency is connected with the autocatalytic character of the thiocarbamide reaction, which results in the formation of concentrated centers of sensitivity (13). The silver sulfide specks on the surface of the grains are supposed to act as concentration centers for the latent-image silver and in this way to produce the development centers (101, 102).

Microscopic evidence for the concentration of the photolytic silver in discrete specks has been given by Trivelli and Sheppard (121), who concluded that the same process takes place in the region of much lower exposure, corresponding to latent-image production. This has recently been justified by means of the electron microscope, which gives results in lower exposure regions than the optical microscope. Figure 1 shows a photograph of the silver specks on a silver bromide grain, obtained by Hall and Schoen (30).

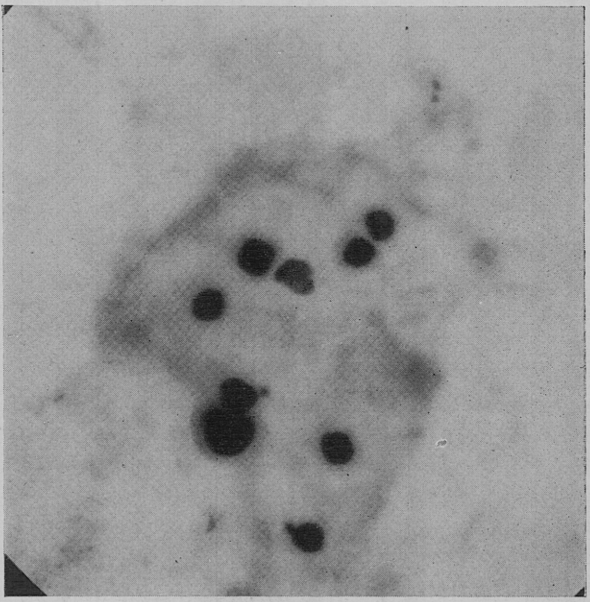


FIG. 1. Photolytic silver particles (Hall and Schoen)

The existence of sensitivity centers is supported by experimental evidence showing that the formation of discrete development centers is not necessarily connected with the action of light, but can also be produced by chemical agents, such as hydrogen peroxide, sodium hypophosphite, sodium arsenite, and others (14, 15, 16, 19, 97, 100, 116). Clark (17) found, further, that the sensitivity to arsenite could be destroyed by treatment with chromic acid in the same way as the sensitivity to light.

C. Formation of the development centers

A theoretical explanation for the action of the sensitivity centers is given by the Gurney–Mott (28) mechanism of latent-image formation. On the basis of this hypothesis it is possible to account not only for the primary act connected with the absorption of light, but also for the subsequent concentration of the reaction products.

The evidence for the primary act was furnished by the inner photoelectric effect. Vanselow and Sheppard (105, 108, 125) studied the instantaneous change of potential on illumination of silver halides, i.e., the photovoltaic effect; Toy (119) and Harrison (120) investigated the photoconductivity. Both phenomena signify the release of electrons by absorption of light, so that they can be shifted over some distance inside the crystal.

Webb (133) interpreted the internal photoelectric effect in the silver halides on the basis of the quantum-mechanics model of the structure of ionic crystals. According to this conception, the electronic levels of the individual lattice elements will be affected by the surrounding elements, so that each electronic level covers a variety of energies which are freely interchangeable between the elements of the same kind. Thus, the electronic levels will be represented by bands or zones instead of the sharp lines characteristic of the gaseous state. In silver bromide an electron in the lowest zone, corresponding to the ground state of the bromide ions, will have no freedom of movement, since all available positions for electrons are filled. A zone of a higher level, however, may have unfilled positions into which the electrons can move. Such a band is called a conduction band. The absorption act in the silver halide was assumed to consist in the elevation of an electron from the ground zone formed by the bromide ions to a conduction band formed by the silver ions where it could move through the crystal.

Gurney and Mott adopted this interpretation of the primary act (74) and supplemented it by a plausible explanation of the formation of centers. The electrons traveling through the crystal will eventually be trapped by some irregularity or impurity in the lattice. An electron trapped in this way would resist the trapping of another electron because of the electrostatic repulsion. This fact presented a serious difficulty to the theory of latent-image formation, until Gurney and Mott bridged the gap by taking account of a crystallographic discovery (51, 129). Silver bromide contains some silver ions which are not situated at the regular lattice positions, but at interstitial places, and the ionic conductivity of silver bromide can be attributed to these interstitial ions. Gurney and Mott pointed out that such interstitial ions can be expected to appear more frequently in the vicinity of an irregularity in the crystal, such as is produced by a silver sulfide speck. An effect of the sensitivity speck on the ions in its vicinity had, indeed, already been suggested in 1928 by Sheppard and Trivelli (103a). An electron trapped at this speck will give it a negative charge and attract an interstitial silver ion from the neighborhood, which then should join the speck and form a silver atom. This process of alternate electron-trapping and silver-ion attraction can be repeated, and the probability of growth should increase with the size of the speck. The part played by the sensitivity centers was very plausibly explained in this way.

The Gurney–Mott mechanism regards latent-image formation as consisting of two different processes: the electron movement and silver-ion migration. The existence of two components in latent-image formation had previously been suggested by Webb (131), because of the fact that reciprocity-law failure at high intensities and at low intensities depends on temperature in an entirely different way. The Gurney–Mott mechanism not only sheds light on the temperature dependence of reciprocity-law failure but explains the phenomenon itself.

The reciprocity law, formulated by Bunsen and Roscoe for photochemical reactions, postulates that the rate should be proportional to the product of time and intensity of exposure and independent of the value of either separately. This law has been recognized as a natural corollary of the law of photochemical equivalence, and both laws are supposed to be valid for any primary photochemical process. The experimental rate of a photochemical reaction, however, includes the effect of subsequent processes which may change the functional dependence altogether.

It was soon recognized that in photography the product of time and intensity is not sufficient to determine the effect of an exposure. This effect is relatively smaller at very high intensities as well as at low intensities. No satisfactory explanation of this failure of the photographic reaction to comply with the reciprocity law appeared until Gurney and Mott introduced the complex mechanism of center formation. The explanation of reciprocity failure at low intensities assumes a thermal activation of the spontaneous disintegration of centers below a certain size (135, 138). This effect is expected to occur at low intensities and high temperatures and to decrease and finally to disappear with the lowering of the temperature—a result established experimentally. At very high intensities the migration rate of the silver ions will play a decisive part, since it will not be high enough to permit neutralization of the electrons in the traps as quickly as they arrive. As the temperature is lowered, the migration rate of the silver ions will be lowered, while the electron migration will not be affected. Thus, with decreasing temperature the high-intensity reciprocity failure will become evident already at lower intensities. The effect will become more and more pronounced until, at very low temperatures, the migration of ions will become negligible, with the result that no photographic effect is produced. Ample experimental support for the theoretical interpretation of the high-intensity reciprocity failure was furnished by Webb and Evans (134) and by Berg and Mendelssohn (5, 6). The former authors demonstrated that exposure at low temperatures can be made efficient if it is applied in short flashes alternated with dark periods at room temperature. In this way, sufficient time is provided for the migration of silver ions.

D. Distribution of development centers

There are two possible sequences of a center disintegration: a true reversal or the formation of one or more new centers. The Herschel effect, consisting in the disintegration of centers by red or infrared radiation, results in a true reversal. Both developed silver and photolytic silver decrease in this case. Reciprocity-law failure, however, is not known to affect the amount of photolytic silver. This can be explained if new centers are formed which are not accessible to the developer.

A developer not containing a solvent for silver bromide will be able to start development only at latent-image centers situated at the surface of the grains. The developer solutions usually contain sodium sulfite, which has some solvent action on silver bromide, and consequently penetrate slightly deeper into the grain at the start of development. Centers in the interior of the grains, however, will still be inaccessible and therefore useless for the start of chemical development.

The existence of latent-image silver in the interior of the grains was suggested as early as 1894 by Kogelmann. Lüppo-Cramer (64) concluded that interior nuclei are present from the fact that treatment with iodide can restore developability which has been destroyed by treatment with chromic acid. He interpreted this as an exposure, by the solvent action of the iodide, of the interior nuclei, after the destruction of the external nuclei by chromic acid (18). This interpretation was supported, for concentrated iodide solution, by Sheppard, Wightman, and Trivelli (98, 99). Evidence for the relative distribution of centers between surface and interior, however, was collected only in recent years.

Meidinger (70) published extensive investigations on the distribution of photolytic silver. He found that increasing exposure favored the surface silver as against the silver in the interior. However, these results are not applicable to normal photographic conditions. The exposures needed for the analytical detection of photolytic silver are much greater than those used for photographic purposes. In addition, the silver bromide grains used in these investigations had several times the size of even the largest grains found in commercial emulsions, and had been prepared in the presence of inert gelatin. The same material was used by Kempf (52), who investigated the distribution of development centers at a single exposure level. The centers were found to be more numerous in the interior than at the surface. For very low exposures of photographic emulsions, however, Kornfeld (54) found the development centers to be almost entirely at the grain surface. Since at these low exposures the latent image can be expected to collect exclusively at the preformed sensitivity centers, this result indicates that nearly all the sensitivity centers are present at the surface of the grains. This, in turn, agrees with the fact that the production of sensitivity centers in after-ripening occurs when crystal growth is practically completed. With increasing exposure, new centers are created in the interior. At very high exposures, the ratio is reversed: practically all the centers are found in the interior. Berg, Marriage, and Stevens (7), in an extensive investigation on the dependence of surface centers and interior centers on temperature, intensity, and exposure time, established the fact that the density curve of the *interior centers* is less affected by temperature than that of the surface centers, that it shows no high-intensity reciprocity-law failure, and that the density increases in the solarization region. This latter result finally confirms the interpretation of solarization as a result of the rebromination of the grain surface (139) and agrees with the increase of photolytic silver in the region of solarization (2).

