

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1963, by the American Chemical Society

VOLUME 85, NUMBER 21

NOVEMBER 5, 1963

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Coagulation of Colloidal Gold

By B. V. ENÜSTÜN AND JOHN TURKEVICH

RECEIVED MAY 31, 1963

Kinetics of coagulation with NaClO_4 of 200 Å. colloidal gold which was stabilized by citrate ions was investigated by electron microscopy. The results were compared with the Derjaguin-Verwey-Overbeek theory and an agreement was obtained only in the very early stage of coagulation at low electrolyte concentration. The discrepancies observed otherwise were explained on the basis of variation of the stabilizing potential due to adsorption of cation and anion of the electrolyte introduced. The Hamaker constant A was calculated as 2.3×10^{-13} erg. The morphology of the aggregates formed under various conditions was also explained on the basis of the behavior of the electrical double layer.

1. Introduction

The subject of coagulation of lyophobic colloids has been studied extensively since the early days of colloid chemistry. The aim of these investigations was to establish the mechanism of coagulation and thus to understand the very existence of the colloidal state.

Certain qualitative observations, such as coagulation by electrolytes, the dependence of the coagulation rate on the electrolyte concentration, the existence of a fairly well defined critical concentration as a border line between slow and fast coagulation, and certain empirical rules, such as that of Schultze-Hardy¹ correlating the critical concentration to the valency of the electrolyte had been accumulated when Von Smoluchowski² put forward his well-known theory of kinetics of coagulation. He treated coagulation as a diffusion process and arrived at a series of equations which give not only the rate of rapid coagulation, but also the relationship between the number of clusters formed containing various numbers of primary particles. To describe the kinetics of slow coagulation, Smoluchowski merely introduced a rate-reducing factor in his equations without going further to consider how this factor depended on the nature of the colloid and on the type and concentration of the electrolyte.

Smoluchowski's rapid coagulation theory has been verified satisfactorily by a number of experimental works.³⁻¹² The methods used were ultramicroscopy, colorimetry, and Tyndallometry. Therefore, the veri-

fication of the theory had been confined to the variation of the total number of particles as a function of time and to the absolute rate of coagulation. Recently, a more stringent test was given to the theory by Turkevich and Baker.¹³ They were able to verify the above-mentioned Smoluchowski relationship for the distribution of cluster multiplicity in the course of fast coagulation of 400 Å. colloidal gold, counting the primary particles in each cluster formed with an electron microscope.

When the Smoluchowski theory was applied to slow coagulation, however, it was found that the actual mechanism of this process was too complex to be accounted for by the theory. Such attempts have shown that in the course of coagulation the rate falls off much faster than the theory predicts.^{4-9,11,12,14} In some cases it has been observed that coagulation even stops completely at a certain stage.^{4,7,8,12}

Anderson⁸ and Garner⁹ considered this behavior as a consequence of unequal charge distribution among the primary particles originally present in the system.

Kruyt,¹⁵ on the other hand, assumed that the stabilizing charge was nonuniformly distributed around the particles. At the early stage of coagulation cohesion took place with a high probability in the spots where the potential was lower than in the rest of the surface, leaving the spots with higher potential to participate in coagulation with lower probability at the later stage.

On the basis of the current theory of stability of lyophobic colloids, developed by Derjaguin, *et al.*,¹⁶ and by Verwey and Overbeek,^{12,17} another explanation was given.^{14,17,18} The theory predicts that, other conditions being equal, the bigger the particle size the higher

(1) H. Schultze, *J. prakt. Chem.*, **27**, 320 (1883); W. B. Hardy, *Proc. Roy. Soc. (London)*, **66**, 110 (1900).

(2) M. Von Smoluchowski, *Physik Z.*, **17**, 557, 585 (1916); *Z. physik. Chem.*, **92**, 129 (1917).

(3) R. Zsigmondy, *ibid.*, **92**, 600 (1917).

(4) A. Westgren and J. Reitstötter, *ibid.*, **92**, 750 (1917); *J. Phys. Chem.*, **26**, 537 (1922); A. Westgren, *Arkiv Kemi Mineral.*, **7**, No. 1, 1 (1918).

(5) H. R. Kruyt and A. E. Van Arkel, *Rec. trav. chim.*, **39**, 656 (1920); **40**, 169 (1921); *Kolloid Z.*, **32**, 29 (1923).

(6) E. Hatschek, *Trans. Faraday Soc.*, **17**, 499 (1921).

(7) J. N. Mukherjee and B. C. Papaconstantinou, *Phil. Mag.*, **44**, 305 (1927); J. N. Mukherjee, *J. Chem. Soc.*, **125**, 785 (1924).

(8) L. Anderson, *Trans. Faraday Soc.*, **19**, 623 (1924).

(9) M. Garner and W. C. M. Lewis, *J. Phys. Chem.*, **30**, 1401 (1926); M. Garner, *ibid.*, **30**, 1410 (1926).

(10) P. Tuorila, *Kolloid Beih.*, **22**, 191 (1926).

(11) D. N. Ghosh, *J. Indian Chem. Soc.*, **10**, 509 (1933).

(12) H. R. Kruyt, "Colloid Science," Vol. 1, Elsevier, Amsterdam, 1952.

(13) J. Turkevich, *American Scientist*, **47**, No. 1, 118 (1959).

(14) N. M. Kudryavtseva and B. V. Derjaguin, *Chem. Abstr.*, **56**, 8043 (1962).

(15) H. R. Kruyt, *Proc. Roy. Acad. (Amsterdam)*, **32**, 857 (1929); "Colloids," John Wiley and Sons, Inc., New York, N. Y., 1930, p. 24.

(16) B. Derjaguin and M. Kussakow, *Acta Physicochim. U.S.S.R.*, **10**, 25, 153 (1939); B. Derjaguin, *ibid.*, **10**, 333 (1939); *Trans. Faraday Soc.*, **36**, 203, 730 (1940); B. Derjaguin and Landau, *Acta Physicochim. U.S.S.R.*, **14**, 633 (1941); *J. Exptl. Theor. Phys. U.S.S.R.*, **11**, 802 (1941).

(17) E. J. W. Verwey and J. T. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, Amsterdam, 1948.

(18) H. Reerink and J. T. G. Overbeek, *Discussions Faraday Soc.*, **No. 18**, 74 (1954).

the stability, at low electrolyte concentration. As aggregates grow by slow coagulation, the system becomes more and more stable.

This explanation, which was based on an otherwise successful theory, as well as that of Kruyt,¹⁵ was recently found as apparently inadequate by Gillespie¹⁹ who investigated the limited coagulation of styrene-butadiene latex of 1.16- μ diameter by ultramicroscopy and observed that there were persistent singlets left in the system at the limiting stage. He interpreted not only his own, but also Westgren's⁴ results on colloidal gold, assuming without evidence that the latter system also contained singlets at the limiting stage, on the basis of coagulation-peptization equilibrium as suggested by Goodeve.²⁰ However, Gillespie's observation must be considered as that of an entirely different type of limited coagulation, since he has carried out his experiments in the region of fast coagulation. It is reasonable to agree with Gillespie's deduction that his latex particles were coagulating into a shallow secondary minimum of the potential energy curve, as predicted by the Derjaguin-Verwey-Overbeek theory. This prediction, which is valid only for large particles, was also recently confirmed by the experiments of Schenkel and Kitchener²¹ on particles of cross-lined polystyrene of 10- μ diameter, having sulfonic acid groups on their surface. Irrespective of whether or not the system investigated by Westgren contained singlets at the limiting stage, the extension of the conclusion drawn from the behavior of rapidly coagulating large (11,600 Å. diameter) styrene-butadiene latex particles to Westgren's slowly coagulating small (240 Å. diameter) gold particles is unjustifiable. In terms of the D.V.O. theory, the latter system should have coagulated into a deep primary minimum and, therefore, re-peptization process would have been out of question (*cf.* p. 324 of ref. 12).

It appears presently that the current theory is not able to describe quantitatively the whole course of slow coagulation because of the retarded or limited nature of the process. Nevertheless, it should be able to predict the rate of coagulation at zero time, as suggested by Reerink and Overbeek,¹⁸ *i.e.*, the rate of combination of primary particles, from the given properties of the system.

Another difficulty which the theory suffers is the fact that the D.V.O. equations contain two parameters, *viz.*, the Hamaker²² constant A as remarked by Tezak,²³ and the surface potential ψ_0 (or charge Q) whose independent measurements are extremely difficult. What is more serious is the fact that in the rigid form of the theory ψ_0 (or Q), which is independent of the concentration of the coagulating electrolyte, is assumed to be the potential which determines the stability. The Stern theory²⁴ of the double layer, on the other hand, requires the replacement of ψ_0 by the Stern potential ψ_s (p. 310 and 321 of ref. 12) which is, in principle, a function of dimension, adsorption potential, and concentration of the ions introduced. The Stern correction makes the theory flexible and indicates the necessity of independent measurement of ψ_s in each specific case in order to compute the stability.

However, recent investigations^{21,25,26} point out that ψ_s , which is more critical than A , can be approximated

to the ζ potential measured at the same electrolyte concentration.

Reviewing the attempts made in recent years to test the D.V.O. theory, one would observe that, in spite of the above-mentioned difficulties, the theory has been reasonably successful in describing coagulation in many cases. Among those are the light extinction experiments on AgI sol by Reerink and Overbeek,¹⁸ who treated not only their own but also the experimental data of the earlier workers on colloidal gold^{4,10} and selenium⁵; the sedimentation experiments of Douglas and Burden²⁵ on ThO₂ suspension; the ultramicroscopic and spectrophotometric experiments of Vatillon, *et al.*,²⁷ on selenium sol; the experiments of Ghosh and Rakshit²⁸ on TiO₂ sol which was applied to the theory by Choudhury²⁶; the turbidimetric experiments of Packter²⁹ on colloidal copper, silver and lead chromates, and silver oxalate; and the sedimentation experiments of Schenkel and Kitchener.²¹

Returning to the question of slow coagulation of colloidal gold, one wonders how the behavior of the same system, *i.e.*, Westgren's gold,⁴ could be explained by the two entirely different theoretical approaches mentioned above, *viz.*, that of D.V.O.¹⁵ and Goodeve-Gillespie,¹⁹ at the same time. Closer inspection of the computed data given by Reerink and Overbeek and by Gillespie shows, however, that the agreement with the theory is not very conclusive in either case.

