THE PHOTOGRAPHIC PLATE. IV

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THE EMULSION. PART IV

The passages quoted[1] from the papers of Lüppo-Cramer, Lobry de Bruyn, Sheppard and Mees, and Eder make it quite evident that the ripening of silver bromide is not due to a reduction. It seems equally clear[2] that we are not dealing with a series of allotropic modifications. Sheppard and Mees[3] have pointed out that a mere increase in the size of the grain for the same mass of material will not account for the increased opacity and resultant increase in sensitiveness. We have thus eliminated: changes in the composition of the silver bromide itself; changes in the chemical state of the silver bromide; and changes in the physical state of the silver bromide alone. That eliminates everything in case we are dealing with pure silver bromide and consequently we are forced to conclude that the so-called silver bromide grain is not pure silver bromide but is a complex of silver bromide, gelatine, and water. The ripening of silver bromide must therefore consist in a change in the composition of the complex. In so far as we can predict these changes in composition, we can predict the changes in sensitiveness. This is really a simplified form of Quincke's hypothesis.[4] It is rather interesting to note that, at one time or another, nearly everybody comes round to some form of Quincke's hypothesis, Ostwald, Lüppo-Cramer, Sheppard and Mees, Lottermoser, Eder, Schaum.[5] The objections to Quincke's point of view are that it is unnecessarily complicated and that he did not apply it to any concrete case.

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[1] Bancroft: Jour. Phys. Chem., 14, 56, 68, 71, 73 (1910).

[2] Cf. Lobry de Bruyn: Ibid., 14, 66 (1910); Sheppard and Mees: "The Theory of the Photographic Process," p. 203 (1907).

[3] Jour. Phys. Chem., 14, 71 (1910).

[4] Ibid., 14, 73 (1910).

[5] Bancroft: Jour. Phys. Chem., 14, 60, 63, 72, 117, 118, 246 (1910).

Before showing what can be done with a simple form of the same hypothesis, it will be desirable to clear up the matter of a possible crystallization in the silver bromide grain.

Schaum[1] says that any spontaneous change to another modification, such as the crystallizing of the silver bromide must be accompanied by a decrease in the free energy and consequently a decrease in the sensitiveness to light. This is an instance of a half-truth which is much more harmful than a deliberate mis-statement. Schaum is entirely right if one grants his premises, which are that he is dealing with pure silver bromide as a one-component system. While his conclusion holds absolutely for the hypothetical case for which it is deduced, it has no bearing at all upon the actual case of a silver bromide emulsion. During a spontaneous change, the free energy of the whole system must decrease; but it does not follow that the free energy of each component decreases during that change. If we have an unsaturated solution which evaporates spontaneously, the chemical potential, and therefore the free energy of the dissolved substance increases until the solution is saturated with respect to it. If we have a supersaturated solution which then crystallizes spontaneously, the chemical potential of the solvent increases. There is therefore no *a priori* reason why the formation of crystalline silver bromide or a crystalline complex of silver bromide, gelatine and water should not be accompanied by an increased sensitiveness to light. When we are once freed from the tyranny of bad thermodynamics, it may be possible for us to find out what the facts really are instead of throwing over our observations[2] because they do not agree with some other fellow's theory.

Not having any analyses of the silver bromide grain as yet, it is impossible to say whether the ratio of gelatine to water is an important factor or not. That point can wait perfectly well till some later date when satisfactory methods

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[1] Jour. Phys. Chem., 14, 64 (1910).

[2] Cf. Bancroft: Jour. Phys. Chem., 14, 71, 102–108, 237 (1910). Sheppard and Mees: "The Theory of the Photographic Process," p. 70 (1907).

of analysis shall have been worked out. We can state definitely however that we get the maximum sensitiveness when we have a definite but small amount of gelatine in the grain, and when we have a definite but small amount of water in the grain. The sensitiveness decreases when the amount of gelatine or of water becomes greater or less than the corresponding, unknown, optimum value. We deduce this from the following facts.

A silver bromide which contains no gelatine or extremely little gelatine[1] is not as sensitive as a silver bromide containing more gelatine. The plate is also not especially sensitive if the silver bromide grain is rich in gelatine,[2] while it is much more sensitive if the silver bromide is precipitated from a solution containing only an extremely moderate amount of gelatine.[3] Since drying a plate increases its sensitiveness up to a certain point,[4] we see that there is a limiting value for which we get a maximum sensitiveness, everything else remaining the same. As further evidence, we have the fact that the original emulsion is more sensitive if a silver-rich solution is used.[5] Incidentally this explains some of the effects due to pressure.[6] It has always seemed absurd to assume that either silver or bromine could be squeezed out of silver bromide by pressures which did not rupture the gelatine film. It takes very little pressure, however, to squeeze water out of a sponge and not much to displace it in a jelly. What we do when we draw lines on an unexposed plate with a smooth glass rod, is to ripen some of the grain to the fogging point. One could probably make a slow plate more sensitive by putting it for a while under a suitable, uniform pressure; but the method does not seem to be one which promises much in the way of results.

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[1] Eder, Schumann: Jour. Phys. Chem., **14**, 41, 252 (1910).

[2] Lobry de Bruyn, Eder: Ibid., **14**, 69, 122 (1910).

[3] Henderson: Jour. Phys. Chem., **14**, 122, 233 (1910).

[4] Baekeland, Eder, Farmer, Schaum: Jour. Phys. Chem., **14**, 35, 126, 127, 128 (1910).

[5] Monckhoven, Schumann: Jour. Phys. Chem., **14**, 121, 249 (1910).

[6] Eder's Handbuch der Photographie, 2nd Ed., **2**, 41 (1897); 5th Ed., **3**, I, 80 (1902); Baekeland: Jour. Phys. Chem., **14**, 34, 38 (1910).

Since ripening, by hypothesis, consists in a change in the gelatine and water concentrations of the silver bromide grain, it follows that there is no necessary connection between sensitiveness and coarseness of grain. While it is pretty generally true that the sensitiveness of a commercial plate increases with increased coarseness of grain, this must be looked upon as purely accidental. It is due to the fact that as yet we do not know any method of obtaining the desired concentrations within the grain without at the same time causing an agglomeration. If it were possible to take a very sensitive plate and to chop up the coarse grains with so sharp a knife that there was no pressure exerted upon them, I do not believe for a moment that such a hypothetical plate would show a decrease in sensitiveness. When we are dealing with silver bromide and water only, the finest grains are the most sensitive.[1] Here we are dealing with a two-component system with one volatile component and it is therefore easy to get any desired composition of the grain. With a three-component system, silver bromide, gelatine, and water, the adjustment of the concentrations is not so simple. Since we have not known that we were trying to adjust concentrations, it is perhaps not surprising that only one type of ripening has been worked out and that people have therefore been led to false conclusions.[2] It should be possible to make a plate which would come nearer to satisfying the astronomers[3] than anything now on the market. It is interesting to note a comparatively recent statement by Wallace:[4] "Messrs. Lumière have introduced a special 'Σ' emulsion, which from measurements by the writer gives a special increase of 2.3 times that of the 'Seed 27 Gilt Edge.' This Σ plate, however, cannot be used generally in astronomical work, as the grain is 1.7 larger than that of the '27.' The Σ plate also fogs badly in development."

