STUDIES ON THE DISPERSOIDAL SYNTHESIS OF GOLD BY MEANS OF ALKALINE FORMALDEHYDE SOLUTIONS. I.(1)

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Preface. In 1922 I carried out a systematic and detailed investigation on obtaining of dispersoidal solutions of gold by means of alkaline (KOH and K_2CO_3) solutions of formaldehyde. I used, in this investigation, beakers made of *ordinary* laboratory glass, which are used in other Departments of our Institute for chemical work; the distilled water and the reagents were also of *ordinary* purity, and not of extra purity.

By applying also to gold, the chief principles of my theory of dispersoidal synthesis, the correctness of which was verified by me almost a quarter of a century ago on more than a hundred substances and by way of thousands of experiments, I arrived in 1922 at the following conclusion: *The dispersoidal synthesis of gold by means of alkaline formaldehyde solutions, carried out by using ordinary distilled water and reagents of ordinary purity (not of extra purity),—provided that it be carried out according to the general principles of my theory of dispersoidal synthesis, —is accomplished as easily, and is as simple and readily reproducible as is for instance the "tannin method" of Wo Ostwald.*(3)

It is evident to every dispersoidologist that these experimental results stand in an extremely sharp contradiction to the experiments of R. Zsigmondy and others.

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(1) Translated from Russian by Mrs. P. P. von Weimarn.

(2) Compare P.P. von Weimarn, "Contributions to the Dispersoidology of Gold," *Reports of the Imperial Industrial Research Institute of Osaka*, **9** (1928), No. 7, 64. For the sake of brevity, in future references to this paper, it will be designated as W_1.

(3) Wo. Ostwald, "Kleines Praktikum der Kolloidchemie," 6 ed. (1926). Theodor Steinkopff, Dresden.

Therefore, previously to repeating my experiments with extra pure distilled water and extra pure reagents, I confined myself in 1923(1) to the publication of some quantitative data of only those experiments in which the extremely high stability of red dispersoidal gold solutions was caused by dispersoidal parasitism at the expense of the products of the resinification of the formoses (Hoppe-Seyler classifies these substances with humous substances, "Humine"; I designated them by the term "H-Dispersoid."

My other experiments,(2) in which the influence of H-Dispersoid cannot even be supposed to exist, are described very briefly thus:

> "Ebenso kann man *rote* dispersoide Lösungen erhalten, indem man sie bloss 5 bis 10 Minuten lang sieden lässt (aber auch bei Zimmertemperatur kann man *nicht weniger beständige rote* dispersoide Lösungen erhalten); nur wären dabei verschiedene Konzentrationen des Formaldehyds oder des KOH anzuwenden, als die in Tabelle 1 angegebenen."(3)

Since 1922(4) I have repeated my experiments of that year with *extra pure* distilled water and *extra pure* reagents. I used in these experiments beakers made not only of different sorts of glass, but also those made of gold and of platinum(5) (all beakers were cylindrical).

The results of my repeated experimenting have only confirmed those obtained in 1922; the influence of the "purity" of the distilled water and of the reagents, manifested itself only in the degree of concentration of the red dispersoidal gold solutions which is obtainable by way of evaporating the water. Other conditions being equal, the higher the degree of purity, the stronger is the concentration which, by the evaporation of the dispersoidal gold solutions, can be reached without any change in the colour of these solutions from the excellent red, noted before, to violet or blue.

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(1) P.P. von Weimarn, *Kolloid-Z.*, **33** (1923), 74 & 242; **36** (1925), 1.

(2) As is known, R. Zsigmondy in his book "Das kolloide Gold" submitted my work to a sharp criticism; for my reply see *Kolloid-Z.*, **39** (1926), 278.

(3) P.P. von Weimarn, *Kolloid-Z.*, **33** (1923), 79. Compare ibid., p. 242 (§ 2) in which are indicated in one series of experiments, the limits of the concentrations of the alkaline formaldehyde solutions, that I have used.

(4) P.P. von Weimarn, *Kolloid-Z.*, **39** (1926), 281 (conclusive sentence).

(5) In my experiments I used water distilled in four manners: 1. Ordinary distilled water. 2. Water 1, redistilled through a condenser made of resistance Jena glass. 3. Water 2, distilled once more through a condenser made of platinum or gold. 4. Water 3, distilled through a platinum condenser, was redistilled again through a gold condenser. KOH and K_2CO_3, $AuCl_3HCl\,4H_2O$ and formaldehyde used were of several Japanese firms as well as of the firms Merck and Kahlbaum, *extra pure*. Moreover, I used formaldehyde of Japanese firms and that of Kahlbaum, redistilling them once more. Beakers were employed of three kinds of Japanese glass, and also those of Jena glass and quartz.