E. Limits of effectiveness for the centers

Various attempts have been made to determine the number of silver atoms necessary to create a development center. This number should not be expected to have a fixed value, since the effectiveness of a center will depend upon orientation, as was emphasized by Sheppard (106). An attempt can be made, however, to find the range of variation for the limiting number of silver atoms under varying conditions.

Reinders and Hamburger (84) and, later, Reinders and DeVries (85) deduced from their experiments the very small and constant limiting number of three to four or, respectively, four silver atoms. Their method was as follows: silver vapor was condensed on a glass plate in invisible minute quantities and then submitted to physical development. In this way, they determined the minimum amount which, after development, could produce one or more silver specks. For this minimum amount, the probability was calculated for the silver being distributed in groups of one, two, three, four, or more atoms. The number of silver specks found experimentally coincided with the calculated number of groups of four atoms. Apart from the fact, however, that these results apply only to physical development under conditions which differ from those for the development of photographic emulsions, it must be realized that the probability calculations rest upon the assumption that condensation of the silver atoms proceeds without any interaction between the groups. It seems rather doubtful that this assumption is justified, in view of possible adlineation.

The mathematical analysis of the characteristic curve (density plotted against logarithm of exposure) gave another method of approach to this problem. Svedberg (116, 116a) was the first to give a statistical evaluation of the surface area of the grains made just developable by a certain exposure. He showed that the dependence on the logarithm of the exposure found in the density curve could be approximated by this function. The assumptions necessary for this approximation were studied thoroughly by various authors, especially Silberstein and deLanghe. Silberstein finally came to the conclusion (111, 112) that the shape of the experimental curves indicated that only a very small part of the absorbed quanta was put to effective use in the grains. He estimated the number of quanta utilized as less than three per grain. It was pointed out by Webb (136, 137, 140), however, that there is an alternative interpretation of the density curve. The very small numbers of utilized quanta must be assumed if no variation of sensitivity exists between the grains. With a very wide range of sensitivity, however, some of the grains must be assumed to utilize several thousand quanta in order to fit a curve of the desired shape. Webb succeeded in reproducing the density curves of many commercial emulsions by his method. He showed (142) that the number of quanta utilized per grain assumed for the various grain-classes is of the same order of magnitude as the number of absorbed quanta per grain, as calculated from the experimental values of time and intensity of exposure, absorption coefficient, and size of grain.

In another attempt to get information on the number of quanta used in the formation of an effective development center, Webb (130, 132, 141) determined the critical frequency of intermittent exposure above which the developed density corresponds to the average intensity of the intermittent light. At low frequencies of intermittent exposure, the density corresponds to the intensity of the flash period instead. The critical frequency thus indicates the rate of intervals necessary to produce the same reciprocity-law failure as the corresponding continuous exposure, and thus gives the rate of quanta accepted by the most effective development center. The time of exposure then gives the number of quanta used for the formation of the development center. With the emulsions employed, some grains required at least sixty-four, and probably more than one hundred, quanta for latent-image formation.

By this method is obtained the number of quanta which actually takes part in the formation of a development center. However, possible losses by partial disintegration of the center make this number only an upper limit for the number of silver atoms added to a center during exposure. It could be taken as an upper limit for the total number of silver atoms forming a development center only in grains which do not contain preëxisting sensitivity centers.

As yet another method of approach, the number of silver atoms which must be produced in order to insure developability of the grain by x-ray exposures can be calculated. Glocker and others pointed out that in the photochemistry of x-rays the primary process of absorption does not play a dominant part, as it does in the photochemistry of ultraviolet and visible rays. The very large quantum releases a number of electrons which is proportional to its energy content. Each of these secondary electrons can start a chemical reaction, and the rate of this reaction is thus proportional to the energy content of the x-ray quantum, or inversely proportional to its wave length. For the photolytic silver in the photographic plate, this relation was confirmed by Günther and Tittel (27) between 0.245 Å. and 1.54 Å. The number of silver atoms per grain at 0.245 Å. was about one thousand. Assuming that the inverse proportionality with the wave length can be extrapolated, one should expect about *thirty-five silver atoms* to be released at 7 Å., and between *five* and *six* at 45 Å. These figures can be used in connection with the investigations by Broili and Kiessig (11), by Mülbach (77) and by Hirsh, Jr. (32, 33). Broili and Kiessig took the numerical (instead of the logarithmic) density curves of four emulsions. With x-rays these should be straight lines, indicating that every quantum absorbed makes a grain developable (26). Straight lines were, indeed, found with a radiation of 1.54 Å., but not with 45 Å., and Agfa Contrast emulsion even showed quite clearly a sensitivity threshold for the longer wave length. Mülbach, on the other hand, found straight lines for 4 Å. and 7 Å. with his emulsions, and no sign of reciprocity-law failure. Hirsh found an inflection point by exposing Eastman IV-0 plates to radiation of 14 Å. and even 11 Å. (His claim does not seem justified for 6 Å.) These results seem to show that, with the emulsions investigated, every grain is made developable if thirty-five silver atoms are produced, while twenty-two are not sufficient and five still less.

Again it should be emphasized that these figures cannot give upper limits for the number of silver atoms present in a development center, since the variation from emulsion to emulsion clearly indicates the participation of sensitivity centers with their unknown content of silver and silver sulfide. They could be regarded as lower limits only if the assumption were made that all the silver atoms formed by the x-ray quantum are collected in one center at the surface. In this connection, it ought to be mentioned that the unripened Lippmann emulsions do not give a straight-line curve, even with α-rays, as was shown by Blau and Wambacher (9). They calculated that α-rays should liberate more than two hundred silver atoms per grain along their path.

II. THE DEVELOPING AGENTS

The known developing agents are both large in number and diversified in chemical composition. The following outline is not intended as a comprehensive listing of the agents known to possess developing power, but rather as an indication of the variation in chemical types encountered among even the more common developing agents.

(*A*) *Inorganic:* (*1*) Metallic: various ferro- and molybdo-complex ions such as the oxalates and malonates, ammoniacal cuprous oxide, ferro-fluoride complex, and probably ferrous ion itself. (*2*) Non-metallic: hydroxylamine, hydrogen peroxide, and sodium hydrosulfite.

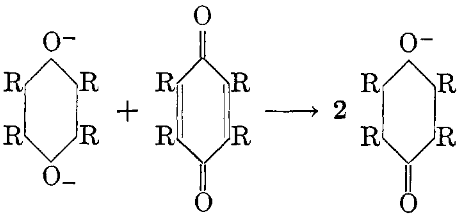
(*B*) *Organic:* (*1*) Aliphatic hydroxyketones: ascorbic acid (vitamin C). (*2*) Aliphatic aminoketones: 1-phenyl-3-methyl-4-amino-5-pyrazolone. (*3*) Aromatic compounds obeying the Andresen–Lumière rules, i.e., compounds possessing at least two hydroxyl or two amino groups, or one of each, in the ortho or para position on a single aromatic nucleus. The amino groups can be substituted, but the hydroxyl groups cannot. The number of such compounds is very large. Included are such relatively simple representatives as hydroquinone, *p*-aminophenol and *p*-phenylenediamine, and such complex structures as hematoxylin and brasilin. The number of active groups may at times extend to the limit. Thus, 1,2,4,5-tetrahydroxy-3,6-diaminobenzene is a usable developer in somewhat acid solution. Not all compounds conforming to the Andresen–Lumière rules are developers, as, for example, dicyanohydroquinone. (*4*) A very limited number of aromatic compounds containing hydroxyl or hydroxyl and amino groups in the meta positions are usable developers, e.g., trioxymesitylene. (*5*) Some aromatic compounds containing not more than one hydroxyl or amino group on any nucleus are developers in sufficiently alkaline solution, e.g., hydrocoerulignone and 1-naphthol.

The developing agents must be capable of reducing silver halides to metallic silver, but this is not a sufficient condition. It was pointed out at the beginning of this article that the developing agent must reduce the exposed silver halide grains at a substantially greater rate than the unexposed grains. Some reducing agents, such as sodium stannite, do not fulfill this condition and therefore are not developing agents.

The theory of the development process is concerned essentially with the reason for the selective reduction of the exposed grains. Before considering the reaction of the developer with the complex photographic emulsion, however, it is desirable to treat the reactions of the developing agents under less complicated initial conditions.

A. Oxygen oxidation

Most of the organic developing agents belong to types which can form semiquinones as oxidation intermediates (71, 72). Durohydroquinone, for example, is oxidized to duroquinone by way of the radical durosemiquinone (73). The percentage of the radical in equilibrium with the fully oxidized and fully reduced forms increases markedly with the alkalinity of the solution. At pH = 8.71 the concentration of durosemiquinone in a solution of partially oxidized durohydroquinone is too small to be detected potentiometrically. However, it has an important bearing on the mechanism of oxygen oxidation of the durohydroquinone in this pH region, since the reaction is markedly catalyzed by the presence of the quinone. The kinetics of this catalytic process suggest that the oxygen mainly attacks the semiquinone which is formed by the interaction of the durohydroquinone and duroquinone (38). The rate of this reaction is proportional to the concentrations of duroquinone and divalent durohydroquinonate ion and is independent of the oxygen concentration. The rate-controlling reaction, therefore, appears to be:



The kinetics of the catalyzed oxygen oxidation of trimethylhydroquinone (ψ-cumohydroquinone) are identical with those of durohydroquinone at very low ψ-cumoquinone concentrations. With increasing concentration of the quinone, the reaction rate in this case becomes increasingly independent of it, and, at the same time, a dependence upon the oxygen concentration appears. In order to explain these results, Kornfeld and Weissberger (53) assumed the interaction of the semiquinone not only with oxygen but with the quinone as well.

The oxygen oxidation of the lower methylated hydroquinones and of hydroquinone itself is independent of added quinone, and the rate varies as the first power of the oxygen concentration (39). One is tempted to assume, for these reactions, that the region in which the reaction rate becomes independent of the quinone concentration is reached at very small concentrations. Qualitatively, the inhibitory action of sodium sulfite and certain thiol compounds could then be explained by their power to react with quinone, thus reducing the concentration of the latter below the critical value for maximum catalytic action. However, the fact that a linear relationship exists between the reaction rate and the reciprocal of the sulfite concentration does not agree with this simple explanation (40).

