VON WEIMARN'S PRECIPITATION
THEORY AND THE
FORMATION OF COLLOIDAL GOLD

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Referring to his law of corresponding states for the precipitation process von Weimarn(1) says: "Without any doubt my law of corresponding states for the crystallization process is truly a quantitative natural law." While this may be the case, Weiser(2) has

(1) Kolloidchem. Beihefte, 18, 55 (1923).

(2) "The Colloidal Salts", (1928).

pointed out that von Weimarn's formulation has been simplified to the point where its usefulness in certain cases may be open to question. Others(3) have likewise questioned the general conclusions and usefulness of von Weimarn's theory. This leads von Weimarn(4) to state: "Recently H.B. Weiser (See his book

(3) Buchner and Kalff: Rec. trav. chim., 39, 135 (1920); Bancroft: J. Phys. Chem., 24, 100 (1920); Freundlich: "Kapillarchemie," 631 (1922).

(4) Kolloid-Z., 53, 366 (1930).

"The Colloidal Salts") has repeated and still further extended the false view of the precipitation theory which has been credited to me. (Rept. Imp. Res. Inst. Osaka, 9, 107 (1928)) The theory which is criticized by the authors named, did not originate with me and I

yield with pleasure the honor of its discovery to one of the critics. Moreover, I have no time to clear up these misunderstandings specifically."

Von Weimarn's theory has been of such outstanding importance in pure and applied colloid science(5)
(5) Cf. Weiser and Moreland: J. Phys. Chem., 36, 1 (1932).

that no one can question its value. At the same time, it can do no harm to call attention to its limitations as a research tool. The recognition of such limitations in usefulness does not result from misunderstanding owing to incomplete knowledge, as von Weimarn seems to think. On the contrary, a broad comprehension of the applicability of the theory is essential to an understanding of its limitations.

In the following paragraphs the applicability and limitations of the von Weimarn theory will be considered briefly after which its inadequacy to predict results in certain instances will be illustrated by the case of the formation of colloidal gold by reduction.

Theoretical

Von Weimarn points out that precipitation from

solution takes place in two stages; the first in which the molecules in solution condense to crystalline nuclei; and the second which is concerned with the growth on the nuclei as a result of diffusion. The initial rate of precipitation $\underline{W}$ is expressed in von Weimarn's equation

$$\underline{W} = K \frac{\underline{Q} - \underline{L}}{\underline{L}} = K \frac{\underline{P}}{\underline{L}}$$

where $\underline{K}$ is a constant; $\underline{Q}$ the total concentration of the substance that is to be precipitated; $\underline{L}$ its solubility; $\underline{Q} - \underline{L} = \underline{P}$ the absolute supersaturation; and $\underline{P}/\underline{L}$ the percentage supersaturation.

The velocity of growth, $\underline{V}$, on nuclei is given by the Nernst-Noyes equation

$$\underline{V} = \frac{\underline{D}}{\underline{S}} \underline{O}(\underline{Q} - \underline{L})$$

where $\underline{D}$ is the diffusion coefficient; $\underline{S}$, the thickness of the adherent film; $\underline{O}$, the extent of surface; and $\underline{Q}$ and $\underline{L}$ have the same significance as above.

In actual practice $\underline{W}$ cannot be measured and $\underline{V}$ either cannot be measured at all or only with greatest difficulty. Accordingly von Weimarn introduced what he termed the "precipitate form coefficient" $\underline{N}$, which is related to the mean magnitude of the single crystals

in gram molecules G_m , by the expression

$$G_m \times N = \text{a constant.}$$

N may be represented qualitatively and in some cases approximately quantitatively by the expression

$$N = \frac{P}{L}$$

which means that in the simplest case, the form of the precipitate is determined exclusively by the prevailing percentage supersaturation at the moment the precipitation starts. If this is approximately true then for the substances x , y , and z :

$$N_x = \frac{P_x}{L_x}; N_y = \frac{P_y}{L_y}; N_z = \frac{P_z}{L_z}.$$

Now if the mean size in gram molecules of the particles in the several precipitates is to be the same; that is, if,

$$N_x = N_y = N_z$$

then,

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z}.$$

This is the simplest form of von Weimarn's law of corresponding states for the precipitation process.