I. Essential Points of Dispersoidal Synthesis.

§ 1. Precipitation of sparingly soluble substances by double decomposition reactions.⁽¹⁾ For example: $\underset{2\,C}{Ba(CNS)_2} + \underset{2\,C}{MnSO_4} \rightleftharpoons \underset{C}{BaSO_4} + \underset{C}{Mn(CNS)_2}$, with water as the dispersion medium.

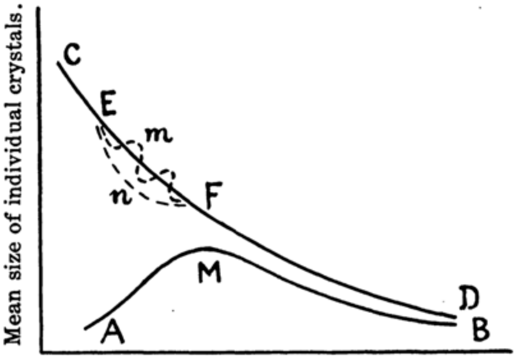

Fig. 1.

If we limit ourselves to knowing only the *qualitative* (or semi-quantitative) direction of precipitation processes, then the expression for the precipitation forms' coefficient is very simple: $N=N_e/J=(C-L)/L$; when L is extremely small—and this is usually the case in dispersoidal synthesis—then the *qualitative* determination of the change, taking place, in accordance with the concentration of the reacting solutions and solubilities, in the mean size of the *individual* crystals of the precipitating substance, may be expressed thus: $N=C/L$.⁽²⁾

When studying only one definite case of precipitation, L may be assumed as of constant value $1/k$, and then: $N=kC$. With the increase in N or in the value C, to which N is proportional, the mean size of the *individual* crystals of the precipitating substance passes at first through a maximum (curve AMB in Fig. 1); after the lapse of some time the maximum disappears⁽³⁾ and the precipitation curve assumes the form CEFD (Fig. 1). For dispersoidal synthesis, it is of importance to take into con-

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(1) For more details, on the same subject, see my papers of previous years in *Kolloid-Z.*, my paper in *Chemical Reviews*, **2** (1925), 217, and a detailed paper in the book " Colloid Chemistry, Theoretical and Applied " edited by J. Alexander, (1926), 27. The translation of this paper into the Japanese language has been recently done by my Assistant, Dr. E. Iwase, and is edited as a separate volume by The Maruzen Co.

(2) It is clear that the expression C/L shows the *qualitative* direction of precipitation processes *only when* of all the variables, C and L are those predominating. See P. P. von Weimarn, " Grundzüge der Dispersoidchemie," (1911), 39. Therefore it is a grave mistake, when comparing two precipitation processes, to change C and L without preserving in both processes, equality or approximate equality with regard to other variables in their influence upon the precipitation. For a more exact expression of N and exact equations of precipitation curves for certain cases of precipitation, see my abovementioned paper in the book edited by J. Alexander.

(3) This appears from practical standpoints only; in theory the maximum does not disappear, but becomes strongly shifted to the left. See P.P. von Weimarn, " Die Allgemeinheit des Kolloidzustandes," (1925), 159, Theodor Steinkopff, Dresden.

sideration the fact that the precipitation curve possesses at first a maximum.

The branch AM of the precipitation curve AMB, under the influence of certain corresponding variables, may be forced to a very slow approach towards the branch CEF of the curve CEFD; in the region of concentration corresponding to the branch AM, the growth of the individual crystals proceeds not only at the expense of the truly dissolved substance, but also by means of "aggregation crystallisation" (Aggregation-Kristallisation) and "contact recrystallisation"(1) (Berührungsumkristallisation).

When the crystallisation is accompanied by processes of desolvation which go at a slower rate than the diffusion process, (for instance the dehydration of molecules of $SrSO_4xH_2O \rightarrow SrSO_4$, etc.) then the precipitation curve retains the maximum for a longer time.(2)

If the precipitation by a double decomposition reaction be accomplished not in pure water, but in an aqueous solution of any substance taken in a definite concentration, (e.g. agar-agar,(3) aniline dyes,(4) or of a truly soluble substance which is strongly adsorbed(5) by the surfaces of the precipitating crystals) then, owing to the contamination of the surfaces of the precipitating crystals, the course of the aggregation crystallisation and contact recrystallisation is hindered; as the result of this, the precipitation curve keeps its maximum. These influences, e.g. account for the successful dispersoidal synthesis of substances of small solubility, realised in water in presence of gelatin by C. A. Lobry de Bruyn,(6) and by others.