It appears quite possible that a chain mechanism of some sort is operative in the oxygen oxidation of hydroquinone and at least its lower homologues. The radical HO_2, which was assumed to play no kinetically significant rôle in the simple quinone catalysis mechanism proposed, may actually be of importance as a chain-carrying intermediate. Gee has used this radical in the mechanism which he suggests for the oxidation of hydroquinone (25), but his mechanism does not include the important rôle of the semiquinone. Chain reactions in similar oxidations have been proposed by Branch and Joslyn (catechol) (10) and by Haber and Willstätter (enzyme-catalyzed oxidation of pyrogallol) (29), but neither mechanism is satisfactory for the oxidation of the hydroquinone series.

B. Reduction of silver salts

There is evidence for a quinone catalysis in the reduction of silver ions by hydroquinone and durohydroquinone (49). A catalysis by the silver formed in the process is, however, far more important.

A pronounced silver catalysis is observed in the reduction of silver ions by hydroquinone, both in acid and in slightly alkaline solution (41, 49, 59). In the slightly acid region, where the catalyzed reaction is most amenable to quantitative study, the dependence of rate upon hydroxyl-ion concentration indicates that both non-ionized hydroquinone and the univalent ion take part in the reaction (pH range 5.15 to 6.27). The rate varies as the first power of the hydroquinone concentration and as about the two-thirds power of the silver-ion concentration. The latter fact suggests adsorption of the silver ions to the metallic silver. Direct experimental confirmation of such adsorption is obtainable from other sources (22, 81, 126). Veselovsky, who was careful to work with oxide-free silver surfaces, found that adsorption begins at a silver-ion concentration of 1×10^{-13}. In the presence of oxide, the null point occurs at a much greater silver-ion concentration, but in the silver catalysis considered here a freshly reduced silver surface is assured.

The kinetics of the reduction of silver ions by hydroquinone supply no evidence for the adsorption of hydroquinone to silver. Direct experimental determinations show that such adsorption, if it occurs at all, is very small (109). Earlier work by Rabinovitch and Peissachovitch (82) must be discounted because of errors in technique. Their procedure was to mix a silver sol with hydroquinone and to determine the concentration of the latter before and after ultrafiltration. Actually, much of the original hydroquinone used escaped analytical detection even before ultrafiltration, owing to oxidation, and no adequate correction was made for oxidation occurring during the ultrafiltration. In the procedure employed by Perry, Ballard, and Sheppard, oxygen and free silver ion were eliminated as far as possible, and all but 0.44 per cent of the hydroquinone used initially was accounted for in the filtrate (pH = 9.0). This they consider to be within experimental error.

The reduction of silver ions by hydroquinone has also been studied in the pH range 8.6 to 9.0, using the soluble sulfite complex as a source of silver ions. The reaction mechanism indicated is the same as in the lower pH region, except that an additional complication arises as a result of quinone catalysis. Principally, the univalent hydroquinone ion is involved in the silver-catalyzed reaction, but the quinone catalysis very probably involves the divalent ion.

A detailed study of the kinetics of reduction of pure silver halide by hydroquinone should prove of great value to the understanding of photographic development. The experimental difficulties, however, are great. An elaborate attempt to carry out such a program was made by Luther and Leubner (65), but the results were largely disappointing. They employed freshly precipitated silver bromide containing an excess of potassium bromide amounting to 0.0247 mole per liter. The work was well planned, but an adequate experimental procedure was lacking, and little of value can be deduced from the scanty data which they were able to accumulate.

Hydroxylamine is by far the most useful developing agent for a general kinetic study of the reduction of silver salts. This agent has the advantage that, over a fairly wide range of experimental conditions, it reacts almost quantitatively to give silver and nitrogen as reaction products. The nitrogen can be readily determined volumetrically without interfering with the reaction.

The reduction of silver nitrate in solution has been studied by this method over the pH range 3.7 to 4.45 (42). Reaction is detected only after a relatively long induction period. Beyond this, an S-shaped reaction curve is obtained. The induction period is considerably shortened by the addition to the reaction mixture of a nuclear gold sol, and results can be satisfactorily duplicated. The reaction curve is the same, whether it is based on measurement of nitrogen or on direct determination of silver (figure 2).

Addition of a silver sol to the reaction mixture at the start practically eliminates the induction period (i.e., the period in which no measured reduction occurs). The rate of the silver-catalyzed reduction varies approximately as the two-thirds power of the silver-ion concentration, in precise agreement with the relation found for the hydroquinone reaction. The dependence of the rate upon the hydroxylamine concentration decreased as the pH increased and also as the hydroxylamine concentration increased. The dependence of the rate upon pH indicated clearly that the ion, NH_2O^-, is the active species, and the variation of rate with concentration of this ion indicates adsorption of the ion to the silver. This latter is in contrast to the hydroquinone mechanism.

Kinetic studies on the reduction of the soluble silver sulfite complex at pH = 8.54 show that the mechanism is essentially the same as for silver nitrate. The undissociated complex itself is not attacked to any detectable extent. The silver-ion concentration supplied by the complex is of the order of 10^{-9}, which is comparable with that which silver chloride could supply during development in the presence of 0.1 M excess chloride.

The reduction of silver chloride, precipitated in the presence of excess chloride ion, yielded the typical S-shaped reaction curve in the region studied (pH 7.0 to 7.5) (45, 46). The initial reaction rate varied directly with the hydroxyl-

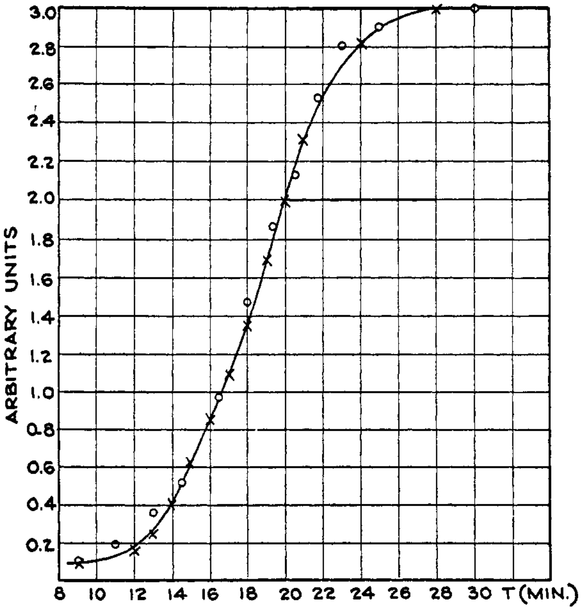


FIG. 2. Reduction of silver ions by hydroxylamine: ○, silver; ×, N_2 volume

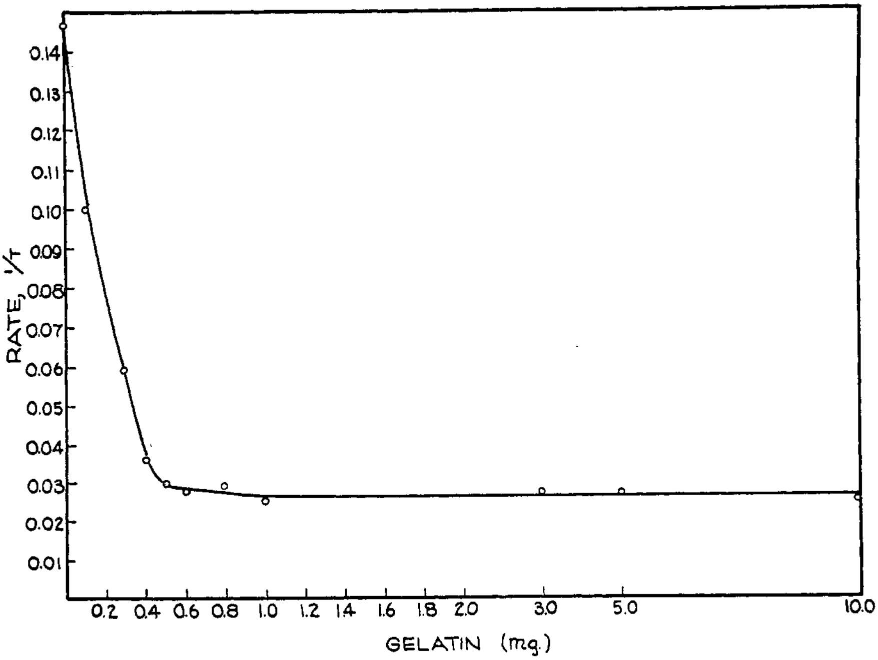


FIG. 3. Variation of initial rate with amount of gelatin

amine concentration and inversely with the chloride-ion concentration when the latter was relatively large. The rate varied approximately with the amount of available surface, and this relation held whether the surface was changed by aging or by partial coverage with a strongly adsorbed cyanine dye, such as 3,3′-diethyl-9-methylthiacarbocyanine. Addition of gelatin to the precipitate caused the reaction rate to drop sharply as the amount of gelatin increased, until a minimum rate was attained (figure 3). Further addition of gelatin had no measurable effect. Evidence from other sources shows that gelatin is rather strongly adsorbed to the halide (107), but probably not so strongly as the cyanine dye just mentioned.

The effects of gelatin and of the cyanine dyes supply important evidence concerning the site of the reaction. The dyes exert scarcely any effect upon the reduction of silver ions from sulfite solution at the same pH. Gelatin decreases the rate of the latter reaction, but the relative effect is much smaller than in the case of silver chloride, and a minimum rate is not attained even at fairly high gelatin concentrations. Indeed, the entire kinetic aspect is different in the reduction of silver ions from solution, showing that the attack on the silver chloride occurs on the solid phase. The fact that the reaction rate varies directly with the amount of available surface as more and more of the surface is covered by the dye suggests that the dye is uniformly and non-selectively adsorbed to the surface. This is in contrast to the reduction of mercurous chloride, where the greatest effect is observed during coverage of the first 10 per cent of the surface by the dye (50), a result which suggests that the active reaction centers selectively adsorb the dye.