It appeared interesting to us to reinvestigate the problem to throw some light on the mechanism of slow coagulation of colloidal gold which has been subject to extensive studies in these laboratories from other aspects. Colloidal gold also lends itself to be treated in terms of the D.V.O. theory, since it can be prepared to contain monodispersed spherical particles of fairly uniform size.

2. Experimental

As mentioned in section 1, the theoretical treatment requires experimental data on reaction between primary particles. We, therefore, used electron microscopy to count the singlets in the system directly, to eliminate the uncertainty which might have existed in the indirect methods used earlier, such as determining the total number of particles by ultramicroscopy^{4,10} and by colorimetry.⁶⁻⁹

In order to confine coagulation, as far as possible, to the simplest case of compression of the double layer, as considered in the D.V.O. theory, we paid attention to selecting the coagulating electrolyte. Some authors,³⁰⁻³² have drawn attention to the fact that various ionic processes may complicate this simple mechanism by changing the stabilizing potential. In the case of colloidal gold used for the present work, which was stabilized by citrate ions, NaClO₄ was chosen as coagulating agent, since Na⁺ does not complex with citrate ion, and ClO₄⁻ is believed to have the least tendency for adsorption.

Throughout these experiments we also paid attention to keeping the concentration of the peptizing citrate ions in the samples constant, while diluting or mixing them with coagulant solutions, not to change the stabilizing potential of the particles (*cf.* p. 322 on ref. 12). Therefore, the molarities of sodium citrate stated in this paper refer to its initial and final concentrations at the same time.

In choosing the suitable particle size, we made a compromise between the ease of detection of large particles and the advantage offered by small particles in minimizing the possible effect of surface roughness on the effective particle radius as discussed by Reerink and Overbeek.¹⁸ Thus, we used gold particles of 200 Å. diameter.

(19) T. Gillespie, *J. Colloid Sci.*, **15**, 313 (1960).

(20) C. F. Goodeve, *Trans. Faraday Soc.*, **35**, 342 (1939).

(21) J. H. Schenkel and J. A. Kitchener, *ibid.*, **56**, 161 (1960).

(22) H. C. Hamaker, *Physica*, **4**, 1058 (1937).

(23) B. Tezak, *J. Phys. Chem.*, **57**, 301 (1953).

(24) O. Stern, *Z. Elektrochem.*, **30**, 508 (1924).

(25) H. W. Douglas and J. Burden, *Trans. Faraday Soc.*, **55**, 350, 356 (1959).

(26) B. K. Choudhury, *Nature*, **185**, 308 (1960).

(27) A. Vatillon, M. Romerowski, and F. Van Grunderbeek, *Bull. soc. chim. Belges*, **68**, 430 (1959).

(28) B. N. Ghosh and S. C. Rakshit, *Science and Culture*, **18**, 498 (1953).

(29) A. Packter, *Kolloid-Z.*, **170**, 48 (1960).

(30) Y. M. Glazman and I. M. Dykman, *Doklady Akad. Nauk USSR*, **100**, 299 (1955); *Chem. Abstr.*, **56**, 10948 (1962); Y. M. Glazman, D. N. Strazhesko, E. F. Zhel'vis, and L. L. Chervyatsova, *Kolloid Zh.*, **21**, 263 (1959); Y. M. Glazman, *Chem. Abstr.*, **56**, 8043 (1962).

(31) A. Packter, *Kolloid-Z.*, **160**, 160 (1958).

(32) J. Duclaux and C. Cohn, *J. chim. phys.*, **56**, 671 (1959).

a. **Preparation and Deionization of Colloidal Gold.**—The preparation of colloidal gold was similar to that described by Turkevich, Stevenson, and Hillier,³³: 100 ml. of HAuCl_4 solution containing 50 mg. of gold was added to 850 ml. of distilled water boiling in a 2-l. flask. When the solution was boiling again, 50 ml. of 1% sodium citrate solution was added while stirring vigorously. After continuous boiling for 30 min., it was allowed to cool and made up to 1 l.

To remove the extraneous ions, the conventional method of dialysis was found unsatisfactory not only because it was time consuming, but also prolonged dialysis caused coagulation before the conductivity could be lowered to the desired level. Instead of dialyzing, we treated the colloid with mixed ion-exchange resin. Preliminary experiments showed that the amount of resin to be used relative to the amount of sol was critical for a successful treatment. A small excess of resin coagulated the sol toward the end of the operation. By trial and error, we were able to find the optimum proportion for routine treatments. The method of treatment was: 400 ml. of gold sol was stirred with 6 ml. of mixed ion-exchange resin Amberlite MB-1 manufactured by Rohm and Haas Co. in a 1-l. beaker by a magnetic stirrer. The conductivity of the sol was observed continuously by means of a pair of dipping electrodes. The specific conductivity dropped from 6×10^{-3} to 6×10^{-7} mho/cm. in about 1.5 hr., depending on the rate of stirring. The sol was then separated from the resin by decantation and filtration through glass wool. We considered the latter conductivity as low enough for the present work, since we observed that its further reduction resulted in coagulation, presumably due to complete removal of the stabilizing ions.

Even at 6×10^{-7} mho/cm. specific conductivity, sols underwent a peculiar type of coagulation in a few days. Their red color, typical for monodispersed sols, changed to violet. Electron micrographs revealed that they consisted of aggregates of mainly 4–5 primary particles arranged exclusively in linear pattern. However, this coagulation did not go any further. There was no indication of sedimentation or further color change 20 months later. Similar observation was reported in the case of dialyzed gold sol of 30 Å. computed particle size and specific conductivity of the order of 10^{-4} mho/cm. by Holliday,³⁴ who, following the light absorption spectrum, concluded that the process was restricted to the pairing of primary particles to form doublets. Another interesting feature of this sol is that electron micrographs taken 3 months after its preparation showed a remarkable degree of fusion between the primary particles where they contacted each other, as distinct from coagulation by electrolytes. We estimated from the specific conductivity of 6×10^{-7} mho/cm. that the final sodium citrate content of the system was about 2×10^{-6} M. In order to stabilize the colloid, we added various amounts of sodium citrate, immediately after the resin treatment, to contain 10^{-5} , 10^{-4} , and 10^{-3} M citrate. None of these sols showed any sign of coagulation for several months.

b. **Particle Size, State of Dispersion, and Concentration.**—Samples were mounted for electron microscopy by adding 2 drops of 0.1% gelatine solutions to 5 ml. of suitably diluted sol, transferring a small drop onto a grid covered with collodion film, and drawing the excess solution 10 min. later by filter paper in the usual manner.³⁵ Electron micrographs of the particles adhering to the collodion film were taken with an RCA type EMU-2 electron microscope. The micrographs were analyzed for particle size distribution and state of dispersion.

The samples were found to be practically monodisperse. The percentage of doublets relative to the total primary particles varied between 1 and 4, depending upon the age of the sample, whereas the percentage of higher aggregates were negligible.

The mean particle diameter was found as 207 Å. The root mean square deviation was 11%. The peak of the size distribution curve, as shown in Fig. 1, was at 204 Å.

The concentration of particles in the sample was also determined by transferring a small aliquot of diluted sample on a grid of known diameter by means of a microcapillary pipet, evaporating, and counting particles by electron microscopy. The concentration was found as 5.0×10^{10} total primary particles per ml. which was in agreement with that calculated from the particle size and the amount of gold used for preparation.

c. **Kinetic of Slow Coagulation.** (i) **Low Particle Concentration.**—In order to reduce the rate of coagulation to a practicable level, in the first series of experiments, we worked with very dilute sols. We investigated the kinetics of slow coagulation of the 200 Å. gold sol diluted 50 times, containing 10^{-6} and 10^{-4} M sodium citrate at various NaClO_4 concentration as follows: 25 ml. of 25 times diluted gold sol and 25 ml. of NaClO_4 solution at appropriate concentration, both containing sodium citrate in

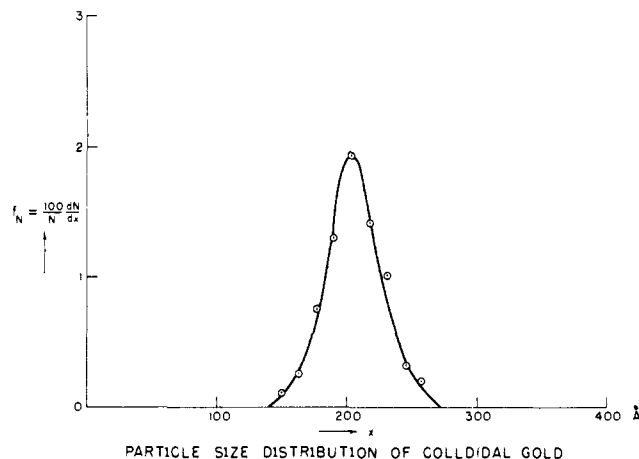


Fig. 1.—Particle size distribution of colloidal gold.

the above-mentioned concentrations, were mixed together by vigorous stirring. At the same time a sample of 5 ml. of gold sol, diluted 50 times, containing sodium citrate in the same concentration, was treated with 2 drops of 0.1% gelatine solution and kept as a blank; 5-ml. samples were drawn from the coagulation system at various times and 2 drops of 0.1% gelatine were added to stop coagulation, as it was found by Turkevich and Baker³⁶ that gelatine was an effective stopping agent.

The blank and the samples were then mounted for electron microscopy. The usual mounting methods could not provide an adequate number of particles in the field at this dilution. Therefore, we had to adopt the following centrifugal method of mounting: A flat bottom glass tube 3.5 mm. in inner diameter and 20 mm. in height was filled up to about $\frac{2}{3}$ of its height with the sample. An electron microscope grid 3 mm. in diameter was introduced into the sample and placed onto the bottom of the tube, so that its membrane side faced upward. The tube was stoppered by a small rubber stopper and centrifuged by an air driven centrifuge, which provided a centrifugal field coaxial with the tube, at 4000 g for 30 min. The grid was then removed from the tube and dried by a piece of filter paper.