In the domain of semi-stable supersaturated solutions, very many variables (e.g. dust in water and from dissolved salts, shaking, sometimes even illumination, etc.) affect the *spontaneous* crystallisation, which becomes *forced*. If the influence of these variables is not removed (and it is sometimes very difficult to remove them) the part EF of the curve CEFD, corresponding to the semi-stable supersaturations, assumes the form either of the dotted line EnF or the dotted wavy line EmF; generally speaking, it assumes the form deviating from the smooth part EF of the curve CEFD.

After performing a great number of experiments, always trying to

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(1) P.P. von Weimarn, e.g. "Grundzüge der Dispersoidchemie," (1911), 27 & 60.

(2) P.P. von Weimarn, *Z. physik. Chem.*, **76** (1911), 215.

(3) P.P. von Weimarn, *J. Russ. Chem. Soc.*, **41** (1909), 322 & 728; *Kolloid-Z.*, **6** (1910), 179. When the concentration of agar-agar is kept constant for every concentration of the reacting solutions, then it is clear that the utmost influence of the agar-agar will manifest itself when the concentrations of the reacting solutions are weak.

(4) P.P. von Weimarn, "Grundzüge der Dispersoidchemie," (1911), 97.

(5) P.P. von Weimarn, "Die Allgemeinheit des Kolloidzustandes," 184–190. "Theory of the Colloid State of Matter" 62 (Fig. 8) in "Colloid Chemistry, Theoretical and Applied," edited by J. Alexander (1926). The Chemical Catalog Co., New York.

(6) C.A. Lobry de Bruyn, *Z. physik. Chem.*, **29** (1898), 562.

eliminate as much as possible the influence of these variables, one becomes convinced of their fortuitous character, and of the fact that after their complete elimination, the precipitation curve would possess the smooth contour CEFD.

When the precipitating substance forms a suspension or a dispersoidal solution, then the individual micro- or ultramicrocrystals at once, or after the lapse of some time, under the influence of variables which are not present in the expression $N_e = JC/L$ may form aggregates (aggregate particles). If such an aggregation does not go too far, the curves, which express the dependence upon concentration of the mean size of particles of a suspension or despersoidal solution, will possess the same form as the curve CEFD in Fig. 1.(1) In the cases of a considerable aggregation of the individual micro- and ultramicrocrystals, these curves (with as coordinates: the mean size of particles, concentration C) can have rather varied forms,(2) particularly when the intensity of the aggregative influences, with the progressive change in concentrations, decreases and increases alternately.

§ 2. **Precipitation of sparingly soluble substances, through the decomposition of a compound by a dispersion medium (solventolysis).**(3) For instance:

$$AlCl_3 + xH_2O = Al(OH)_3 + 3HCl + (x-3)H_2O\ ;^{(4)}$$

$$AlO_2Na + xH_2O = Al(OH)_3 + NaOH + (x-2)H_2O.$$

I introduced the term "Precipitation forms' coefficient" as a substitute for the rate of formation(5) of a solid phase, which rate in many cases of dispersoidal synthesis is practically unmeasurable, and it is evident that in the case of the formation of a solid phase by hydrolysis, owing to the increase in the velocity of hydrolysis with dilution,(6) this coefficient, for the purposes of *qualitative* investigation of precipitation processes will have to be expressed thus: $N = (C_w - c_w)/L = C_{aw}/L$, where c_w stands for the dilution, beyond which the hydrolysis does not practically go; and C_w is the total dilution of the given solution; thus C_{aw} is the active dilution; when it is possible to assume L as constant, then $N = k_1 C_{aw}$ · For solutions sufficiently diluted, N may be expressed thus: $N = k_2/CL = k_3/C$, where C is the

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(1) P.P. von Weimarn and S. Morishima, see figs. 10–13 (238–239), for the disperse systems of selenium, *Chem. Reviews*, **2** (1925).

(2) P. P. von Weimarn, *Kolloid-Z.*, **36** (1925), 8–9 (Fig. 2); *Chem. Reviews*, **2** (1925), 225 (Scheme C).

(3) Compare P.P. von Weimarn, *Kolloid-Z.*, **33** (1923), 230; *Chem. Reviews*, **2** (1925), 227.

(4) In reality the hydrolysis processes are more complicated and are accompanied by the formation of intermediate compounds, see e.g. J. Matula, "Allgemeine Chemie," (1923), 162.

(5) For the formulation of the precipitation law, see *J. Russ. Chem. Soc.*, **38** (1906), 267. This formulation appeared in German in *Kolloid-Z.*, **43** (1927), 26.

(6) H.M. Goodwin, *Z. physik. Chem.*, **21** (1896) 1–15, especially pp. 11 & 15.

concentration of the hydrolysed substance previous to the beginning of the hydrolysis (in the cases analogous to the hydrolysis of $AlCl_3$, concentration C represents also the concentration of the product after the termination of the hydrolysis).