Exposure of the silver chloride precipitate to white light, or nucleation by other means, largely eliminates the induction period. This effect, together with the regression which occurs when sufficient time elapses between exposure and reduction, is illustrated in figure 4. The rate of reduction of the nucleated precipitate varies with the 0.8 power of the hydroxylamine concentration. The temperature coefficient of the catalyzed reaction is substantially smaller than that of the initial reaction in the unnucleated precipitates. This is shown by the data in table 1. In this table, R_i is the rate of the initial reaction of the pure precipitate in terms of the reciprocal of the induction period; R_c is a measure of the rate of the silver-catalyzed reaction beyond the induction period; and R is the rate of the reaction in the nucleated precipitates in terms of cubic centimeters of nitrogen per minute. All values represent the average of triplicate runs.

The reduction of silver salts by hydrazine presents some points of similarity to the action of hydroxylamine, but also some important points of difference. The reduction of the soluble silver sulfite complex (47) and of the soluble ammonia complex (37) are both strongly catalyzed by colloidal silver. The reduction of silver chloride by hydrazine shows a definite induction period which, in some cases, is relatively large. However, in contrast to the hydroxylamine reduction, exposure of the precipitate to white light has only a slight effect upon the induction period or upon the subsequent course of the reaction. Nucleation of the precipitate by the action of hydroxylamine decreases the induction period without eliminating it and produces little or no effect upon the subsequent course of the reaction. Addition of the dye 3,3′-diethyl-9-methylthiacarbocyanine produces no effect until the surface of the precipitate is more than half covered. Further increase in the amount of dye added produces an irregular decrease in the reaction rate which is completely atypical of the hydroxylamine reaction. Gelatin decreases the reaction rate, but to a smaller extent than in the case of hydroxylamine, and a minimum rate is not attained. The data point to a mechanism involving the catalyzed reduction of silver

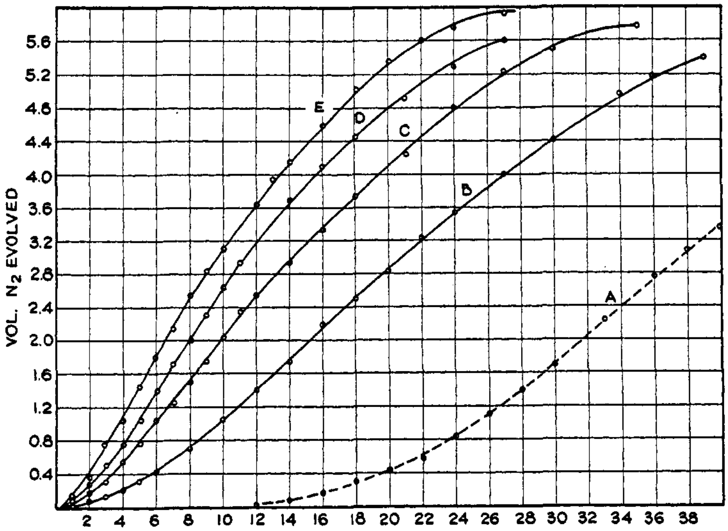


FIG. 4. Effect of age of exposure on reduction of silver chloride by hydroxylamine. Curve A, no exposure; curve B, exposure 17 hr. old; curve C, exposure 6 hr. old; curve D, exposure 2 hr. old; curve E, exposure 20 min. old.

TABLE 1

Temperature coefficients of reaction

TEMPERATURE	PURE PRECIPITATES				NUCLEATED PRECIPITATES			
					By NH_2OH		By light	
	R_i	Temperature coefficient	R_c	Temperature coefficient	R	Temperature coefficient	R	Temperature coefficient
°C.								
12.00	0.022		0.0090		0.058		0.145	
		4.46		3.35		3.25		2.80
20.03	0.073		0.0237		0.149		0.332	
		3.78		3.15		3.12		2.87
29.80	0.27		0.073		0.454		0.925	

ions from solution, a conclusion which is further supported by the effect of excess chloride ion upon the reaction rate.

The essential difference between the reduction of silver chloride by hydroxylamine and by hydrazine thus appears to be the following: reaction by the former agent involves direct attack upon the solid; reaction by the latter agent involves a preliminary solution of the silver chloride. Hydrazine is known to form complexes with the silver halides which are similar to the ammonia complexes, except that they are much less stable and decompose into nitrogen and silver at moderate temperatures (24). It is quite possible that the solvent action of the hydrazine plays an important part in determining the difference in action between this agent and hydroxylamine.

The comparative behavior of hydroxylamine and hydrazine in the reduction of silver chloride becomes quite suggestive when it is remembered that hydroxylamine is a rather clean-working developing agent, yielding good image development and reasonably low fog, whereas hydrazine yields an uneven image development and high fog. We can proceed a step further in comparisons and consider the action of sodium sulfite. This compound reduces silver ions, and the reaction is markedly catalyzed by colloidal silver, but the compound has a strong solvent action on silver chloride and bromide and it fails completely to develop an image. The silver catalysis is clearly in evidence in the reaction which occurs in a solution of the complex containing an excess of sulfite (48, 94) and the kinetics show that the silver ion, rather than the undissociated complex, is involved. Silver catalysis has also been observed in the reduction of silver bromide by sodium sulfite (13). The rate of even the catalyzed reaction is quite small at room temperature, however. The temperatures employed in the studies mentioned ranged from 50°C. to 88°C. Normal photographic emulsions become "fixed out" in the sulfite solution before much reduction is in evidence at room temperature. At higher temperatures, the silver formed is largely colloidally dispersed in the solution, and no image development is obtained.

Not all reductions of silver salts are characterized by autocatalysis. Fischbeck and Schnaidt (23) found that the reduction of single crystals of silver chloride by gaseous hydrogen proceeded without an induction period and without influence by reaction products. The reaction velocity was proportional to the silver chloride surface. The heat of reaction is about 9.6 kcal. The activation energy obtained for the reduction of silver chloride solidified from a melt was 61.0 kcal., numerically equal to the heat of dissociation of the salt (61.2 kcal.). However, precipitated silver chloride yielded the much lower value of 20.7 kcal.

Furoin and desylamine reduce silver ions in solution without evidence of silver catalysis (48). The reaction here appears to involve the enolization of the reducing agent as the rate-controlling process. The reaction is largely independent of the silver-ion concentration, and the rate is the same as that of reaction with oxygen. Sodium stannite is a very vigorous reducing agent, and the rate of reduction of most silver salts by this agent is very high. The only reaction of this agent in which silver catalysis has been detected is the reduction of the very slightly dissociated soluble silver iodide complex, where reaction probably involves the complex itself and not the silver ions. No silver catalysis is observed in the reduction of the silver thiosulfate complex, where reaction definitely involves the undissociated complex ion.

C. Development of the photographic emulsion

Two methods of approach which have been applied with some success to the solution of the mechanism of development in the photographic emulsion itself depend upon microscopic observations of the partially developed or developing grains and upon a study of the over-all kinetics of the process. We shall consider the results obtained by each method in turn.

It was pointed out in section I that development starts from latent-image centers and proceeds until eventually the entire grain is reduced. A hydroquinone developer containing only a small amount of sodium sulfite will effect the reduction of a pure silver bromide grain in a quite orderly fashion so far as the optical microscope reveals, and the silver particle remaining at the end of the process is a fairly good pseudomorph of the original grain (62). On the other hand, some of the more energetic developers such as Elon produce considerable distortion in the shape of the grain. During the development process, the grain as a whole appears to be constantly vibrating, and threadlike protuberances are thrown out. The mass of silver remaining at the end of the reduction bears little resemblance to the original (123).

Scheffer, in one of the earliest microscopic investigations of partially developed grains, observed the presence of fine filaments of silver jutting out from the surface of the grain (86). Some were so fine as to be barely visible at 2000 × magnification. Subsequent workers failed to obtain the striking display of fine filaments which Scheffer observed. The photolytic reaction proceeding under the influence of the very intense radiation applied has to be considered in his case. However, a formally similar phenomenon has recently been observed in photographs taken through the electron microscope.

Hall and Schoen (30) observed a seaweedlike mass of filaments formed when silver bromide grains were developed on the electron microscope object holder (20,000 to 50,000 × magnification). Grains developed on a photographic plate were not the same in general appearance, but, when completely developed, showed a filamentary structure only around the edges. The major portion of the grain was completely opaque. Similar observations were made by von Ardenne (1). Figure 5 shows an electron micrograph of a silver bromide crystal which was developed for a very short time, after which the unreduced silver bromide was dissolved out in sodium thiosulfate solution. A faint outline can be seen in the background where the original crystal has left its trace in the gelatin. A number of dots can be observed where development has just started. In the larger areas of silver, development has proceeded much farther and has extended rather irregularly over the crystal surface.

The filament phenomenon is not observed with physical development in which the grain is first dissolved and the latent image then developed by means of a silver-producing solution (silver salt and suitable reducing agent). The reduced silver in this case is observed only in the form of regular clumps.

Kinetic studies on the reduction of individual silver halide grains are difficult experimentally, and the data available from direct observation are quite limited. Steifon has made a series of photomicrographs of the progress of development by hydroquinone of very large (6 to 8 microns) insensitive silver bromide grains, and from these has determined the rate of reduction of the individual grain (83). In these photographs, the silver area spread over the surface of the grain in a regular fashion, and the length of the radius of the silver area increased linearly with the time of development. Thus, the rate of reaction was proportional to the visible interface between silver and silver bromide.

FIG. 5. Partially developed silver bromide crystal. Undeveloped portion dissolved out (Hall and Schoen).

