Formation and Aging of Precipitates. VIII. Formation of Monodisperse Particles (1) Gold Sol Particles by Sodium Citrate Method*

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Recently many investigations on the precipitation from homogeneous solution have been made to prepare pure and filterable precipitates. The author prepared a few kinds of monodisperse particle by the homogeneous solution method to study the reaction of precipitation. In this paper the formation of gold sol, containing monodisperse particles, is reported. A great many methods for preparing the gold sol have been investigated, but only the sodium citrate method, reported by Turkevich, Stevenson and Hillier(1), seems to be suitable to produce monodisperse gold particles. The author took advantage of the sodium citrate method to prepare the gold sol, and studied the relationship between the condition of formation and the properties of particles produced, and the growth process of gold particles by electron microscopy.

Experimental

Formation of Gold Sol.—Varying amounts (1, 2, 5, 7.5, 10, 15, 20 and 25 ml.) of chlorauric acid solution (0.10% Au) were taken into Erlenmeyer flasks with two openings and diluted with

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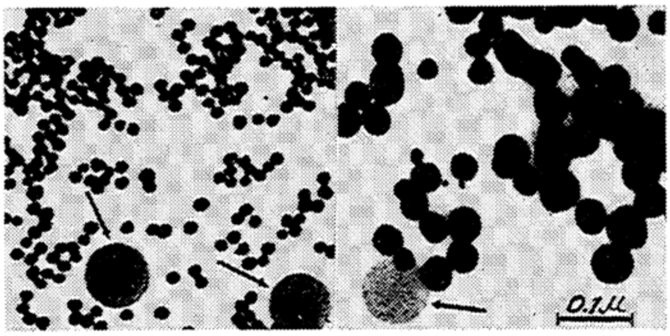
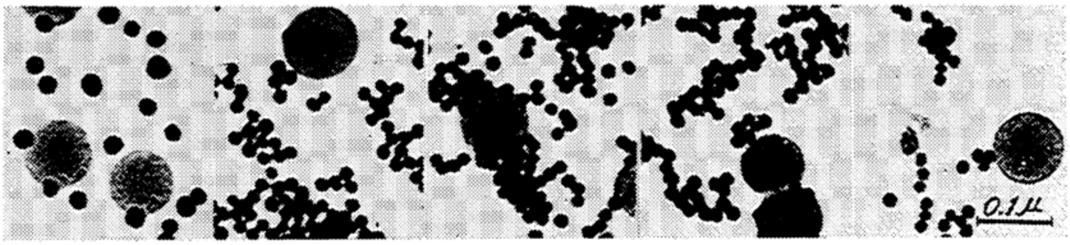
* The seventh paper of this series, This Bulletin, **31**, 555 (1958).

1) J. Turkevich, R. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, **11**, 55 (1951).



(a) (b) (×100,000)

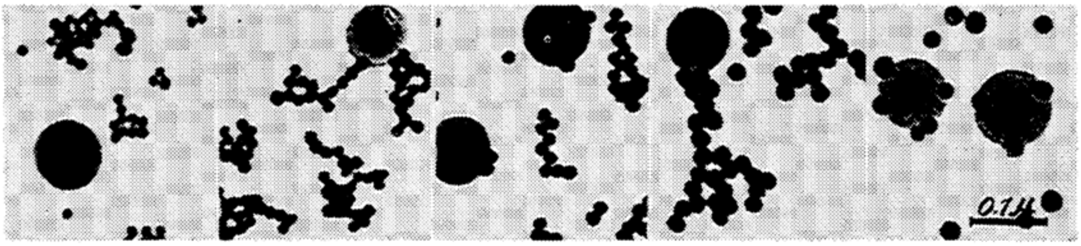
Fig. 1. Electron micrographs of gold sol particles.
a: Sodium citrate sol b: Zsigmondy sol
(Larger particles in micrographs (arrow) are polystyrene latex particles (880 Å in diameter) using as calibration standard)



(a) (b) (c) (d) (e)
(×100,000)

Fig. 4. Electron micrographs of gold particles prepared from the various initial concentrations of auric ion at 80°C.

a : 10.15×10^{-5} moleAu/l. (2 mg.Au/100 ml.)
b : 25.37×10^{-5} moleAu/l. (5 mg.Au/100 ml.)
c : 50.75×10^{-5} moleAu/l. (10 mg.Au/100 ml.)
d : 76.13×10^{-5} moleAu/l. (15 mg.Au/100 ml.)
e : 101.50×10^{-5} moleAu/l. (20 mg.Au/100 ml.)