Therefore, the experimentally established fact (W. Bilz),(1) that in the formation of a solid phase by hydrolysis, the mean size of particles of the precipitating substance, decreases with the growing dilution, is not in contradiction to, but in full accord with, my theory of precipitation. That is, in the case of solventolysis also, after the lapse of some time from its commencement, with the increase of N, the mean size of the individual crystals decreases, i.e. the precipitation curve has the shape of the curve CEFD (Fig. 1).(2)

The producing of AgI or $BaSO_4$ dispersoidal solutions, in an alcohol-aqueous medium from their double compounds, AgIxKI or $BaSO_4xMnSO_4$, represents also an example of solventolysis. *And in general, cases of solventolysis are very often met with in dispersoidal synthesis.*(3)

II. Several Instances of the Obtaining of Red Dispersoidal Gold Solutions by means of Alkaline Solutions of Formaldehyde.(4)

§ 1. **General.** For acquiring a clear idea of the process of the reduction of gold by alkaline formaldehyde solutions, it is essential to remember the reactions:

$$\text{I.}\quad AuCl_3+3H_2O \rightleftarrows Au(OH)_3+3HCl;$$

$$\text{II.}\quad AuO_2K+2H_2O \rightleftarrows Au(OH)_3+KOH.^{(5)}$$

Further it is advisable to recall to mind the existence of aurous hydroxide, AuOH, producing in water a dispersoidal solution of an indigo-blue colour; the latter fact and Reaction II are most important for experimentation by the formaldehyde method.

When we experiment upon a stable, weak, but highly disperse AuOH solution, the reduction, in the case of an insufficient quantity of the

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(1) Quoted from Th. Svedberg's "The Formation of Colloids," (1921), 105, London.

(2) It is clear that in the case of complete solventolysis, when the concentration of the solutions approach the saturation concentration of the precipitating solid substance, the crystallisation goes on from the more or less stable supersaturated solutions, i.e. in this case, the expression $N=(C-L)/L$ must be assumed in which C is the concentration of the substance being precipitated. In substances which are actually sparingly soluble, the concentration corresponding to their solubility is so vanishingly weak, that in practice such infinitely diluted solutions are not used.

(3) Compare P.P. von Weimarn, *Chem. Reviews*, **2** (1925), 227.

(4) Compare P.P. von Weimarn, Paper W_1. A more detailed exposition is given in a paper which is in preparation, "Contributions to the Dispersoidology of Gold II." *Reports of the Imperial Industrial Research Institute of Osaka.* In future references this paper will be designated by W_2.

(5) What is said in Footnote (4) in page 39 is also applicable to these cases.

reducing agent, proceeds very protractedly, but in spite of this, a beautiful red dispersoidal gold solution is obtained. It is evident that in a dispersoidal AuOH solution, of coarser dispersity, but at the same time of greater concentration (possessing a greater number of particles in unit volume) the addition of larger quantities of reducing agent, proportionally to the increased concentration, will at first accelerate the reduction.

This happens because the molecules of the reducing agent meet a greater number of AuOH particles. But the particles being coarser, the resulting dispersoidal gold solution is of a coarser dispersity, and the transformation of AuOH particles totally into pure gold particles is more protracted than it is in weaker dispersoidal AuOH solutions with highly disperse particles. In general, the coarse dispersity of AuOH particles, acts in greatly hindering their transformation into pure gold, and AuOH can, for an extremely long time, remain embodied within the ultramicrocrystals (or their aggregates) of gold.

§ 2. Several instances of the obtaining of red dispersoidal gold solutions, the stability of which is caused by the presence of small quantities of unreduced gold compounds.(1) **§ 2a. Formaldehyde in a KOH-solution.** $A_1 \cdot 500\ H_2O\ (20°C.) \leftarrow 10\ AuCl_3HCl4H_2O\ (0.1\%) \leftarrow 0.7–1.4\ F^{10}_{0.2KOH}$(2) The numbers preceding the formulae indicate the number of c. c.

The reagents (of room temperature) are poured rapidly, in succession, and the whole quantity of each, all at once,(3) into water which meanwhile is being vigorously stirred with a thermometer.

When 0.7 c.c. $F^{10}_{0.2KOH}$ are added, although the reaction proceeds instantaneously i.e. on the surface of contact, the reduction is not complete, and an intensely indigo-blue liquid is obtained, which is perfectly transparent and has no opalescence. When allowed to remain at room tem-

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(1) On red dispersoidal gold solutions, the stability of which, over a period of six years, without change of the red colour into violet, is accounted for by the presence of a small quantity of „H-Dispersoid," see *Kolloid-Z.*, **33** (1923), 78. The repetition of these experiments with extra pure reagents has also fully confirmed the results obtained by me in 1922, with reagents of ordinary purity.