As would be expected the simple formulation is seldom applicable quantitatively since in most cases there a number of factors other than percentage super-

saturation which influence the value of $\underline{N}$ and hence the mean particle size; and the magnitude of these factors is, in general, different for different substances. To take care of these several factors von Weimarn introduces a multiplier, $\underline{J}$, into the equation for $\underline{N}$ which now becomes

$$\underline{N} = \underline{J} \frac{\underline{P}}{\underline{L}} .$$

But the value of $\underline{J}$ is in general not the same for different states; hence the expression for von Weimarn's law of corresponding states becomes

$$\underline{J}_x \frac{\underline{P}_x}{\underline{L}_x} = \underline{J}_y \frac{\underline{P}_y}{\underline{L}_y} = \underline{J}_z \frac{\underline{P}_z}{\underline{L}_z}$$

in which $\underline{J}_x$, $\underline{J}_y$, and $\underline{J}_z$ are specific variable multipliers "the product of all other factors in addition to $\underline{P}/\underline{L}$ which influence the crystallization process." These factors must be expressed in abstract numbers equivalent to that for $\underline{P}/\underline{L}$. (1) This means that von Weimarn's

 Von Weimarn: Kolloidchem. Beihefte, 18, 48 (1923).

law becomes quantitative and generally applicable by using variable multipliers which may include as indefinite number of unevaluated variables. Among the several factors which are lumped together in the var-

iable multipliers are: the effect of the viscosity of the reaction medium, solvation as connected with molecular association, polymerization of the reactant molecules, molecular complexity of the reactants, adsorption, the presence of dust particles, the extent of agitation on mixing, the specific tendency to form nuclei, the specific tendency to grow on nuclei, etc.

The significance of the expression $N = J \frac{P}{L}$ is that the mean size of the particles in a precipitate is determined by the product of the initial percentage supersaturation and of all the other factors in addition to supersaturation which enter into the process. In other words, the size of the particles is determined by all the factors which enter into the precipitation process. One cannot question the truth of this statement but it is obvious that it may not be particularly helpful in certain cases.

Fortunately, in a number of cases the von Weimarn formulation may be used to advantage in its simplest form. This is true under the following conditions:

(1) if the factors influencing the precipitation process which are lumped together in von Weimarn's J are relatively unimportant as compared with the prevailing $\frac{P}{L}$

value at the moment of precipitation; (2) if the factors included in $\bar{I}$ are significant but are approximately equal for the precipitation of the two or more substances under consideration. On the other hand, the von Weimarn formulation may cease to be helpful in case the $\bar{I}$ values in the precipitation processes being compared are far from equal. This is especially true if the factors collected together in $\bar{I}$ should happen to be of greater importance than the prevailing percentage supersaturation in determining the form of the precipitate. This appears to be the case in the formation of colloidal gold by certain reduction processes to be considered in the next section.

The Formation of Colloidal Gold

In 1906 von Weimarn(1) formulated the rule that

(1) J. Russ. Phys.-Chem. Soc., 38, 267, 624 (1906).

the mean magnitude of the individual crystals of precipitates will progressively decrease with progressively increasing concentrations of the reacting solutions, providing the process of direct crystallization is complete. If the form of the precipitate is determin-

ed in large measure by the prevailing percentage supersaturation it follows from the expression

$$N = \frac{J \frac{Q - L}{L}}{L} = \frac{P}{L}$$

that N will be larger and hence the mean size of the particles will be smaller ~~the~~ the larger the value of Q , that is, the higher the concentration of the reactants. The formation of colloidal gold by certain reduction processes is an apparent contradiction to this rule. Thus Zsigmondy(1) showed in the case of the reduction by formaldehyde of HAuCl_4 made slightly alkaline with K_2CO_3 , that the greater the dilution of HAuCl_4 the higher the degree of dispersion and vice versa. A similar behavior was noted by Svedburg(2)