(a) (b) (c) (d) (e)
(×100,000)

Fig. 6. Electron micrographs of gold particles prepared at various temperatures. (25.37×10^{-5} moleAu/l.)
a: 50°C b: 60°C c: 70°C d: 80°C e: 100°C

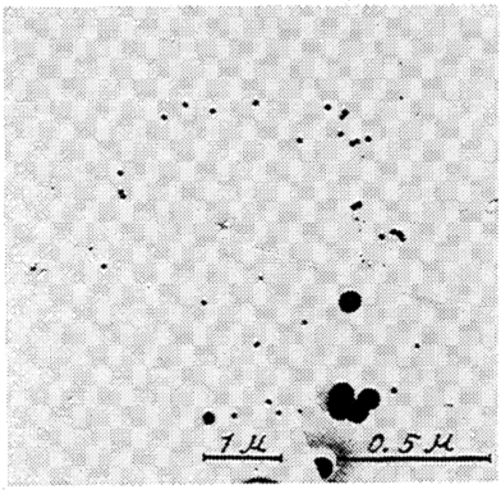
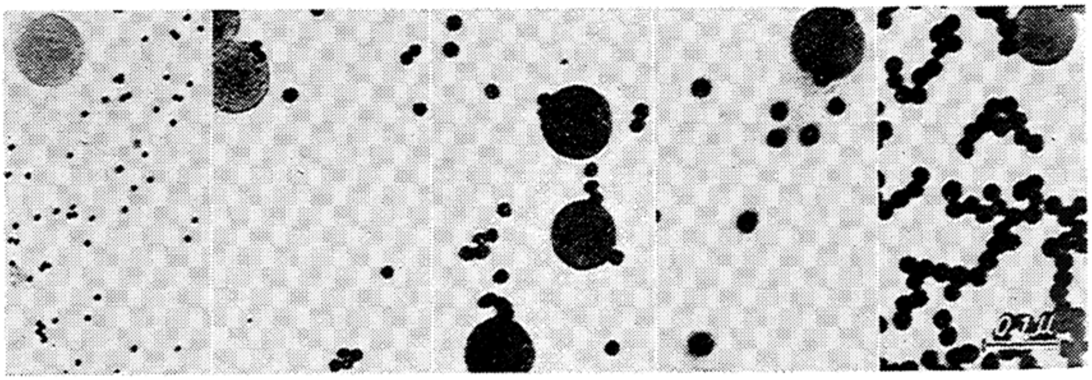


Fig. 8. Electron micrograph of spray mounted drop pattern of gold sol. (Small particles are gold and large particles are polystyrene latex.) (×10,000)
One segment further enlarged. (×40,000)



(a) (b) (c) (d) (e)
(×100,000)

Fig. 9. Electron micrographs of gold particles during the growth process. (25.37×10^{-5} moleAu/1., 80°C)
a: 5 min. b: 10 min. c: 20 min. d: 30 min. e: 60 min.

water to 90 ml. After the solutions were warmed to a desired temperature (50, 60, 70, 80 and 100°C), 10 ml. of sodium citrate solution (1.0%) was added to them, the reaction flask connected with a reflux condenser and a thermometer was held in a thermostatted bath.

Measurement of Size of Gold Particles with Electron Microscope.—The diameter of gold sol particles has been determined by electron microscopy. Particle-diameter measurement was made from micrographs enlarged at ten-fold magnification. The particle-diameter distribution, the mean particle-diameter** and the standard deviation*** were obtained. The monodisperse polystyrene latex, run No. LS-040-A (880 Å in mean diameter)[2], of the Dow Chemical Co., has been used as calibration standard to measure the particle-diameter****. At different intervals during the course of a reaction, a drop of the reaction mixture was taken onto a small Formvar film, and the film with the drop was floated on the surface of cold water. About ten minutes, the drop on the film was allowed for diffusion of mother liquid ions from the drop into the water below. The film was scooped up with a grid for electron microscopy and was mounted with polystyrene latex. The specimen was observed with electron microscope to determine the growth rate of gold particles.