Electron micrographs of all samples were taken and analyzed in terms of the number of singlets, doublets, triplets, etc., relative to the total number of primary particles, counting at least 1000 primary particles in each case. The results are given in Table I (a) to (d).

TABLE I

KINETICS OF SLOW COAGULATION OF 200 Å. GOLD SOL

n_0 = total concn. of primary particles = 10^9 part./ml.; n_1 = concn. of singlets; Σn_i = total concn. of kinetic units (singlets and clusters)

(a) 10 mM NaClO_4 , 10^{-6} M sodium citrate			(c) 30 mM NaClO_4 , 10^{-5} M sodium citrate		
Time, hr.	n_1/n_0 , %	$\Sigma n_i/n_0$, %	Time, min.	n_1/n_0 , %	$\Sigma n_i/n_0$, %
0	94.9	96.7	0	80.8	86.6
1.50	68.2	81.9	1	6.3	26.1
3.25	56.8	72.7	4	4.7	25.0
14.75	52.9	68.9	67	1.0	5.5
30.50	52.3	67.1			
(b) 20 mM NaClO_4 , 10^{-5} M sodium citrate			(d) 40 mM NaClO_4 , 10^{-4} M sodium citrate		
Time, hr.	n_1/n_0 , %	$\Sigma n_i/n_0$, %	Time	n_1/n_0 , %	$\Sigma n_i/n_0$, %
0	88.0	91.9	0	88.9	91.5
0.20	65.4	79.5	2 min.	69.8	79.1
0.50	47.8	66.0	12 min.	63.5	71.4
1.50	45.6	65.4	2.20 hr.	57.1	70.1
7.00	42.5	63.4	18.75 hr.	54.5	65.6
19.00	45.6	63.3	31.83 hr.	56.2	67.0
31.00	43.8	67.3			

(ii) **High Particle Concentration.**—For the reasons to be given in section 3, we also investigated the rate of coagulation in the earliest possible stage of the process, i.e., within the first 10 sec. after mixing the sol and the coagulant. In order to produce measurable coagulation in the slow region in such a short time, the particle concentration was kept much higher in these experiments than in the experiments described in (i).

(33) J. Turkevich, P. S. Stevenson, and J. Hillier, *Discussions Faraday Soc.*, No. 11, 58 (1951).

(34) A. K. Holliday, *Trans. Faraday Soc.*, **43**, 661 (1947); **46**, 440, 447 (1950).

(35) C. E. Hall, "Introduction to Electron Microscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p. 319.

(36) J. Turkevich and C. Baker, unpublished data.

Fresh colloidal gold (20 ml. containing $10^{-5} M$ sodium citrate) was treated with 1 ml. of 0.1% gelatine solution and kept as a blank; 10-ml. samples taken from the same stock of sol, each containing $10^{-5} M$ sodium citrate and gold particles in appropriate concentrations, were then mixed with 10 ml. of coagulating solution containing $10^{-5} M$ sodium citrate and NaClO_4 in various concentrations, in 50-ml. erlenmeyer flasks by pouring the coagulant into the sol while stirring vigorously by a magnetic stirrer. At the end of 10 sec., 1 ml. of 0.1% gelatine was added to stop coagulation. The blank and the samples were then mounted for electron microscopy by transferring small drops onto collodion grids and drying them as described in (i) 10 min. later. The treatment of grids with samples and subsequent drying was repeated a few times when needed in the case of the samples which were relatively dilute with respect to colloidal particles. The micrographs were analyzed for singlets as described in (1). The range of NaClO_4 concentration covered in these experiments was 2-50 mM. The results are given in Table 11.

TABLE II

COAGULATION OF 200 Å. GOLD SOL CONTAINING $10^{-5} M$ SODIUM CITRATE IN 10 SECONDS

Concn. of NaClO_4 , mM	n_0 , part./ml. $\times 10^{-10}$	n_1/n_0 , % in sample	n_1/n_0 , % in blank
2	3.75	85.5	92.6
3	3.75	82.1	92.6
5	2.50	75.4	86.8
8	1.25	75.6	86.8
10.5	0.75	42.6	92.6
13	.50	43.4	86.8
20	.25	49.9	86.8
50	.25	37.2	92.6

It will be shown in section 3 that coagulation at 50 mM NaClO_4 was well in the fast region. Yet, judging from the color of the samples coagulated at higher concentrations, we observed that the rate of coagulation was increasing further by increasing NaClO_4 concentration from 50 mM. To measure the rate of coagulation in this region, we used the following comparative method: More samples were coagulated as described above, which ultimately contained primary particles in the same concentration as that of the last sample in Table 11, and more than 50 mM of NaClO_4 , stopping coagulation in 10 sec. Then a series of samples were coagulated similarly, which contained 50 mM NaClO_4 , stopping coagulation in various times little longer than 10 sec. The color of both series of samples varied from purple to blue. The color of each of the first series of samples was then compared with those of the second series, placing both samples in two identical test tubes and viewing from the top against a uniformly illuminated white background. The samples with matching colors were noted. Assuming that two samples with identical colors have the same state of aggregation, the rate of coagulation of the first series of samples was estimated, relative to that at 50 mM NaClO_4 . The results are given in Table 111.

TABLE 111

RELATIVE RATE OF COAGULATION OF 200 Å. GOLD SOL CONTAINING $10^{-5} M$ SODIUM CITRATE AT VARIOUS NaClO_4 CONCENTRATIONS

NaClO_4 concn., mM	Stopping time of standard (50 mM), sec.	Relative rate of coagulation
50	(10)	(1.0)
100	13.5	1.35
200	15	1.5
400	15	1.5

To investigate the effect of citrate concentration on stability, we also estimated the rate of coagulation of samples containing $10^{-5} M$ sodium citrate, at various NaClO_4 concentrations. This estimation was also based on color comparison with the samples containing $10^{-5} M$ sodium citrate for which the rate of coagulation was determined microscopically as mentioned above. The procedure was similar to that described in the preceding paragraph. The samples containing $10^{-5} M$ sodium citrate were coagulated for 10 sec. and compared in the same manner with those containing $10^{-5} M$ sodium citrate, which were also coagulated for 10 sec. at various NaClO_4 concentrations; NaClO_4 concentrations which produced identical colors in the sample and in the standard are given in the first and second columns of Table IV.

Finally, we investigated the effect of pre-addition of NaClO_4 on the stability of sols containing $10^{-5} M$ citrate by similar experiments. We have found that no observable coagulation is caused by the presence of 1 mM NaClO_4 in the standard sol

TABLE IV

NaClO_4 CONCENTRATIONS PRODUCING IDENTICAL COLORS IN 10 SEC.

(Corrected for Na^+ due to sodium citrate)

In $10^{-5} M$ citrate (standard), mM	In $10^{-5} M$ citrate, mM	In $10^{-5} M$ citrate + $10^{-3} M$ NaClO_4 , mM	$10^{-10} n_0$ part. ml. ⁻¹
5	23	6.7	2.50
8	31.5	9.5	2.50
10	35.5	..	1.25
10.5	..	12.5	1.25
13	..	15.5	1.25
20	63	23	0.25
32.5	400	..	.25
40	800	..	.25
45	..	50.5	.25

containing $10^{-5} M$ citrate in 15 min. Sol samples containing $10^{-5} M$ citrate were, therefore, mixed as above with solutions to contain 1 mM NaClO_4 ; 15 min. later they were coagulated by further addition of NaClO_4 for 10 sec. and compared with standard samples coagulated for the same period of time, at various NaClO_4 concentrations without pre-addition, as described above. The results of these experiments are given in the first and third columns of Table IV.

3. Discussion

a. Kinetics of Slow Coagulation.—Considering a completely monodispersed system and starting with a bimolecular equation of the form

$$(-dn/dt)_{t=0} = Kn^2 \quad (1)$$

where n is the concentration of primary particles, t is the time, and K is given by

$$K = 8kT/3\eta W \quad (2)$$

in which K is the Boltzmann constant, T is the absolute temperature, η is the viscosity coefficient of the dispersion medium, and W is the retardation or stability factor; Smoluchowski^{2,12} derived equations for the concentration of singlets and of total particles in a coagulating system as functions of time. They can be written as

$$\sqrt{n_0/n_1} = 1 + 1/2Kn_0t \quad (3)$$

and

$$n_0/\Sigma n_1 = 1 + 1/2Kn_0t \quad (4)$$

respectively, where n_0 is the concentration of singlets at $t = 0$ or that of primary particles in the system at any time, n_1 is the concentration of singlets and Σn_1 is the sum of the concentrations of singlets and all aggregates. If the colloid is already coagulated to some degree at the zero time, as in actual practice (see Tables Ia-Id), then the eq. 3 and 4 can be rewritten as

$$\sqrt{n_0/n_1} - \sqrt{n_0/(n_1)_0} = 1/2Kn_0t \quad (5)$$

and

$$n_0/\Sigma n_1 - n_0/(\Sigma n_1)_0 = 1/2Kn_0t \quad (6)$$

respectively, where $(n_1)_0$ and $(\Sigma n_1)_0$ are the values of n_1 and Σn_1 , respectively, at $t = 0$.