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[1] Cf. Weisz: Jour. Phys. Chem., **14**, 248 (1910).

[2] Cf. Bancroft: Jour. Phys. Chem., **14**, 98, 99, 102, 106, 109, 115 (1910).

[3] Wallace: Jour. Phys. Chem., **14**, 120 (1910).

[4] Astrophys. Jour., **28**, 42 (1908).

Now that we know what constitutes ripening, we can draw some interesting conclusions in regard to the limits of ripening. Under ordinary conditions the limit of ripening is reached when the unexposed plate fogs in the developer.[1] Since the plate is never uniform,[2] we may easily have a small portion of the emulsion in an over-ripened state while the bulk of it is not up to standard pitch. I have not been able to find any published accounts of anyone having taken special precautions to obtain an exceptionally uniform product, though it is probable that something of this sort is done by some manufacturers.

Van Bemmelen[3] has already shown that a silicic acid gel contains more water when precipitated from a dilute solution than when precipitated from a concentrated solution. These gels change in composition with time, temperature, partial pressure of water vapor, and concentration of other substances. This is exactly what the photographic emulsion does except that we measure the change of concentration indirectly by means of the sensitiveness. The silicic acid gel changes slowly on standing under ordinary conditions, much more rapidly when heated. The silver bromide emulsion ripens slowly in the cold and very much more rapidly when heated. If the silicic acid gel is precipitated from a concentrated alkaline solution of silicic acid, it comes down in a form similar to that obtained by aging a gel precipitated from a more dilute solution. This is very like what happens with a silver bromide emulsion.

In all matters affecting the emulsification and ripening of silver bromide we are dealing with phenomena which are not really photochemical at all. We make use of photochemistry to show that the emulsion has ripened; but the phenomena of ripening are common to all emulsions whether sensitive to light or not. Until we have a fairly satisfactory theory for emulsification and ripening in general we cannot

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[1] Bancroft: Jour. Phys. Chem., 14, 41, 42 (1910).

[2] Eder: Ibid., 14, 45 (1910).

[3] Zeit. anorg. Chemie, 13, 233 (1897).

hope to clear up all the details of the special case. It is worth while however to consider what we know about the general theory of emulsification and of ripening. We can then see in how far we can apply this knowledge to the particular case of silver bromide emulsions.

Wolfgang Ostwald[1] discusses the phenomena of emulsification but comes to the conclusion[2] that we are still far from a satisfactory theory of the emulsifying action of certain ions. Freundlich[3] gives us more facts and makes us think that we are getting ahead.

"We may picture to ourselves the action of a protecting colloid somewhat as follows: The formation of an outer film when the particles have the same charge depends chiefly on straight adsorption; when the particles have different charges, it depends also on the electrical adsorption. If the film is once formed, it protects to the extent that the sol can now be considered as an emulsion colloid and is therefore less sensitive to electrolytes, for instance. If this film is tough, the uniting of two particles of the suspension colloid is of course made very much more difficult thereby. *But even though the film is not especially tough and merely consists of substances which lower the surface tension very much*—which is necessarily the case since they are adsorbed—*this alone must check agglomeration very markedly.*

"Donnan[4] has shown that when there is a contact between two particles, each surrounded by a film, there is necessarily an increase in the concentration of the adsorbed substance at the surface of contact. The surface tension will therefore be decreased still more at that point and the higher surface tension at the other portions of the surface will not favor a fusion at that point but will rather tend to tear the particles apart because the substances in the surface film will always

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[1] Grundriss der Kolloidchemie, 289–309 (1909).

[2] Ibid., p. 308 (1909).

[3] Kapillarchemie, 456, 459, 473 (1909).

[4] Zeit. phys. Chem., 31, 42 (1899).

tend to pass from the place of lower surface tension to that of higher surface tension.

"These changes make it intelligible that the protecting colloids, previously mentioned, are able to preserve an already existing or just formed mass of very fine particles and *are also able to emulsify a solution in mass.* The emulsifying action of alkali on oils has long been known. If one pours a layer of dilute alkali over a commercial oil such a olive oil, a very slight shaking is enough to form a milky liquid. After Gad[1] had made a number of qualitative experiments, Quincke[2] increased our knowledge of the phenomena very considerably by showing that oil is emulsified only by such dissolved substances as lower very much the surface tension between oil and water." "The reason why colloidal solutions of soaps, albumen, starch, and glue are so effective in forming emulsions, seems to be that, with these substances which diffuse so slowly, the adsorption and the equalizing of the concentrations does not take place rapidly. Consequently, the differences in the surface tension are maintained long enough to enable the mechanical effect to take place.

"The mechanism of the conditions for stability with emulsion colloids was previously referred generally to the solubility of the colloid phase; but it is now very probable that it may be due to the mutual reaction with the dispersing medium, in that the *liquid, dispersed phase is separated from the dispersing medium by an adsorption film containing a substance or substances formed by inter-action with the dispersing medium.* Thus the stability of an oil emulsion depends on the soap solution due to the action of alkali on oleic acid. This is the explanation which Quincke has given for the stability of colloidal solutions because the 'oily liquid' which he mentions so often is merely the adsorption film."

"We have already described how we are to picture to ourselves the emulsifying action of soap on oil. In the ex-

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[1] Du Bois-Reymond's Archiv. anat. Physiol., **1878**, 181.

[2] Wied. Ann., **35**, 380 (1888).

periments then under consideration, there was an external pressure driving the oil into the dispersing medium. We must now consider how the emulsification takes place under ordinary conditions. From the experiments of Quincke[1] we know that oleic acid is not emulsified in pure water and that soap must be present. The tendency of the oleic acid to emulsify is especially marked if the acid is brought in contact with an alkaline solution and this solution then diluted with, or replaced by, water. From the oleic acid there protrude globular and worm-like growths—the myelin forms—which show a tendency to split off drops of oil, so that finally the oil is emulsified in the water. Similar phenomena are obtained by adding a solution of an alkali oleate to oil and water. The following sequence of events is quite probable. The alkali oleate tends to distribute between the oleic acid and the water. An alkali oleate is soluble in a good deal of water; but with oleic acid it forms masses which are sparingly soluble in water. At the surface between oleic acid and water, there is formed a film of an acid oleate, this film being permeable to water. Just as in Traube's experiments, some water will tend to pass into the oleic acid phase in order to dissolve more alkali oleate, and consequently we have an arching of the oleic acid phase. This then becomes more marked because the surface tension is lowered by the adsorption of the alkali oleate dissolved in the water. This does not take place entirely regularly and the surface tension consequently varies from point to point. These differences of surface tension set in motion the outgrowths from the oleic acid phase and cause the formation of drops.

