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A colloid, in chemistry, is a substance in which one substance of microscopically dispersed insoluble particles is suspended throughout another substance

A STUDY OF THE NUCLEATION AND GROWTH PROCESSES IN THE SYNTHESIS OF COLLOIDAL GOLD

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After a preliminary survey with the electron microscope of various preparations of colloidal gold, a study was made of the process of nucleation and growth in gold colloids. It was shown that nucleating agents may be identified with reducing agents which form a mixed polymer with chlorauric ion before the reduction to the nucleus takes place. It was also shown that the law of growth is exponential. The average size, the deviation from the average size and the character of the particle size distribution curve are determined by the amount of gold, the nucleation process and the law of growth.

Colloidal gold may be considered as a typical hydrophobic colloid with particle size falling below the resolution limit of the optical microscope. With the development of the electron microscope which has a resolution permitting the examination of the individual colloidal particles [1] it was natural to make an extensive study of the shape, mean size and size distribution of the various preparations of colloidal gold and determine the factors that govern these properties. Previous work on the subject was limited to one or two preparations.[2]

Experimental

Electron Microscopic Examination of Various Preparations of Colloidal Gold.—In order to gain an insight into the colloidal gold system, a systematic survey was made of all standard preparations of colloidal gold. Due precautions were taken to ensure cleanliness of the distilled water, reagents and the glass vessels used. The water was distilled water purified from nuclei by ultrafiltration. The glass vessels used were not only cleaned with aqua regia to remove traces of colloidal gold which might subsequently serve as nuclei, but were also treated with chromic acid and steamed for 20 min. to remove any grease film. Contact with rubber tubing or rubber stoppers was scrupulously avoided. The colloidal gold preparations were examined in an RCA electron microscope by placing a drop of the colloid on a collodion screen and allowing it to evaporate. The resolution of the microscope was about 10-20 Å.

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[1] Turkevich and Hillier, *Anal. Chem.*, 1949, **21**, 475.

[2] (*a*) Beischer and Krause, *Z. angew. Chem.*, 1938, **51**, 331; (*b*) Ardenne, *Z. physik. Chem. A*, 1940, **187**, 1; (*c*) Koch, *Z. Elektrochem.*, 1941, **47**, 717; (*d*) Feitknecht, Signer and Bergern, *Kolloid-Z.*, 1942, **101**, 12; (*e*) Roginski, Shekhter and Sacharova, *Compt. rend. U.R.S.S.*, 1946, **52**, 687; (*f*) Borries and Kausche, *Kolloid-Z.*, 1947, **90**, 132; (*g*) Harris, Jeffries and Siegel, *J. Appl. Physics*, 1948, 791.

BREDIG SOL[3] was prepared by striking an arc from two gold wires under very dilute sodium hydroxide solution with a 115 V, 60-cycle potential. The gap between the electrodes was about $\frac{1}{4}$ mm. and the electrodes were agitated to keep them from fusing. A purple cloud was observed to drift away from the arc, gradually darkening the entire solution. The process was continued until a fairly intense purple colour had developed and the colloid so obtained was examined with the electron microscope. The particles ranged in diameter from 30-100 Å but due to their small size and extensive clumping no precise measurements of size distribution could be made.

FARADAY SOL[4] was prepared in the following way. A saturated solution of white phosphorus in freshly distilled diethyl ether was diluted with three times its volume of diethyl ether. 50 ml. of chlorauric acid solution (50 mg. of Au) was diluted with 45 ml. of distilled water and with 5 ml. of 0·1 N KOH. This solution was treated, using good mechanical stirring, in one case with 2·0 ml. of the phosphorus-ether solution and in the other case with 1·0 ml. of the same solution. The solution turned first brown, then grey, purple and red, finally giving a deep-red product. The sol was then heated to boiling and a stream of filtered air was drawn through it in order to oxidize any remaining phosphorus. Electron microscopic examination revealed that both sols contained extremely fine particles more or less clumped. The sol reduced with 2 ml. of phosphorus solution consisted of particles of mean diameter of 50 Å with a root-mean-square deviation of 30 %. This preparation was grown to double, quadruple and eight-fold of the original diameter by means of the hydroxylamine development technique (described below) in an attempt to deduce the smallest particle size in the original Faraday preparation. An electron microscopic examination of these developed preparations showed that the smallest particle in the original Faraday sol was about 30 Å diam. This is interpreted to mean either that particles smaller than 30 Å are not formed by the Faraday method or if they are formed they do not serve as nuclei in the hydroxylamine + gold chloride growth medium. The size distribution of the Faraday sol particles is not symmetrical having a gradual rise on the small diameter size passing through a sharp maximum to a rapid drop on the large diameter size and showing a small tail of larger particles. The significance of this distribution curve characteristic of many gold sols will be discussed later. The sol made by the reduction with 1 ml. of phosphorus diethyl ether solution consisted of particles of mean diameter of 70 Å with a root-mean-square deviation of about 25 %. Rinde[5] studied Faraday sols by growing them in a hydrogen peroxide + gold chloride medium and determined the particle size distribution by gravity and ultracentrifugal sedimentation. His curves have a similar general appearance to those found in the present investigation. Rinde, however, deduced the average particle diameter to be 19 Å.

ACETONE SOL.[6] 98 ml. of chlorauric acid solution (containing 12 mg. of Au) were heated to boiling and treated with 1 ml. of acetone purified by distillation from alkaline permanganate. On boiling, a faint coloration appeared in the solution after about 90 sec., darkening gradually to deep red. Under the electron microscopic investigation the particles appeared in clusters of about 50. The individual particles were non-spherical with a probable diameter of about 200 Å and a root-mean-square deviation 13 %.

TANNIN GOLD SOL.[7]—10 ml. of chlorauric acid (containing 10 mg. of Au) was added to 100 ml. of water, the solution was made neutral to litmus with sodium carbonate and heated to boiling. A fresh 1 % tannin solution was added dropwise until no colour change was observed on further addition. The sol was pink and had a slight opalescence. Electron micrographs showed that the sol consisted of small spherical particles of 120 Å mean particle diameter and a root-mean-square deviation of 28 %. The particles occurred singly or in small clusters. It is of interest to note that the particles making up the clusters were *not* in contact but were separated by a space of not less than 40 Å. This may be interpreted to indicate that the particles are surrounded by a skin of protective colloid (tannin) of too low a contrast to be visible in the electron microscope.

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[3] Bredig, *Z. angew. Chem.*, 1898, **11**, 951.

[4] Faraday, *Phil. Trans.*, 1857, **147**, 145.

[5] Rinde, *The Distribution of Sizes of Colloidal Gold Sols prepared according to the Nuclear Method* (Uppsala, 1928).

[6] Davies, *J. Physic. Chem.*, 1929, **33**, 276.

[7] (*a*) Wieser, *Inorganic Colloid Chemistry*, **1** (John Wiley and Sons, New York, 1933), p. 40; (*b*) Garbowski, *Ber.*, 1903, **36**, 1215; (*c*) Ostwald, *Kleiner Praktikum der Kolloidchemie*, 2nd edn. (1920).

OXALIC ACID SOL.—38 ml. of chlorauric acid solution (containing 20 mg. Au) was treated at the boiling point with 2 ml. of 1 % oxalic acid. Turbidity appeared in about 5 sec. and the reaction seemed complete in 20 sec. The sol was light blue in colour while the scattered light was yellow. The particles were about 2000 Å diam., irregular in shape and the size distribution was rather broad.

HYDROXYLAMINE SOL.[8]—Hydroxylamine hydrochloride in slightly acid solution has been described by a number of investigators as an inhibitor for the nucleation of colloidal gold. In neutral or basic solution, however, it is a nucleating agent. 20 ml. of 0·027 % hydroxylamine hydrochloride solution was added to 20 ml. of chlorauric acid solution (containing 2 mg. of Au) previously neutralized with potassium carbonate. A dark blue colloid formed instantaneously. Unlike the ordinary unstable blue colloidal gold, this colloid was stable. The blue colour had been ascribed to this preparation by Thiessen[9] as due to the presence of aurous oxide. The sol was found to consist of small non-spherical particles aggregated into clusters. The distribution curve was broad with a maximum at about 150 Å and a root-mean-square deviation of 44 %.

DONAU SOL.[10]—Carbon monoxide gas was bubbled through a chlorauric acid solution (containing 0·001 % Au) at room temperature. The solution darkened assuming finally a purple colour. The sol was found to consist of highly irregular particles of about 200 Å diam. and 400-800 Å long. Their appearance suggested that the particles were formed by the deposition of gold on straight or bent chains of smaller particles and that the growth took place during coagulation (Fig. 1).

ACETYLENE SOL.—18 ml. of chlorauric acid solution (containing 10 mg. of Au) were treated with 2 ml. of water saturated with acetylene gas. A pink colour appeared in 20 sec. and in 2 min. the sol became dark ruby-red. Electron microscope examination of this sol revealed small particles mostly spherical in shape with a mean diameter of 285 Å and a root-mean-square deviation of 22 %. The size distribution curve was definitely skewed, the slope on the large diameter side of the maximum being markedly steeper than on the smaller diameter side. An unusual feature of the separation was the presence of a few particles in the form of triangular plates. Since the acetylene sol was definitely acidic, the effect of the hydrogen ion concentration was investigated. Solution of pH 10·4 and 8·0 gave no sol formation. Solution with a pH of 5·8 obtained by adding an appropriate amount of sodium carbonate to the original reagents, produced a sol slowly, taking 5-7 min. to develop full colour while the non-neutralized acetylene + chlorauric acid solution required 2-3 min. The particles in the neutralized medium were smaller having a mean diameter of 170 Å with a root-mean-square deviation of 16 %. The size distribution curve was again skew-shaped. No plates were found. If the starting reagents were of lower pH value containing 20 and 64 mequiv. of added HCl the sols formed had a definite blue tint and contained a large number of irregularly-shaped flat plates and bipyramids. The distribution in size was very broad.