Using the experimental data tabulated in the third columns of Tables Ia-Id, we plotted the left-hand sides of eq. 5 and 6 against t . The interesting portions of these plots are reproduced in Fig. 2 and 3, respectively. It will be seen that the Smoluchowski relationships break down in the case of relatively slow coagulation, as already established by the previous workers (cf. section 1). After a certain time, coagulation practically stops. At $10^{-5} M$ sodium citrate concentration, when NaClO_4 concentration exceeds a certain critical value between 20 and 30 mM, not only the rate of coagulation increases abruptly, but also the coagulation goes to completion without appreciable retardation (see Table Ic). When sodium citrate concentra-

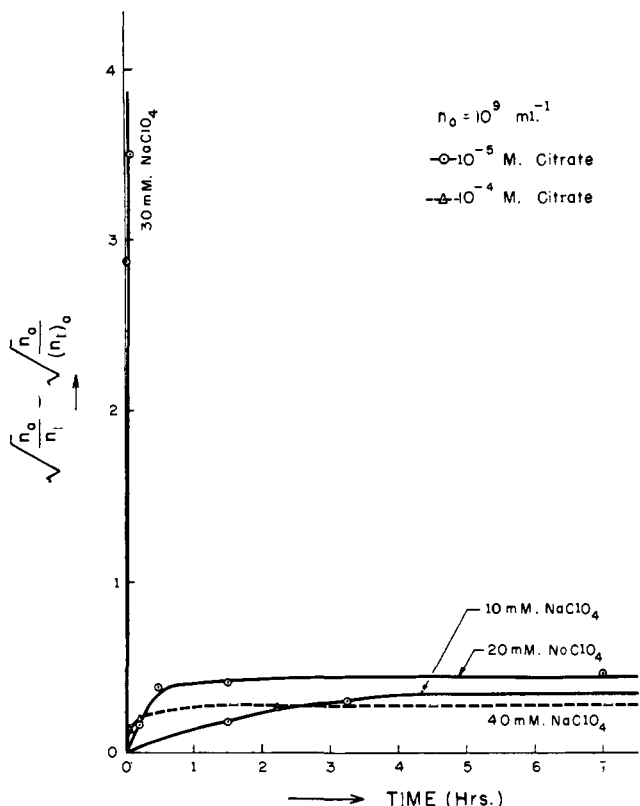


Fig. 2.—Dependence of difference of singlet and total particle concentrations as a function of time.

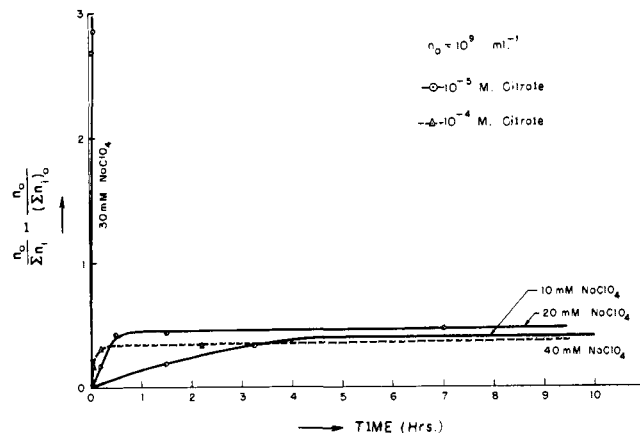


Fig. 3.—Relationship between total particle and kinetic unit concentrations as a function of time.

tion is increased to 10^{-4} M , stability also increases, indicating the stabilizing effect of citrate ions.

Figures 2 and 3 reveal three interesting features of limited coagulation, namely: (i) Substantial amounts (45–55%) of singlets (see Tables Ia, b, and d, and Fig. 2), as well as multiplets are left at the limiting stage. (ii) The faster the initial coagulation, *i.e.*, the higher the electrolyte concentration, the sooner the system reaches the limiting stage. (iii) Although the initial rate of coagulation increases sharply with the concentration of the electrolyte added, the advancement of the limiting stages does not depend critically on this concentration.

The first observation, which means that the increasing stability in the course of slow coagulation is not confined to aggregates only, invalidates the explanation of limited coagulation as given by Kruyt¹⁵ and by Overbeek, *et al.*,¹⁷ and Derjaguin, *et al.*¹⁴

The fact that not only singlets, but also multiplets, exhibit an added stability at the limiting stage also

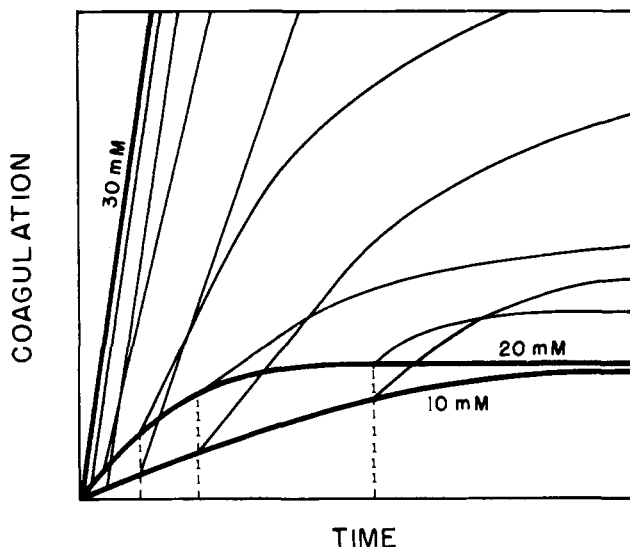


Fig. 4.—Smoluchowski type plot of coagulation with time.

rules out the assumption by Anderson⁸ and Garner⁹ of unequal charge distribution among primary particles.

As far as the presence of singlets is concerned, Gillespie's assumption, as discussed in section 1, might have been correct. But the idea of coagulation-peptization equilibrium appears to be incompatible with the third observation. Indeed, an increase in the electrolyte concentration which accelerates the initial coagulation, supposedly by deepening the secondary minimum of the potential energy curve, should also have shifted the equilibrium state appreciably to the direction of coagulation.

These considerations together with the second observation stated above suggested that the colloid system attained the additional stability gradually as coagulation proceeded, by an unknown mechanism. This was confirmed by the following experiments: Samples of 20 times diluted colloidal gold containing 10^{-5} M sodium citrate were coagulated rapidly by 30 mM NaClO₄ (*cf.* Table Ic and Fig. 2 and 3) for various short periods of time, stopping coagulation by gelatine as described in section 2,c,(ii), and kept as standards for color comparison. Then, more samples were coagulated by adding 30 mM NaClO₄ in two successive steps instead of a single addition. By comparing colors, as described in section 2,c,(ii), the times required for the samples to reach the same color as standards were noted. Not only the time interval between the two additions of NaClO₄, but also the NaClO₄ concentration at the first addition, was varied in these experiments. The results showed that when the electrolyte was added in two steps, coagulation took place slower than when it was added in one increment. This was true only when the time interval between the two additions was more than *ca.* 20 sec. and the NaClO₄ concentration at the first addition was not too small. This behavior is shown schematically by a Smoluchowski type of plot in Fig. 4 where the thick lines represent coagulation at 10, 20, and 30 mM NaClO₄, as indicated. The thin lines originating from the 10 and 20 mM lines represent coagulation on further addition of NaClO₄ to make its total concentration 30 mM at various times.

One possible explanation of this phenomenon is that when cohesion takes place between particles, the stabilizing ions are desorbed from the vicinity of the contact points because of electrostatic repulsion, and become available for the free particle surfaces and thus increase the stabilizing potential. However, this explanation cannot be valid for two reasons: (a) Con-

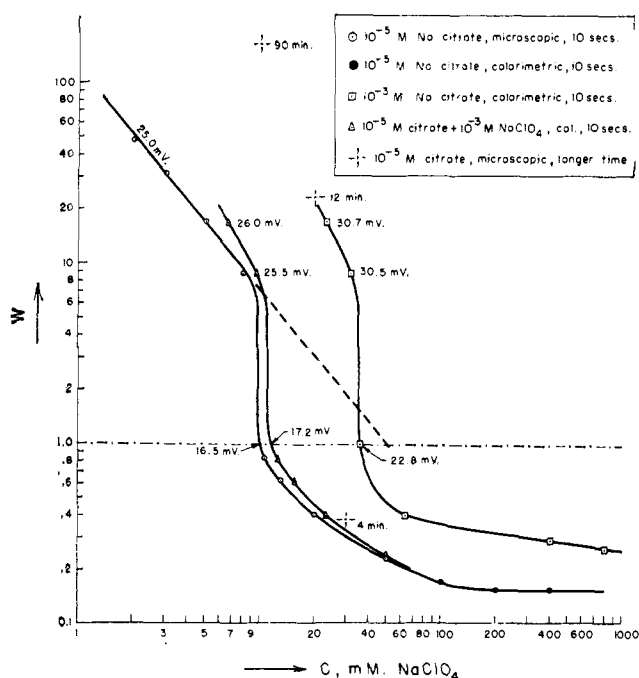


Fig. 5.—The stability factor W as a function of the perchlorate concentration.

sidering the surface areas of a citrate ion which is presumably the stabilizing ion concerned, and of a 200 Å. gold particle, the maximum number of citrate ions which can be accommodated on one particle as a monomolecular layer was calculated as 7000. Even if all these ions were desorbed they would increase the citrate concentration in the bulk phase from 10^{-5} only to $10^{-5} + 10^{-8}$ M under the present experimental conditions. Obviously, this could not have caused any detectable shift in the adsorption equilibrium.

(b) Two limiting coagulation stages which are reached at two different NaClO_4 concentrations correspond to two different stabilizing potentials. The higher the concentration, the higher the potential. In the light of the observation stated above under (iii), this means, however, that at two different NaClO_4 concentrations almost the same state of aggregation but different stabilizing potentials are reached at the limiting stage.

The last argument leads us to another explanation of the limited coagulation. Indeed, it follows from this argument that the attainment of additional stability is not because of coagulation, but because of the addition of the coagulant. As a matter of fact, this accounts for all three observations stated above, and other characteristics of coagulation represented by Fig. 2, 3, and 4, satisfactorily. It appears that as soon as NaClO_4 is added to the system, coagulation starts as a result of instant compression of the electrical double layer, and at the same time the stabilizing potential is gradually raised possibly due to addition of ClO_4^- ions to the adsorption layer around the colloidal particle. When the order of magnitude of the concentration of NaClO_4 added (*i.e.*, 10^{-2} M) is compared with that of sodium citrate (*i.e.*, 10^{-5} to 10^{-4} M) (which is the only electrolyte present in the system to control the adsorption equilibrium and thus controls the stabilizing potential before the addition of NaClO_4), the assumption of ClO_4^- adsorption becomes justifiable.