"The behavior of the oleic acid has been taken as typical. It seems probable that we have similar conditions whenever amorphous substances or gels are emulsified in liquids, as for instance when albuminoids are dissolved in alkali or stannic acid in ammonia. A part of the phase which is to be emulsified dissolves in the dispersing medium as a substance which is adsorbed very gently. Protuberances arise from swelling

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[1] Pflüger's Archiv., **19**, 129 (1879); Wied. Ann., **53**, 593 (1894).

or from liquid passing through a semipermeable wall and the rest of the emulsification is caused by movements due to differences in adsorption and resulting differences in surface tension. In other cases it seems to be essential that the natural gel shall be freed from a protecting film before the dispersing medium can act. After a dilute solution of permanganate or any other oxidizing agent has acted on a starch, this substance dissolves more readily in water than it did before the treatment."[1]

There are some specific facts in regard to the reversible coagulation of gelatine solutions which we need and which I therefore quote.[2]

"Electrolytes and other foreign substances affect the reversible change of sol to gel to a great extent and in a very complex way for we have to distinguish between two fundamentally different things. The equilibrium between sol and gel may actually be displaced and the rate of gelatinization may be changed. This is easily seen from the following considerations: At higher temperatures a pure gelatine sol is practically a stable sol and its viscosity does not increase. If cooled, a range of temperatures is reached where the viscosity is not constant. It increases rapidly or slowly until the sol has solidified to a gel. The foreign substances may not only displace the critical range of temperatures; they may also alter the rate of change. Since we have not been able to separate these two effects, it is not surprising that the action of foreign substances seems complex. It is pretty certain that both must be taken into account, because otherwise one must postulate enormous retarding effects, since many substances (sulphocyanates for instance) are able to keep a gelatine solution containing fifty grains to the liter, liquid for an indefinite time at temperatures well below that of the 'point of modification.'

"We can however say that, with electrolytes, the effects

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[1] Wolff: Comptes rendus, 141, 1046 (1905).

[2] Freundlich: Kapillarchemie, 418, 420, 423 (1909).

are always lyotropic.[1] Sulphates, tartrates, etc., raise the point of solidification, decrease the period of solidification, and increase the rate of change of the viscosity with the time. They therefore help the solidification. Chlorides, nitrates, bromides, iodides, sulphocyanates act in the opposite way and in that order. We therefore have again the series

$SO_4 > CH_3CO_2 > Cl > NO_3 > Br > I > SCN$ ($>$ benzoates, salicylates).

"The effect of the cations is very limited and counts only in the neutral region. Hydrogen and hydroxyl ions act like chlorides and nitrates; they check gelatinization."

"The electrolytes show another peculiarity beside that of affecting the gelatinization. They may precipitate the gelatine or salt it out. When the concentration of the electrolyte is high, the gelatine precipitates in clots which do not form a sol spontaneously when the solution is diluted. This precipitation can be brought about both by electrolytes which increase gelatinization and by those which check it. This is a proof that we are dealing with a phenomenon quite distinct from the one affecting the reversible change of sol to gel. . . . Although potassium chloride lowers and sodium sulphate raises the temperature of solidification, concentrated solutions of both salts cause the precipitation of flocks. . . . If we arrange the salts according to the strength of their precipitating powers we get again a lyotropic series.

$SO_4 >$ Citrate $>$ Tartrate $>$ Acetate $>$ Chloride.

That salt is said to have the highest precipitating power which precipitates with the lowest concentration.

"The precipitation differs from the change in the gelatinization because non-electrolytes do not precipitate gelatine. They often prevent the precipitation and, sometimes, change the flocks back into a colloidal solution. The action

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[1] (Affecting the internal pressure. Freundlich: Kapillarchemie, p. 54 (1909)).

of several electrolytes is not additive and in such solutions a number of complications arise.[1]

"There is still a third phenomena which complicates the properties of a gelatine sol. A pure sol is not stable even at the higher temperatures at which it does not gelatinize. The viscosity decreases continuously until it reaches a definite, final value. At the same time the sol loses the power to gelatinize. It changes from the α form to the β form; it becomes saponified.[2] Hydrogen and hydroxyl ions accelerate this irreversible change very much and this must always be kept in mind in experiments in which the sol is heated, no matter for how short a time.

"Although the multiplicity of these properties is very perplexing, the transfer of water must be the important factor in all cases. If this were not so, the lyotropic influences would not be so prominent. From the experiments on viscosity, we concluded that gelatine sols contain a very viscous phase which is rich in gelatine and poor in water. This phase preserves to a great extent the viscous and solid properties of the amorphous gelatine. Gelatinization must be due to the fact that these finely divided masses, which are chiefly in the form of drops at high temperatures, coalesce as the temperature falls and become ever more viscous. This is certainly due in part, if not entirely, to a decrease in solubility. These viscous masses finally form the skeleton throughout which the drops of the solution are distributed; in other words, a gel is formed. The effect of the foreign substances must be due to the fact that they change the solubility of gelatine in water and to the fact that by dissolving in the gelatine phase they change its viscosity. Since the effects of the foreign substances are largely additive, it looks as though it were more a case of solubility than of a surface condensation."

"A large number of other emulsion colloids behave like the gelatine sol. The best known of these is the sol

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[1] Pauli and Rona: Beiträge chem. Physiol. und Pathol. 2, 25 (1902)

[2] v. Schroder: Zeit. phys. Chem., 45, 94 (1903).

of agar-agar, a substance whose chief constituent is a polyose, δ-galactone. Its power of gelatinizing is much greater than that of gelatine since a sol containing only one gram to the liter gelatinizes at 0°. Foreign substances affect the agar-agar sol much as they do the gelatine sol. Nitrates, iodides, sulphocyanates, benzoates, urea, thio-urea, increase the time of gelatinization while salts of polybasic acids, acetates, bromides and chlorides decrease it."

Freundlich[1] also gives some special facts with regard to silver salts which are of distinct interest to us.

"Lottermoser and Rothe[2] have shown clearly that there is always adsorption of the salt present in excess when the silver iodide sol is formed; and that this salt can be displaced by others. Thus, silver iodide, precipitated from an ammoniacal solution contains ammonia which can be displaced by nitric acid, whereby some ammonium nitrate remains in the surface. This was finally removed by careful washing. The adsorption of silver nitrate by this precipitated silver iodide is described by an exponential formula. Within certain ranges of concentration a similar formula holds good for the adsorption of potassium iodide, although at the higher concentrations there is a surprising decrease in the amount adsorbed. This last is probably to be accounted for by the assumption that silver iodide changes its structure and consequently its adsorbing power."