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- (1) Zsigmondy: "Colloids and the Ultramicroscope" (Alexander), 132 (1909).
 (2) Kolloid-Z., 4, 168 (1909).
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who employed $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ in alkaline solution as the reducing agent. This result would have never been predicted by the von Weimarn relationship but after the fact, von Weimarn explains the apparently anomalous behavior by assuming that hydrolysis of the gold salt, HAuCl_4 or KAuO_2 with the formation of $\text{Au}(\text{OH})_3$ sol

which is subsequently reduced to blue AuOH sol, is the initial and therefore the significant state in determining the degree of dispersity as it is influenced by the concentration of the reactants. In such instances, "the principle reacting molecules are obviously the molecules of water, and it is by the ratio of their number to the number of hydrolysing salt molecules that the velocity, as well as the completeness, of the hydrolytic process, is determined." (1) In

(1) Von Weimarn: Chem. Review, 2, 227 (1926).

other words, the greater the active mass of the water and not the lower concentration of HAuCl_4 in the dilute solutions is assumed to account for the higher dispersion in such solutions, since the higher the dilution the greater the number of nuclei formed by hydrolysis and hence the smaller the individual particles. From this point of view, it follows that if the primary particles of the AuOH⁽¹⁾ sol which is assumed

(1) Probably hydrous Au_2O .

to form as an intermediate product, are very small and the reducing agent insufficient, the reduction will be slow and yet the particles will be small. On the other

hand, if the originally formed particles of AuOH are relatively large the complete transformation to gold takes place slowly and the particles will be large. That is, the mean size of the primary particles in a gold sol prepared by the formaldehyde method stands in direct relation to the size of the particles of AuOH sol, the reduction of which results in the formation of colloidal gold.

The mechanism of the formation of colloidal gold which von Weimarn proposes in order to show that the process is strictly in accord with his theory is in-
genueous but there are certain lines of evidence which indicate that it is not correct.

In the first place Thiessen(1) has shown that all
(1) Kolloidchem. Beihefte, 29, 122 (1929).

the conditions which increase the degree of hydrolysis of HAuCl_4 solution decreases the number of particles that are formed in a given time on adding a suitable reducing agent. This is well illustrated by observations of the effect of temperature and age of HAuCl_4 solutions on the number of particles formed in a given time with hydrogen peroxide as reducing agent. In these experiments 1 cc of 0.6% $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solution was add-

ed to 100 cc of water and treated with 500 cc of 5% H_2O_2 . After a definite time interval 50 cc of 0.8% $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ was added. The latter reducing agent is known to cause rapid growth on the nuclei already present and to inhibit the formation of new nuclei. A count of the number of particles gives the number of nuclei that was present after a given time interval. The results of some observations are given in Fig. 1. The upper curve was made with freshly prepared solutions at 15° ; the middle curve with freshly prepared at 21° ; and the lower curve with solutions previously heated to boiling and cooled suddenly to 15° . The conductivity of the fresh solution at 15° was 1.25×10^{-4} mhos and of the boiled solution at 15° was 1.37×10^{-4} . The increased conductivity is indicative of an increase in hydrolysis; yet the number of particles formed with the more highly hydrolyzed solution was much less and the size correspondingly greater than for the less hydrolyzed solutions. Similarly, the number of particles in a sol formed with a 10 minute old solution having a conductivity of 1.27×10^{-4} mhos was twice as great

Fig 1

as with a 40 minute old solution with a conductivity of 1.34×10^{-4} mhos. Similar results were obtained with CO as the reducing agent. These observations show that the greater the hydrolysis of the solution prior to the addition of the reducing agent, the fewer the number and hence the larger the particles. This result is diametrically opposed to what one would predict from the von Weimarn mechanism. The presence of larger particles in the more highly hydrolysed solutions is attributed by Thiessen to a retardation of the spontaneous formation of nuclei by the hydrolysis products.