Determination of the Number of Gold Particles by Spray Method[3].—At fixed intervals during the reaction of sol formation, about 10 ml. of the reaction mixture was taken and was poured into a test tube, dipped in an ice bath, to stop the reduction of the auric ion. 5.0 ml. of this sample was mixed thoroughly with 1.0 ml. of polystyrene latex to a definite concentration, and then the mixture was sprayed with a Vaponefrin Nebulizer onto a film made on grid for electron microscopy, which was placed about 20 cm. away from the nozzle of the nebulizer. The specimen was observed with an electron microscope. The number of gold particles during the course of sol formation was estimated by counting the number of gold and polystyrene latex particles in droplet patterns.

Determination of Gold Sol Concentration by Absorption Spectroscopy.—An absorption spectrum of gold sol was measured with Hitachi spectrophotometer, using 1-cm. cell, at intervals of 5 mμ over a range of 350 to 700 mμ and a relation between concentration and absorbance was obtained at the wave length of absorption maximum. Absorption spectra of the reaction mixture during the course of sol formation were also obtained.

Experimental Results

Size of Gold Sol Particles.—*Uniformity of gold sol particles.*—The gold sol particles prepared by sodium citrate method were almost spherical. An electron micrograph of particles in one of the gold sol, which was formed from chlorauric acid solution at the initial concentration of 25.37×10^{-5} mole per liter (5 mg. Au/100 ml.) at 80°C, is shown in Fig. 1 a and the particle-diameter distribution of gold particles is shown in Fig. 2 a. The mean particle-diameter was 172 Å and the standard deviation was 13 Å. To compare the property of the gold sol, an electron micrograph of particles in the Zsigmondy's sol (25.37×10^{-5} mole Au/l.) prepared by the reduction with an alkaline formaldehyde solution is shown in Fig. 1 b, and the particle-diameter distribution is shown in Fig. 2 b. The shape of particles in Zsigmondy's sol was also spherical, but the mean diameter was 417 Å and the standard deviation was 145 Å. Then the particles in Zsigmondy's sol were polydisperse. Larger spherical particles contained in the electron micrographs (arrows) are polystyrene latex particles. The polystyrene latex particles are also contained in every micrograph indicated below. The size of gold sol particles was affected by the condition of formation as described in the next section. An example of the change of standard deviation by the variation of the condition of formation

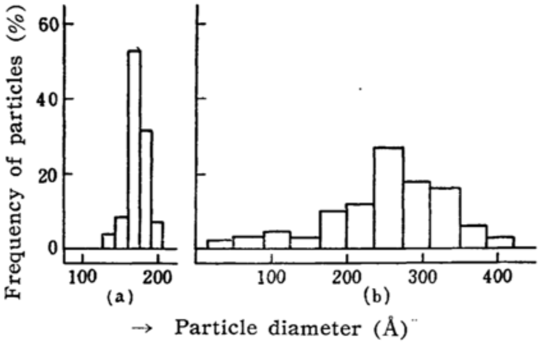


Fig. 2. Particle-diameter distribution of gold sol particles.
a: Sodium citrate sol
b: Zsigmondy sol

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[2] E. B. Bradford and J. W. Vanderhoff, *J. Appl. Phys.*, **26**, 864 (1955).

** The mean particle-diameter used here is the arithmetic mean obtained by

$$d_0=\frac{\sum n_i d_i}{N}$$

where d_0 is the arithmetic mean particle-diameter, n_i is the frequency of particles having diameter d_i, and N is the total number of particles.

*** The standard deviation, σ, is obtained by

$$\sigma=\sqrt{\frac{\sum(d_i-d_0)^2 n_i}{N}}$$

**** Polystyrene latex used here was sent from Dr. E. B. Bradford of Dow Chemical Co. to whom the author's thanks are due.

[3] R. C. Backus and R. C. Williams, *J. Appl. Phys.* **21**, 11 (1950).