"Lottermoser prepared sols of silver halides by letting a dilute solution of a silver salt flow into a dilute solution of an alkali chloride. *The silver halide remained if there were a slight excess of alkali halide in the solution.* The sol precipitated in flocks, however, if the two solutions were exactly equivalent, so that the whole of the halide reacted with the silver. When the sol was dialyzed, a trace of alkali halide always remained adsorbed, just as happens with other electrolytes and other sols. These sols were negative and the halogen ion was therefore adsorbed more strongly than the

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[1] Kapillarchemie, 323, 360, 361 (1909).

[2] Zeit. phys. Chem., **62**, 359 (1905).

alkali ions. The experiments were made chiefly with iodides.

"With the silver halide it was also possible to prepare a positive sol. If Lottermoser let a dilute solution of an alkali halide flow into a dilute solution of a silver salt, he obtained a positive sol, so long as there was an excess of silver salt, owing to the greater adsorption of the silver ion. Here too there was flocculation when the solutions were equivalent."

"If the disperse phase is precipitated as flocks, the suspension is not so simple a matter, while one may consider the submicrons as loose groups of amicrons in which the Brownian movements help out the disintegrating action of a charge. The stationary, precipitated flocks are not in a state of equilibrium. As we shall later describe more in detail, they change from the amorphous, finely-divided form into even coarser and more crystalline forms and, with the smaller surface, offer ever fewer points of attack to each disintegrating influence. Freshly precipitated flocks are therefore easily brought into colloidal solution again under certain conditions, whereas it is more difficult with older ones and requires the use of mechanical means, fine grinding, powerful stirring and the like. Such a behavior has been observed by many different investigators[1] during the formation of colloidal sulphides, hydroxides, etc."

We can now discuss some of the facts in regards to the peptonizing of silver halides.[2] Silver bromide can be precipitated in aqueous solution and subsequently emulsified by a hot solution. Since we know that gelatine is adsorbed by silver bromide, this is right in line with the general facts in regard to emulsification. The silver iodide hydrogel is converted into a hydrosol by potassium iodide and there is an optimum concentration of the iodide. Since the iodide is adsorbed, it should tend to peptonize the gel. While we

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[1] For instance, Spring: Ber. chem. Ges. Berlin, **16**, 1142 (1883); Linder and Picton: Jour. Chem. Soc., **61**, 114 (1892); Wissinger: Bull. Soc. chim. Paris, **49**, 452 (1888).

[2] Bancroft: Jour. Phys. Chem., **14**, 15–23 (1910).

do not know in this case just what determines the optimum concentration, it seems to depend on a balance between the peptonizing action and the precipitating action. We get a similar phenomenon with salts, gelatine and water. We have another form of the same thing in Lüppo-Cramer's experiments, where a hydrosol is obtained if silver halides are precipitated with a slight excess of halide, whereas no hydrosol is obtained when there is no excess or when there is a very large excess of the halide. We must keep in mind, however, that the balance here is not between the peptonizing and the precipitating actions; but between the peptonizing and the solvent actions, because the silver halides form true solutions with an excess of the alkali halide. Since gelatine will emulsify a silver halide, it is not surprising that gelatine and potassium bromide should emulsify silver chloride. What does not seem clear, however, is Lüppo-Cramer's statement that silver chloride, formed by precipitation from aqueous solution, shows no tendency to emulsify in gelatine under the influence of chlorine ions. It looks as though this experiment would have to be repeated. It is quite natural that the gelatine should decrease the pectizing effect of an excess of bromide. Since gelatine is a much more efficient protecting colloid than dextrine, gum arabic, or albumen in the case of colloidal gold,[1] it is not surprising that Lüppo-Cramer should also have found it more effective with respect to silver bromide. I do not at present know how we could have predicted the great emulsifying power of collodion in presence of potassium bromide, nor why it should not emulsify silver bromide in presence of ammonia. That a heated silver bromide or iodide should not peptonize readily with gelatine and bromide is not surprising because heating in that way ages the gel and it is an entirely general fact that a gel, which has aged, is not readily converted back into a sol. One must be permitted to doubt the absolute accuracy of Lüppo-Cramer's statement. It seems probable that he has not paid sufficient attention to the time factor though,

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[1] Freundlich: Kapillarchemie, 451 (1909).

of course, irreversible changes are not out of the question. However this may be, it is clear that the failure to peptonize a ripened Schleussner plate with bromide comes under the same head. Lüppo-Cramer was dealing with a silver bromide gel which had been aged or ripened. Carey Lea's experiments with colloidal silver are in harmony with this. When his reducing agent gave him a silver containing little or no water, a gray silver, it could not be peptonized. When he obtained a silver with more water in it, the silver could be converted into a sol.

In view of the fact that ammonia ripens silver bromide and therefore removes water and probably gelatine from it, the silver bromide from an ammoniacal solution is probably in a higher stage of ripening than a silver bromide precipitated from a neutral solution. If this proves to be the case the following paragraph contains nothing surprising.[1]

"If the silver bromide is formed from ammoniacal silver oxide instead of from silver nitrate, it differs in shape and color from that precipitated from a neutral solution and it cannot be peptonized in presence of gelatine. Even when not precipitated in presence of ammonia, it only requires a few minutes shaking of the silver bromide with a very dilute solution of ammonia to bring the silver bromide into such a state that ammonia does not cause an emulsification in presence of gelatine. Bromides cannot peptonize a silver bromide precipitated from an ammoniacal silver oxide solution."

Under conditions of precipitation we must consider the statement[2] that a moderate excess of potassium bromide is desirable. An excess of silver nitrate would not be possible because it would react with the gelatine during ripening and cause fogging. A moderate excess of potassium bromide would make the silver bromide less soluble and would, there-

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[1] Lüppo-Cramer: Jour. Phys. Chem., **14**, 23 (1910). Through an inadvertence the words "silver nitrate" and "ammoniacal silver oxide" have been transposed in the original paragraph.