(2) The beakers of glass, gold and platinum used were of 1 litre capacity; the beaker of quartz was of 300 c.c. Reagents $F^{10}_{0.2\,KOH}$, $F^{10}_{0.1\,KOH}$, $F^{5}_{0.2\,KOH}$ etc. are concise designations for the following solutions. To 90 c.c. 0.2 norm. KOH solution, is added – to form 100 c.c. – a concentrated (about 35% by weight) formaldehyde solution; to 90 c.c. 0.1 norm. KOH-solution is added – to form 100 c.c. – the same formaldehyde solution; to 95 c.c. 0.2 norm. KOH-solution is added – to form 100 c.c. – the same formaldehyde solution, etc.

(3) I measured the reagent F in conical vessels of 5 c.c. capacity, graduated in half c.c. It must be pointed out that a part of the reagent (in my experiments amounting to about 0.2 c.c. for 3 c.c. of the reagent) adheres to the walls of the vessel. If in the producing of an intensely indigo-blue dispersoidal solution it is desirable to obtain always the same *quantitative* results, the quantity of the reagent $F^{10}_{0.2\,KOH}$ added, must be varied a little, in dependence upon the amount of water and upon the acidity of the commercial chloride of gold.

perature, the blue colour of this dispersoidal solution, passes through violet, to red (50–46–42–38–33–29); red 33 appears(1) after the lapse of 24 hours, and red between 33 and 29, after 48 hours. These red dispersoidal solutions are very stable. If the indigo-blue liquid, just after its being obtained, be heated over a powerful Teklu burner, the colour, after 10 minutes' heating, at the beginning of boiling, becomes red 25, and after 10 minutes' boiling, a beautiful red appears, with an orange nuance, 25–21, without any opalescence. By the addition of more than 0.7 c.c. of $F^{10}_{0.2KOH}$, at once a violet or reddish-violet dispersoidal solution is obtained. During the transition of colour of the dispersoidal solution into pure red, the intensity of colouring falls off sharply.

The experiments, carried out with ordinary distilled water, in beakers of every kind of ordinary laboratory glass, (made in Japan) and with reagents of different preparation, of ordinary purity, as well as of extra purity, have proved always successful.

By means of boiling off, this red dispersoidal solution may be concentrated to 1/3 of its original volume, without change in colour and without the appearance of opalescence. A further concentration is also practicable; but when reagents of only ordinary purity are used (this applies chiefly to all commercial solutions of formaldehyde)(2) the dispersoidal solutions which have so far preserved their beautiful red colouring, on cooling become blue (there is an increase in adsorption on cooling, owing to the decrease of solubility of the adsorbing coagulants); when after being sufficiently concentrated (e.g. to 120–100 c.c.) the hot solution with its beautiful red colour (possessing an orange nuance) is being poured in a thin stream into another beaker, the stream itself becomes at once bluish.

The concentration of the red dispersoidal gold solution, without any change in its red colour, by means of boiling off to 1/6 of the initial volume (80–85 c.c.) is accomplished always with success when redistilled formaldehyde solution is used; the use in this case of water redistilled through a condenser of Jena glass is only to be commended.

The red dispersoidal solutions, concentrated to 1/3 of their initial volume, may be mixed, without the colour's changing into blue, with concentrated (extra pure, freshly distilled) ammonia; under the ammonia test, the surface of separation remains red during e.g. two hours. However, these red dispersoidal solutions still contain traces of unre-

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(1) According to the standards established by W. Ostwald, "Die Farbenfibel." 10 ed. (1924), 19.

(2) The bottles in which the formaldehyde solution is kept are not of a high quality, therefore after a long preservation in such bottles, the formaldehyde solutions, whether of Japanese or of German preparation, take up considerable quantity of coagulants.

duced gold compounds which may be revealed by means of the ammonia test; in order to minimize these, more of the diluted KOH-solution (without formaldehyde) should be added (see below).