What is to happen to the system after the initiation of coagulation will depend on the relative rates of the two processes, *viz.*, (1) coagulation and (2) rising of the potential due to ClO_4^- adsorption. Both rates increase with NaClO_4 concentration. The first rate also in-

creases with particle concentration, but decreases critically as the stabilizing potential rises. It appears that the second process is a relatively slow one. The system reaches the practically stable state, which corresponds to complete attainment of the additional potential, in *ca.* 4, 1, and 0.5 hr. (Fig. 3) in 10, 20, and 40 mM NaClO_4 , respectively. Also, as described earlier, no additional stability was observed within 20 sec. in the experiments of successive addition of NaClO_4 . Therefore, if the original stabilizing potential is small, the particle and the electrolyte concentrations are big enough, the system will coagulate completely before the second process can take place, as in the case of the sample containing 10^{-5} M citrate and 30 mM NaClO_4 (*cf.* Table Ic, Fig. 2 and 3). If the electrolyte concentration is lower, coagulation will be slower and the second process will come into play slowing down coagulation as it proceeds. If the original stabilizing potential is already high, the system may ultimately reach a stable state. The higher the electrolyte concentration, the quicker the system will reach this state. This is the case with the systems coagulating in 10, 20, and 40 mM NaClO_4 shown in Fig. 2 and 3. If the original potential and the electrolyte concentration are low, the system may still coagulate slowly, but not reach a stable state before coagulation is complete. Such a case was actually observed with a sol which was diluted to contain 2×10^{-7} M citrate and coagulated in 7 mM NaClO_4 .

If the particle concentration is too high, the initial coagulation may be so fast that coagulation may go to completion without appreciable retardation at any electrolyte concentration.

b. Application of the Derjaguin-Verwey-Overbeek Theory.—Obviously, the experimental data so far discussed are not suitable for comparison with the D. V. O. theory in its rigid form, as they reflect a variation in the stabilizing potential (*cf.* section 1). The experiments of successive addition of electrolyte revealed, as discussed above, that in order to obtain any data on coagulation rate which refers to the original ψ , measurements must be taken within the first 20 sec. after mixing. Even the earliest measurements given in Table I were taken outside of this safe interval.

For this reason, we carried out the 10-sec. experiments described in section 2,c,(ii). Assuming the validity of Smoluchowski equations for such a short period, we obtain from eq. 2 and 5

$$\Pi' = \frac{4kTn_0t}{3\eta(\sqrt{n_0/n_1} - \sqrt{n_0/(n_1)_0})} \quad (7)$$

Using the experimental data in the second, third, and fourth columns of Table II, we calculated the stability factor W at each NaClO_4 concentration up to 50 mM . These calculations were then extended to 400 mM NaClO_4 by dividing the value of W at 50 mM by the relative rate factors given in Table III. The results of these calculations are given in Table V.

Combining the treatment developed by Fuchs³⁷ with the D.V.O. theory and assuming that the surface potential ψ_0 remains constant as two particles approach each other, Verwey and Overbeek^{12,17} were able to correlate the stability factor W to the electrolyte concentration. It follows from this treatment that $\log W$ varies linearly with the logarithm of the electrolyte concentration C for $W > 1$,^{12,18} provided, of course, that ψ_0 is also independent of this concentration. This theoretical requirement has met with experimental confirmation in a number of cases.^{12,18,27,29,31}

Accordingly, we plotted the data given in Table V, in log-log scale, in Fig. 5. Also in the same figure, we

(37) N. Fuchs, *Z. Physik*, **89**, 736 (1934).



Fig. 6.—Aggregates formed by fast coagulation of colloidal gold containing 10^{-5} M sodium citrate, by 30 mM NaClO_4 ; time of coagulation, 1 hr. Note dark regions where individual primary particles are indistinguishable. They are the regions of three dimensional formation. Magnification 60,000 \times .

plotted the W -values calculated from the first series of coagulation experiments carried out over longer periods (Tables Ia–Ic). The large discrepancies between the two sets of data when the observation times are greatly different, and the agreement when the time difference is small, indicate the rise in the stabilizing potential as discussed in subsection a.

TABLE V
STABILITY FACTOR OF 200 Å. GOLD SOL CONTAINING 10^{-5} M SODIUM CITRATE AT VARIOUS NaClO_4 CONCENTRATIONS

NaClO_4 concn., mM	W	NaClO_4 concn., mM	W
2	48	20	0.40
3	31	50	.73
5	17	100	(.17)
8	8.9	200	(.15)
10.5	0.84	400	(.15)
13	0.62		

It will be seen from Fig. 5 that the data obtained by the 10-sec. experiments fit into the theory rather well up to a concentration of 8 mM , as the points fall on a straight line. Somewhere near 10 mM , however, W falls off sharply indicating a significant deviation from the straight line relationship. In terms of the theory, this corresponds to a drop in the stabilizing potential. Packter³¹ interpreted the similar trends observed with other systems as a result of coagulation, which is confined to that induced only by compression of the

double layer at low concentration, affected by a reduction in ψ due to precipitation, chelation, or neutralization of the adsorbed peptizing ions at higher concentration. As these processes are out of the question for the present system, the Stern adsorption of Na^+ ions (*cf.* section 1) appears to be the only explanation. That this is the actual mechanism is suggested by the fact that, unlike the potential rise as discussed in subsection a, the potential drop must be the result of a fast process which takes place in less than 10 sec., such as electrostatic rearrangement of labile ions. The same fact also suggests that the adsorption of ClO_4^- ions, responsible for slow potential rise, involves localization of these ions in the Helmholtz layer, whereas the adsorption of Na^+ ions, responsible for fast potential drop, takes place in the Stern layer.

Although the abrupt change in the rate and mode of coagulation, as shown in Fig. 2 and 3, apparently takes place at a higher electrolyte concentration under the conditions of the first series of coagulation experiments (section 2,c,(i)), the existence of a break in the curve near 10 mM (Fig. 5) explains this abruptness: At 20 mM , at the beginning, the system coagulates rapidly because of the reduced stabilizing potential (*cf.* Fig. 5). However, since the particle concentration is low (*cf.* subsection a), coagulation soon slows down and eventually comes to a standstill at a certain time because of an increase in the potential which more than compensates for its early decrease. At 30 mM , on the other hand, the early rapid coagulation proceeds

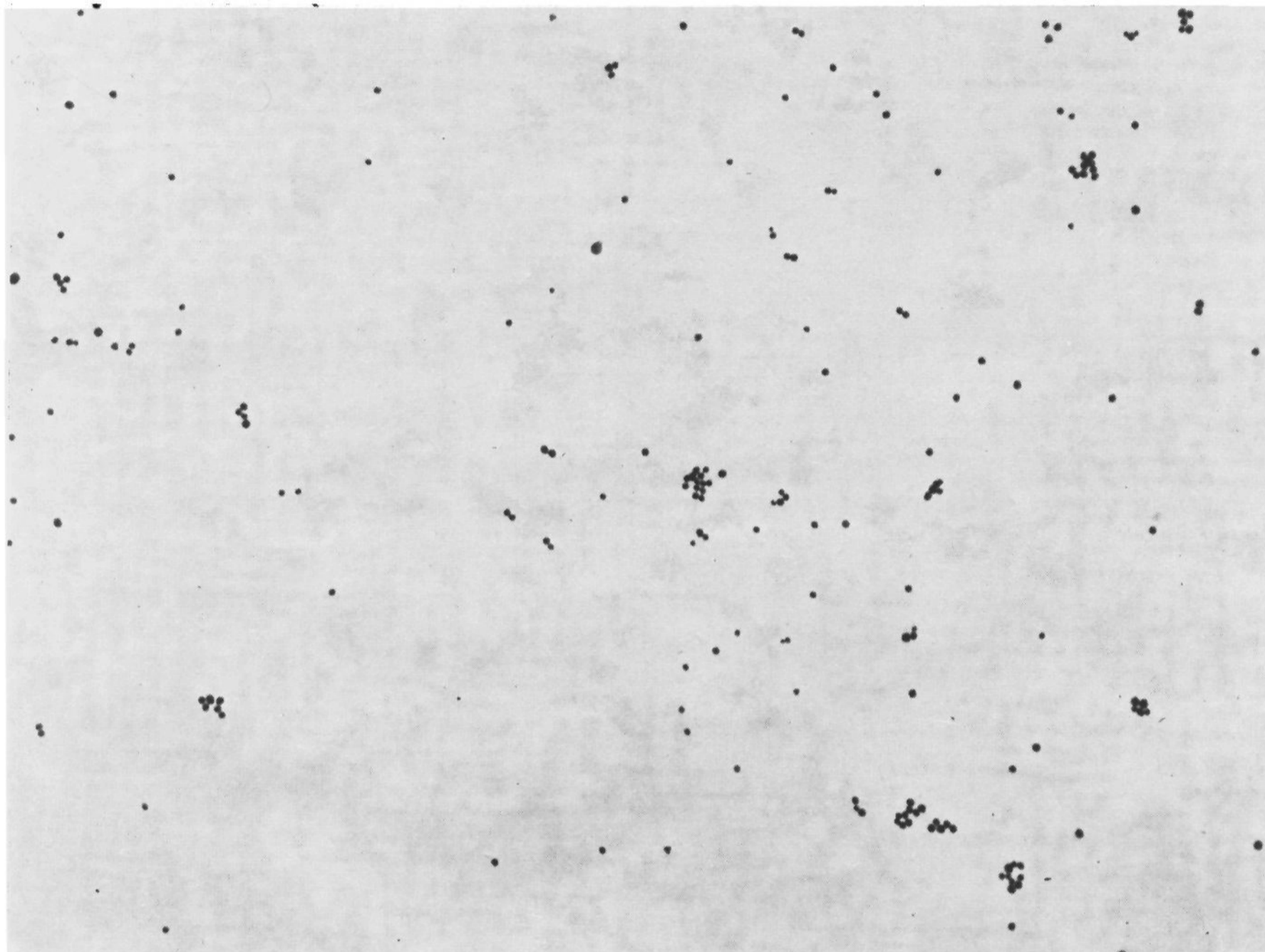


Fig. 7.—Aggregates formed by slow coagulation of colloidal gold containing 10^{-5} *M* sodium citrate, by 10 mM NaClO_4 ; time of coagulation, 15 hr. Magnification, 75,000 \times .

even faster, so that before the potential just begins to rise the system coagulates almost completely.