Previously, Meidinger had made microscopic observations on the development of large silver bromide grains prepared in the same way as those employed by Steifon. Meidinger used a heavily bromided Elon–hydroquinone developer, and collected the following data: (*1*) the number of grains which had begun to develop after a determined time; (*2*) the number of completely developed grains; (*3*) the mean time elapsing between the first trace of development detected under the microscope and the complete reduction of the grain (68, 69). The time elapsing between the beginning of penetration of the developer into the layer and the first detected trace of development (the initiation period) decreased with increasing illumination until the solarization region was reached. The rate of development beyond the initiation period, however, was independent of the amount of exposure. At the lower bromide concentrations employed, the rate of initiation decreased much more sharply with increasing bromide-ion concentration than the rate of development beyond the initiation period. Meidinger concludes that the velocity of development is made up of two components: The first depends essentially upon the probability of initiation of development in the crystal, and is dependent upon the exposure. The second is the rate of reduction of the crystal once reaction starts and is independent of the exposure.

It is unnecessary to assume that Meidinger's two components require two distinct reaction mechanisms. The observed dependence of the initiation period upon exposure and bromide-ion concentration are well accounted for by an effect which the electric charge on the silver bromide grain has upon the rate of development. This effect is particularly evident in the early stage of the reaction.

The lower portion of the density–time of development curve will be concave, approximately straight, or convex, depending upon several factors. Experiments covering the action of fourteen developing agents belonging to several chemical types and employed under simplified conditions showed that a close correlation exists between the shape of the lower portion of the curve and the *charge on the effective developing agent* (43). The charge on the agents employed varied from 0 for certain members of the *p*-phenylenediamine group to -3 for sodium hydroquinonemonosulfonate. Each charge-group yielded its own particular type of curve (figure 6), irrespective of considerable diversity in the chemical nature of the constituents.

Certain surface-active agents which reduce the effective charge on the silver halide grains, such as phenosafranine and thallous ion, markedly increase the rate of development by members of group -2 or -3, but have only a slight effect upon development by members of group -1 and none whatsoever upon group 0. A similar observation applies to Lüppo-Cramer's neutral-salt effect (63).

The charge effect has been explained as follows: The repelling force exerted upon an approaching developer ion by the negative charge of the adsorbed halide layer will be proportional to the charge of the ion itself. Only a fraction of the negatively charged ions will possess sufficient kinetic energy to overcome this repulsion, and the percentage will decrease rapidly as the charge increases. Those ions which, by virtue of their excess kinetic energy, approach closely enough to the latent-image centers and which, in addition, possess sufficient activation energy will react to produce metallic silver. As the silver speck grows in size, the protective layer becomes more and more disrupted in this region. The resulting decrease in charge permits an increase in the effective concentration of the developing agent at the reaction zone, and hence an increase in the reaction rate. The greater the charge of the developing ion, the greater will be the relative increase.

The effect described will be pronounced only in the early stages of development of the individual silver halide grains, and will probably disappear before the silver speck becomes very large. As expected, increase in the concentration of excess bromide ion has a greater effect upon the induction period of the charged developers than upon the subsequent reduction rate, in line with Meidinger's observations, and the greater the charge on the developing agent, the greater is the relative effect upon the induction period.

The autoaccelerating effect just described is quite distinct from the catalytic autoaccelerating action of silver produced during development. The effect of the increased silver interface becomes evident in development by such uncharged agents as diaminodurene, if the amount of silver formed is plotted against the time of development. Generally, the optical density is taken as a measure of the amount of silver, with the implication of a linear dependence. This proportionality, however, does not always hold (*cf.* footnote 2). Under the conditions employed in the preceding work on the shape of the development curve, the relationship

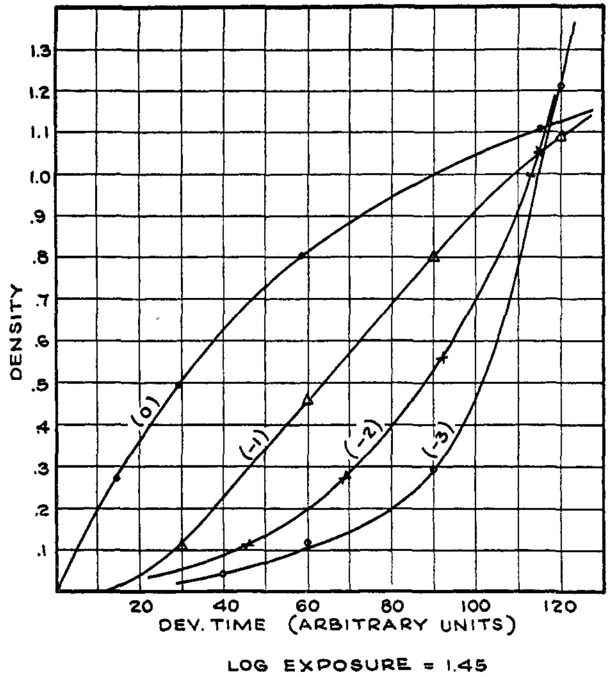


FIG. 6. Effect of charge of reducing agent upon shape of development curve. ×, hydroquinone; △, *p*-aminophenol; ●, diaminodurene; ○, sodium hydroquinonemonosulfonate.

$$\log \text{Ag} = 1.5 \log D + \text{Constant}$$

held good to fair approximation for constant exposure. When density is plotted against time, this non-linear relation between silver and density obscures the increase in reaction rate with increasing size of the silver–silver halide interface during the early stages of development.

Kinetic studies of the development of a simple commercial emulsion by hydroquinone have been carried out under specially simplified development conditions (44). The emulsion was a thin, unsensitized, pure bromide material of fairly uniform grain size. The developer solutions contained only the reducing agent and buffer and were used in the absence of oxygen. In the pH range employed (8.0 to 8.9) the development rate was sufficiently low to minimize diffusion effects. Analysis of the data showed that the rate of development throughout the entire course varied quite accurately as the 0.55 power of the concentration of the divalent ion $C_6H_4O_2^{--}$. The same variation was obtained when small amounts of sodium sulfite were added to the hydroquinone solution, even though the sulfite reduced the actual rate of development severalfold. The oxidation product, quinone, when added to the sulfite-free developer at the start of the reaction produced an increase in rate, supporting Staude's earlier observation of the accelerating effect of oxidation products (113, 114). The probable reason for the retarding effect of sulfite lies in its ability to react rapidly with quinone, forming the soluble hydroquinonemonosulfonate.

The unique dependence of the development rate upon the concentration of the divalent ion, rather than upon the non-ionized hydroquinone or the univalent ion, supports the suggestion of Sheppard and Mees that the active developing agent is the divalent ion (93). The occurrence of this ion to the one-half power in the kinetic expression is evidence that the ion becomes adsorbed prior to reaction. The site of the adsorption must be deduced from other evidence. Rabinovitch has suggested that the adsorption is to the silver, but the experimental evidence available does not support this assumption (109). A direct investigation of adsorption to silver bromide in alkaline solution is not feasible because of the chemical reaction which occurs. Wulff and Seidl, however, demonstrated that resorcinol is adsorbed from alkaline solution by silver bromide (152), and argued by analogy that hydroquinone likewise would be adsorbed. Sheppard and Meyer had suggested earlier that the first step in development is the adsorption of the reducing agent to the silver halide, forming a complex between the silver ions and the developing agent (95).

The importance of the accelerating action of oxidation products in the development process has been strongly emphasized by Staude and other workers in Luther's laboratory. Staude has even suggested that development would not take place at all in the complete absence of the oxidation product, and states that a reducing agent is a photographic developer "if it can form with its next oxidation product an addition compound which needs to be stable only in the solid phase or adsorbed to an interface, respectively" (115). However, the maximum accelerating effect which Staude observed was obtained with hydroquinone and amounted to only sixfold. In some cases, such as development by Elon or *p*-aminophenol, the oxidation product produces an acceleration only at the very start of development and retards the subsequent reduction (43). No acceleration at all has been observed with the *p*-phenylenediamine developers. On the contrary, agents which combine with the oxidation products in this case markedly increase the rate of development throughout the entire range. Staude's generalized definition obviously fails to account for this fact and for the developing power of hydroxylamine, whose oxidation product is nitrogen. Furthermore, addition products of the type he suggests are very improbable in a number of other cases, such as those of ferro-oxalate, ascorbic acid, and diaminodurene.

III. THE MECHANISM OF DEVELOPMENT

There has been a tendency in photographic theory to treat development as a unique phenomenon. Actually, there is ample evidence to link development to a whole series of reactions which proceed at an interface between reactant and product. The thermal decomposition of silver oxalate and the reduction of cupric oxide by hydrogen are well-known examples of such reactions. The general significance of the interface was first recognized by Langmuir (58).

The original explanation of the action of photographic developers is the classic Ostwald–Abegg supersaturation mechanism, which is now of no more than historical importance. A development hypothesis centered upon one particular aspect of the process, the electric charge effect, was proposed by Schwarz and Urbach. The excess halide ions adsorbed to the grains in the normal emulsion form a protective layer which will resist the approach of negatively charged developer ions. Schwarz and Urbach assumed that absorption of light by the silver halide grains resulted in the ejection of electrons from the surface halide ions into the interior of the grain, where they were caught by silver ions (89, 90, 91). The latent image was in this way identified with a loss of negative charge, regardless of the formation of silver specks. This extreme position was later abandoned, and the silver specks at the surface were regarded as responsible for the break or weakening of the protective charge (57). This hypothesis was employed with considerable success to explain certain development effects, such as the accelerating action of a few surface-active agents and the neutral-salt effect (60, 61), although some strongly adsorbed dyes, such as erythrosine and pinaflavol, showed the opposite of the effect expected (124).

As a general explanation of development, however, the surface charge mechanism cannot be accepted. If the selective rate between exposed and unexposed grains results from the charge effect, the indiscriminate reduction of silver bromide grains by the negatively charged stannite ion remains unexplained. Equally unexplained is the fact that certain acid emulsions containing excess silver ion, rather than halide, may be developed by conventional agents (12). If a negative charge layer exists at all in this case, which is doubtful, it must be very weak and could not afford the required protection. The most serious objection to the proposed mechanism is the existence of a whole series of developing agents, the substituted *p*-phenylenediamines, which must be considered to act as neutral molecules. Acid ionization of aromatic amines, when it has been measured at all, is too slight to be of kinetic significance. For example, the dissociation constants indicated for aniline and *p*-toluidine are of the order of 10^{-27} (66). The rate of development by the substituted *p*-phenylenediamines increases with increasing pH, but not in the manner expected for an ionization effect. Thus, the rate of development by diaminodurene is scarcely doubled by an increase in pH from 9 to 11. Many of these agents are good developers, and electron micrographs of the developed grains reveal the same general structure as that obtained with the charged developers. Physical development, which is so prominent in the action of *p*-phenylenediamine itself, does not play a significant part with these substituted agents.