CITRIC ACID GOLD SOL.—95 ml. of chlorauric acid solution (containing 5 mg. of Au) were heated to the boiling point and 5 ml. of 1 % citric acid solution was added to the boiling solution with vigorous mechanical stirring. The solution remained clear for about 15 sec. and then suddenly a dark blue-purple sol was formed. There was no further change of colour on prolonged boiling. When examined in the electron microscope, this sol proved to be identical in appearance to the one prepared in acidified acetylene solution. Large numbers of flat triangles and hexagons were seen. There were also some bipyramidal forms. The particle " diameter " ranged from 100 to 500 Å. Because of the extensive variability in shape no size distribution curve was determined (Fig. 2).

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[8] (*a*) Rinde, ref. (15) ; (*b*) Thiessen, *Z. anorg. Chem.*, 1929, **180**, 57 ; (*c*) Thiessen, *Kolloidchem. Beihefte*, 1929, **29**, 122.

[9] Thiessen, *Z. anorg. Chem.*, **134**, 1924, 393.

[10] (*a*) Donau, *Monatsh.*, 1905, **25**, 525 ; (*b*) Weiser, ref. (7*a*), p. 41.

Sodium Citrate Sols.—This preparation, of great importance in our investigation, is a modification of the one described by Hauser and Lynn.[11] The following is a description of a preparation which we shall term the " standard " sodium citrate sol : 95 ml. of chlorauric acid solution (containing 5 mg. Au) were heated to the boiling point and 5 ml. of 1 % sodium citrate solution was added to the boiling solution with good mechanical stirring. After about a minute a very faint greyish-pink or greyish-blue tone appeared gradually darkening over a period of about 5 min. The final colour was deep wine red. Electron microscopic examination of a number of preparations showed that this colloid is highly reproducible and gives spherical particles (Fig. 3) with a mean diameter of about 200 ± 15 Å and a root-mean-square deviation of 12·5 %. The size distribution curve based on a count of 1046 particles is not symmetrical but shows a distinct " tail " on the small diameter side (Fig. 4). The effect of temperature, concentration of reagents and dilution was investigated. The effect of the temperature is given in Table I. Lowering the temperature by 10° C. increases by a factor of two the time necessary for the completion of the reaction as judged by the deepening of colour. Both the mean particle size and the root-mean-square deviation decrease slightly with decreasing temperature. The effect of decreasing the amount of sodium citrate (Fig. 5) in the preparation on the properties of the gold sol are given in Table II. The colour changes accompanying the reaction show marked variation as the amount of the citrate is decreased. The early stages become more definitely blue and the transition from the blue to the red becomes more sharply defined. The overall reaction appears to take place more rapidly at the lower citrate concentration. Using 1/10th the standard amount of citrate, the reaction could be divided sharply

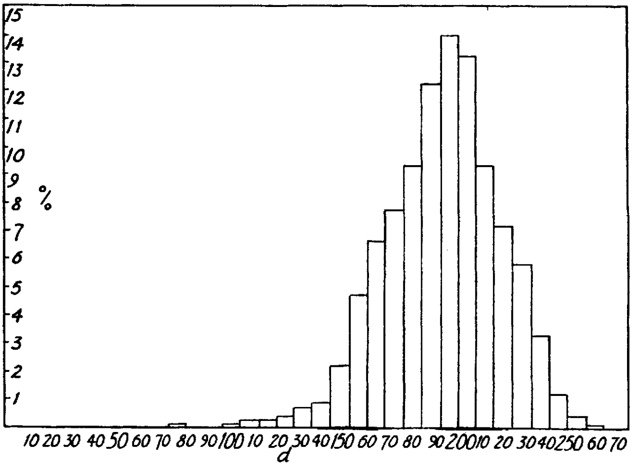

Fig. 4.—Size distribution of a standard citrate sol. Ordinate : % particles ; abscissa : diam. (Å).

TABLE I.—The Effect of Temperature on the Sodium Citrate Sol

Temp. °C	Approximate Time for the Completion of Reaction in min.	Mean Particle Size in Å	% Deviation
100 (standard)	5	200	12·5
80	25	165	8·1
70	45	180	8·6

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[11] Hauser and Lynn, *Experiments in Colloid Chemistry* (McGraw Hill, 1940), p. 18.

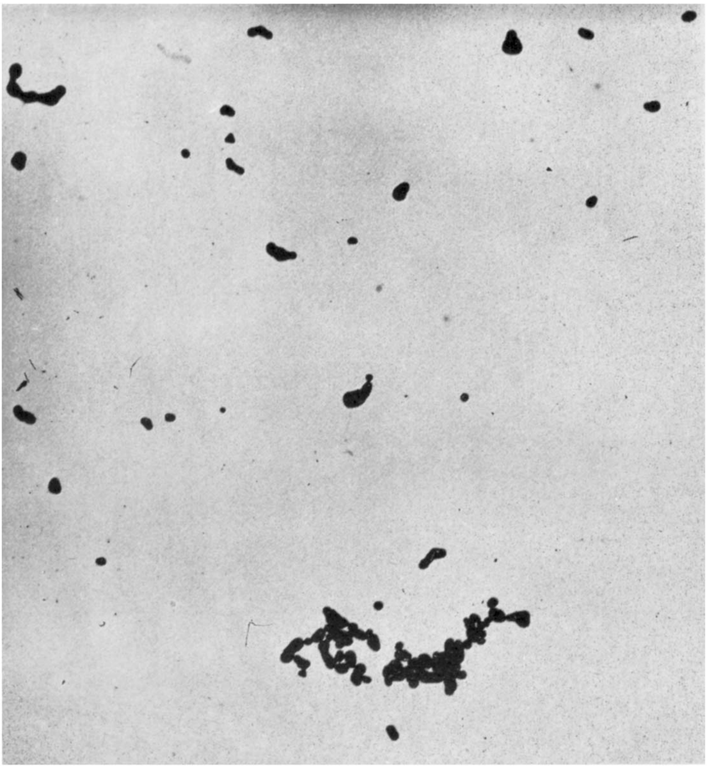

FIG. 1.—Electron micrograph of a gold sol reduced with carbon monoxide, magnification of 50,000 diameters.

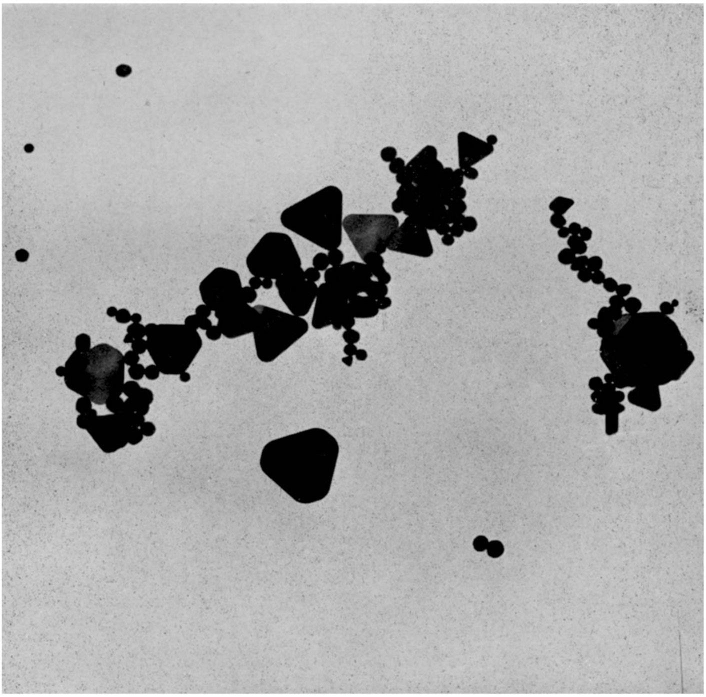

FIG. 2.—Electron micrograph of a gold sol reduced with citric acid, magnification of 50,000 diameters.

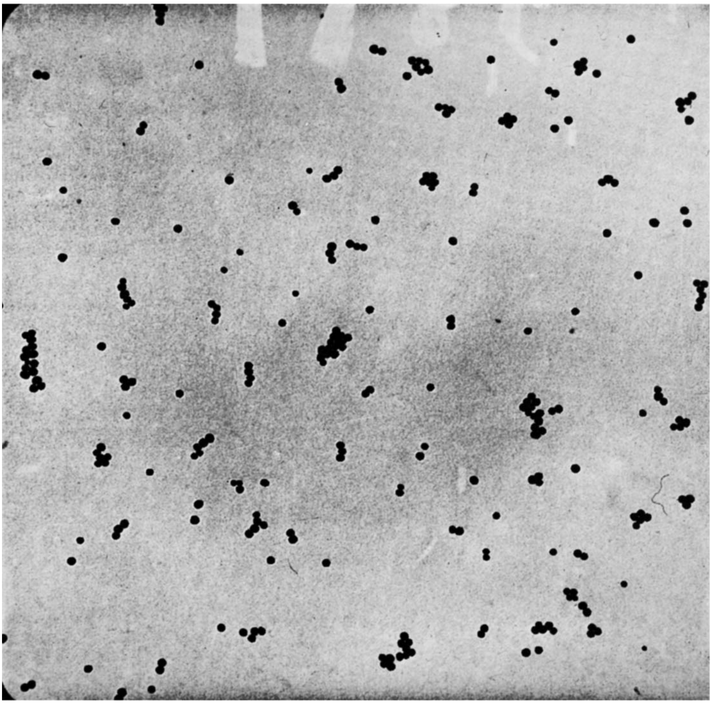

FIG. 3.—Electron micrograph of a gold sol reduced with sodium citrate (standard citrate sol) magnification 50,000 diameters.