[2] Jour. Phys. Chem., **14**, 14, 15, 44, 106 (1910).

fore, presumably make it precipitate with less water and therefore in a more sensitive form. When we come to the effects of an excess of bromide, the matter is not so simple. The bromide will make the silver bromide more soluble, which would accelerate crystallization and would therefore make the silver bromide more sensitive. The potassium bromide may also lower the setting-point of the gelatine which would presumably be bad for the plate. It therefore seems possible only to predict that a large excess of bromide will be beneficial or will be deleterious, depending on which of two unknown factors one assumes to be the more important. This harmonizes only too well with the experimental data. The following two sentences will illustrate my meaning: "A very finely divided, extremely satisfactory silver bromide is obtained by dissolving this salt hot in potassium bromide and then causing it to separate either by cooling the solution of by diluting it with a gelatine solution." "When an emulsion contains too large an excess of potassium bromide it is apt to be flat or even fogged after ripening by cooking." It is quite clear that these experiments must be repeated by the same man so that we may have comparable data. It is quite possible that the sentences quoted are both correct; but that does not help us until we know what the other conditions were.

Since ripening, by hypothesis, consists in bringing the composition of the silver bromide grain toward certain values of silver bromide, gelatine and water, there are at least three different ways in which this can be done. For lack of better names we will call these processes: recrystallization, dehydration, and degelatinization. We may add something which will first dissolve the silver bromide and then let it separate in a more nearly crystalline form. Abney's explanation[1] for the advantage in using an excess of potassium bromide when precipitating silver bromide is that "silver bromide is soluble in potassium bromide and crystallizes, on cooling, in yellowish crystals which yield a green, highly

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[1] Jour. Phys. Chem., 14, 14 (1910).

sensitive silver bromide when washed." Lüppo-Cramer[1] notes that "an excess of halide salt causes a crystallization of the grain more readily with silver bromide than with silver chloride, while ammonia changes silver chloride to the crystalline state more readily than it does silver bromide. Silver iodide is extraordinarily readily soluble as a complex salt and we shall see in the following paper that it becomes crystalline especially easily when a large excess of iodide is used, while ammonia seems to have no effect of that sort at all." Everybody knows that the solubility in ammonia decreases from silver chloride to silver iodide and it is this property which determines the rate of ripening.

A beautiful instance of the same thing occurs in the case of silver nitrate and silver iodide.[2] "Silver nitrate also has a marked ripening action on grainless silver iodide gelatine. The greenish yellow, opalescent emulsion becomes at once intensely yellow. If it is heated it soon becomes entirely opaque and the grain even coarsens until the plate lets grayish blue light through whereas a pure silver iodide emulsion scarcely changes at all. The ripening, or grain-coarsening action, of an excess of an iodide is much less than that of an excess of silver nitrate when the emulsion is hot, while the reverse is the case when the emulsion is cold. With the grainless silver bromide gelatine, silver nitrate checks the ripening process as I have already pointed out, and the same effect is produced with silver chloride gelatine." In Dammer's Handbuch there is no reference to the solubility of silver iodide in silver nitrate and one might easily suppose that some other explanation would have to be found.[3] Fortunately Hellwig[4] has shown not only that silver iodide is soluble in silver nitrate but that it is much more soluble than either silver bromide or silver chloride. At 25° silver iodide is less soluble in a given silver nitrate solution than it is in

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[1] Jour. Phys. Chem., 14, 105 (1910).

[2] Lüppo-Cramer: Jour. Phys. Chem., 14, 119 (1910).

[3] Cf., however, Comey: Dictionary of Chemical Solubilities, 374 (1896).

[4] Zeit. anorg. Chem., 25, 157 (1900).

an equivalent solution of potassium iodide. While Hellwig does not give solubilities at higher temperatures, the following passage makes it probable that the solvent action of silver nitrate increases more rapidly with the temperature thand does that of potassium iodide.[1]

"If silver iodide is added to a hot concentrated solution of silver nitrate, the silver iodide clots to a compact mass, the surface of which is covered with a film of whitish crystals. These crystals are probably the double salt $Ag_3I(NO_3)_2$. If the mass is stirred thoroughly with a glass rod, the silver iodide and the adhering crystals dissolve slowly, and there is formed a colorless liquid with a high refractive index. If still more silver iodide is added, there comes a point where the iodide melts at the bottom of the vessel to a pale yellow oily liquid. This oily liquid and the supernatnnt aqueous solution form two clearly-marked liquid layers. If these two phases are shaken together vigorously, a dirty yellow emulsion is formed which soon separates into the two clearly marked liquid layers. If the upper colorless layer is poured off quickly and carefully, and is allowed to cool slowly, colorless, pointed needles crystallize. The oily layer solidifies to a dirty yellow crystalline mass. The oily phase is certainly to be considered as a solution of silver nitrate, water and complex salt in silver iodide, the melting point of which has been lowered from 527° to below 100°."

We can remove water from the emulsified silver bromide grains by dehydration and when we do so we increase the sensitiveness.[2] This loss of water is very possibly also accompanied by an extrusion of gelatine; but we have no direct proof of this as yet. In any event the elimination of gelatine does not keep pace with the elimination of water because there seems to be a limit to the sensitiveness which can be obtained by merely drying a plate.

There is also the possibility of degelatinization, in other

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[1] Hellwig: Zeit. anorg. Chem., **25**, 166 (1900).

[2] Baekeland, Eder, Farmer, Schaum: Jour. Phys. Chem., **14**, 35, 126, 127, 128 (1910).

words that our ripening agent may remove gelatine from the silver bromide grain either directly, by acting as a solvent for the gelatine, or indirectly, by changing the temperature of solidification of the gelatine or something of that sort. Since we invariably get an agglomeration during ripening, it is clear that every ripening agent must either act as a solvent for silver bromide or must remove from the surface of the silver bromide grain substances which lower the surface tension, in other words, gelatine and water. This last conclusion may be considered a strong argument in favor of the theory under discussion or it may be looked upon as an ingenious case of reasoning in a circle. Personally, I am a little doubtful how to classify it.

So far as one can judge from the paragraphs quoted,[1] the hard gelatine is not so readily adsorbed as the soft gelatine and consequently it is easy to overdo the ripening and to get plates which fog. With the soft gelatine this difficulty is eliminated to a certain extent but we then get a film which does not adhere so well to the glass. When plates are made on a commercial scale, it may be safer, as Eder says, to have the soft gelatine constitute one-third to one-half the mixture. If one wishes to make a special plate for a special purpose, it would seem wiser to take no chances and to use the hard gelatine. As against that, we have Schumann's statement[2] that the best gelatine to use is soft gelatine, Nelson's No. 1. This apparent contradiction seems to be due to two things. The statement that "a hard gelatine fogs readily" is very vague and does not mean much of anything until one knows the conditions. In the second place Schumann was not ripening his plates and he was working under such conditions that the danger from frilling was reduced to a minimum. Consequently, what holds good in this case does not necessarily apply in other cases.

Since we are maintaining that there is no necessary connection between the coarsening of the grain and the in-

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[1] Bancroft: Jour. Phys. Chem., 14, 52 (1910).