TABLE I

THE SIZE OF GOLD PARTICLES PREPARED FROM VARIOUS INITIAL CONCENTRATION OF AURIC ION AT 80°C

Concn. C_0 (moleAu/l. $\times 10^5$)	5.07	10.15	25.37	38.06	50.75	76.13	101.50	126.87
Mean particle dia. d_0 (Å)	149	191	172	173	168	155	140	146
Standard deviation σ (Å)	31.5	9.4	7.5	8.1	8.3	7.1	21.5	28.1
Particle weight $M\times 10^{-5}$	203	430	312	317	290	233	168	191
Particle number* $N\times 10^{-10}$	29	28	97	144	209	390	720	793

* Particle number per ml. of sol. $N=(C_0/\text{mole number of one particle})\times 10^{-3}$

is listed in Table I, and the summarized results are indicated in Fig. 3. For the gold particles in sodium citrate sols prepared over a range of the initial concentration from 20×10^{-5} to 80×10^{-5} mole auric ion per liter and at the reaction temperature above 70°C, the values of standard deviation ranged below 10% of the particle-diameter. Thus the particles are recognized to be monodisperse. The size distribution of the gold sol particles prepared outside the range of concentration and reaction temperature described above became wide, and the particles were not monodisperse.

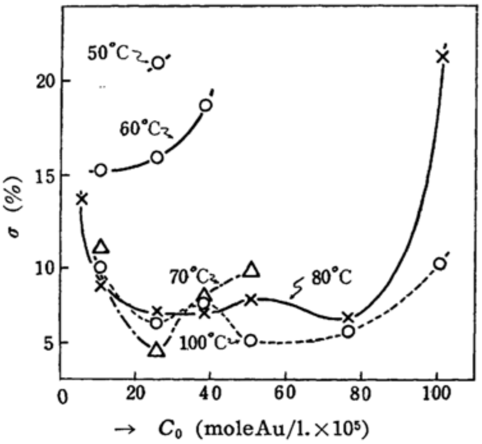

Fig. 3. Relation between the standard deviation of particle-diameter (σ%) and the initial concentration of auric ion (C_0 mole Au/l.$\times 10^5$) of sodium citrate sol.

Relation between initial concentration of the auric ion and size of gold sol particles.— The size of particles in the gold sols was only affected by the initial concentration of auric ions and was not affected by the concentration of sodium citrate over the range from five-fold to ten-fold mole of the auric ion. As the initial concentration of auric ion was increased, the particles became smaller as indicated in Fig. 4 and in Table I. The size of particles is expressed by the particle weight in molecular weight unit, M, calculated according to the following equation:

$$M=(4/3)\pi(d_0/2)^3\rho A$$

where d_0 is the mean particle diameter (cm.), ρ is the density of gold, and A is Avogadro's number. The logarithm of particle weight of the gold sol particles prepared at 70, 80 and 100°C, log M, was linear with the initial concentration of auric ion, C_0 (mole Au/l.), as shown in Fig. 5. Then the particle weight, M, is represented by

$$M=\alpha e^{-\beta C_0} \tag{1}$$

where α and β are constants. α is dependent upon the reaction temperature showing the values of 3.63, 4.79 and 6.31×10^{-7} at 70, 80 and 100°C respectively. β is always constant and is 1000.

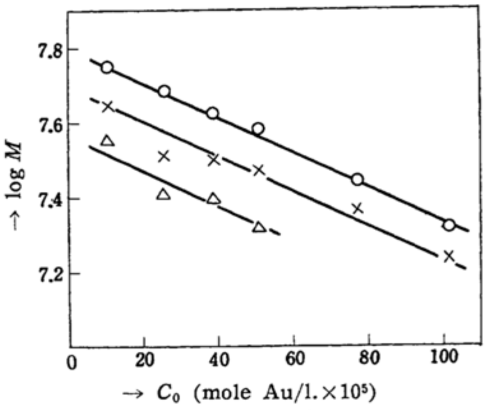

Fig. 5. Relation between the initial concentration of the auric ion and the size of gold particles.

○ 100°C × 80°C △ 70°C

The number of particles per ml. gold sol was related to the size of particles and increased with increasing initial concentration of the auric ion.