The experimental data on the photographic induction period in development, discussed in a preceding section, enables us to consider the rôle of the protective charge layer in its true perspective. The effect of the charge upon the kinetics of the reduction is apparently a purely secondary one, in contrast to the primary catalytic effect of the silver nuclei. The charge effect can be detected with the singly charged developing agents, but it only becomes of real significance as a contributory cause of the difference in the rate of reduction of exposed and unexposed grains when the charge is 2 or greater. However, a double negative charge does not guarantee developing action, for stannite ion is completely nonselective.

Another special aspect of development was generalized by Staude, who assumed that the oxidation products of the developing agents were responsible for the developing action. This hypothesis, which is quite inadequate, was considered in the preceding section.

Still another special hypothesis was proposed by Gurney and Mott, in an attempt to apply their well-supported mechanism of latent-image formation to the development reaction (28, 75, 76). According to this mechanism, "the molecules of the developer hand over electrons to the metallic silver speck, and raise its potential relative to that of the halide grain. The interstitial silver ions which are present in the halide are then attracted to the silver speck; they will move up to it and adhere to it. Of course, as fast as the (interstitial) silver ions in the grain are used up, new ones are formed. The halogen escapes from the surface of the crystal, and not from the metal-compound interface. Interstitial ions, which may have come from quite distant parts of the crystal, flow through the crystal and join the metal at the interface."

If true, this extension would give a beautifully unified theory of latent-image formation and development. Unfortunately, there are serious objections. Inherent in the theory itself is the difficulty of providing a mechanism whereby the excess bromide ions can escape from the crystal. There is no experimental evidence that bromide ions can migrate through the crystal even at temperatures considerably higher than those normally employed in development. Theoretical calculations (35) show that the activation energy required for the migration of a bromide ion is at least five times greater than that required for the silver ion, and the activation energy of formation of the interstitial bromide ion is more than three times greater than that of the silver ion.

Moreover, the expected correlation between conductivity and development kinetics is completely lacking. According to this hypothesis, the rate of development should be a simple function of the number and mobility of the interstitial silver ions. Experimentally, this is not the case. The concentration of interstitial silver ions decreases in the series AgI > AgBr > AgCl, yet the development rate generally increases in this series.

The amount of current passing through the silver bromide crystal is proportional to the applied potential. However, no simple relationship exists between the rate of development and the redox potential of the developer. Even among the iron developers, where the redox potentials are well defined, it is observed, for example, that a ferro-citrate solution develops at a much smaller rate than a ferro-malonate solution of identical redox potential (8, 110). With hydroquinone, an increase in ΔE may even produce a decrease in the development rate (44).

Furthermore, the temperature coefficient of development is a function of the developer, not the silver halide, and the coefficient is usually much smaller than that of electrical conductivity. Dyes adsorbed to the silver halide surface should not affect the mobility of internal interstitial silver ions, yet they may reduce the rate of development by 100- to 1000-fold. Finally, it has been shown that the kinetics of reduction of mercurous chloride are formally very similar to those of silver chloride, although the Gurney–Mott mechanism is impossible in the former case (50).

Piper, in 1908, suggested (80) that development is an "action of a catalytic nature, the latent image being the catalyzer." Sheppard (94) pointed out that colloidal silver markedly accelerates the formation of silver in a silver nitrate–sodium sulfite solution and suggested that the latent-image silver facilitates the decomposition of an adsorption complex formed between the developer and silver ions. This hypothesis was amplified by Sheppard and Meyer in the following year (95). Volmer showed that the oxygen oxidation of several developing agents is accelerated by colloidal silver, and likewise suggested a catalyzing action of silver in development (127, 128). However, at least in the case of hydroquinone, it appears that adsorption of oxygen to the silver is responsible for the effect Volmer observed, rather than any activation of the developing agent (*cf.* 3, 4). Rabinovitch suggested adsorption of the developing agent to silver as the basis for the catalysis in development. His data have been considered in a preceding section and shown to be inadequate. It is possible that adsorption of developing agent to silver plays a kinetic rôle in some cases, such as that of hydroxylamine, but experimental results with hydroquinone show that it cannot be considered the fundamental reason for development.

The real key to the fundamental mechanism of development probably lies in a suggestion made by Sheppard in 1929: "The importance of a suitable nucleus, e.g., silver or silver sulfide . . . becomes twofold. On the one hand, its interface with the silver halide provides the necessary ionic deformation for reactivity; on the other hand, it provides a break in the adsorption layer, a platform for displacement processes" (104). In some interface reactions, it is probable that the reaction product acts merely as a crystallization center, but in many reactions involving true catalysis, a reduction of the activation energy is strongly indicated. The boundaries at which these reactions occur are the "lines of especially unsaturated character at which synergetic effects are to be expected. That this is so is directly supported by other observations; the reaction product can often be replaced by other substances" (88). Thus, the thermal decomposition of silver oxide, in addition to being accelerated by silver and platinum which could act as crystallization nuclei, is accelerated by manganese which could not; the decomposition of mercuric oxide and barium peroxide is accelerated by a series of other oxides (117); the decomposition of silver permanganate is even accelerated by powdered pumice stone.

The observations of Wischin on the thermal decomposition of crystals of barium azide (151) include data on the energy of activation both of nuclear formation and of growth. The rate of growth of each nucleus follows the law:

$$\mathrm{d}r/\mathrm{d}t = B$$

where r is the radius and B is dependent only upon the temperature. The energy of activation of nuclear growth is approximately 23.5 kcal., compared with 74 kcal. for nuclear formation.

In the development process an external molecule, the developing agent, is brought into reaction at the interface. The basic mechanism of the silver catalysis in this reaction and in the silver-catalyzed reduction of silver ions from solution is essentially the same. It will be simpler to treat the latter first.

Evidence from several sources showing rather strong adsorption of silver ions to the silver has already been discussed. The reaction system may be treated (*cf.* 56) as consisting of three reactants—the silver ions, the developer, and the adsorption site on the surface of the catalyst; thus:

$$\mathrm{D} + \mathrm{Ag}^{\bullet} + \mathrm{S} \rightleftharpoons (\mathrm{D{-}Ag}^{\bullet}\mathrm{{-}S})^{\ddagger} \rightarrow \text{products} \quad (5)$$

The difference between the energy of activation required for this catalyzed reaction and that required for homogeneous reaction will equal the difference in potential energy of the activated states $(\mathrm{D{-}Ag}^{\bullet}\mathrm{{-}S})^{\ddagger}$ and $(\mathrm{D{-}Ag}^{\bullet})^{\ddagger}$, i.e., the *heat of adsorption* of the activated complex minus the heat of adsorption of the reactants. This is illustrated schematically in figure 7. Here, the solid curve refers to the homogeneous reaction, the broken curve to the heterogeneous reaction; E_{hom} is the activation energy of the homogeneous reaction; E_{a} is the apparent or measured energy of activation of the heterogeneous process, whereas E_{het} is the true activation energy; E_{a} differs from E_{het} by the heat of adsorption, λ, i.e., $E_{\mathrm{a}} = E_{\mathrm{het}} - \lambda$.

At the silver–silver halide interface, the silver ions are already present in an "adsorbed" condition. The significant difference is imposed by the presence of the silver halide lattice. The concentration of the activated complex will depend upon the availability of the silver ions for combination with the developer, and this, in turn, will depend upon the lattice forces. In addition, external materials strongly adsorbed to the halide, such as gelatin or the cyanine dyes, will greatly decrease the concentration of activated complex, as will adsorbed excess halide ion. This effect, due either to adsorption already involving the silver ions or to a steric shielding of them, is quite distinct from the electrical repulsion effect previously discussed and is operative with the uncharged developers as well as with the charged ones.

Differences are to be expected between the physical form of the silver obtained by reduction of the solid silver halides and that obtained by the silver-catalyzed reduction of silver ions from solution. In the latter case, the silver ions and reducing agents have free access to all parts of the silver surface, and the particles grow in a uniform manner. In the former case, however, free contact of the reducing agent is attained only at the triple interface between silver, silver halide, and solution. The silver formed in the reaction does not occupy as much space, if it forms a compact lattice, as did the original silver bromide. As reaction proceeds and bromide ions pass into solution, the silver–silver halide interface will progress in an erratic fashion, depending upon the presence of flaws in the crystal structure, accessibility of the interface to the developer, and localized breaks in the interface due to differences in space requirements. Reaction proceeding chiefly along surfaces and producing silver filaments within the approximate confines of the original grain, such as is revealed by electron micrographs, is to be expected on this basis. Filaments projecting beyond the original confines of the grain probably arise from other causes, although the silver filaments in the absence of rigid support (as is the case in the electron microscope technique) may possess considerable mobility.