It is interesting to note that the transition of colloidal systems from the stable to the coagulated state usually takes place in a narrow region of electrolyte concentration (p. 81 of ref. 12). If no allowances are made for a reduction of the potential in this region, the theory fails to predict such a sharp transition. It may be, therefore, that a fast coagulation is affected not only by compression of the double layer, but also by neutralization of the stabilizing charge by the counter ions, as considered in the older theories (*cf.* p. 311 of ref. 12).

c. Effects of Citrate and Perchlorate Ions on Stability.—Making use of the experimental data in the second and third columns of Table IV, we were able to construct the W vs. C curve for the sol containing 10^{-3} *M* sodium citrate from the curve for 10^{-5} *M* sodium citrate in Fig. 5. The general shape of the curve so obtained is similar to that of 10^{-5} *M* citrate. The striking separation of these two curves, however, indicates that citrate is the main potential-determining ion in the present system.

We discussed in subsection a the retarded or limited coagulation and interpreted it by the stabilizing effect of ClO_4^- ions. In order to find an independent support for this interpretation, we carried out the experiments described in section 2,c,(ii) by adding 10^{-3} *M* NaClO_4 to a sol containing 10^{-5} *M* citrate, prior to coagulation. From the results given in the second and fourth columns of Table IV, we obtained the W vs. C curve for this system, which is also shown in Fig. 5. Although the

effect is not so pronounced as in the case of sodium citrate added in the same concentration, it will be seen that pre-addition of 10^{-3} *M* NaClO_4 definitely increases the stability.

In order to find further experimental evidence, we also made the following experiment: A fresh sample of colloidal gold was deionized, as described in section 2,a, to the usual specific conductivity of 6×10^{-7} mho/cm. To one portion of this sol NaClO_4 was added in 10^{-3} *M* concentration immediately after deionization. Another portion was kept under observation as it was. To a third portion, 10^{-5} *M* sodium citrate was added. The second coagulated in two days. The first sample, on the other hand, was stable for two weeks. Only at the end of two weeks it showed the first sign of coagulation. The third sample, of course, did not coagulate at all, as we knew by experience (*cf.* section 2,a). These observations showed once more the relative stabilizing powers of citrate and ClO_4^- , as revealed in Fig. 5.

d. Stabilizing Potential and Hamaker's Constant.—Let us now consider the quantitative aspects of the treatment. Reerink and Overbeek¹⁸ was able to correlate the slope of the theoretical straight line in the $\log W$ vs. $\log C$ plot, by a useful approximation. The relationship derived by them reads

$$d \log W / d \log C = -2.15 \times 10^7 a \gamma^2 / v^2 \quad (8)$$

where a is the radius of particles in cm., v is the valency of the counter ion, and γ is given by

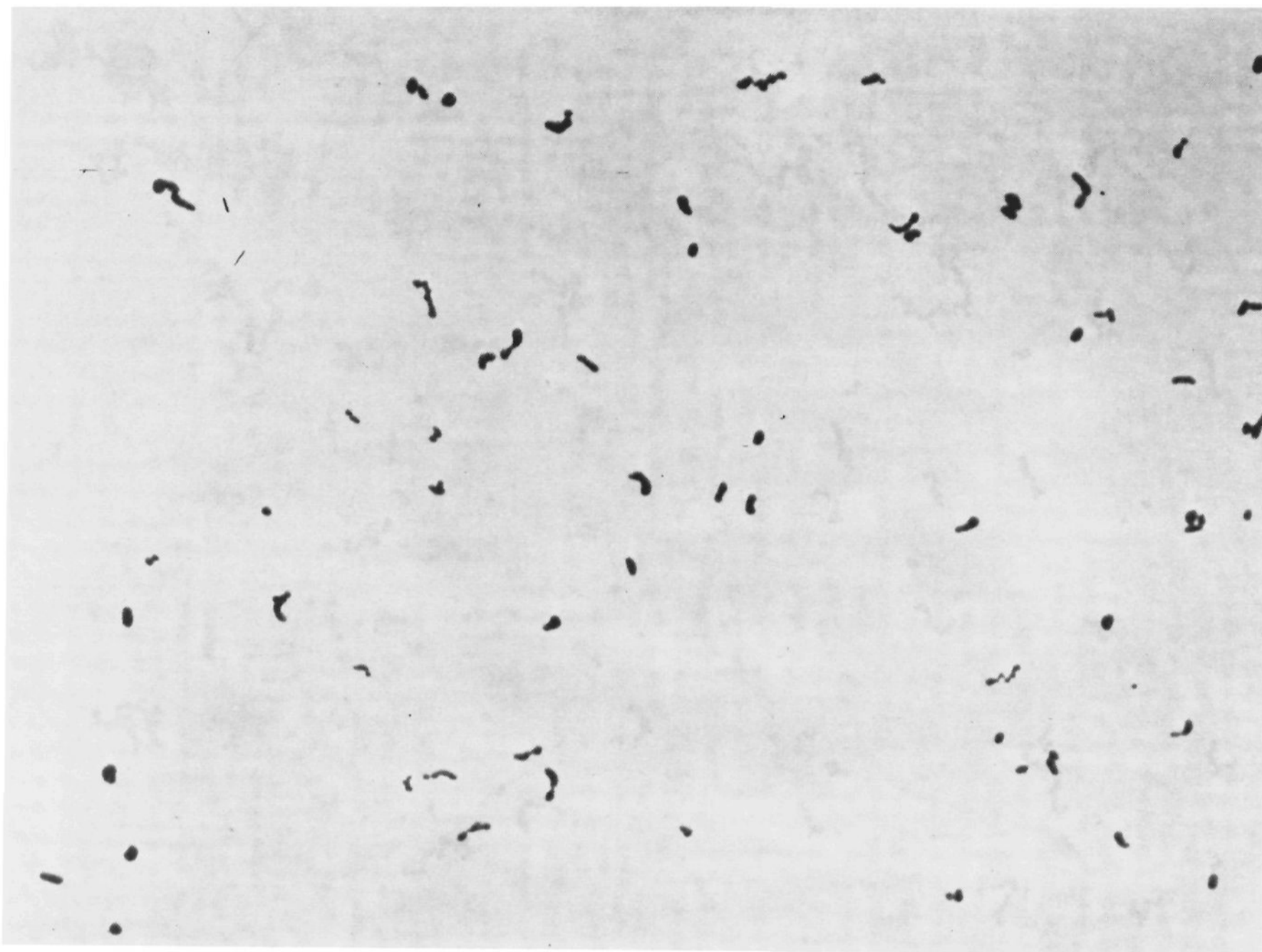


Fig. 8.—Aggregates formed by slow spontaneous coagulation of deionized (spec. cond. 6×10^{-7} mho/cm.) colloidal gold. Sample was mounted 3 months after preparation. Note fusion between primary particles (*cf.* section 2,a). Magnification, 75,000 \times .

$$\gamma = \frac{\exp(v\psi/51.2) - 1}{\exp(v\psi/51.2) + 1} \quad (9)$$

where ψ is in mv.

It appears from the plots of Verwey and Overbeek (p. 175 of ref. 17) that the intersection of the $\log C$ axis with the exact theoretical curve lies very close to that with the extension of the straight portion of the curve. Therefore, the latter intersection can be taken as the point where W becomes unity, without committing a serious error. The $W = 1$ point can be taken, however, as the critical concentration at which the potential energy barrier just becomes zero.

Integrating eq. 8 with this condition, we obtain

$$\log W = 2.15 \times 10^7 a \gamma^2 / v^2 \log (C_c / C) \quad (10)$$

where C_c is the above-mentioned critical concentration.

Following Vatillon, *et al.*,²⁷ a further approximation can be introduced by assuming the validity of the equation

$$C_c = 8 \times 10^{-22} \gamma^4 / A^2 v^6 \quad (11)$$

in the case of spherical particles, which was derived by Verwey and Overbeek¹⁷ for two interacting plates.³⁸

(38) This second approximation can be justified as follows: It appears from Verwey and Overbeek's¹⁷ potential energy curves that at critical concentration the peak of this curve becomes tangent to the distance axis at $R \approx 2.1a$, where R is the distance between the centers of two interacting particles. At $R = 2a$ the potential energy is $-\infty$. If the potential energy curve were absolute a vertical straight line located at $R = 2a$ in one instance, and at $R = 2.1a$ in another, these would correspond to fast Smoluchowski coagulations (*cf.* p. 278 of ref. 12) with an effective radius of $2a$ and $2.1a$, or in other words, to $W = 1$ and $W = 2/2.1 = 0.95$, respectively. Since the theoretical curve lies in between these two extremes, the actual W at the critical concentration must have a value between 0.95 and 1.00.

This equation gives the critical concentration in moles/liter. Thus, from eq. 10 and 11 we get

$$\log W = 2.15 \times 10^7 a \gamma^2 / v^2 \log (8 \times 10^{-22} \gamma^4 / A^2 v^6 C) \quad (12)$$

where C is also in mM. This is the equation of the straight line mentioned above. Although eq. 11 is expected to be applicable to large particles, it appears that eq. 12 can be used to calculate the parameters ψ and A fairly accurately from the experimental straight line for $a = 10^{-6}$ cm., without going through the tedious operations of the exact treatment. This was checked with $a = 10^{-6}$ cm., $v = 1$, $\psi = 76.8$ mv., and $A = 2 \times 10^{-12}$ erg, for which the exact curve was given by Verwey and Overbeek (p. 175 of ref. 17). Using these values we found -8.7 for the slope and 33 mM for the intercept on $\log C$ axis from eq. 12 against actual -7.0 and 36 mM, respectively.

From the slope and the intercept of the straight line obtained in Fig. 5 with the system containing 10^{-5} M citrate at low concentrations, we found $\psi = 25.0$ mv. and $A = 2.3 \times 10^{-13}$ erg, using eq. 12 with $a = 10^{-6}$ cm. (200 Å. diameter) and $v = 1$.

Substituting $A = 2.3 \times 10^{-13}$ erg, $a = 10^{-6}$ cm., and $v = 1$ in eq. 12, we get

$$\log W = 21.5 \gamma^2 \log (15,370 \gamma^4 / C) \quad (13)$$

which represents the stability of the present system for $W \geq 1$, as a function of stabilizing potential and concentration of 1-1 type electrolyte expressed in mM.