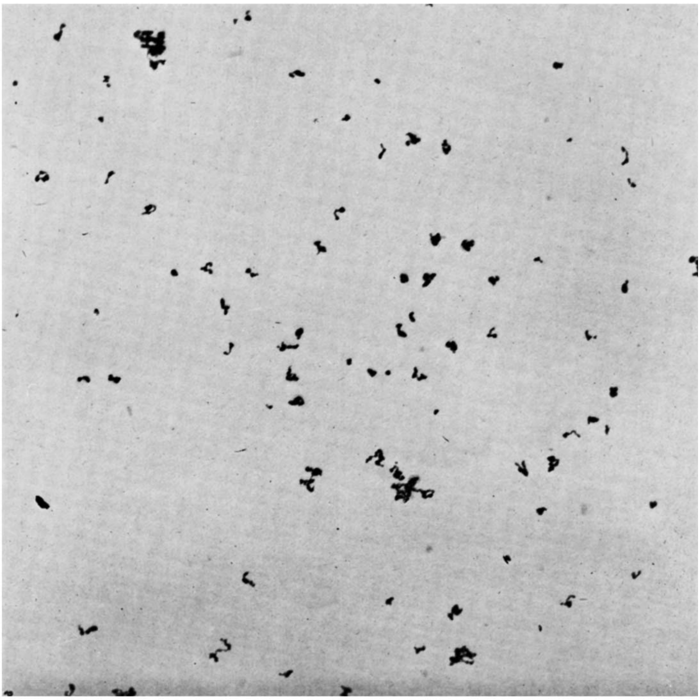

FIG 12 —Electron micrograph of nuclei for colloidal gold isolated by the ion exchange resin method, magnification 43,600 diam.

[*See page* 65.

into three stages. The reaction mixture was colourless for 12 sec. after the addition of the citrate, then it turned blue within a fraction of a second. After a total reaction time of 72 sec. it suddenly turned clear red. The colour changes accompanying this reaction were very striking. Size distribution curves were obtained for all preparations but the one using 1/20th of the amount of citrate used in the standard preparation. This latter sol was highly turbid and coagulated very rapidly. Decreasing the amount of citrate caused the mean particle diameter to increase somewhat and the size distribution curve showed a definite " hump " on the large diameter side of the average diameter. The effect of dilution of reagents on the properties is given in Table III and Fig. 6. Sols made in the more concentrated solutions had a smaller particle diameter but were somewhat contaminated. Further detailed studies on the sodium citrate

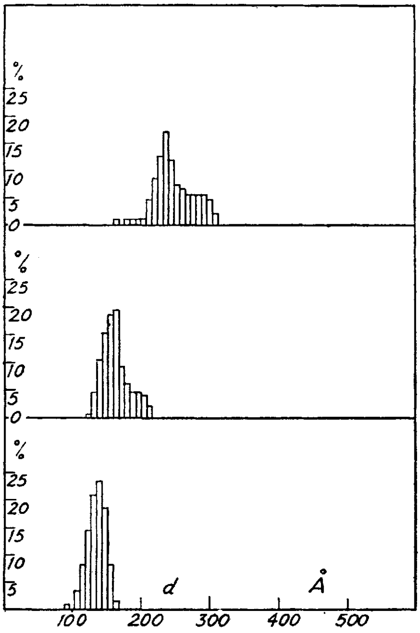

FIG. 5.—Size distributions of sols reduced with varying amounts of sodium citrate. Upper curve: one-tenth the standard amount of citrate; middle curve: one-fifth the standard amount of citrate; lower curve: half the standard amount of citrate.

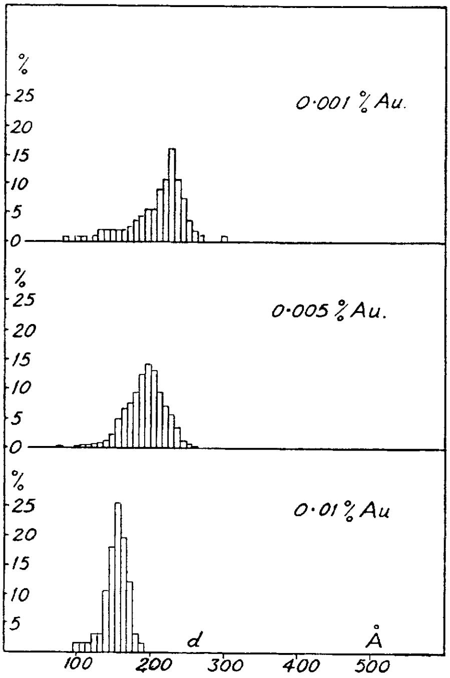

FIG. 6.—Size distribution of sols reduced with sodium citrate at different dilutions. Upper curve: twice standard dilution; middle curve: standard dilution; lower curve: half standard dilution.

TABLE II.—THE EFFECT OF CITRATE CONCENTRATION ON THE SODIUM CITRATE SOL

Citrate (mg.)	Approximate Time for the Completion of Reaction in min.	Mean Particle Size in Å	% Deviation
50 (standard)	5·0	200	12·5
25	5·0	145	9·4
10	2·0	165	11·8
5	1·2	240	12·1
3·75	2·0	dirty and clumped	
2·5	2·0	dirty and clumped	

sol will be considered in connection with the process of nucleation and growth of colloidal gold.

TABLE III.—THE EFFECT OF DILUTION ON THE SODIUM CITRATE SOL PREPARATION

Dilution	Approximate Time for the Completion of Reaction in min.	~~Mean Particle~~ Size in Å	% Deviation
1/2	2	174	10·4
1 (standard)	5	200	12·5
2	6	235	12·6

The Nucleation Process.—An electron microscopic survey of the methods of preparation of gold colloids has shown that the nature of the product formed was highly dependent on the reagent used and on the conditions. The particle shape, the particle size and the nature of the size distribution curve have been shown to vary within quite large limits. The shape of the size distribution curve will be shown to depend largely on the relative rates of two separate processes, nucleation and growth. Nucleation will be defined as the process whereby a discrete particle of a new phase forms in a previously single-phase system, in our case, a homogeneous solution. Growth will be defined as a process in which additional material deposits on this particle causing it to increase in size. It has been shown that these two processes are indeed separable. Zsigmondy and Thiessen[12] have studied the nucleation using several reducing agents. This section will deal with sodium citrate and hydroxylamine hydrochloride as reducing agents of auric ion, the former acting as both a nucleating agent and a growth agent while the latter functioning only as a growth agent.

Nucleation in the formation of gold sols is a difficult phenomenon to investigate directly. Preliminary evidence indicated that the nuclei are very small, of the order of 50 Å or less in diameter and consequently not susceptible of effective direct examination with the electron microscope. Furthermore these nuclei have only a transitory existence in the reaction mixture during the ordinary methods of gold sol preparation. The experimental criterion for the presence of nuclei that was used was the following: the solution suspected of containing nuclei is added to the growth medium consisting of a solution of 12×10^{-4} parts of hydroxylamine hydrochloride and 10×10^{-4} parts of chlorauric acid. If the nuclei are present in the solution tested, reduction takes place either to colloidal gold, a coagulated gold sol, or to large particles of gold depending on whether the number of nuclei is large or small. Each particle produced in this growth medium is presumed to have formed from the nucleus present in the solution tested, at the time of its addition to the growth medium of chlorauric acid and hydroxylamine hydrochloride. In the absence of nuclei and in a dust-free atmosphere the growth medium undergoes no reduction of the auric ion for several hours. This test for the existence of nuclei may be adapted for the growth of nuclei to a size convenient for observation by the choice of a proper amount of the growth medium (development technique). It was decided to study the nucleation process in the production of colloidal gold by the sodium citrate reduction taking advantage of this development technique to bring the nuclei formed at various times into a range of size capable of ready evaluation. The number of particles in the sols so developed and consequently the number of nuclei were determined either by counting in the slit ultramicroscope or deduced from the optical properties of the developed sol. In addition a method was developed for determining the rate of nucleation from the ultimate particle size distribution curve as revealed by the electron microscope. Furthermore a study was made of the disappearance of the auric ion as a function of time and this was correlated with the nucleation rate. In addition a method was found for removing the auric ion from solution after nucleation was essentially complete, and examining the isolated nuclei with an electron microscope. Finally an oxidation product of sodium citrate was studied as a nucleating agent.

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[12] (*a*) Zsigmondy, *Z. physik. Chem.*, 1906, **56**, 65; (*b*) Thiessen, ref. (8*b*) and (8*c*).