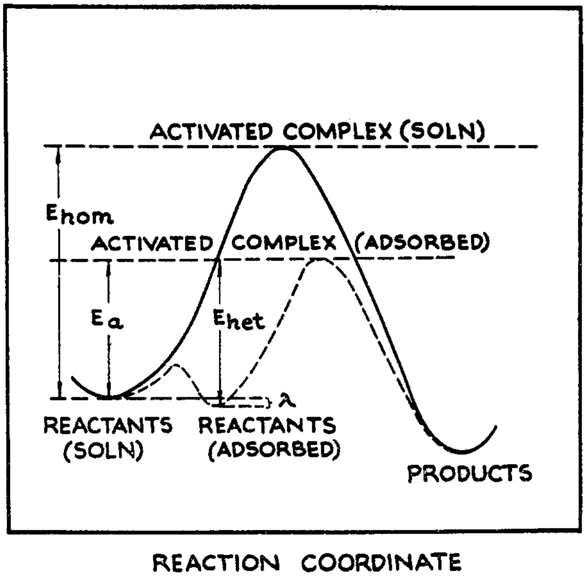


Fig. 7. Comparison of activation energies for homogeneous and heterogeneous reactions

An auxiliary factor which may markedly influence the final physical result in some cases arises from the finite solubility of the silver halides. This solubility is enhanced by the sodium sulfite present in most conventional developers and by additions such as potassium thiocyanate which are made to the "fine-grain" developers. These solvents will not increase the *equilibrium* silver-ion concentration attainable, but they will increase considerably the rate at which silver ions may pass into solution and, in addition, their action will expose silver nuclei existing within the original grains. Competition between the silver-catalyzed reduction of silver ions from solution and the interface reaction is to be expected in all cases. The former reaction may be negligible, as in the case of the pure hydroquinone developers previously discussed. It may also be large, as indicated by microscopic studies of the action of the fine-grain developers (62). The fundamental basis of development is not changed in any case. Only the practical result is altered.

Further complications may arise, owing to the localized solvent action of excess halide ion which is liberated around the development centers during reduction. Such action may be responsible for the streamers of silver observed under the microscope when perfect crystals of silver bromide are attacked by a rapidly acting developer, such as a metal–hydroquinone developer containing carbonate. A slowly acting developer, such as that used by Yano (153), does not produce the streamers. This effect offers one of the explanations for the filaments which, under the electron microscope, are observed to project out from the grain surface.

The amount of experimental material on the mechanism of fog formation, i.e., the unselective reduction of the silver halide, is very small. However, on the basis of the experimental material already given, the factors leading to fog formation can be foreseen. The reduction of silver ions in solution not catalyzed by silver will be independent of light exposure. In time, this will lead to the formation of nuclei which can then grow by silver-catalyzed reduction of silver ions. Fog silver produced in this way will have a smaller covering power than image silver and may even be of different color. A direct attack of the developing agent on the grain occurs, as evidenced by the reduction of pure silver chloride by hydroxylamine. Nuclei are thus formed which can catalyze the continued reduction of the grain (development fog). Catalytic nuclei may already exist in some grains prior to exposure as a result of reactions during the ripening process (emulsion fog). Finally, any additional reaction which can give rise to catalytic nuclei, such as the interaction of silver ions and sulfide, will lead to fog. Successful development depends upon adequate control of all of these factors, so that the rate of the fogging reactions is small compared with that of normal development.

The direct attack of the developing agent upon the unexposed silver halide forms the basis for a special type of developing action. The experiments with hydroxylamine and pure silver chloride showed clearly that the rate of initiation of reduction is markedly decreased by adsorption of protective substances, such as the cyanine dyes, gelatin, and chloride itself. Any abrasive action which tears such a layer from a portion of the surface, or splits the crystals and thereby exposes a fresh surface, causes an increase in the rate of initiation of reduction, provided conditions do not permit a rapid and complete reëstablishment of the productive layer. On this basis, the Poindexter effect and the production of a developable image by abrasion are easily understood. A silver nucleus is not required initially, and development arises from a cause which is qualitatively distinct from the more usual one.

REFERENCES

(1) ARDENNE, M. VON: Z. angew. Phot. **2,** 14 (1940).
(2) ARENS, H.: Z. wiss. Phot. **30,** 127 (1931).
(3) BENTON, A. F., AND BELL, R. T.: J. Am. Chem. Soc. **56,** 501 (1934).
(4) BENTON, A. F., AND DRAKE, L. C.: J. Am. Chem. Soc. **56,** 255 (1934).
(5) BERG, W. F., AND MENDELSSOHN, K.: Proc. Roy. Soc. (London) **A168,** 168 (1938).
(6) BERG, W. F.: Trans. Faraday Soc. **35,** 445 (1939).
(7) BERG, W. F., MARRIAGE, A., AND STEVENS, G. W. W.: J. Optical Soc. Am. **31,** 385 (1940).
(8) BEUKERS, M. C. F.: "Fotografische Ontwikkelaars", Dissertation, Delft, 1934.
(9) BLAU, M., AND WAMBACHER, H.: Z. wiss. Phot. **31,** 243 (1933).
(10) BRANCH, G. E. K., AND JOSLYN, M. A.: J. Am. Chem. Soc. **57,** 2388 (1935).
(11) BROILI, H., AND KIESSIG, H.: Z. Physik **87,** 425 (1934).
(12) CARROLL, B. H., AND HUBBARD, D.: Bur. Standards J. Research **1,** 565 (1928).
(13) CARROLL, B. H., AND HUBBARD, D.: Bur. Standards J. Research **12,** 329 (1934).
(14) CLARK, W.: Brit. J. Phot. **69,** 462 (1922).
(15) CLARK, W.: Phot. J. **63,** 230 (1923).
(16) CLARK, W.: Brit. J. Phot. **70,** 763 (1923).
(17) CLARK, W.: Brit. J. Phot. **70,** 717 (1923).
(18) CLARK, W.: Trans. Faraday Soc. **19,** 309 (1923).
(19) DOMBROWSKY, C.: Dissertation, Leipzig, 1908.
(20) EGGERT, J., AND NODDACK, W.: Z. Physik **20,** 299 (1923).
(21) EGGERT, J., AND NODDACK, W.: Z. Physik **31,** 922 (1925).
(22) EULER, H. VON: Z. Elektrochem. **28,** 446 (1922).
(23) FISCHBECK, K., AND SCHNAIDT, K.: Z. Elektrochem. **38,** 299 (1932).
(24) GALL, H., AND ROTH, H.: Z. anorg. Chem. **214,** 201 (1933).
(25) GEE, G.: J. Chem. Phys. **5,** 801 (1937).
(26) GLOCKER, R., AND TRAUB, W.: Physik. Z. **22,** 345 (1921).
(27) GÜNTHER, P., AND TITTEL, H.: Z. Elektrochem. **39,** 646 (1933).
(28) GURNEY, R. W., AND MOTT, N. F.: Proc. Roy. Soc. (London) **A164,** 151 (1938).
(29) HABER, F., AND WILLSTÄTTER, R.: Ber. **64,** 2844 (1931).
(30) HALL, C. E., AND SCHOEN, A. L.: J. Optical Soc. Am. **31,** 281 (1941).
(31) HIGSON, G. J.: Phot. J. **60,** 161 (1920).
(32) HIRSH, F. R., JR.: J. Optical Soc. Am. **25,** 229 (1935).
(33) HIRSH, F. R., JR.: J. Optical Soc. Am. **28,** 463 (1938).
(34) HODGSON, M. B.: J. Franklin Inst. **184,** 705 (1917).
(35) HUGGINS, M. L.: Private communication.
(36) HURTER, F., AND DRIFFIELD, V. C.: J. Soc. Chem. Ind. **9,** 455 (1890).
(37) JABLCZYNSKI, K., AND KOBRYNER, S.: Roczniki Chem. **9,** 715 (1929).
(38) JAMES, T. H., AND WEISSBERGER, A.: J. Am. Chem. Soc. **60,** 98 (1938).
(39) JAMES, T. H., SNELL, J. M., AND WEISSBERGER, A.: J. Am. Chem. Soc. **60,** 2084 (1938).
(40) JAMES, T. H., AND WEISSBERGER, A.: J. Am. Chem. Soc. **61,** 442 (1939).
(41) JAMES, T. H.: J. Am. Chem. Soc. **61,** 648 (1939).
(42) JAMES, T. H.: J. Am. Chem. Soc. **61,** 2379 (1939).
(43) JAMES, T. H.: J. Phys. Chem. **43,** 701 (1939).
(44) JAMES, T. H.: J. Phys. Chem. **44,** 42 (1940).
(45) JAMES, T. H.: J. Am. Chem. Soc. **62,** 536 (1940).
(46) JAMES, T. H.: J. Am. Chem. Soc. **62,** 1649 (1940).
(47) JAMES, T. H.: J. Am. Chem. Soc. **62,** 1654 (1940).
(48) JAMES, T. H.: J. Am. Chem. Soc. **62,** 3411 (1940).
(49) JAMES, T. H.: J. Phys. Chem. **45,** 223 (1941).
(50) JAMES, T. H.: J. Am. Chem. Soc. **63,** 1601 (1941).
(51) JOST, W.: Trans. Faraday Soc. **34,** 860 (1938).
(52) KEMPF, A.: Z. wiss. Phot. **36,** 235 (1937).