In the second place the number of particles in a gold sol is greater the higher the dilution of the gold salt even when the latter undergoes little or no hydrolysis. This conclusion is reached as a result of the following experiments.

Experimental

Although a number of procedures have been described for the preparation of colloidal gold, in all but a few cases the gold was reduced from a solution of chlorauric acid. This is prepared by dissolving metallic gold in aqua regia and evaporating to dryness. The

The product when dried over CaCl_2 is considered to be $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. (1) However, some AuCl_3 will be present

(1) Lengfeld: Am. Chem. J., 26, 328 (1901).

unless the chlorauric acid is purified in some manner. Since von Weimarn believes that the hydrolysis of the gold salt plays a significant if not predominate part in the mechanism of the reduction of gold compounds to colloidal gold, it was thought desirable to use a gold solution in which there is little likelihood of hydrolysis. Potassium chloraurate was chosen as the most suitable gold compound for the present experiments since it is the salt of such a strong base and strong acid that it will hydrolyze but little if at all.

Preparation of KAuCl_4 . Pure sheet gold was allowed to dissolve in aqua regia, the excess acids removed by boiling, and the resulting chlorauric acid extracted from the aqueous solution with ethyl acetate. (2)

(2) Lenher and Kao: J. Phys. Chem., 30, 126 (1926).

The chlorauric acid was crystallized from the ethyl acetate, dissolved in distilled water, and allowed to react with the calculated quantity of re-crystallized potassium chloride. The resulting potassium chlor-

aurate was crystallized from aqueous solution by slow evaporation in a vacuum desiccator over H_2SO_4 . Finally the best crystals were separated mechanically, washed with anhydrous ether, (1) and the excess ether removed

(1) Mylius and Huttner: Ber., 44, 1315 (1911).

in a vacuum desiccator. The gold content of the crystals was obtained without attempting to dry them to any definite composition. A 0.01 molar stock solution of KAuCl_4 was made up from which other solutions were prepared by dilution.

The Distilled Water. The purity of the distilled water used is an important factor in the preparation of colloidal gold. Much has been written by Zsigmondy and others (2) concerning the necessary purity of the distilled water. In view of the fact that a solution

(2) Zsigmondy-Thiessen: "Das Kolloide Gold", (1926).

of electrolytes is reduced and electrolytes are formed as products, it is apparent that slight traces of electrolyte impurities in the water employed will have little or no effect. Organic material, dust particles, etc., which can serve as nuclei are the undesirable, variable impurities that may be present in the distilled water. Accordingly water of minimum

conductivity is not necessarily the best to use. In the present investigation water prepared by a single distillation of ordinary laboratory grade distilled water in a copper still with a block tin condenser gave the same results as the same water distilled twice more from KmnO_4 and H_2SO_4 respectively, in a pyrex still with a block tin condenser. However, care was used to let the distilled water stand for several days in an aged bottle, and to syphon off the water, taking the precaution to not disturb the lower layer, into which the undesirable dust particles had settled. (1)

(1) Zsigmondy-Alexander: "Colloids and the Ultramicroscope".

This distilled water was used in the experiments about to be described.

Size of Au Particles in Sols formed by Reduction of KAuCl_4 with H_2O_2 . Amounts of solution as indicated in Table I were mixed together in the following manner: To the water in a 250 cc pyrex flask was added first the KAuCl_4 solution and then 0.2 cc of 30% H_2O_2 . The latter was allowed to flow in from a pipette while the contents of the flask were shaken with a rotary motion. The reduction was carried out at room temperature. A tint of color appeared in about 30 seconds, and the reaction was complete as evidenced by no further change

in color in two or three minutes. Tests disclosed that un-reduced gold was absent in the supernatant solution after coagulation of the sol. A clear, red colloidal solution resulted in each case. The number of particles in a definite volume of the sol was counted in the usual way by means of the Zeiss Slit Ultramicroscope. From the data so obtained the particle size was calculated assuming the crystals to be cubic. The results are given in Table I and are shown graphically in Figure 2.