[2] Jour. Phys. Chem., 14, 257 (1910).

crease in sensitiveness, it will be wiser to consider these two phenomena separately and we will therefore take up first Lüppo-Cramer's[1] experiments on the coarsening of the grain in so-called grainless emulsions. Lüppo-Cramer found that ammonia, ethylene diamine, ammonium sulphocyanate, sodium sulphite,[2] sodium amino-acetate, potassium cyanide, the thiocarbamides, bromides, chlorides, and hydrochloric acid "coarsen the grain of a so-called Lippmann emulsion quickly and visibly when the latter is heated in presence of one of them." He refers this very properly to the solvent action on silver bromide. He finds however that soda and also sulphuric acid increase the size of the grain fairly rapidly, and he says:[3]

"The acceleration of the coarsening of the grain by soda, bisulphite, and sulphuric acid cannot be accounted for in the same way because these substances have no solvent action at all upon silver bromide, as is easily shown by the fact that they do not prevent the precipitation of silver bromide. Since the growth of the grain is obviously affected by the greater or lesser viscosity of the colloidal medium, we might account for the effect of these reagents, and especially of sulphuric acid, by postulating that they increase the rate of growth indirectly by decreasing the cohesive action of the glue and by thus permitting the grains to coalesce more readily."

Since there is no solvent action on silver bromide, we must be dealing with a degelatinization. It is interesting to note that sulphates head one of Freundlich's lyotropic series;[4] but I fear that this is merely a coincidence. While sulphates act one way on gelatine, acids act the other way and consequently we could only have a differential effect with sulphuric acid at best. If the coarsening of the grain is due to the acid, nitric acid should be more effective than sulphuric acid,

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[1] Jour. Phys. Chem., 14, 110–116 (1910).

[2] On p. 110, eighth line from top, read sulphite instead of bisulphite.

[3] Lüppo-Cramer: Jour. Phys. Chem., 14, 112 (1910).

[4] Kapillarchemie, p. 418 (1909).

which is not the case. If the coarsening of the grain is due to the sulphate, then nitric acid should have no effect. The results are therefore inconsistent and more experiments will have to be done before this matter is settled.

The experiments with bathed plates are identical in principle with those on recrystallization, p. 636. Lüppo-Cramer[1] added silver nitrate solution or ammoniacal silver oxide solution to gelatine films containing potassium iodide, potassium bromide or sodium chloride. He found that when silver nitrate is added, the iodide plate becomes opaque more rapidly than the bromide plate or the chloride plate, while the reverse is true in case of an ammoniacal silver solution. Silver nitrate dissolves silver iodide more readily than it does silver bromide or chloride, while ammonia dissolves silver chloride and bromide more readily than it does silver iodide. Since the composition of the silver bromide grain changes during ripening and since the change in composition consists in an elimination of gelatine and water, there is no longer any difficulty in accounting for the increasing opacity.[2]

The effect of different substances in changing the sensitiveness of a photographic plate has been summed up by Sheppard and Mees[3] in the following words: "Generally silver solvents facilitate ripening. Oxidizing agents retard it, but this has been dealt with under desensitizers, while reducing agents are said to have a favorable influence. But this may be merely due to a destruction of a desensitizer."

While this summing is not complete and is not entirely correct, it will do admirably as a starting point. Everybody is agreed that substances which dissolve silver bromide promote ripening, provided no other reaction takes place. Not having any theory to guide them, Sheppard and Mees have overlooked the possibility of dehydration and of degelatiniza-

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[1] Jour. Phys. Chem., 14, 77 (1910).

[2] Sheppard and Mees, Gaedicke: Jour. Phys. Chem., 14, 71, 98 (1910).

[3] Jour. Phys. Chem., 14, 70 (1910).

tion. Sheppard and Mees[1] consider oxidizing agents as desensitizers and they show that the action of such substances as cupric,[2] ferric, mercuric, and uranic salts "occurs *during exposure by reversal of the photochemical action*, and not by any modification of the sensitive salt." "From all these results it appears justifiable to conclude that a definite quantity of the metallic salt is irreversibly absorbed by the silver halide, and that this subsequently counteracts the photochemical action during exposure. It is probable that something of the nature of a solid solution is formed, the maximum effect with any salt being the quantity which forms a saturated solution of the halide."

If one is to call these oxidizing agents desensitizers, it would seem the natural thing to call reducing agents sensitizers instead of considering their effect as limited to the destruction of a desensitizer. In so far as a substance acts as an oxidizing agent or a reducing agent, it is a depolarizer and consequently has an effect on the sensitiveness. Before this point of view can be accepted, it is necessary to discuss some of Lüppo-Cramer's objections[3] to the theory of sensitizers.

Lüppo-Cramer bathed collodion plates in specified solutions for one minute and then washed the plate thoroughly. He found that there was a marked decrease in apparent sensitiveness when the bath contained ferric chloride, acidified ammonium persulphate, potassium permanganate, acidified bichromate, cupric chloride, or potassium ferricyanide. Since these are all oxidizing agents, the results are exactly what they should be, though that is not the conclusion that Lüppo-Cramer draws.

He next tried substances which absorb halogen. "If a collodion plate is bathed for one minute in a one percent aqueous solution of aqueous hydroquinone and the plate is then washed thoroughly, the sensitiveness is doubled and

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[1] "The Theory of the Photographic Process," 247, 254, 257, 260 (1909).

[2] Cf. Eder: Jour. Phys. Chem., **14**, 215 (1910).

[3] Jour. Phys. Chem., **14**, 129–145, 147–149 (1910).

there is not the slightest formation of fog. Adurol, the halogen-substituted product of hydroquinone, behaves just like the latter; but no increase of sensitiveness is to be noted when the plate is bathed in pyrogallol, metol, gallic acid or iron vitriol. On the other hand, it seems as though these substances behave like hydroquinone if the plates are left in the solutions for a longer time. An effect is obtained with pyrogallol by allowing the emulsion to stand in an alcoholic pyrogallol solution for several hours. Exactly the same thing happens with narcotine, in regard to which von Hübl[1] also established that its action as a sensitizer only appears after a long time."

This again is exactly what should happen provided we supplement the theory of sensitizers by the very probable assumption that some substances take longer than others to diffuse into, or be adsorbed by, the silver bromide grain. Lüppo-Cramer considers these results as fatal to the theory of sensitizers because "the increase in sensitiveness caused by the sensitizers occurs when the sensitizer has been in contact with the unexposed silver bromide for a greater or lesser time but has been removed completely from the film." The whole difficulty lies in the last half a dozen words. Lüppo-Cramer believes that the sensitizer has been removed completely from the film while most people doubt it.