I should like to point out especially that the concentrations, indicated in Experiment A_1, should in no wise be regarded as *fixed;* quite the contrary, there exist variations of concentrations which are difficult to enumerate, with which red gold solutions are obtained and may be always reproduced. It is only necessary, that either the dispersoidal AuOH solution, *produced instantaneously*, should be stable, or that the reduction reaction of this solution into gold at first goes as rapidly as possible, whilst the AuOH is still in statu nascendi.⁽¹⁾

For instance, by working with the following concentrations, there are obtained after 5–10 minutes' boiling, dispersoidal gold solutions which are also coloured a beautiful red with an orange tinge.

$$A_2 \cdot 500\ H_2O(20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.1\%) \leftarrow 1.4\ F^{5}_{0.2\,KOH};$$

$$A_3 \cdot 500\ H_2O(20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.1\%) \leftarrow 1.4\ F^{5}_{0.5\,KOH};$$

$$A_4 \cdot 500\ H_2O(20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.1\%) \leftarrow 1\text{-}1.4\ F^{10}_{0.1\,KOH}.$$

In the instance A_4 (with the presence of a larger quantity of unreduced gold compounds) by boiling, it is possible to concentrate the dispersoidal solution, without change in its red colour, to 1/10 (50 c.c.) of the initial volume. Instead of pure reagent F there may of course be added its mixture with KOH-solution, e.g. $(0.75\ F^{10}_{0.2\,KOH} + 0.75\ KOH,\ 0.2$ norm.) etc.

All the above-mentioned solutions, after the dissolution of gold⁽²⁾ by the addition of 1/10 norm. KCN solution, leave behind a liquid as perfectly transparent and colourless as water (even in a layer of 11 cm.); the influence on the stability of H-Dispersoid, cannot be even supposed to exist, because in the presence of even small quantity of H-Dispersoid, after the dissolution of gold by KCN solutions, the liquid left behind is coloured yellow.

The diminution of the amount of formaldehyde and the fall in the concentration of KOH-solutions below certain limits, make it either totally impossible to obtain red dispersoidal gold solutions, or else to produce them only by chance. For instance, if we add to 500 c.c. distilled water (20°C.) e.g. 1 c.c. $F^{10}_{0.05\,KOH}$ there is obtained a blue liquid, which under boiling does not change to red; even after the addition $3\ F^{10}_{0.05\,KOH}$, either strongly opalescent red dispersoidal solutions are obtained, or violet ones;

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(1) For more details see Paper W_2.

(2) Compare Paper W_1. In this case one fails to obtain a liquid coloured pure orange, by the incomplete dissolution of gold by KCN-solutions; however, there may be obtained an orange-red coloured liquid, with orange predominating.

provided only the concentration of the commercial preparation of formaldehyde is normal (35%).

In order to avoid the long procedure of eliminating formaldehyde by boiling it off from red dispersoidal gold solutions, and to decrease the quantity of coagulants introduced if the formaldehyde solution is employed without redistillation, it is advisable to take as small a quantity as possible of reagent F, diluting it with a pure (*without formaldehyde*) solution of KOH (i.e. $xF+yKOH$, where $y>x$). The temperature of water may be of course also varied; I worked with the water of 20°C. and also with that of temperatures from 2.5°C. At low temperatures (below 20°C.) the colour of the dispersoidal solution at first tends to blue-violet, but after boiling, it changes to the beautiful red with an orange nuance, possessing no opalescence.(1)

The above-discussed dispersoidal solutions prove to be extremely stable; on the grounds of my experiments of 1922, I can say that dispersoidal solutions, obtained by the addition of 1 c. c. of $F^{10}_{0.2\,KOH}$ are stable for more than a year at least.

The obtaining at one time of large amounts of dispersoidal gold solutions with a beautiful red colour, of considerably higher concentration, may be carried out (see Footnote (3) in page 41), for instance, thus: $B_1 \cdot 500\ H_2O(20°C.) \leftarrow 60\ AuCl_3 \cdot HCl \cdot 4\ H_2O\ (0.1\%)$, or $10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.6\%) \leftarrow 3.5\ F^{10}_{0.2KOH}$, or better thus: $B_2 \cdot 500\ H_2O\ (20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O\ (0.6\%) \leftarrow (1.5\ F^{10}_{0.2\,KOH} + 2\ KOH,\ 0.2\ norm.)$ or $(2\ F^{10}_{0.2\,KOH} + 2\ KOH,\ 0.2\ norm.)$ etc. If we keep the solution B_1, for instance, at room temperature, then after the lapse of approximately 1 hr. 40 min., its dark-red colouring (claret-red), very intense initially, changes as by leaps into the beautiful red with an orange tinge without perceptible opalescence; in this transition of colour, its intensity falls off sharply. Heating to boiling, accelerates the rate of this change of colour; and in the case when the quantity of $F^{10}_{0.2\,KOH}$ taken is somewhat less than that indicated, the intensity of colour on heating, at first increases very strongly and the liquid becomes quite opaque; but on further heating, the intensity of colour suddenly falls off sharply, and a beautifully coloured red dispersoidal solution results which is perfectly transparent (in a layer of 11 cm.) and possesses no perceptible opalescence in diffused day light.