Table I
Size of Au Particles formed by Reduction of KAuCl_4
with H_2O_2

Solutions mixed			Resulting concentration of KAuCl_4 Molarity $\times 10^{-5}$	Mean linear dimension of Au Particles <i>mμ</i>
KAuCl_4 .001 M cc	H_2O cc	H_2O_2 30% cc		
7	92.8	0.2	7	160
6.75	93.05	0.2	6.75	155
6.5	93.3	0.2	6.5	109
6	93.8	0.2	6	92
5	94.8	0.2	5	78
4	95.8	0.2	4	68
3	96.8	0.2	3	56

Size of Au Particles in Sols Formed by Reduction of KAuCl_4 with $\text{NH}_2\text{OH} \cdot \text{HCl}$. In the reduction with H_2O_2 a constant amount of reducing agent was used. This was permissible since the excess H_2O_2 has little or no effect on the size of the particle.(1) Since this is

(1) Westgren: Z.anorg. Chem., 93, 154 (1915).

not the case with many reducing agents, in the subsequent experiments a constant mole ratio of the KAuCl_4 and the reducing agent was maintained. Solutions A and B were mixed as indicated in Table II. In every case a clear, red colloidal gold solution was obtained. The particle size in each case was determined with the results recorded in the Table and shown graphically in Figure 2.

Table II

Size of Particles formed by Reduction of KAuCl_4
With $\text{NH}_2\text{OH} \cdot \text{HCl}$

Solutions mixed				Resulting concentration of KAuCl_4 Molarity $\times 10^{-5}$	Mean linear dimension of Au <i>m</i>
A KAuCl_4 .001M cc	H_2O cc	B $\text{NH}_2\text{OH} \cdot \text{HCl}$.00375 M cc	H_2O cc		
8	42	8	42	8	70
7	43	7	43	7	58
6	44	6	44	6	46
5	45	5	45	5	41
4	46	4	46	4	37

Size of Au Particles in Sols formed by Reduction of KAuCl_4 with $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$. The reducing agent was added to the several concentrations of KAuCl_4 solutions as given in Table III. The size of the particles in each of the clear, red sold was determined. The results are given in the Table and shown graphically in Figure 2.

Table III

Size of Au Particles in Sols Formed by Reduction of KAuCl_4 with $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$

Solutions mixed			Resulting Concentrations of KAuCl_4 Molarity $\times 10^{-5}$	Mean linear dimension of Au Particles <i>mm</i>
KAuCl_4 .001 M cc	H_2O cc	$\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ 0.001 M cc		
12	76	12	12	62
11	78	11	11	57
10	80	10	10	54
9	82	9	9	52
8	84	8	8	50

Fig 2

Conclusions

The particles of colloidal gold formed by reduction processes are larger the higher the concentration of the gold salt reduced. This is not in accord with von Weimarn's theory which states that provided the crystallization is complete the mean size of the individual crystals is greater the higher the dilution of the reactants. Von Weimarn explains this anomalous behavior by postulating that hydrolysis of the gold salt with the formation of $\text{Au}(\text{OH})_3$ which is subsequently reduced to AuOH and finally to Au is the initial and therefore the important step in determining the degree of dispersity as it is influenced by the concentration of reactants. From this point of view the greater hydrolysis at lower concentrations accounts for the greater number of nuclei and hence the smaller size of the particles in low concentration. Against this point of view is (1) Thiessen's observations that the greater the hydrolysis of the gold solution prior to the addition of the reducing agent, the fewer the number and hence the larger the particles; and (2) the observations herein recorded which show that in the absence of appreciable hydrolysis of gold salt the gold

particles are smaller the more dilute the solution.