(53) Kornfeld, G., and Weissberger, A.: J. Am. Chem. Soc. **61,** 360 (1939).
(54) Kornfeld, G.: J. Optical Soc. Am. **31,** 598 (1941).
(55) Kreveld, A. van, and Jürriens, H. J.: Physica (IV) **4,** 297 (1937).
(56) Laider, K. J., Glasstone, S., and Eyring, H.: J. Chem. Phys. **8,** 667 (1940).
(57) deLanghe, J. E.: Z. wiss. Phot. **35,** 201 (1936).
(58) Langmuir, I.: J. Am. Chem. Soc. **38,** 2263 (1916).
(59) Livingston, R., and Lingane, J. J.: J. Chem. Education **15,** 320 (1938).
(60) Lottermoser, A., and Steudel, R.: Kolloid-Z. **82,** 319 (1938).
(61) Lottermoser, A., and Steudel, R.: Kolloid-Z. **83,** 37 (1938).
(62) Loveland, R. P.: Private communication.
(63) Lüppo-Cramer, H.: Kolloid-Z. **15,** 164 (1914).
(64) Lüppo-Cramer, H.: *Kolloidchemie und Photographie*, 2nd edition. T. Steinkopff, Dresden (1921).
(65) Luther, R., and Leubner, A.: Brit. J. Phot. **59,** 632 *et seq.* (1912).
(66) McEwen, W. K.: J. Am. Chem. Soc. **58,** 1124 (1936).
(67) Meidinger, W.: Z. physik. Chem. **114,** 89 (1924).
(68) Meidinger, W.: Physik. Z. **36,** 312 (1935).
(69) Meidinger, W.: Phot. Ind. **34,** 1305 (1936).
(70) Meidinger, W.: Physik. Z. **38,** 564, 737, 905 (1937).
(71) Michaelis, L.: Chem. Rev. **16,** 243 (1935).
(72) Michaelis, L., and Schubert, M. P.: Chem. Rev. **22,** 437 (1938).
(73) Michaelis, L., Schubert, M. P., Reber, R. K., Kuck, J. A., and Granick, S.: J. Am. Chem. Soc. **60,** 1678 (1938).
(74) Mott, N. F.: Trans. Faraday Soc. **34,** 822 (1938).
(75) Mott, N. F.: Reports on Progress in Physics **6,** 186 (1939).
(76) Mott, N. F., and Gurney, R. W.: *Electronic Processes in Ionic Crystals.* The Clarendon Press, Oxford (1940).
(77) Mülbach, E.: Z. wiss. Phot. **36,** 269 (1937).
(78) Nutting, P. G.: Phil. Mag. **26,** 421 (1913).
(79) Ollendorff, G., and Rhodius, R.: Z. wiss. Phot. **35,** 81 (1936).
(80) Piper, C. W.: Brit. J. Phot. **55,** 196 (1908).
(81) Proskurnin, M., and Frumkin, A.: Z. physik. Chem. **A155,** 29 (1931).
(82) Rabinovitch, A. J., and Peissachovitch, S.: Z. wiss. Phot. **33,** 94 (1934).
(83) Rabinovitch, A. J.: (a) Trans. Faraday Soc. **34,** 920 (1938); (b) Photo Kino Chem. Ind. (U.S.S.R.) **3** (1938).
(84) Reinders, W., and Hamburger, L.: Z. wiss. Phot. **31,** 32, 265 (1932).
(85) Reinders, W., and deVries, R. W. P.: Rec. trav. chim. **56,** 985 (1937).
(86) Scheffer, W.: Brit. J. Phot. **54,** 116, 271 (1907).
(87) Scheffers, H.: Z. Physik **20,** 120 (1923).
(88) Schwab, G. M., Taylor, H. S., and Spence, R.: *Catalysis.* D. Van Nostrand Company, New York (1937).
(89) Schwarz, G., and Urbach, F.: Z. wiss. Phot. **31,** 79 (1932).
(90) Schwarz, G., and Urbach, F.: Phot. Korr. **68,** 61 (1932).
(91) Schwarz, G.: Phot. Korr. **69,** 27 (1933).
(92) Sheppard, S. E., and Mees, C. E. K.: Proc. Roy. Soc. (London) **A76,** 217 (1905).
(93) Sheppard, S. E., and Mees, C. E. K.: *Investigations on the Theory of the Photographic Process.* Longmans, Green and Company, London (1907).
(94) Sheppard, S. E.: Phot. J. **59,** 135 (1919).
(95) Sheppard, S. E., and Meyer, G.: J. Am. Chem. Soc. **42,** 689 (1920).
(96) Sheppard, S. E., Elliott, F. A., and Sweet, S. S.: Trans. Faraday Soc. **19,** 261 (1923).
(97) Sheppard, S. E., and Wightman, E. P.: J. Franklin Inst. **195,** 337 (1923).
(98) Sheppard, S. E., Wightman, E. P., and Trivelli, A. P. H.: J. Franklin Inst. **196,** 653, 779 (1923).

(99) SHEPPARD, S. E., WIGHTMAN, E. P., AND TRIVELLI, A. P. H.: J. Franklin Inst. **198,** 507 (1924).

(100) SHEPPARD, S. E., WIGHTMAN, E. P., AND TRIVELLI, A. P. H.: J. Franklin Inst. **198,** 629 (1924).

(101) SHEPPARD, S. E., TRIVELLI, A. P. H., AND LOVELAND, R. P.: J. Franklin Inst. **200,** 51 (1925).

(102) SHEPPARD, S. E.: Phot. J. **65,** 380 (1925).

(103) SHEPPARD, S. E., AND BALLARD, A.: J. Franklin Inst. **205,** 659 (1928).

(103a) SHEPPARD, S. E., AND TRIVELLI, A. P. H.: Phot. Korr. **64,** 145, 173, 242, 273 (1928).

(104) SHEPPARD, S. E.: Phot. J. **69,** 330 (1929).

(105) SHEPPARD, S. E., VANSELOW, W., AND HALL, V. C.: J. Phys. Chem. **33,** 1403 (1929).

(106) SHEPPARD, S. E.: Phot. J. **71,** 313 (1931).

(107) SHEPPARD, S. E., LAMBERT, R. H., AND KEENAN, R. L.: J. Phys. Chem. **36,** 174 (1932).

(108) SHEPPARD, S. E., VANSELOW, W., AND HAPP, G. P.: J. Phys. Chem. **44,** 411 (1940).

(109) SHEPPARD, S. E., BALLARD, A., AND PERRY, E. S.: J. Am. Chem. Soc. **63,** 2357 (1941).

(110) SHISHKINA, N. N.: J. Phys. Chem. (U. S. S. R.) **10,** 848 (1937).

(111) SILBERSTEIN, L., AND TRIVELLI, A. P. H.: J. Optical Soc. Am. **28,** 441 (1938).

(112) SILBERSTEIN, L.: J. Optical Soc. Am. **31,** 343 (1941).

(113) STAUDE, H.: Fot. Rundschau **72,** 390 (1935).

(114) STAUDE, H.: Z. wiss. Phot. **38,** 65 (1939).

(115) STAUDE, H.: Z. wiss. Phot. **38,** 137 (1939).

(116) SVEDBERG, T.: Z. wiss. Phot. **20,** 36 (1920).

(116a) SVEDBERG, T., AND ANDERSSON, H.: Phot. J. **61,** 325 (1921).

(117) TAYLOR, H. S.: J. Phys. Chem. **28,** 933 (1924).

(118) TOY, F. C.: Phot. J. **61,** 417 (1921).

(119) TOY, F. C.: Nature **120,** 441 (1927).

(120) TOY, F. C., AND HARRISON, G. B.: Proc. Roy. Soc. (London) **A127,** 613 (1930).

(121) TRIVELLI, A. P. H., AND SHEPPARD, S. E.: *The Silver Bromide Grain of Photographic Emulsions*, Monograph No. 1 on the Theory of Photography from the Research Laboratories of the Eastman Kodak Co., Rochester, New York (1921).

(122) TRIVELLI, A. P. H., RIGHTER, F. L., AND SHEPPARD, S. E.: Phot. J. **62,** 407 (1922).

(123) TUTTLE, C., AND TRIVELLI, A. P. H.: Phot. J. **68,** 465 (1928).

(124) URBACH, F.: Proc. IX Intern. Congr. Phot., Paris, p. 432 (1935).

(125) VANSELOW, W., AND SHEPPARD, S. E.: J. Phys. Chem. **33,** 331 (1929).

(126) VESELOVSKY, V. I.: Acta Physicochim. U. R. S. S. **11,** 815 (1939).

(127) VOLMER, M.: Z. wiss. Phot. **20,** 189 (1921).

(128) VOLMER, M.: Phot. Korr. **58,** 226 (1921).

(129) WAGNER, C.: Trans. Faraday Soc. **34,** 851 (1938).

(130) WEBB, J. H.: J. Optical Soc. Am. **23,** 157 (1933).

(131) WEBB, J. H.: J. Optical Soc. Am. **25,** 4 (1935).

(132) WEBB, J. H.: J. Optical Soc. Am. **26,** 347 (1936).

(133) WEBB, J. H.: J. Optical Soc. Am. **26,** 367 (1936).

(134) WEBB, J. H., AND EVANS, C. H.: J. Optical Soc. Am. **28,** 249 (1938).

(135) WEBB, J. H., AND EVANS, C. H.: J. Optical Soc. Am. **28,** 431 (1938).

(136) WEBB, J. H.: J. Optical Soc. Am. **29,** 309 (1939).

(137) WEBB, J. H.: J. Optical Soc. Am. **29,** 314 (1939).

(138) WEBB, J. H.: J. Applied Phys. **11,** 18 (1940).

(139) WEBB, J. H., AND EVANS, C. H.: J. Optical Soc. Am. **30,** 445 (1940).

(140) WEBB, J. H.: J. Optical Soc. Am. **31,** 348 (1941).

(141) WEBB, J. H., AND EVANS, C. H.: J. Optical Soc. Am. **31,** 355 (1941).

(142) WEBB, J. H.: J. Optical Soc. Am. **31,** 559 (1941).

(143) WIGHTMAN, E. P., AND SHEPPARD, S. E.: J. Phys. Chem. **25,** 181 (1921).

(144) WIGHTMAN, E. P., AND SHEPPARD, S. E.: J. Phys. Chem. **25,** 561 (1921).

(145) Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E.: J. Franklin Inst. **194,** 485 (1922).
(146) Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E.: J. Phys. Chem. **27, 1** (1923).
(147) Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E.: J. Phys. Chem. **27,** 141 (1923).
(148) Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E.: J. Phys. Chem. **27,** 466 (1923).
(149) Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E.: Trans. Faraday. Soc. **19,** 270 (1923).
(150) Wightman, E. P., Trivelli, A. P. H., and Sheppard, S. E.: J. Phys. Chem. **28,** 529 (1924).
(151) Wischin, A.: Proc. Roy. Soc. (London) **A172,** 314 (1939).
(152) Wulff, P., and Seidl, K.: Z. wiss. Phot. **28,** 239 (1930).
(153) Yano, T.: J. Soc. Chem. Ind. Japan (Suppl. Bind.) **43,** 44B (1940).

In addition to the specific references, the following books may be consulted:

Mees, C. E. K.: *The Theory of the Photographic Process.* The Macmillan Company, New York (1942).
Meidinger, W.: *Handbuch der wissenschaftlichen und angewandten Photographie,* Vol. V. J. Springer, Berlin (1932).