The reduction process, carried out according to B_2, proceeds quite

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(1) By pouring even extra pure reagents into *boiling* water, distilled even thrice, in spite of experimenting in a gold beaker, there are obtained strongly opalescent and even turbid dispersoidal solutions, and their red colouring changes to violet-red. Compare K. Hiege, *Z. anorg. Chem.*, **91** (1915), 148. When working with water of 20°–2.5°C., it may with success be used distilled ordinarily, as well as redistilled thrice. If it is desirable to concentrate as much as possible, by way of evaporation, the dispersoidal solution obtained, it suffices to use water redistilled once.

similarly to that of B_1; when to a portion of dispersoidal solution, cooled to room temperature, be added, after the fall of intensity in the colour, concentrated (extra pure) ammonia, (dispersoidal solution 2/3 + concentrated ammonia 1/3), the solution becomes at once blue; this is a proof, as it is also for the dispersoidal gold solutions obtained by the "phosphorus method," of the presence of certain quantities of unreduced gold compounds.(1) The quantity of these unreduced compounds may be minimized in various simple ways. If it is desirable to attain this rapidly, strongly diluted KOH-solutions, e.g. 0.02 norm., are poured as soon as the intensity of colouring has fallen, by small portions (in order not to stop boiling), into boiling mixture B_2; after the addition of only 50 c.c., the intensity of colour of the dispersoidal solution falls off somewhat, and a slight brown opalescence in reflected light appears; this solution may be mixed with concentrated ammonia and the mixture remains for a time red. The same is observed after the addition of 100–150 c.c. of a diluted KOH-solution. However, after the addition of 300 c.c. KOH-solution of 0.02 norm. (in certain experiments even of 200 c.c.) and after the reducing by boiling of the volume of the dispersoidal solution to 500 c.c., it becomes again extremely sensitive to ammonia; an immediate change of colour to violet and blue ensues, after the addition of ammonia to this solution.

Thus a minimum of sensitiveness to ammonia exists. It corresponds to the addition of about 150 c.c. of a diluted KOH-solution (more details are given in Paper W_2). The greater sensitiveness to ammonia, observed after the addition of 300 c.c. of a diluted KOH-solution, is accounted for by the increased activity, caused by the ammonia, of coagulants(2) which are present in the dispersoidal solution.

Previously to the addition of diluted KOH-solution, dispersoidal solutions B_1 and B_2 can be easily concentrated by way of boiling, to 1/5 of their original volume. Dispersoidal solutions of double concentration can be obtained at once by the addition to 500 c.c. water (20°C.) of 20 c.c. 0.6% $AuCl_3HCl4H_2O$, and by increasing correspondingly the quantities of mixture $F^{10}_{0.2KOH}$ and KOH solution of 0.2 norm.

Of course, beautiful red dispersoidal gold solutions may be also obtained by taking instead of 500 c.c., 1 litre of water and by doubling the quantities of the reagents. The use of a mechanical stirrer makes it possible to apply much larger volumes of water.

Thus, by my modification of the formaldehyde method, very large quantities of beautifully coloured red dispersoidal gold solutions may be obtained in a short time with ordinary distilled water and reagents of ordi-

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(1) See Paper W_1; more details will appear in Paper W_2.

(2) For more details see Paper W_2. In the presence of H-Dispersoid, when the eduction is complete, no coagulation is observed by the addition of ammonia, even when the content of KOH is great.

nary purity; these solutions, whether in the *minimal* contents of unreduced compounds of gold, or in other properties are not inferior to the dispersoidal gold solutions obtained by the prescript given by R. Zsigmondy; according to which they can be prepared only with extra pure distilled water and extra pure reagents; in spite of these precautions the obtaining of the dispersoidal gold solutions by this prescript is not always successful.(1)

The less the unreduced compounds of gold, contained in a dispersoidal gold solution the more is this solution sensitive to coagulants; therefore the dispersoidal solution containing a minimum of unreduced compounds, when very long preservation is desired, must be kept in bottles of resistant glass of high quality.

§ 2b. Formaldehyde in K_2CO_3-solution. For the understanding of this case, the following reactions for salts of iron and especially for those of silver, must be remembered: $2\,FeCl_3 + 3\,K_2CO_3 + 3\,H_2O = 2\,Fe(OH)_3 + 6\,KCl + 3\,CO_2$; $FeCO_3 + CO_2 + H_2O = Fe(HCO_3)_2$; $4\,FeCO_3 + 6\,H_2O + O_2 = 4\,Fe(OH)_3 + 4\,CO_2 \cdot 2\,AgNO_3 + K_2CO_3 = Ag_2CO_3 + 2\,KNO_3$; $Ag_2CO_3 + K_2CO_3 = Ag_2CO_3 \cdot K_2CO_3$; $Ag_2CO_3 \cdot K_2CO_3 + aH_2O = Ag_2CO_3 + K_2CO_3 + aH_2O$; $Ag_2CO_3 + H_2O + CO_2 = 2\,AgHCO_3$; $Ag_2CO_3 + (b+2)H_2O = 2\,AgOH + CO_2 + (b+1)H_2O$.