Relation between reaction temperature and size of particle. — The size of gold sol particles increased with temperature as shown in Fig. 6. The logarithm of particle weight of gold particles prepared at various concentrations, log M, is linear with the reaction temperature, T (°C), as shown in Fig. 7. Then the particle weight, M, is represented by

$$M=\gamma e^{\delta T} \qquad (2)$$

where γ and δ are constants. γ is a function of initial concentration of the auric ion. They are 9.55, 7.08, 6.76, 6.17, 5.01 and 3.55×10^{6} at 10.15, 25.37, 38.06, 50.75, 76.13 and 101.50×10^{-5} mole Au/l. respectively. δ is always constant and is 0.0184.

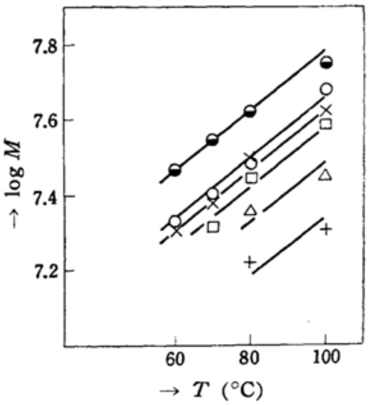

Fig. 7. Relation between the reaction temperature of sol formation and the size of gold particles.

◒ 10.15×10^{-5} moleAu/l.
○ 25.37 〃
× 38.06 〃
□ 50.75 〃
△ 76.13 〃
+101.50 〃

The number of particles per ml. sol prepared at a fixed concentration decreased with the rise of the reaction temperature.

Formation Process of Gold Sol Particle.—*Number of gold particles determined by spray method.*—A spray mounted drop pattern of the reaction mixture during the sol formation is shown in an electron micrograph of Fig. 8. Every droplet sprayed is deposited individually in a circular form and it is possible to determine the number of gold and polystyrene latex particles in each droplet pattern. The relationship between the number of particles of gold and polystyrene latex in the droplet patterns prepared at different times after the commencement of the reaction of the sol formation, is shown in Table II. The polystyrene latex sol used here was the same, so its concentration was unchanged throughout the experiment. The ratio of the number of particles of gold and polystyrene latex in the same run was kept almost constant, and it was recognized that the number of gold particles during the reaction of sol formation was constant over the range of time spent in measuring the number of particles.

Observation of growth process of gold particles with electron microscope.—The growth process of gold particles during the course of sol formation is shown in a series of electron micrographs of Fig. 9. The particles were monodisperse from the initial stage of the reaction. The size of a particle measured at the time t (min.) is expressed by the mole number of one particle, x (mole), calculated from the mean particle-diameter, d (cm.), according to the following equation:

$$x=(4/3)\pi(d/2)^{3}\rho/W$$

TABLE II

THE NUMBER OF PARTICLES OF GOLD AND POLYSTYRENE LATEX IN DROPLET PATTERNS PREPARED BY THE SPRAY METHOD DURING THE FORMATION OF GOLD SOL

No.	Initial concn. of auric ions C_0 (mole Au/l.$\times10^5$)	Reaction time t (min.)	Number of gold particles A_n	Number of polystyrene latex particles P_n	$(A_n/P_n)\times100$
1	25.37	5	329	386	85.2
		10	502	579	86.7
		30	1142	1319	86.6
		60	358	417	85.8
2	25.37	5	142	169	84.1
		10	64	73	88.0
		20	231	271	85.0
		30	304	352	86.5
3	50.75	5	193	103	187
		10	130	72	180
		20	429	229	186
		30	152	82	185

where W is the molecular weight of gold. The plot of x vs. t in two runs exhibits S-shaped curve as shown in Fig. 10.

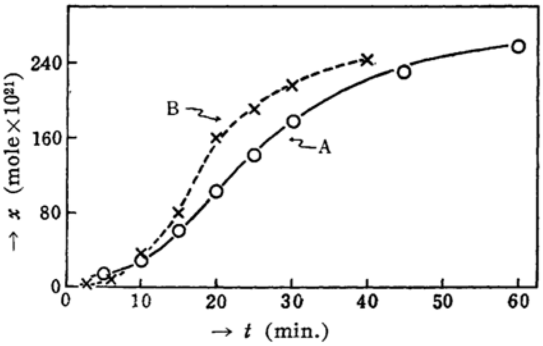

Fig. 10. Growth curve of gold particle measured by electron microscopy.
A: 25.37×10^{-5} mole Au/l.
B: 50.75×10^{-5} mole Au/l.