Slit-Ultramicroscopic Examination.—Since nuclei are difficult to see in slit-ultramicroscope, the following procedure due to Zsigmondy [13] was adapted to the study of the rate of formation of nuclei from gold chloride by sodium citrate. Reagents necessary for the production of the standard sodium citrate sol were mixed in clean glass-stoppered Erlenmeyer flasks and kept in a thermostat. At fixed intervals samples were drawn from the nucleating solution and were added to a volume of the growth medium so chosen empirically as to give developed particles of a size chosen to minimize coagulation during the counting operation. The samples so obtained were diluted to standard volume and aliquots were introduced into a cell of a Bausch and Lomb slit-ultramicroscope for counting. Nucleation curves for the formation of gold sol were measured

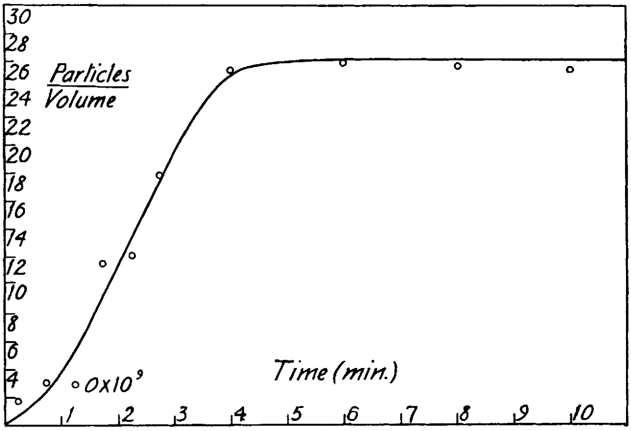

FIG. 7.—Nucleation curve at 58·5° C measured with the slit ultra-microscope.

in the sodium citrate + chlorauric acid solutions at 23·0° C and at 58·5° C and are presented in Fig. 7. Examination of the data shows that it takes about 40 min. to complete nucleation at 23° C and 4 min. at 58·5° C indicating a high temperature coefficient for the nucleation process. Furthermore the curves indicate that the rate at the start is reasonably constant and then drops off suddenly at the end. The nuclei formation is complete *long* before the process of colloidal gold formation ends because the colour of the solution deepens at 23° C for 12 hr. and at 58·5° C for 2 hr. Previous investigations of the rate of nucleus formation were carried out by Thiessen [14] who used the same technique for the study of the nucleation of gold by potassium oxalate, hydrogen peroxide, sodium citrate, potassium thiocyanate and ultra-violet light. The experiments with sodium citrate were carried out at one temperature. The general character of his sodium citrate nucleation curve is similar to the one reported in this investigation. It is felt that the method of counting particles in the slit-ultramicroscope has definite disadvantages. In the first place the method is subjective and involves errors arising from dark adaptation and subsequent fatigue of the eyes. Secondly the time of count is often comparable to the time of stability of the developed colloids. Thirdly there is always an error arising from defining the depth of the liquid examined. Finally the question arises as to whether very small particles can be detected with as much assurance as the larger ones. For this reason it was thought that other methods should be developed to determine the rate of nucleation.

[13] Zsigmondy, ref. (12*a*).

[14] Thiessen, ref. (8*c*).

Nephelometric Method.—In this method sodium citrate + chloraurate mixture was allowed to nucleate and aliquot portions were developed by addition to a *constant* amount of the hydroxylamine growth medium. A series of developed gold sols were obtained having the same total gold content but differing among themselves in the number and consequently size of the gold particles. The number was determined by nephelometric comparison with an appropriate standard set of colloids of the same gold concentration but different known particle concentration. This graded set of standards was obtained in the following way. A gold sol was prepared by allowing a nucleating mixture identical to the one under investigation to go to completion. This sol contained the maximum number of particles which could be determined experimentally. This number corresponded to the final number of nuclei formed. The particles in this completed sol were of minimum size compared to the other members of the graded set. Other members of the standard series were prepared by taking known volumes of this final solution (containing known number of particles) and developing them in a hydroxylamine hydrochloride + chlorauric acid solution of such a strength in gold that the total gold concentration was the same as in the developed samples from the sodium citrate run under investigation. The particle concentration of the developed aliquot sample from the run was obtained by comparison with an appropriate standard in a nephelometer. Using this procedure it was not difficult to prepare a curve for each run showing the fraction of nuclei formed as a function of time. The number of nuclei per ml. in the completely nucleated sol could be easily determined either by a nephelometric comparison based on the 200 Å standard sol or by an electron microscopic investigation of their particle size. A typical nucleation curve obtained in this way is shown in Fig. 8. The curve is similar in nature to the one obtained with the slit-ultramicroscope. It is more convenient to determine and its accuracy and reproducibility are much greater. An assumption is made that the total scattering observed is determined primarily by the mean particle volume and is independent of small variations in the particle size distribution curve.

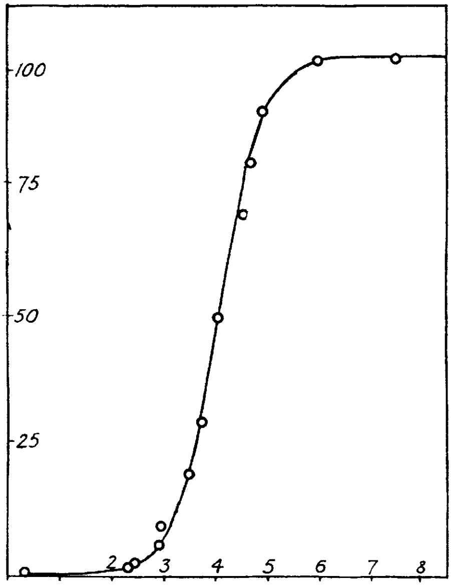

Fig. 8.—Nucleation curve at 49° C measured with a nephelometer.

Ordinate : particles per unit volume ;
abscissa : time (sec.).

Electron Microscopic Methods.—There are two methods that can be used to determine the nucleation curve using the electron microscope. The first method consists of stopping the nucleation process at various times and developing the samples. Each individual developed sample is examined in the electron microscope and a size distribution curve is obtained. The mean particle volume of each sample is determined from these curves. Since the total gold content is known one can determine the number of particles per unit volume present in the nucleating mixture at the time of development of each sample. This procedure, however, is rather time-consuming and tedious.

The second method consists of determining the nucleation curve from the particle size distribution curve of the completed preparation of the gold sol. The method is based on the assumption that the principal cause of the *spread in particle size* of a gold colloid is the *spread in time in the nuclei formation.* Particles formed early in the nucleation process begin to grow immediately so that in the final sol the particles that first form and hence have the longest time to grow, attain the largest size. Nuclei which form later attain smaller and smaller sizes corresponding to shorter and shorter growing times. The size distribution of a sol can be considered as a regularly distorted mirror image of the nucleation curve. In Fig. 8 are shown schematically a size distribution curve (upper curve) and a nucleation curve (lower curve) of the same colloid. The marked diameter D in the size distribution curve was chosen to be the diameter finally attained by those particles formed during nucleation at the time t marked on the nucleation curve. The ordinate of the nucleation curve at t represents the total number of particles present in the unit volume of the solution at time t, i.e. all those particles which have formed up to and including time t. It is convenient to express this number as the fraction of the number of particles that are going to be eventually formed at infinite time, $N(t)$. The total number of particles formed up to time t is simply the total number of particles with diameter greater than $D(t)$ or

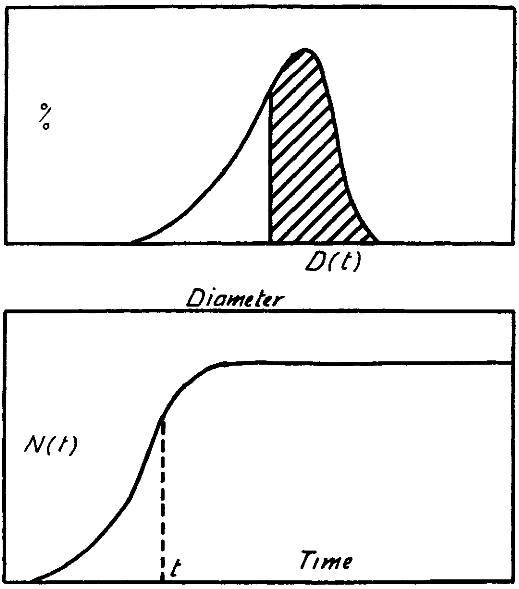

FIG. 9.—Schematic diagrams to illustrate the calculation of nucleation curves from size distributions. Upper curve : schematic size distribution ; ordinate : % total particles ; abscissa : diameter $D(t)$; lower curve : schematic nucleation curve : ordinate : $N(t)$; abscissa : time.

$$N(t) = \int_{D(t)}^{\infty} n(D)\mathrm{d}D. \qquad (1)$$

The value of this definite integral is the shaded area under the distribution curve and this can be determined as a fraction of the total area. In the section on growth it will be shown that a gold particle grows according to the law

$$\mathrm{d}D/\mathrm{d}t = K(C, T)D, \qquad (2)$$

where D is the diameter of the particle and k is the velocity constant dependent on the temperature and reagent concentrations. In the integrated form it becomes

$$t = (a - \log D)/b, \qquad (3)$$

where a is a function of time at which an arbitrarily-selected reference particle forms and of the rate constant k, while b is proportional to k. If one obtains from independent observations the values of a and b one can derive a nucleation curve from a particle size distribution curve by means of the equations above.

Since knowledge of these constants was incomplete at the time of the investigation it was decided to modify the procedure by taking at least three samples from a nucleating sol and developing them. These three developed samples taken at three definite times and the completed sol were examined in the electron microscope. (Actually two samples taken at two times during nucleation are sufficient, but the third was taken to obtain check values.) Distribution curves were taken of these four sols. Three incompletely nucleated sols were used to determine the mean diameter and thus the number of nuclei present in the reaction mixture at the three definite times when the nucleation was stopped by development. One therefore obtains three points on the nucleation curve and these points will be used later to convert the time size scale into a time scale. One then examines the size distribution of the completed sol. The area lying to the right of a particular D value is determined from the experimental distribution curve for a number of arbitrarily chosen D values. The values of these areas, the fraction of particles having a diameter greater than D, are plotted against log D. We thus have a plot of the number of nuclei against log D. In order to convert this to a time scale one uses the relation

$$t = (a - \log D)/b,$$

the constants a and b being determined from the three values of the number of nuclei at three different times previously obtained by the study of the distribution curves of the three partially nucleated sols. The size distribution curve has been converted into a nucleation curve.