Similar reactions take place under suitable conditions, for gold salts also, and the possibility of a temporary formation of gold carbonate, gold bicarbonate and of double carbonates of gold and potassium,(2) must be kept in mind. It must also be especially emphasised that the rate of decomposition of "carbonates of gold" is influenced not only by the CO_2, which is in the water, but also by the oxygen from the air dissolved in water.

In order to obtain results, approaching those described in § 2a for formaldehyde solutions in KOH, the following is one of the ways recommended: $A'_1 \cdot 500\,H_2O\ (50°C.) \leftarrow 10\,AuCl_3HCl\,4\,H_2O\ (0.1\%) \rightarrow 1.5\,F^{10}_{0.2\,K_2CO_3}$; $B'_1 \cdot 500\,H_2O\ (50°C.) \leftarrow 10\,AuCl_3HCl\,4\,H_2O\ (0.6\%) \leftarrow 3.5\,F^{10}_{0.2K_2CO_3}$. On being heated to boiling and on further boiling, mixtures A'_1 and B'_1 behave very similarly to mixtures A_1 and B_1 in § 2a.

The completion of the reduction is achieved by the addition of a diluted K_2CO_3 solution (0.2 norm. is also possible), similarly to that described in § 2a. Reagent $F^{x}_{0.2\,K_2CO_3}$ is more sensitive than Reagent $F^{x}_{0.2\,KOH}$ to the decrease in the amount of formaldehyde. Under other conditions, equal to $F^{x}_{0.2\,KOH}$, turbid, red dispersoidal solutions are obtained, when only the quantity of formaldehyde in K_2CO_3 is somewhat decreased.

§ 3. On the degree of dispersity possessed by dispersoidal gold solutions, obtained by the author's modification of the formaldehyde method.(3)

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(1) With more details, in Paper W_2.

(2) I propose to devote a special paper to the transformation of "carbonates of gold" into gold.

(3) For more details see Paper W_2.

The mean size of particles of dispersoidal gold solutions, stands in direct dependence upon the mean size of particles of dispersoidal AuOH solutions, the transformation of which particles into gold, causes the appearance of dispersoidal gold solutions. If in the course of the reduction process, the aggregation of particles in a dispersoidal AuOH solution, has not proceeded too far, there exists between the mean size of particles of the dispersoidal gold solution and the dilution, the same dependence as this is in AuOH dispersoidal particles, i.e. with the increase in $N=k_1C_{aw}$ (see § 2, Chapter I) or in $N=k_3/C$ the mean size of particles decreases. Of course, a far-reaching aggregation of AuOH particles, alters completely this dependence.

By applying for the dispersoidal gold synthesis, the formaldehyde method modified by me, in the reduction carried out at low temperatures (approaching e.g. that of the room), amicroscopical dispersoidal gold solutions are very easily obtained; it is also possible to obtain dispersoidal gold solutions possessing any degree of dispersity, including of course those with the degree of dispersity obtained by Zsigmondy's prescript, which requires the use of extra pure water and extra pure reagents.

Conclusion.

In one of my papers(1) I have already directed attention to the fact that without a scrupulous mental analysis of the vast number of variables governing dispersoidal processes, one may easily go astray and approach the solution of the problem from a wrong angle.

When conditions are created according to my old theory of dispersoidal synthesis,—the observance of which conditions is necessary for its success,—then by using ordinary distilled water and reagents of ordinary purity, as the reader has already learned from the previous pages *it is possible, working by the formaldehyde method, to obtain easily dispersoidal gold solutions of a splendid red colour, which are always reproducible.*

I wish here also to thank once more Prof. Emer. Y. Osaka, for his kind hospitality which I enjoyed from 1922 to 1926, in his laboratory at the Kyoto Imperial University; in this laboratory were carried out the first ultramicroscopical investigations of the dispersoidal gold solutions, obtained by my modification of the formaldehyde method. The author takes it as his pleasant duty, to express here many cordial thanks to Mr. I. Shoji, President of the Imperial Industrial Research Institute of Osaka, for the opportunity kindly afforded him to repeat the experiments of 1922, with extra pure reagents and with very expensive distilling apparatus.

1922–1928 Dispersoidological Department of the
Imperial Industrial Research Institute of Osaka.

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(1) P.P. von Weimarn, *Journal of Chemical Education*, **3** (1926), 373.