From eq. 13, we also calculated ψ at other points of the curves in Fig. 5. The results of these calculations,

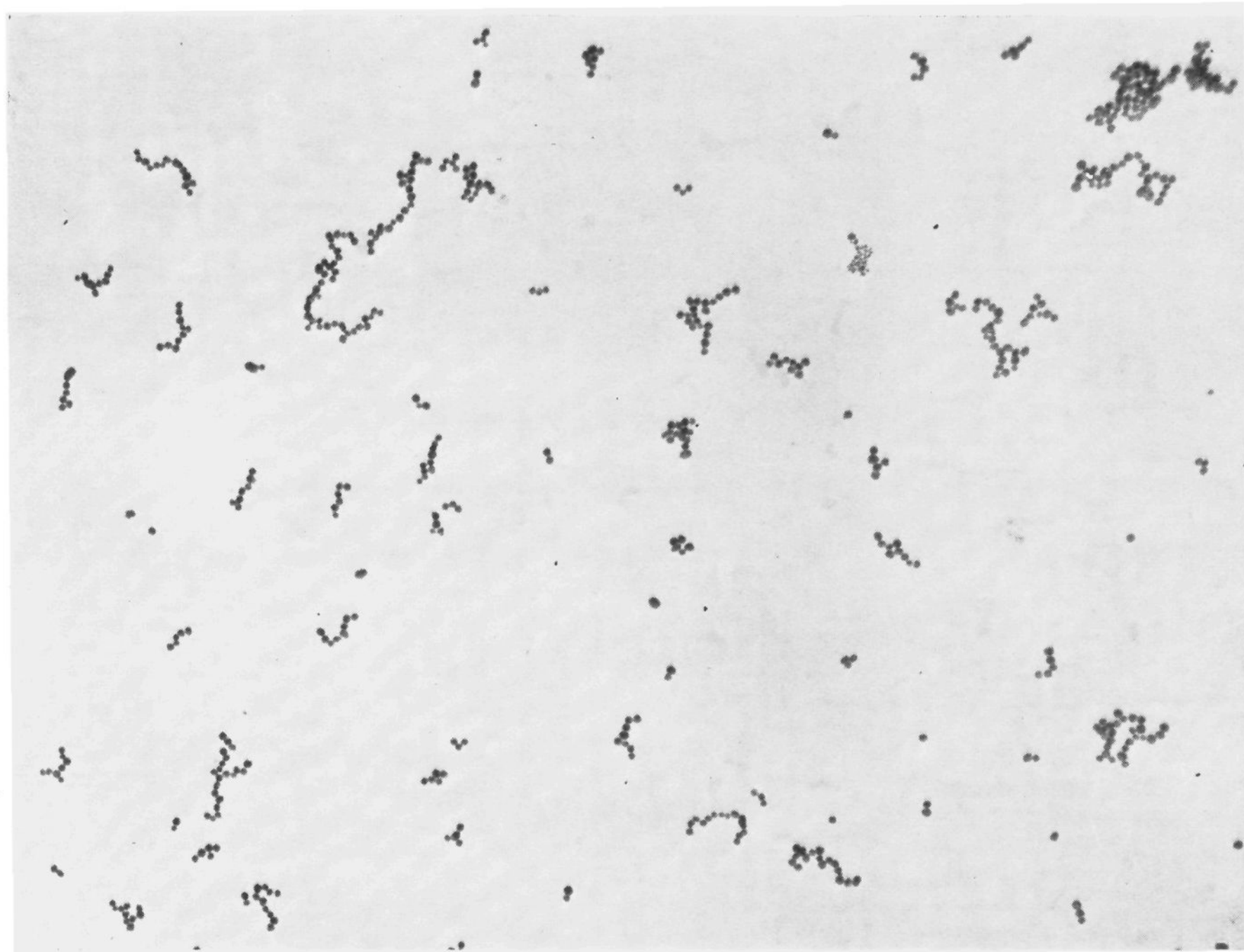


Fig. 9.—Aggregates formed by slow coagulation of colloidal gold containing $10^{-5} M$ sodium citrate, by $1.2 mM$, $HClO_4$; time of coagulation, 1 day. Magnification $75,000\times$.

which are also given in the same figure, form a basis for quantitative description of the potential variations discussed in subsections b and c. It follows from these values that increasing citrate concentration from 10^{-5} to $10^{-3} M$ increases the stabilizing potential by *ca.* 6 mv., whereas the addition of $10^{-3} M$ $NaClO_4$ causes only *ca.* 1 mv. increase. The potential drop at the critical concentration is at least 8 mv.

It does not seem permissible to compare the present data of ψ with those computed by Reerink and Overbeek¹⁸ from the experimental results of Westgren⁴ and Tuorila,¹⁰ not only because the latter workers used different methods of preparation which involve reduction of gold chloride by reducing agents other than sodium citrate, but also their other experimental conditions were different from ours. Nevertheless, the present data appear to be between 48 mv. obtained from Tuorila's results on 370 Å. gold sol and 10–15 mv. computed from Westgren's data on 900 Å. gold sol.

The most comparable data are, perhaps, the ζ potentials obtained by Turkevich and Baker³⁶ from electrophoretic mobility, which range from 32 to 47 mv. They investigated 200 Å. gold sol prepared by the same method as in the present work, but dialyzed (*cf.* section 2,a) to have a conductivity approximately equal to that of $10^{-5} M$ sodium citrate.

Our estimation of the Hamaker constant A for gold as 2.3×10^{-13} erg is also in between 6×10^{-13} and $(0.5-1) \times 10^{-13}$ erg computed by Reerink and Overbeek from Tuorila's and Westgren's results, respectively.

e. Superfast Coagulation.—Theoretically, as C is increased indefinitely, W decreases and approaches a limiting value smaller than 1. This is because of the fact that at such high concentrations the repulsive potential disappears, and the van der Waals–London attraction potential accelerates coagulation beyond the rate of fast Smoluchowski coagulation. The general trend exhibited by the curves in Fig. 5 is in qualitative agreement with this requirement. The stronger the attraction, *i.e.*, the bigger the value of A , the faster the coagulation, *i.e.*, the smaller the limiting W . According to Overbeek's calculations (p. 286 of ref. 12), for $A = 10^{-12}$ erg this limit is 0.67. For $A = 2.3 \times 10^{-13}$ erg, which we estimate, the limiting W value is expected to be bigger than 0.67. We find, however, that the experimental W drops much below this value (Table V and Fig. 5). In the case of $10^{-5} M$ citrate, for example, the apparent limiting W is 0.15. The rate of coagulation of 400 Å. gold sol with $Ba(ClO_3)_2$, measured also in small fractions of a minute by Turkevich and Baker³⁶ in the fast region, corresponds even to a lower W value ($W = 0.08$).

The reason for this superfast coagulation may be related to the instant potential drop which occurs near the critical concentration, as discussed in subsection d. This drop may become so large at higher electrolyte concentrations that the charge of the particle is even reversed. Now, if the reversal of charge is a fast process compared to mixing, which may well be the actual case, only a fraction of the particles will suffer charge reversal at the earliest stage of mixing. In other words,

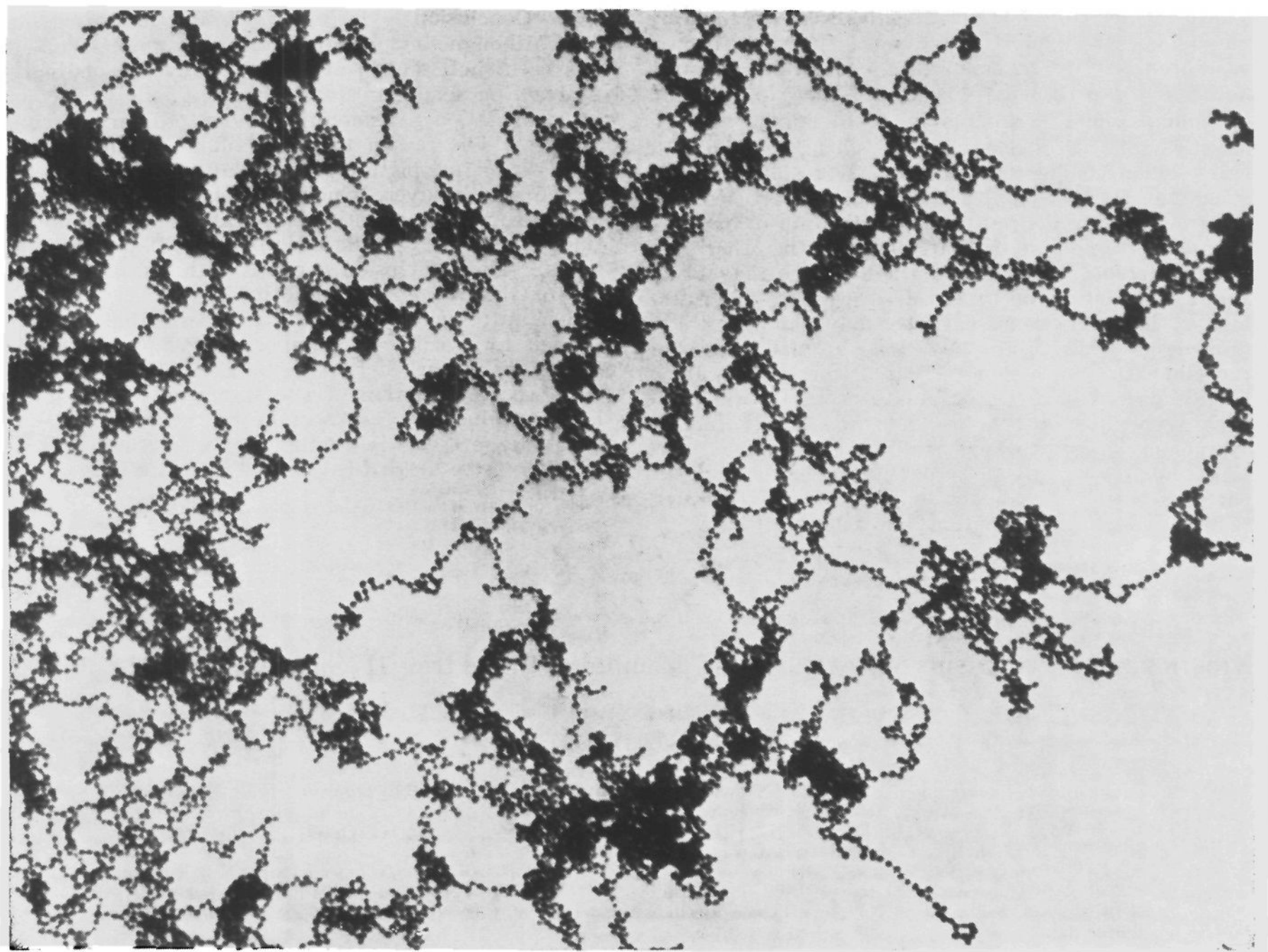


Fig. 10.—Aggregates formed by mixing 70% negative and 30% positive particles of colloidal gold. Magnification 75,000 \times .

at this stage the system will be a mixture of negatively and positively charged particles and coagulate faster than the theory predicts because of electrostatic attraction between oppositely charged particles (*cf.* p. 315 of ref. 12).

f. Morphology of Aggregates.—In view of the potential barrier around the colloidal particles as predicted by the theory, it was of some interest to investigate the morphology of aggregates formed under various coagulation conditions. As revealed by the electron microscope, the aggregates can be classified morphologically as follows:

I. Three Dimensional Formation: The aggregates formed as a result of fast coagulation at high electrolyte concentration are in this group, as shown in Fig. 6. Since the potential barrier practically disappears at high concentration, every random encounter results in cohesion and the primary particles are preferably held together in a compact three dimensional fashion, by the resulting attractive potential.