Several implicit assumptions were made in this treatment. In the first place all nuclei were assumed to form with the same original diameter, secondly the law of growth was assumed to hold for nuclei as for the larger particles and finally it was assumed that the addition of hydroxyl amine hydrochloride in the development process stopped the nucleation instantly. Thiessen [15] has stated that in nucleation with citrate the nucleation process is stopped immediately by the hydroxylamine. His statement is based, however, on his failure to observe an induction period. As will be shown below our experiments indicate that there is a definite induction period in the nucleation with sodium citrate.

Finally before leaving the subject of the relation of the size distribution curves as determined by the electron microscope to the nucleation curve, it was of interest to see how the partial nucleation curve (obtained from the samples for which the nucleation was stopped at definite times by development) fit into the complete nucleation curve. The nucleation curves were determined for the three samples from their distribution curves using the method described above. The constant b was the same for all the three developed samples and was taken as that of the final sol since prior to development these partially nucleated samples were mere undifferentiated portions of the nucleating solutions. The curves so obtained were translated along the time axis to obtain for their lower parts the best fit with the complete nucleation curve (Fig. 10). A study of the curve so obtained shows an excellent fit for the lower portions of the nucleating curve of each developed sol. The upper portions of the curve, however, show marked deviations. Instead of a sharp break from the overall curve, the three partially developed sols approach their final nucleus number gradually. Part of this rounding-off of the expected sharp break is undoubtedly due to the imperfect resolution of the electron microscope and to errors in the measurement of the smaller particles. It is thus seen that a good insight can be obtained into the kinetics of nucleation of gold sols by the study of the particle size distribution curves by means of the electron microscope.

The Rate of Disappearance of the Auric Ion.—A study was made of the rate of disappearance of the auric ion during the formation of a gold sol in a sodium citrate + chloraurate system by withdrawing at definite times aliquot portions, running them into concentrated potassium iodide solution, reducing the iodine liberated by a measured excess of standard thiosulphate solution and titrating the remaining thiosulphate with standard iodine solution.[16] The results of a typical experiment are given in Fig. 11. It will be observed that the nucleation process is essentially complete before as much as 5 % of the auric ion has been reduced. The statement of Thiessen [17] that nucleation stops due to the exhaustion of the ionic gold is therefore not applicable to our system. The rate of disappearance of the auric ion is proportional to the concentration of the nuclei and an indication of the size of the nuclei may be obtained in the following way. About one-twentieth of the auric gold has disappeared by the end of nucleation. The ratio of diameters is the cube root of this fraction or 0·36. Since the final diameter of the sol is about 170 Å the mean nuclear size at the end of the nucleation is about 60 Å. From the size distribution curve the smallest particle has a diameter between one-half to two-thirds of the mean, the smallest nucleus should have a diameter of about 30-40 Å.

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[15] Thiessen, ref. (8*c*).

[16] Scotts, *Standard Methods of Chemical Analysis* (ed. N. H. Furman) (D. van Nostrand Co.), 5th edn., **1**, p. 437.

[17] Cf. ref. (8*b*).

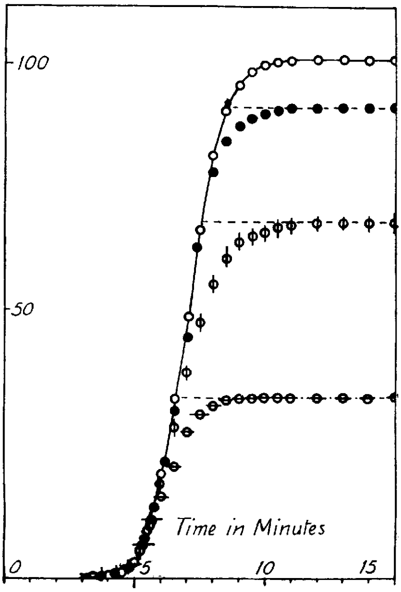


FIG. 10.—Nucleation curves calculated from particle size distribution for a completed sol and three samples developed during nucleation.

Ordinate : number of particles per unit volume ; abscissa : time (min.).

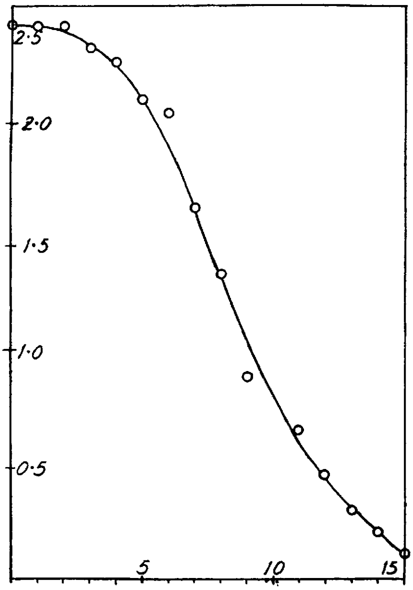
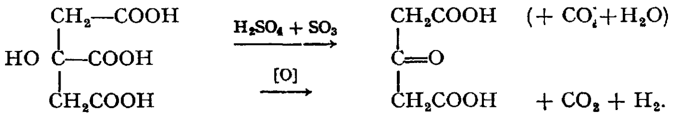


FIG. 11.—Concentration of auric ion as a function of time during reduction with sodium citrate at 49° C.

Ordinate : concentration of $[Au^{+++}] \times 10^5$; abscissa : time (min.).

Isolation of the Nuclei.—An attempt was made to isolate the nuclei for direct examination and the use of ion exchange resins suggested itself for the removal of the auric ion. Four ion exchange resins were used, the cation exchange resins being charged with sodium ion and the anion exchange resins with hydroxyl ions (sodium carbonate). They were well washed with distilled water. A nuclear solution was prepared by incubating the standard sodium citrate + chloraurate system for 19 min. at 30·5° C. The colour of the solution at this time was pale grey. Dowex-50 cation exchange resin had no appreciable effect on the reaction mixture and both nuclei and auric gold passed through the column. Amberlite IRC-100 cation exchange resin proved to be a rapid reducing agent for the nuclear solution ; a clear red colloid came from the bottom of the column. This resin did not, however, reduce pure solution of chlorauric acid. Amberlite IR-4 and IR-4*b*, both anion exchange resins produced no visible effect on the colour. The emergent solution did not liberate iodine from potassium iodide and was therefore substantially free of auric ions. Furthermore it was stable toward boiling and produced a colloid when introduced into growth medium. Electron microscopic examination showed that the particles were surprisingly large and diffuse. Their irregular shape did not permit the determination of a size distribution curve (Fig. 12). Their form and lack of opaqueness suggests that they may contain organic material because irregular bodies such as were seen often result from the decomposition of organic material by the electron beam. The ionic gold could not be eluted from the column by solutions of sodium carbonate, sodium hydroxide, sodium chloride, sodium sulphate, hydrochloric acid, sulphuric acid or nitric acid. The latter attacked the resin vigorously. It is therefore believed that the auric ion was reduced to gold on the surface of the resin.

Role of the Sodium Citrate.—An investigation was made of the chemistry of the process and particularly the role of the citrate ion. The final products and the intermediates, if any occur, of the citrate + chloraurate reaction have not been reported in the literature. However, in the oxidation of citric acid by various reagents, acetone dicarboxylic acid has been described as the first intermediate step.[18] This substance can be prepared from citric acid either by intensive dehydration or by mild oxidation, the reactions being



$$\begin{matrix} & CH_2\text{—}COOH \\ & | \\ HO & C\text{—}COOH \\ & | \\ & CH_2COOH \end{matrix} \quad \begin{matrix} \xrightarrow{H_2SO_4 + SO_3} \\ \\ \xrightarrow{[O]} \end{matrix} \quad \begin{matrix} CH_2COOH \\ | \\ C{=}O \\ | \\ CH_2COOH \end{matrix} \quad \begin{matrix} (+ CO + H_2O) \\ \\ \\ \\ + CO_2 + H_2. \end{matrix}$$

It was proposed to study the action of acetone dicarboxylic acid on chlorauric acid.

Acetone dicarboxylic acid was prepared in the following way.[19] 25 g. citric acid were treated in an Erlenmeyer flask with 50 g. fuming sulphuric acid (15 % excess SO_3). After standing for 15 min. the flask was cooled in an ice-salt mixture for ½ hr. and 25 g. of crushed ice were added. Crystals of acetone dicarboxylic acid were filtered off this viscous mixture, washed with ethyl acetate and dried in air. A solution of 0·05 M of the sodium salt was made by dissolving the acid in 0·1 N NaOH.

10 ml. of chlorauric acid (containing 1 mg. of Au) was diluted with 9 ml. of water and treated at the boiling point with 1 ml. of the sodium acetone dicarboxylate solution. A clear red colloid formed with great rapidity passing swiftly through the blue state similar to that observed during the synthesis using the citrate ion. A faint but definite odour was observed similar to that noted during the synthesis with the citrate ion and resembling the odour of formaldehyde. Kuyper[20] reports that the oxidation products of acetone dicarboxylic acid are formic acid, formaldehyde and CO_2. An identical reaction mixture prepared at room temperature (23° C) showed the first detectable colour of faint pink in 1 min. growing darker over a period of several hours. The reaction was believed to be complete in 4 hr. The synthesis with acetone dicarboxylate exhibits little or no induction period and this is verified from the nucleation curve (Fig. 13) obtained from the size distribution curve (Fig. 14).

The Character of the Nucleation Curves.—An examination of the nucleation curve (Fig. 15, 16) shows that it has in general four regions: an induction period, followed by a rapid rise at the beginning of the nucleation, a " linear " portion and finally a decay portion. The general nature of the curve is characteristic of an autocatalytic reaction.