The rate of growth of a single gold particle is supposed to be expressed by the following equation:

$$\mathrm{d}x/\mathrm{d}t = kx^{2/3}(x_\infty - x) \tag{3}$$

where x and x_∞ are the size of particles at time t and after the completion of the sol, respectively; k is the rate constant. The value of $x^{2/3}(x_\infty - x)$ was calculated and $\mathrm{d}x/\mathrm{d}t$ was obtained from the tangent of the growth curve at time t, and the value of k was calculated from equation 3 and was shown in Fig. 11. The value of k was constant except the very initial stage of the reaction. Then the rate of growth of a gold particle was proved to obey equation 3.

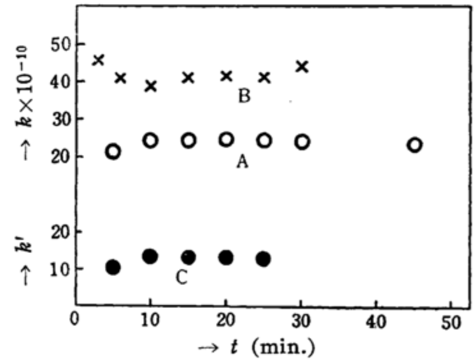

Fig. 11. Constancy of the rate constant.
A: 25.37×10^{-5} mole Au/l.
B: 50.75×10^{-5} mole Au/l. obtained from Fig. 10
C: 25.37×10^{-5} mole Au/l. obtained from Fig. 12

A study was made of the rate of disappearance of the auric ion during the formation of gold sol in the reaction mixture by withdrawing at definite times aliquot portions and analysing by means of iodometry*. The results of the experiment are given in Fig. 12.

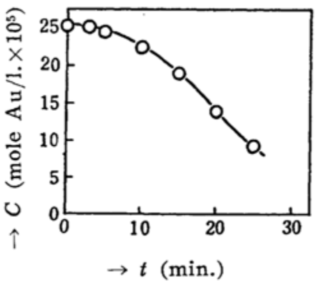

Fig. 12. Reaction rate of gold sol formation measured by the titration.
25.37×10^{-5} mole Au/l.

The rate of disappearance of the auric ion is supposed to be shown by the following equation:

$$-\mathrm{d}C/\mathrm{d}t = k'(C_0 - C)^{2/3}C \tag{4}$$

where k' is the rate constant, and C_0 and C are concentrations of auric ion at initial and at time t during the sol formation. k' calculated from the experimental data is constant as shown in Fig. 11, and it is confirmed that equation 4 was proper.

Absorption Spectra of Gold Sol.—The absorption spectra of the reaction mixture

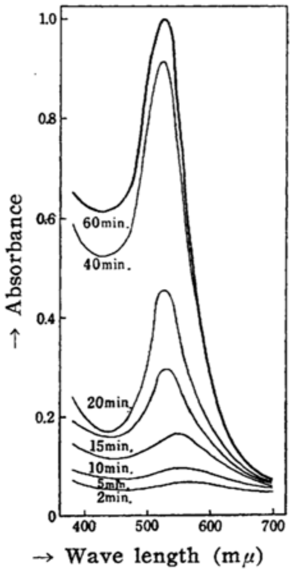

Fig. 13. Absorption spectra of gold sol.
(25.37×10^{-5} mole Au/l., 80°C)

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* Iodine liberated by the reduction of Au^{3+} to Au^{+} oxidize gold particles to Au^{+} and the experimental data were obtained from the corrected volume of standard thiosulfate solution.