The following quotation from Sheppard and Mees[2] seems to have a bearing on this point: "Lumière and Seyewetz have shown the tenacity with which this 'hypo' is retained. A parallel experiment with potassium bromide showed that the film retained sufficient bromide after five minutes' washing to influence considerably the *subsequent development*. However, increased washing only slightly affected the result with thiosulphate. Experiments on the characteristic curve showed that it was impossible to wash out the hypo completely. Treatment with hypo destroyers lessened the effect partially, but not entirely. It appears

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[1] Die Collodiumemulsion, 35, 52.

[2] "The Theory of the Photographic Process," 135 (1907).

probable that the thiosulphate is strongly absorbed by the silver bromide, possibly forming to some extent a solid solution, or traces of a solid double thiosulphate.

In another place Sheppard and Mees[1] point out that "freshly precipitated silver bromide treated with bichromate or chromic acid takes a yellow coloration, which is not removed by long washing." Since the results obtained by Lüppo-Cramer are exactly those which would be obtained in case the sensitizers were not washed out of the silver bromide and since Lüppo-Cramer offers no proof that he did wash the sensitizers out completely, the simplest assumption is that they were not removed completely. This assumption has the further advantage of expediency because otherwise we are left without any explanation of the phenomena since Lüppo-Cramer offers none.

Lüppo-Cramer is even less fortunate in his statement that "ammonia, hydroquinone, the ready mixed developers, and the bromine absorbers decrease the sensitiveness of silver to light when they are present during the exposure." It did not seem possible that bathing a plate in a metol solution should reduce the sensitiveness to one-half and we therefore repeated the experiment. Instead of decreasing the sensitiveness, this treatment increases the sensitiveness to such an extent that Lüppo-Cramer evidently over-exposed his plates badly. I had suspected this from the start;[2] but it was rather a comfort to have it confirmed.

Lüppo-Cramer makes a good deal of the fact that an intimate mixture of silver chloride and silver citrate is blackened by light a good deal more rapidly than either one alone. From the point of view of the Grotthuss theory, this is precisely what should happen. The citrate is a depolarizer for chlorine. We have had analogous cases before. Ferric chloride is not readily decomposed by light but ferric citrate is.

While these experiments of Lüppo-Cramer are just what

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[1] "The Theory of the Photographic Process," 238 (1907).

[2] Bancroft: Jour. Phys. Chem., **14**, 150 (1910).

one would have predicted, this is not at all the case in the experiment[1] with nitrite solutions and silver chloride. Lüppo-Cramer found that precipitated silver chloride or a silver chloride gelatine plate blackened less rapidly when immersed in a five percent solution than when immersed in pure water. On the other hand, a sensitizing action was obtained when a silver chloride plate was bathed in a nitrite solution and then dried. With the dried plate the concentration of the nitrite was high and its sensitizing action correspondingly great. That would not account for a retarding effect of the five percent solution. Since the retarding action does not occur to any great extent when the silver chloride plates are merely moistened with the nitrite solution, Lüppo-Cramer attributes the difference in result to the difference in the absolute amount of the solution, though he does not explain why this should produce such a result. We do know cases of this sort. If filter paper is moistened with a potassium iodide solution, a small current will set free visible amounts of iodine while this will not happen if the electrodes are placed in a beaker of solution. The reason for this is that the iodine dissolves in the large mass of the iodide solution, while the diffusion is so slow in the pores of the filter paper that there is a local excess of iodine. This cannot be the explanation of Lüppo-Cramer's experiment because we should not then get a sensitizing action with the so-called dried plate containing the high concentration of nitrite. If we bar diffusion phenomena, it seems quite impossible for the absolute mass of the solution to have an effect if the conditions at the surface of the silver chloride layer are the same in both experiments. I see only one way in which these conditions could vary and that is that the nitrite solution absorbs certain rays which are active in changing silver chloride. If this proves to be the case, the difficulties disappear, because the experiments are not comparable if the intensity and quality of the lights also varied.

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[1] Lüppo-Cramer: Jour. Phys. Chem., 14, 149 (1910).

The sensitiveness[1] of different silver bromide emulsions to the solar spectrum is quite in harmony with the view that ripening consists in a change in the amount of gelatine and water in the silver bromide grains. There is always a maximum sensitiveness for silver bromide gelatine about wave-lengths 420–460, regardless whether "the bromide is precipitated hot or cold, whether the emulsion is boiled or not boiled, digested or not digested. Boiling, digesting or treating silver bromide gelatine with ammonia, has the effect only of increasing the sensitiveness for the other colors, violet, ultraviolet, green, and red, the increase being less for the less refrangible rays." Of course we might have different modifications of silver bromide in gelatine, each with the maximum absorption at the same place; but it is not very probable and it certainly is not the simplest assumption. With increasing opacity we get a broadening of the absorption band, which is what one would expect. The differences between a long exposure and a short exposure are also qualitatively what they should be. With a very short exposure, we get only an effect at the point of maximum sensitiveness whereas a longer exposure gives us a developable effect due to the less active rays.

When silver bromide and silver iodide emulsions are mixed together or silver chloride and silver iodide emulsions, we should expect to recognize an effect due to each salt, which is just what happens. If the mixed emulsions are ripened or if the two salts are precipitated together, we should expect to get results approximating equilibrium conditions whatever they might be. Now Küster[2] has shown that silver chloride and silver bromide form a continuous series of solid solutions. Consequently this pair of salts would show a double maximum if mixed after precipitation and a single maximum if precipitated together or if ripened together after having been mixed. Unfortunately, the cases cited by

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[1] Vogel, Eder: Jour. Phys. Chem., **14**, 228–236 (1910).

[2] Zeit. anorg. Chem., **19**, 81 (1899); **23**, 25 (1900).

Eder[1] do not include this particular pair; but the results given by him are just what they should be if we assume that silver iodide forms a continuous series of solid solutions with silver chloride and with silver bromide. If this is true, we can go one step further. If silver chloride and silver iodide are precipitated together in varying proportions, the position of maximum sensitiveness can be made to shift continuously from the position corresponding to silver chloride to the one corresponding to silver iodide. The assumption of a continuous series of solid solutions between silver bromide and silver iodide accounts for the peculiarities in the behavior of brom-iodide plates,[2] whereas if we assume the existence of a double salt as Eder does, we should then have silver bromide plus double salt in the emulsion and we should not get the continuous variation in properties which we seem to have. If silver iodide formed a double salt with silver bromide, it would be possible to sensitize the excess of silver bromide with dyes such as eosine, whereas we find[3] that "brom-iodide emulsions with more than two percent iodide are much less readily sensitized than pure silver bromide emulsions. It is practicable, however, to sensitize emulsions containing up to five percent of silver iodide." The fact that silver bromide and silver iodide affect silver chloride in the same way[4] is another reason for believing that silver iodide and silver chloride form a continuous series of solid solutions just as silver bromide and silver chloride do. I must admit, however, that I do not see why the addition of potassium iodide to the developer should have a beneficial effect on ultraviolet plates.[5] As this may be a question of development, we can ignore this difficulty for the present.