It is apparent from these considerations that the percentage supersaturation at the beginning of precipitation is not the only factor and may not be the most important one in determining the primary particle size in the formation of colloidal gold. In the absence of added nuclei, the size of the primary gold particles in a sol will be determined, for a given concentration of reactants by the velocity with which nuclei form spontaneously and with the velocity with which the particles grow on the spontaneously formed nuclei. Now it is to be expected from the Nernst-Hoyes formulation that the velocity of growth on added nuclei will be greater the greater the absolute supersaturation of the solution with respect to gold; in other words, the greater the initial concentration of gold salt. The same thing will apply to the rate of growth on nuclei formed spontaneously. In general to obtain very highly dispersed particles, the velocity of formation must be relatively rapid and the growth on the effective nuclei must be relatively slow. Since gold is extremely insoluble, the

percentage supersaturation of the metal is relatively high at all concentrations of the gold salt under consideration. Accordingly the rate of formation of nuclei will not differ widely at the various dilutions; but at the high dilutions, the rate of growth on nuclei is relatively slower so that relatively more nuclei can form before the supply of gold is used up. For both these reasons the particle size is smaller for the sol formed from dilute solutions of the gold salt.

Von Weimarn may contend that larger particles formed in the more concentrated solutions are aggregates rather than primary particles. There is no evidence to support this view under the experimental conditions herein described. All the sols were perfectly clear and the untramicroscopic examination showed no indication of aggregate formation. Moreover, it is well known that particles grow by direct precipitation of gold on gold nuclei added to the reduction mixture and there is no reason to believe that the process is any different in the presence of spontaneously formed nuclei. In this connection, if one insists that $\text{Au}(\text{OH})_3$ and AuOH are precipitated as intermediate

products in the reduction process, then the growth on nuclei must result from initial precipitation of $\text{Au}(\text{OH})_3$ on such particles followed by reduction to AuOH and subsequently to gold. While this could be true to a certain extent, it seems to be altogether unnecessary to assume such a mechanism since it is probably not in general accord with the facts.

Summary

The following is a brief summary of the results of this paper:

(1). Von Weimarn's formulation of the precipitate form coefficient and the law of corresponding states for the precipitation process have been considered from the standpoint of their applicability and limitations as a research tool.

(2). The particles of colloidal gold formed by reduction processes are in general larger the higher the concentration of the gold salt reduced. This would not be predicted from the von Weimarn theory which states that provided the process of direct crystallization is complete, the mean magnitude of the in-

dividual crystals is smaller the higher the concentration of reactants (the higher the percentage supersaturation at the moment precipitation begins).

(3). Von Weimarn explains the apparently anomalous behavior noted in (2) by postulating that hydrolysis of gold salt with the formation of $\text{Au}(\text{OH})_3$, which is subsequently reduced to AuOH and finally to Au , is the initial and therefore the important step in determining the degree of dispersity as it is influenced by the concentration of reactants.

(4). Against von Weimarn's general point of view are the observations: (a) The greater the hydrolysis of gold solution of a given concentration, prior to the addition of reducing agent, the fewer the number and hence the larger the particles of gold (Thiessen), (b) The observations recorded in this paper which show that in the absence of hydrolysis of gold salt, the gold particles are smaller the lower the concentration of the salt reduced. This was found to be true for the reduction of KAuCl_4 solutions with H_2O_2 , $\text{NH}_2\text{OH} \cdot \text{HCl}$, $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$.

(5). Because of the very low solubility of gold in water, the percentage supersaturation of the metal is relatively high at all concentrations of gold salt reduced. Accordingly the rate of formation of nuclei will not differ widely at the various dilutions; but at the higher dilutions the rate of growth on nuclei is relatively slower, so that relatively more nuclei can form before the gold supply is exhausted. For both these reasons the particle size is smaller for the sol formed from the dilute solution of gold salt.

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