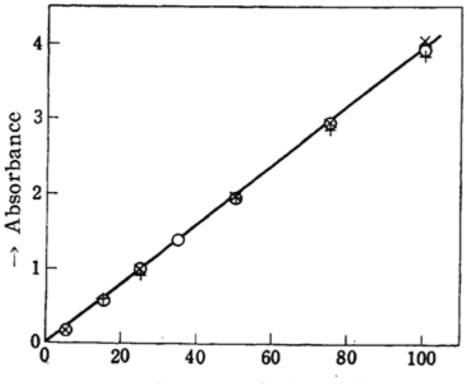

Fig. 14. Calibration curve of gold sol at 525 mμ.

measured at various times after the commencement of the reaction of sol formation are shown in Fig. 13. The maximum absorption shifted slightly toward the shorter wave length as the reaction proceeded. But after the lapse of about one fourth of the total reaction time, the wave length of maximum absorbance was fixed at 525 mμ. The maximum absorbance of gold sol formed under various conditions lay also at 525 mμ. The absorbance of gold sol at 525 mμ was linear with the initial concentration of auric ion as shown in Fig. 14, and the plots of absorbance vs. initial concentration of auric ion of the gold sols prepared above 70°C gave the same straight line.

Discussion

Gold particles in sodium citrate sol were the monodisperse and highly reproducible. Then particles can be used as a calibration standard in the measurement of particle sizes.

The size of particles decreased exponentially with increasing initial concentration of the auric ion. It has been reported that the gold sol particles prepared with various reducing agents in a basic medium increased in size with increasing initial concentration of the auric ion$^{4)}$ and these phenomena were caused by the auric hydroxide produced as an intermediate. The sodium citrate sol is slightly acidic and the pH value is about 5.5. It is supposed that the auric ion exists as a chloride complex$^{5)}$ before the reduction, and that free auric ion produced slowly from the complex reacts with citrate. Turkevich, Stevenson and Hillier$^{1)}$ asserted that acetone dicarboxylate, generated from sodium citrate, reduced chlorauric acid. But as a pure sodium citrate solution was not known to be changed by heating, a certain kind of complex ion may be formed at first between gold and citrate ions, and the complex may be changed to acetone dicarboxylate. It seems that the formation of acetone dicarboxylate is the reaction from homogeneous solution and that the formation of gold sol proceeds homogeneously.

In order to prepare monodisperse particles it is necessary that the nucleation in the formation of gold sol should occur rapidly at the initial stage of the reaction, and that the new particle should not be produced during the growth period of gold particles. It was proved that new particles were not created during the growth process of gold sol particles by the spray method. Turkevich, Stevenson and Hillier$^{1)}$ studied the rate of nucleation in gold sol. But it seems that at high temperature when a certain quantity of substance (acetone dicarboxylate) is generated homogeneously as described above, nuclei of gold are formed rapidly$^{6)}$, and after the nucleation the growth of the particles seems to balance the deposition of gold, and the new particles are not formed.

The growth of gold particles after the nucleation is slow in the initial stage, then rapid and finally the size of particles approaches a definite value. The rate of growth is represented by equation 3. The general nature of the growth process is of an autocatalytic type with respect to the surface of gold particles. This process is also proved by equation 4 obtained from the rate of the disappearance of the auric ion.

The absorption maximum of gold sol shifts toward the shorter wave length as the reaction proceeds; that is, as the size of particle is increased and finally to 525 mμ. The relation between the absorbance at 525 mμ of gold sol produced and the initial concentration of auric ions gives the same straight line for every gold sol containing monodisperse particles ranging from 100 to 200 Å in diameter and the relation is not affected by the reaction temperature. This phenomenon is proved by Mie's theory that the absorbance of

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4) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **36**, 1950 (1930).

5) H. M. Irving and D. Phil, *Quart. Rev.*, **5**, 200 (1951).

6) V. K. LaMer and R. H. Dinegar, *J. Am. Chem. Soc.*, **73**, 380 (1951).

gold sol containing very fine particles is proportional to the product of the volume of one particle with the number of particles in unit volume. Then the small quantity of gold can be determined by the sodium citrate method using the calibration curve described above.

Summary

Gold sol particles prepared by sodium citrate method were monodisperse. The size of gold particles decreased exponentially with increasing initial concentration of the auric ion, and increased exponentially with the reaction temperature. At the initial stage of the reaction of the gold sol formation, the gold nuclei were formed rapidly. After the nucleation the number of particles was kept constant over the whole period of reaction and the particles grew with the autocatalysis-like reaction at the surface of the particle.

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