The induction period can best be examined by the nephelometric techniques. Its exact duration is difficult to determine for it involves extrapolation, to zero of a curve of rapidly changing curvature. One can say, however, that its duration decreases with increase in temperature as the approximate induction times of 26 min. at 15° C, 5 min. at 30° C, 3 min. at 39° C and 2 min. at 49° C indicate. One can use these values to calculate an approximate activation energy of about 10 kcal./mole. The process responsible for the induction might be interpreted as the removal of an inhibitor of the nucleation process. However, the fact that when one uses acetone dicarboxylate, an oxidation product of the citrate ion, there is an induction period of less than 1 min., indicates that the induction period is the time necessary to form an amount of acetone carboxylate ion necessary for nucleation. Examination of the effect of dilution on the induction period at 100° C with the citrate ion as the reducing agent shows that it increases with dilution. Varying the citrate ion does not affect the induction time. Finally the decrease in the auric ion concentration during the induction period is less than 1 %. Since the production of acetone dicarboxylate ion involves the reduction of auric ion, this indicates that only a small number of acetone dicarboxylate ions can have been produced during this time.

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[18] Bruce, *Ind. Eng. Chem.* (*Anal.*), 1943, **6**, 283; Kuyper, *J. Amer. Chem. Soc.*, 1933, **55**, 1722.

[19] *Organic Synthesis* (Ed. Marvel) (John Wiley and Sons Inc.), **5**, p. 5.

[20] See ref. (18).

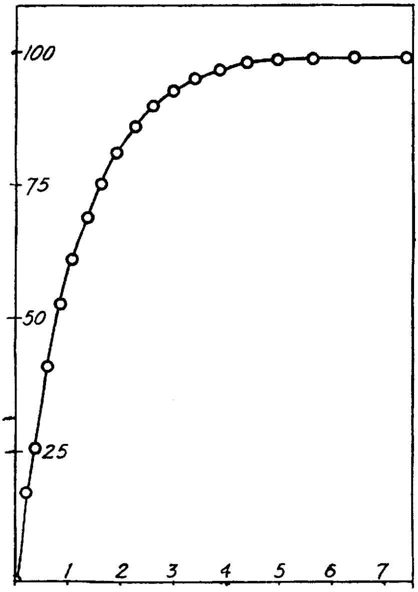

FIG. 13.—Nucleation curve of a gold sol produced by acetone dicarboxylic acid. Ordinate : % total number of particles per unit volume ; abscissa : time (min.).

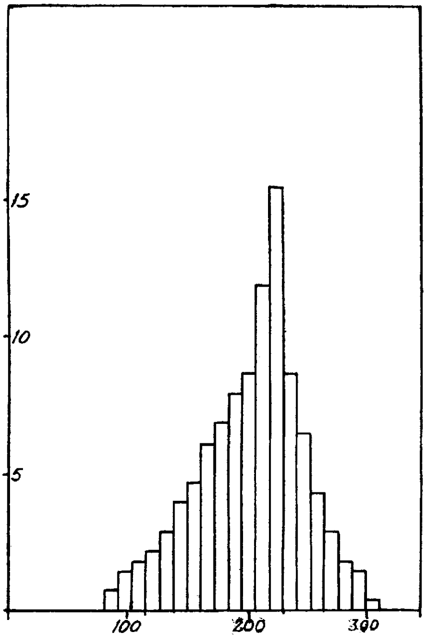

FIG. 14.—Size distribution of a sol reduced with acetone dicarboxylic acid. Ordinate : % particles ; abscissa : diam. (Å).

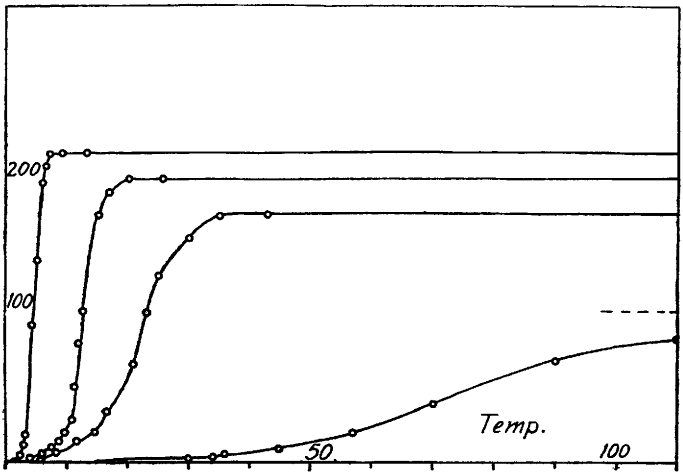

FIG. 15.—Nucleation curves at 49·5°, 39·0°, 30·0° and 15·4° C (nephelometric method). Ordinate : particles per unit volume ; abscissa : time (min.).

The second portion of the nucleation curve is one of rapid increase in the number of nuclei with the rate of increase increasing with time. On increasing the temperature this autocatalytic character becomes more pronounced in that d^2n/dt^2 is greater the higher the temperature (n is the number of nuclei and t is the time). Dilution markedly decreases the autocatalytic character indicating a high order dependence of this rate on the total concentration of the reactants. Decrease in the citrate ion concentration produces a similar effect. It should be noted that this autocatalytic character is absent from the nucleation curve produced by the acetone dicarboxylate. The rate of nucleus formation is a maximum at the *start* of nucleation and falls off exponentially indicating a first-order mechanism. One is therefore led to the conclusion that the autocatalytic nature of the nucleation reaction is due to the autocatalytic nature of the formation of the acetone dicarboxylic acid from the citric acid or some complicated phenomenon involving acetone dicarboxylate.

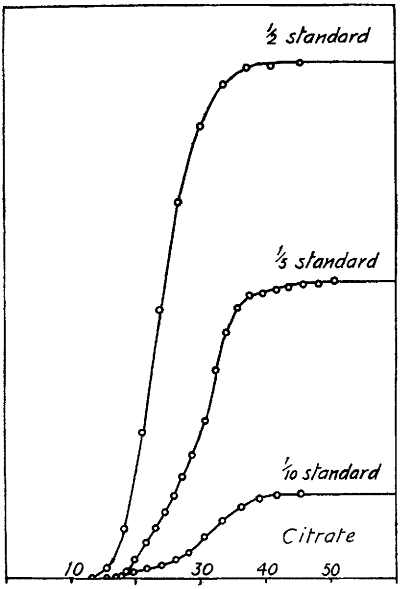

FIG. 16.—Nucleation curves at various citrate concentrations at 100° C (size distribution method).
Ordinate : particles per unit volume ; abscissa : time (min.).

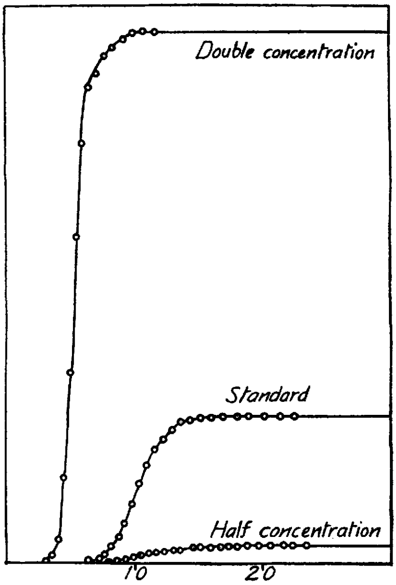

FIG. 17.—Nucleation curves at various dilutions (size distribution method) ; ordinate and abscissa same as Fig. 16.

The third portion of the curve, the " linear " portion, is most pronounced for experiments at high concentration or high temperatures. It is significant to note that under these conditions it resembles the nucleation curve observed with acetone dicarboxylate. We are again inclined to ascribe to the acetone dicarboxylate an important role in this region of the nucleation curve. If one plots the logarithm of $(N_\infty - N_t)$ against time for the nucleation by acetone dicarboxylate at 100° C one obtains a curve given in Fig. 18. The straight-line character of the relationship shows that we have a kinetic expression of the type

$$N_t = N_\infty(1 - e^{-kt}) \quad . \quad . \quad . \quad . \quad (4)$$

and this suggests that the rate-determining step in the nucleation process is the unimolecular decomposition of a complex of gold and acetone dicarboxylate. The kinetics of this decomposition will be a subject of further study.

The slope of the last portion of the nucleation curve decreases rapidly with time as if one of the reagents is being exhausted. The explanation of this phenomenon is just as important as the explanation of why nuclei form. It is a region most difficult to examine experimentally because one is dealing with a system undergoing small changes in large absolute values of the observables. One cause contributing to the decrease in the rate of formation of the nuclei is the competition of the growth process. For as the particles grow larger and are present in greater number, they grow more rapidly and begin to exhaust the " active " species of the nucleation process. This active species cannot be the auric ion for it has been previously established that about 95 % of the original auric ion is present at the time when the nucleation process has ceased. The active species cannot be the citrate ion because it is present in three to tenfold excess over the auric ion. One is thus led to the conclusion that the active species that is exhausted must be closely identified with acetone dicarboxylate. It is this compound that creates the nuclei and it is quite possible that when there is a sufficient number of nuclei present they adsorb the acetone dicarboxylate on their surface and either utilize it as a reducing agent for the growth process or merely decompose it catalytically. In support of this idea we wish to cite from an experiment on the growth process which will be presented in more detail in the section on the growth process.