II. Two Dimensional Formation: Slow coagulation at moderate electrolyte concentrations yields aggregates of this type, as shown in Fig. 7. In this case the repulsive potential and its range, *i.e.*, the double layer thickness, are small enough for an approaching particle to adhere to a primary particle of an aggregate entering additional repulsion fields of up to about two neighboring primary particles. Under these conditions two dimensional small aggregates are first formed, which preferably grow around the edges for the same reason and maintain the planar arrangement.

III. One Dimensional Formation: Slow coagulation at very low ionic strength always produces aggregates of linear (or fibrous) form. At low ionic strength the double layer thickness is large. Needless to add, therefore, that coagulation can take place only if the stabilizing potential is low enough. One dimensional formation was observed only if these two requirements, *i.e.*, low ionic strength and moderately low stabilizing potential, are fulfilled as in the following cases: (a) spontaneous slow coagulation of highly deionized colloid (Fig. 8) (*cf.* section 2,a); (b) slow coagulation induced by partly neutralizing the citrate charge on particles by introducing a small amount of a strong acid (Fig. 9), (c) slow coagulation induced by mixing negative and positive colloids under special conditions (see below).

Under these conditions, particles possess weak but long range repulsive fields, so that after the formation of doublets, a singlet approaching a doublet enters the repulsion fields of both primary particles of the doublet at the same time, if its direction of approach differs substantially from the axis of symmetry of the doublet. Such encounters will not, therefore, result in cohesion, and thus the formation of linear triplets, quadruplets, etc., will be more favorable than any other more compact arrangements.

If the stabilizing potential is too low, however, such selectivity becomes unimportant, and type I aggregates are formed again, in spite of low ionic strength.

It is possible to observe any conceivable combination of these three types of formation of aggregates under various conditions. An interesting example of this is

shown in Fig. 10. These aggregates were obtained by mixing negative and positive sols. The positive sol was prepared by reversing the charge of deionized negative sol with poly-*N*-isopropyl-4-vinylpyridinium bromide. The experiments made by mixing 400 Å. negative sol with 200 Å. positive sol had shown that this kind of coagulation was not the result of simple interaction between oppositely charged particles, but the result of instant mutual neutralization of opposite charges. If one kind of charge exceeds the other by a small difference, the residual small charge may bring about coagulation of type III. Owing to imperfect mixing, however, some particles may get practically discharged, while others possessing a small charge of the same kind, for a short period of time during which the discharged particles coagulate rapidly, form compact aggregates of type I, and thus hinder further charge exchange through diffusion of ions. This process is followed by slow coagulation of the primary particles with the compact masses. This is believed to be the case in the formation shown in Fig. 10.

g. Conclusions.—It follows from this discussion that although the current theory of lyophobic colloids has been successful in explaining many aspects of the problem on semiquantitative basis, it fails to account for coagulation satisfactorily under ordinary circumstances. The reason for this failure lies in the fact that the simple picture of coagulation by compression of the double layer, which the theory is mainly concerned with, is frequently complicated. The complications arise from specific adsorbability of ions of both kinds. This conclusion parallels with the recent findings of Glazman, *et al.*,³⁰ and Mirnik, *et al.*³⁹

The introduction of the Stern correction in some explicit form will be an important refinement of the theory, as remarked by Overbeek (p. 312 of ref. 12). Also, the formulation of the stabilizing effect of the ions introduced (*cf.* subsection b), which appears to be a rate process, is another important and difficult problem to be tackled by the theoretical workers.

(39) M. J. Herak and M. Mirnik, *Kolloid-Z.*, **179**, 130 (1961); M. Mirnik, *Nature*, **190**, 689 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON, WIS.]

Kinetics and Mechanisms of Reactions of Chromium(VI) and Iron(II) Species in Acidic Solution¹

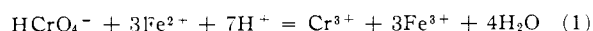
BY JAMES H. ESPENSON² AND EDWARD L. KING³

RECEIVED MAY 24, 1963

The rates of reaction of chromium(VI) with aquoiron(II) ion and tris-(1,10-phenanthroline)-iron(II) ion have been determined as a function of concentrations of reactants and products. The rate law for reaction of aquoiron(II) ion is $-d[\text{Fe}^{2+}]/dt = ([\text{H}^+]^3[\text{Fe}^{2+}]^2/[\text{Fe}^{3+}])\{k_1[\text{HCrO}_4^-] + k_2[\text{HCrO}_4^-]^2\}$. In interpretation of kinetic data on this reaction, account was taken of interaction of iron(II) and chromium(VI); spectrophotometric data yield a value $Q_{38} = [\text{FeCrO}_4^+][\text{H}^+]/([\text{Fe}^{3+}][\text{HCrO}_4^-]) = 1.4$ at 0° in solutions of ionic strength 0.0839 *M*. The reaction of tris-(1,10-phenanthroline)-iron(II) ion and chromium(VI) is not retarded by tris-(1,10-phenanthroline)-iron(III) ion. Fewer mechanistic details of this latter reaction are revealed by the kinetic data.

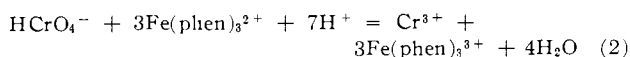
Chromium(IV) and chromium(V) may be unstable intermediates in reactions of stable +3 and +6 oxidation states of chromium with oxidizing and reducing agents, respectively. Reactions with one-equivalent reagents are particularly informative, and the kinetics of oxidation of chromium(III) by cerium(IV) indicate that reaction of cerium(IV) and chromium(IV) is rate determining.⁴ The present study deals with rates of reaction of chromium(VI) with two one-equivalent reducing agents, aquoiron(II) ion and tris-(1,10-phenanthroline)-iron(II) ion.

The first of these reactions



was studied by Benson,⁵ and her results have been discussed by Westheimer.⁶ The present work done at 0° using titrimetric and spectrophotometric procedures extends concentration ranges of the earlier work, characterizes the reaction order with respect to iron(III) ion more completely, and takes into account the interaction of iron(III) and chromium(VI) to form a relatively stable complex ion, FeCrO_4^+ .

The second of the reactions



the kinetics of which have not been studied previously,

(1) Taken from the Ph.D. Thesis of James H. Espenson, University of Wisconsin, 1962. This work was supported in part by the United States Atomic Energy Commission (Contract AT(11-1)-1168).

(2) Procter and Gamble Fellow, 1961-1962.

(3) Department of Chemistry, University of Colorado, Boulder, Colo.

(4) J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).

(5) C. Benson, *J. Phys. Chem.*, **7**, 1 (1903); **7**, 356 (1903).

(6) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

was studied spectrophotometrically at temperature between 0 and 40°.

Experimental Details and Results

Reagents.—At least two independent sources of each reagent except tris-(1,10-phenanthroline)-iron(III) ion were used. Doubly distilled water was used in preparation of some solutions; the second distillation was from alkaline permanganate in a Barnstead still. A redistillation of this water from an all-glass still provided another source of water. Reagent grade potassium dichromate was used both without further purification and also after it was recrystallized two or three times from water and dried at 110°. Perchloric acid solutions were prepared by dilution of 60 and 72% reagent grade acids. Lithium perchlorate solutions were prepared either from twice-recrystallized reagent grade material or from material made by reaction of lithium carbonate and a slight excess of perchloric acid. Lithium perchlorate prepared in the latter way was recrystallized from water. Iron(III) perchlorate was prepared from both iron(III) chloride and iron(III) nitrate by prolonged fuming with perchloric acid. Hydrated iron(III) perchlorate was crystallized from this medium and once or twice more from 60% perchloric acid. These solids contained appreciable perchloric acid, the concentration of which was determined in each iron(III) stock solution as the difference between the total normality and the iron(III) normality. The former quantity was determined by titration of the perchloric acid solution resulting from passing an aliquot of stock solution through a column containing cation-exchange resin in the hydrogen ion form. Sources of aquoiron(II) ion used in reaction solutions were iron(II) sulfate heptahydrate, dianmonium iron(II) disulfate, and iron(II) perchlorate. Stock solutions of the first two iron(II) compounds were prepared by dissolving reagent grade solids in dilute (*ca.* 0.01 *M*) perchloric acid. Iron(II) perchlorate solutions were prepared by dissolution of iron wire in *ca.* 0.5 *M* perchloric acid at temperatures below 80°. The absence of iron(III) and chloride ion in these solutions was proved by tests with thiocyanate ion and silver ion, respectively. The iron(II) stock solutions were stored under purified nitrogen in bottles equipped with self-sealing rubber disks; aliquots were removed by hypodermic needle and syringe. Aqueous solutions of tris-(1,10-phenanthroline)-iron(III) sulfate