There are some points about staining plates with optical sensitizers which call for more experiments. It seems as

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[1] Jour. Phys. Chem., 14, 232 (1910).

[2] Eder: Jour. Phys. Chem., 14, 79–82 (1910).

[3] Eder: Ibid., 14, 240 (1910).

[4] Eder: Ibid., 14, 82 (1910).

[5] Schumann: Jour. Phys. Chem., 14, 258 (1910).

though the best way to get the dye into the silver bromide grains would be to add it to the melted emulsion; but that is apparently not the case. Schumann[1] says that "finished plates, when bathed in an eosine solution are four times as sensitive to yellow green as is the case when the dye is added to the melted emulsion. The same thing is true for erythrosine and for the colors of the eosine and cyanine groups." If this is really a fact, there seems to be only one explanation possible, that the melted gelatine takes up more dye than the solid gelatine and that this dye cannot be washed out readily from the solidified gelatine. In other words, the difference in the two cases must be due to a screening action of the dye in the gelatine, though, in that case, it is surprising that neither Schumann nor Eder should have given this explanation.

The theory that the silver bromide grains in a dry plate consist of silver bromide, gelatine and water in varying amounts is enough to account for the effect of developers on the exposed and unexposed plates.[2] We also get differences between silver bromide with one content of water and silver bromide with another water content, as is shown by Schaum's experiments on silver bromide containing no binder.[3]

We have now merely to consider the question of the medium in which the silver bromide is emulsified.[4] The medium can act in two ways, as an emulsifier and as a sensitizer. Gelatine is one of the best of the protecting colloids[5] and it is partly to this that it owes its superiority over caseine, gum arabic, dextrine, starch, etc. Collodion has high emulsifying powers; but it is not a sensitizer and therefore collodion plates are not as sensitive as the best dry plates. Schumann's

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[1] Jour. Phys. Chem., 14, 241 (1910).

[2] Lüppo-Cramer, Schaum: Jour. Phys. Chem., 14, 119, 243–248 (1910).

[3] Schaum: Ibid., 14, 247 (1910).

[4] Eder, Lüppo-Cramer, Lobry de Bruyn, Schloemann, Cooper and Nuttall, Schumann: Jour. Phys. Chem., 14, 12, 19, 20, 26, 69, 113, 202, 204–209, 211–227, 252–254 (1910).

[5] Freundlich: Kapillarchemie, 451 (1909).

experiments[1] with ultra-violet plates are conclusive proof that gelatine acts as a sensitizer and I cannot see that Lüppo-Cramer's[2] experiment with a gelatine film superposed on a collodion plate is of any value. "Collodion plates were washed thoroughly with water, were then covered with a film of a one percent gelatine solution, and were exposed with a check-plate. When the plates were developed, the one covered with gelatine developed somewhat more slowly than the other, but when allowance was made for this it was found that the gelatine layer had not increased the sensitiveness in any way." Since a sensitizer must be incorporated in the silver bromide grain to work, and since such substances as pyrogallol and metol are only adsorbed slowly[3] it is not surprising that no effect was obtained with a superposed film of gelatine.

In some ways, agar-agar is more promising than gelatine. It has a much higher jellying power.[4] "The viscosity of agar is much greater than that of gelatine with the same percentage of solid. We have estimated that a solution of gelatine of definite strength is about as 'thick' as a solution of agar containing 1/8 percent of the amount present, this agreeing with the figures given by Stanford."

"A solution of 3 percent is difficult to use, as it is too thick. We find a 1 percent solution is most convenient, though a 2 percent solution is quite easily worked. A 1 percent solution is about as thick as an 8 percent solution of gelatine. If two emulsions contain the same amounts of chemicals, except that the medium in the one is gelatine and in the other is agar, and if the solutions are of the same 'thickness,' then the amount of agar will be one-eighth the amount of gelatine; in coating a plate or paper with these solutions and drying, one will get the same amount of silver per square foot, but only one-eighth the amount of medium

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[1] Jour. Phys. Chem., 14, 252 (1910).

[2] Ibid., 14, 145 (1910).

[3] Lüppo-Cramer: Jour. Phys. Chem., 14, 130 (1910).

[4] Cooper and Nuttall: Jour. Phys. Chem., 14, 215, 216 (1910).

when using agar. In the case of paper this would not matter so much perhaps but with plates it means that the pellicle will be extremely thin. It will be of great interest to ascertain what influence this has on the sensitiveness of the emulsion and on the development. If the pellicle is so much thinner, the light will be able to act more rapidly on the sensitive salt and should give increased rapidity. One would expect that in development, the developer would penetrate more rapidly and therefore develop more energetically; on that account also less exposure should suffice.[1] In that case, one should be able to obtain plates of extreme rapidity, great latitude, and with a fine grain."

As yet no agar plates have been made which are anything like as fast as the best gelatine plates; but we do not know whether this is because agar is a less effective sensitizer than gelatine or because the possibilities of the agar plate have not yet been realized experimentally. For that matter, there is no reason to suppose that the last word has been said in regard to fast gelatine plates. If a suitable depolarizer is incorporated with the silver bromide grain and if a suitable developer is used, there seems to be no *a priori* reason why we should not have an infinitely fast plate with as fine a grain as one pleases. It is possible that gelatine is the ideal protecting colloid for silver bromide, though I doubt it; but it certainly is not the ideal sensitizer. Instead of trying to combine the two properties of the protective colloid and the sensitizer in one substance, it will be more rational to add the ideal sensitizer, when found, to gelatine or agar or whatever may prove to be the best, protecting colloid. By working along these lines, with a clear understanding of the factors on which sensitiveness depends, it seems to me quite probable that photographic plates can be made which will be enormously superior to anything which can now be obtained.

The general results of this paper may be summed up as follows:

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[1] [This conclusion seems to be based on faulty reasoning. W. D. B.]

1. The silver bromide grain is a complex of silver bromide, gelatine and water.
2. The process of ripening consists in changing the composition of the silver bromide grain towards an unknown, optimum concentration.
3. There is no necessary connection between sensitiveness and coarseness of grain.
4. Chemical and optical sensitizers are depolarizers.
5. Gelatine acts as an emulsifying agent and as a sensitizer, whereas collodion apparently acts only as an emulsifying agent.
6. The peptonization of silver bromide is merely a particular case of the general problem of the peptonization of any precipitate.
7. The peculiarities of mixtures of silver chloride, silver bromide and silver iodide can all be explained on the assumption that each of these salts can form a continuous series of solid solutions with either of the two. This is known to be the case for silver chloride and silver bromide.
8. It seems theoretically possible to make an almost infinitely fast plate having a very fine grain.

Cornell University,
March, 1910