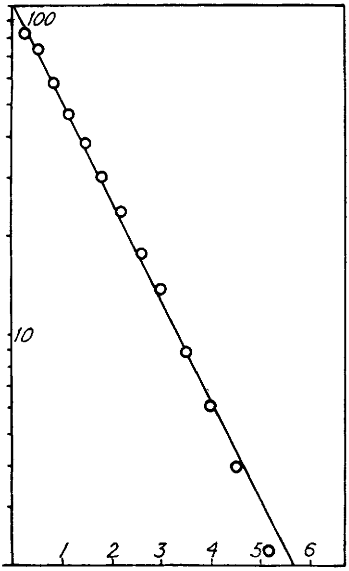

FIG. 18.—Demonstration that nucleation with acetone dicarboxylic acid resembles a first order reaction.

Ordinate : log $[N(\infty)-N(t)]$; abscissa : time (min.).

A solution of sodium citrate and chloraurate was allowed to interact at 70° C. A few minutes after mixing these reagents a known amount of 200 Å gold sol was added. Examination of the product in the electron microscope revealed but one maximum in the distribution curve. If, however, the 200 Å sol was added to the sodium citrate + chloraurate system several minutes after the completion of the nucleation the sol obtained had two maxima, one due to the growth of the added 200 Å particles and one due to the growth on the nuclei already formed. The absence of a second maxima in the first case is taken as evidence that a large number of nuclei, artificially introduced, inhibit the nucleation process. Thus we are inclined to ascribe the slowing-down of the nucleation process to the removal of the acetone dicarboxylate by the increasing number of gold particles. Further evidence that a gold-containing species is strongly adsorbed on the growing particles during the growth stage of the citrate reaction, will be presented in the following section.

The total number of nuclei per unit volume increases with the concentration of the gold and citric ions and appears to reach a maximum at some temperature between 40° and 70° C. This unusual temperature dependence may be associated with the observation that dilute aqueous solutions of acetone dicarboxylic acid begin to decomposed at about 60° C. Hence above this temperature the tendency of increased temperature to produce a greater number of nuclei is more than compensated by the lower concentration of the acetone dicarboxylate ions due to its decomposition. This point will be the subject of further study.

Mechanism of Nucleation.—No completely satisfactory theory concerning the precise mechanism of the formation of nuclei in dilute solution has yet been worked out. One possible theory is that nuclei are artificially introduced. This " impurity " theory in its various forms reduces simply to the hypothesis that the nuclei are introduced into the system as dust particles, bacteria, spores, bits of glass or sharp points on the inside of glass containers. There is no doubt that very often such substances produce nucleation, and lack of cleanliness and flagrant disregard of certain common-sense precautions such as cleaning vessels from nuclei of previous preparations can explain the varying success of many previous workers in the field of colloidal gold. Again it should be pointed out that a few nuclei accidentally introduced do not produce colloidal gold, but a coagulum of metallic gold. Because of the consistent behaviour obtained in this investigation under different conditions of concentration, temperature, time of the year, starting materials and glass apparatus, we have come to the conclusion that impurities were not a variable in our investigation.

The fluctuation theory is one of great tradition. It postulates the formation of a supersaturated solution of atoms of metallic gold some of which coalesce into a nucleus only when the statistical fluctuation of their concentration brings a sufficiently large number of them together to form a particle of a size that is thermodynamically stable. Thiessen [20] has stated that this number is about a hundred. This theory has been shown by LaMer and Kenyon [21] to apply to the formation of colloidal sulphur. It is possible that it might apply to our case but it is difficult to understand the marked temperature dependence of the rate of nucleation from the fluctuation point of view. Furthermore our investigation indicates that the nuclei are about 30 Å diam. and this would involve a fluctuation of the order of a million of gold atoms.

We wish to advance the following " organizer " mechanism for the formation of a nucleus. The fundamental difficulty in building up a nucleus is the accumulation of a large local concentration of atoms to produce a particle whose size is greater than that just demanded by the stability of the particle. The fluctuation theory describes such an event as being rare but significant and due primarily to the statistical nature of physical events. One may attain the same result by postulating that the nucleating agent gradually builds up a complex between the gold ions thereby chemically binding a large number of both gold ions and reducing agent molecules into large macromolecules which at some stage or other will undergo a molecular rearrangement to produce metallic gold particle of sufficiently large size. This event will be accompanied by the production of oxidation products of the reducing agent. This precursor of the nucleus may be considered as a copolymer of the gold ion and the organizer—a reducing agent which is polydentate and thus capable of forming cross-links between gold ions. This hypothesis finds some support in the nature of the reducing agents capable of causing nucleation. All of these are polydentate containing in the same molecule more than one group capable of forming a bond with the gold ion. Acetone dicarboxylic acid is known to form a stable complex with mercury [22] and is functionally related to acetoacetic acid, a well-known complex-former. Citric acid is known to form complexes with copper and iron [23] and is tetradentate in these complexes. Carbon monoxide forms carbonyls [24] which are stated to be polymeric for elements of odd atomic number such as gold. Acetylene forms complexes with silver and copper acting as a dibasic acid.

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[20] See ref. (8*b*).

[21] LaMer and Kenyon, *J. Colloid Sci.*, 1947, **2**, 257.

[22] Bruce, ref. (18).

[23] Lanford and Quinan, *J. Amer. Chem. Soc.*, 1948, **70**, 2900 ; Fales and Kenney, *Inorganic Quantitative Analysis* (The Century Company, New York, 1939), p. 345.

[24] Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1945), p. 453.

An ether solution of phosphorus has been suggested by Faraday as a reducing agent for the production of colloidal gold. In our point of view it is the fine emulsion of phosphorus in water produced by the mixing of the ether solution with the gold chloride solution that acts as an organizer. The gold ions are adsorbed on the surface of the phosphorus droplets, are reduced there to metallic gold, and migrate on the surface to form a particle of sufficient size to exist as a nucleus. It is the binding on the surface in this case, just as the binding of the gold atoms by the polydentate reducing agents in the macromolecule, that ensures the continued high concentration of gold atoms on the surface of the phosphorus droplet thereby permitting the gold particle to reach a size great enough for an independent existence as a nucleus.

Growth Process.—In order to complete the experimental study of the process of the formation of colloidal gold in solution it was thought desirable to study the process of growth. Most reagents used for the preparation of gold colloids by reduction, cause both nucleation and growth. Fortunately two substances, hydrogen peroxide and hydroxylamine hydrochloride have been found by previous workers to act under certain conditions as solely growth reagents. The study of the growth reaction differs markedly from that of nucleation in that in the latter one studies the number of particles as a function of time while in the former the size of the individual particle is examined.

GROWTH IN HYDROXYLAMINE HYDROCHLORIDE REAGENT.—It was shown in the previous section that particles of gold prepared by the reduction of gold chloride with sodium citrate at 100° C are very uniform in size at about 200 Å diam. It was thought desirable to use the method of Zsigmondy [25] to prepare a graded series of gold sols of different but predetermined particle size. Accurately measured amount of the growth medium (equal volumes of chlorauric acid (0·01 % Au) and hydroxylamine hydrochloride (0·027 % by weight) were added to various amounts of sodium citrate gold sol containing a known concentration of 200 Å particles. Reduction commenced immediately on mixing and proceeded rapidly and smoothly, the gold sol developing completely within a few minutes of the mixing. In cases where the preparation of sols of a very large diameter was desirable, it was felt advantageous to carry out the reaction in steps using sols grown from the 200 Å particles for the inoculation of the growth medium. In this method advantage is taken of the fact that a slightly acid solution of chlorauric acid and hydroxylamine hydrochloride (growth medium) in a scrupulously clean closed vessel will not produce colloidal gold until a sufficient number of nuclei are introduced. When the growth medium is inoculated with nuclei, the chlorauric acid is reduced by the hydroxylamine and the metallic gold so formed is deposited only on the nuclei so that they increase in size but not in number. The mean diameter of the resulting particles can easily be shown to be

$$D_f = D_0 \sqrt[3]{\frac{M_i + M_m}{M_m}}, \quad . \quad . \quad . \quad . \quad (5)$$

where D_f is the mean diameter of the final colloidal particle, D_0 is the mean diameter of the nuclei used, M_i and M_m are the respective masses of the ionic gold in the growth medium and the metallic gold of the gold nuclei used in the growth medium. The results are presented in Table IV. The observed mean particle size compare very favourably with those predicted on the basis of the above formula. In addition to this confirmation of the formula it was noted that the percentage root-mean-square deviation changed but relatively little with quite large changes in the particle size. A definite trend in this change was observed however in that the percentage root-mean-square deviation decreased from 13 % for the 200 Å nuclear sol to about 8·5 % for the 1000 Å sol. This decrease is believed to be more apparent than real for the following reasons. In the first place the average experimental error in the particle size measurement due to imperfect resolution of the electron microscope and to personal errors in the image measurement was approximately constant in amount from sample to sample and hence contributed more to the percentage deviation of the distribution of the smaller particles. In the second place a study of the small angle X-ray scattering [26] of the 200 Å sol has revealed that the root-mean-square deviation of particle diameters is not 13 % but may be about 8·5 %. We are thus led to the conclusion that the percentage root-mean-square deviation does not change with growth in particle size in the range size investigated. Our observations confirm the experiments of Rinde [27] on the particle size determinations by sedimentation studies. It can be easily seen that the law of growth consistent with the observation that the root-mean-square deviation does not change is

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[25] Zsigmondy and Thiessen, *Das Kolloide Gold* (Leipzig, 1925) and ref. 8(*b*) ; and Rinde, ref. (5).

$$dD/dt = kD, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where D is the diameter of the particle, t is the time and k is a constant whose magnitude depends on the temperature and reagent concentration but not on particle size.

A further insight into the law of growth was obtained from the following experiment. From a standard 200 Å mean diameter sol, a sol was prepared by the method described above with a mean diameter of 300 Å, 27 ml. of this sol were mixed with 8 ml. of the 200 Å sol and the size distribution curve of the mixed sol was measured. The mean diameter of the mixed sol was then increased by a factor of two by growth in a hydroxylamine+auric chloride solution. The size distribution of the particles of the resulting sol was also measured. In both cases two maxima were observed. In the first sol the maxima were at 200 Å and 300 Å while in the second case they were 400 Å and 600 Å (Fig. 19). Integrating the law of growth leads to the conclusion that during growth the *ratio* of the particle sizes is

$$\ln \frac{D'}{D} = c(t - t')$$

remains constant and not the difference in particle sizes. The above experiment clearly confirms this deduction.

A chemical study was also made of the growth reaction using hydroxylamine hydrochloride. Observations with the glass electrode indicated that the pH dropped during the growth reaction. It was not found possible to study the rate of formation of the hydrogen ions. The iodometric method of Gooch and Morley [28] was applied to the study of the kinetics of the disappearance of the auric ion. Runs were made at four temperatures, at several nuclear concentrations, with nuclei of different sizes and several hydroxylamine concentrations. The reaction was found to be first order with respect to the auric ion, hydroxylamine, added metallic gold nuclei and hydroxyl ion concentrations, indicating that none of these reagents is strongly adsorbed. The first-order dependence on the added nuclei is stated on the basis of added gold *atoms*, i.e., the rate observed when a large nuclei were added was the same as observed when the smaller nuclei were added provided that the total concentration of metallic gold was the same (more smaller particles). This is equivalent to the law of growth stated above. The experimental activation energy was found to be 9·1 ± 0·6 kcal./mole for two sizes of nuclei.

[26] Turkevich and Hubbell, *J. Amer. Chem. Soc.*, 1951, **73**.

[27] Rinde, ref. (5).

[28] Kolthoff and Furman, *Volumetric Analysis* (John Wiley and Sons), **2**, p. 469 ; Kurtenacker and Wagner, *Z. anorg. Chem.*, 1922, **120**, 26.

The stoichiometry of the reaction was also investigated. The gold ion solution used was standardized iodometrically as described above while the hydroxylamine hydrochloride was oxidized in strong hydrochloric acid solution by the method of Kurtenacker and Wagner.[29] The metallic gold colloid must be removed by adsorption on TiO_2 previous to titration since acid bromate solutions readily oxidize metallic gold and give false readings. It was found that 1·00 mmole of $HAuCl_4$ oxidizes 1·0 ± 0·5 mmoles of hydroxylamine. The reaction is probably

$$HAuCl_4 + NH_2OH \,.\, HCl \rightarrow Au + 5HCl + NO.$$

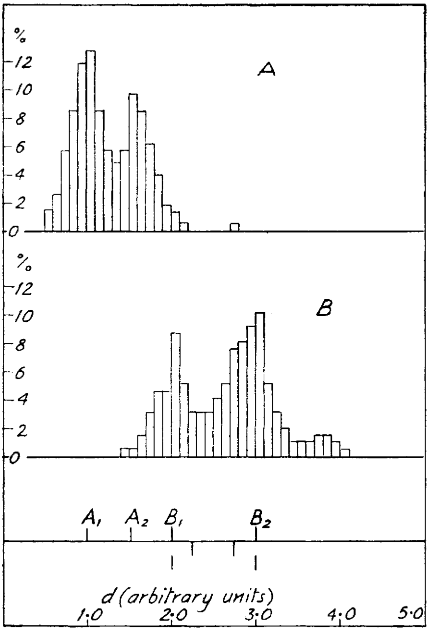

FIG. 19.—Demonstration of the law of growth using the electron microscope.

GROWTH IN SODIUM CITRATE REAGENT.—It is quite possible that the exponential law of growth obtained for the hydroxylamine hydrochloride reagent may be peculiar to reduction by the hydroxylamine hydrochloride. It was therefore decided to investigate the law of growth in the sodium citrate system. In a subsequent communication on the optical properties of monodisperse gold sols of different diameters it will be shown that the absorption spectrum of uncoagulated colloidal gold has a single absorption maximum in the visible region which varies in a regular way with the particle size after 300 Å and that the optical density of the sol per particle for the absorption maximum follows the law

$$d = \text{const.}\ nD^{2\cdot 8}, \quad . \quad (7)$$

where n is the number of colloidal particles per ml. and D is the mean particle diameter. Since we have shown in the preceding section that the number of particles per unit volume becomes constant very soon after the mixing of the reagents at the higher temperature, this relationship can be used to obtain the particle size as a function of time from the equation

$$\frac{D(t)}{D(\infty)} = \left[\frac{\mathrm{d}(t)}{d(\infty)}\right]^{\frac{1}{2\cdot 8}}, \quad . \quad . \quad . \quad . \quad (8)$$

the final diameter $D(\infty)$ being determined by the electron microscope. Three runs were made on the standard sodium citrate preparation at 70° C using a Beckmann spectrophotometer to measure d. The readings were found to be reproducible, the points for the three runs falling close to the same smooth curve. Points obtained for very short reaction times were not considered reliable as the number of particles was not constant. A plot of log D against t gives a straight line up to times until almost all of the gold is reduced, indicating that the growth reaction follows the growth law given above but is zero order in the reagents used (Fig. 20). This zero-order behaviour is consistent with a surface reaction in a strongly adsorbed layer of reactants. It may be recalled that the cessation of the nucleation process was ascribed by us to the strong adsorption of the active species by the gold particles formed. Extrapolation of the straight line to zero time gives a value of 48 ± 5 Å for the diameter of the nucleus, a value consistent with estimates given in the section on nucleation.

Some further evidence was desired to show that the exponential law of growth did indeed hold for the growth process using sodium citrate. It was shown above that when the law of growth was exponential, the ratio of the diameters of two particles growing in the same reaction medium does not change with time. Experiments were devised in which particles of known large size were added to the growing colloid at several times during the growth process. It was expected that the size distribution curve of the resulting sol on completion of the reaction would show two maxima, one due to the added particles and one due to those present when the particles were added. The ratio of the diameters at which these maxima occurred should be the ratio of the mean particle size in the growing sol to the mean diameter of the added particles at the instant of mixing. Since the latter is known, the former can be easily evaluated. Several samples were prepared using sodium citrate as the nucleating and growth agent at 70° C. The first of these was allowed to go to completion. At definite times the other samples were diluted with equal volume of the completed sol. Size histograms were obtained with the electron microscope for these sols after the reaction was completed. In most cases two maxima were observed in the size distribution curve. When these occurred the ratio between the diameters at which these peaks occurred were used to calculate the diameter of the growing colloid at the time of the addition of the completed sol. The points so obtained agree with those derived by the optical method (Fig. 21). In the sample prepared by adding the completed gold colloid immediately after mixing of the sodium citrate and the chlorauric acid solutions only a single maximum in the size distribution curve was produced. This was interpreted to mean that a large number of gold particles in solution inhibits nucleation by successful competition for the active species.

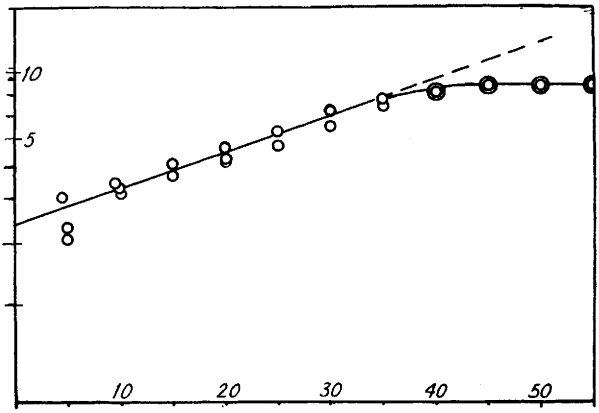

FIG. 20.—Growth in the citrate sol. Ordinate : log relative diameter ; abscissa : time (min.).

Mechanism of Particle Growth.—Consideration of the law of growth of a particle in a solution which deposits material on the surface by a typical heterogeneous reaction leads to a formula of the following type

$$\frac{\mathrm{d}D}{\mathrm{d}t} = \frac{K\Delta}{KD + \Delta} C_{\infty} V, \qquad (9)$$

where K is the specific rate constant for unit area for the surface reaction, D is the diameter of the particle, Δ is the diffusion coefficient of the active species, V is the molal volume of the metallic gold and c_∞ is the concentration of the active species at large distances from the particle. It is seen that if the diffusion is the rate-determining quantity, then the rate of change of diameter is inversely proportional to the diameter; while if the process is limited by the surface reaction, then the rate of change of the diameter with time is independent of the diameter. The observed law is neither and demands that the rate of change of diameter with time be proportional to the diameter. A mechanism of this exponential law of growth must await further experimental studies of the growth reaction.

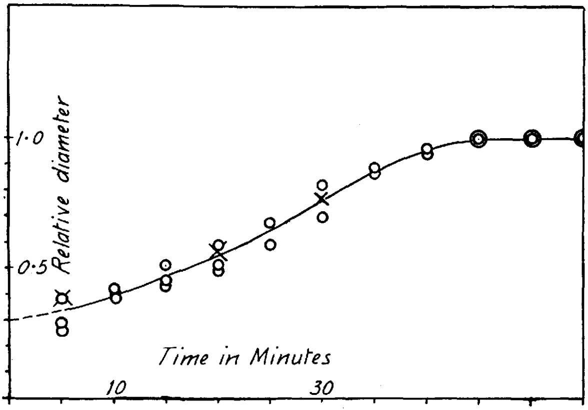

FIG. 21.—Growth in the citrate sol. Open circles are from optical data, crosses are from electron microscope data.
Ordinate: relative diameter; abscissa: time (min.).

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