

463. *The Effect of Peptising Agents on the Crystal Growth of Insoluble Metal Salts. Part I. Precipitation in Aqueous Solution.*

By A. PACKTER.

The average crystal diameter of the precipitates of insoluble silver, copper, and lead salts has been followed as a function of the stability of the sol from which crystal growth occurs. Highly "supersaturated" systems may be stabilised by addition of simple organic acids, ammonia, etc., and the rate of coagulation of the sols is then appreciably reduced.

Slow growth leads to large crystals of diameter $>20 \mu$, in solutions of silver, complex copper, and lead salts, peptised by organic acids and pyridine, but, in the ammonia-peptised sols, only when the complex ammonia salt is present in excess during the whole period of crystal formation.

The experimental results support Balarev's and Traube's hypothesis¹ that the basic unit from which crystal growth occurs in such supersaturated systems is the micelle of the peptised sol.

THE peptisation of insoluble metal salts by solutions of organic acids and ammonia, and their subsequent precipitation by one of the reacting ions (after a specific time lag), has already been studied,² and the two main hypotheses proposed to explain this phenomenon

¹ (a) Balarev, *Kolloid-Beih.*, 1939, **50**, 1; (b) Traube, *Z. phys. Chem.*, 1929, *A*, **146**, 1.

² Packter and Matalon, *Discuss. Faraday Soc.*, 1954, **18**, 161.

have been discussed in some detail. The peptisation of silver, copper, and lead salt sols by organic acids is caused by orientated adsorption of the molecules of the added reagent on to the surface of the sol micelles, and their subsequent stabilisation against coagulation; the sol stability then varies as an exponential function of the concentration of the peptising agent. The peptisation by ammonia, on the other hand, is due to formation of a sol of the complex metal salt, protected by further adsorption of ammonia.³

Mass-action and coagulation hypotheses have also been proposed to explain the nature of crystal growth from supersaturated aqueous solutions of these insoluble metal salts. Balarev^{1a} and Traube^{1b} suggested that the basic units from which a crystal grows are not the "seeds" or lattice-cell "embryos,"⁴ but the "submicrons," which may consist of thousands of such lattices, and reach colloidal dimensions. The latter may be stable in solution, until under further stimulus they aggregate together in rows and layers and finally form the microcrystals of the precipitate. But whereas the peptisation of insoluble metal-salt systems has been extensively studied, the effect of additives on the properties of the crystals grown from such peptised solutions has been rarely investigated; and although Reinders⁵ and Miles⁶ have presented qualitative data for the effects of dyes and dextrans on the crystal growth of silver halides and lead chloride, respectively, no quantitative correlation between crystal size and concentration of peptising agent was noted by these earlier workers.

The present work is an investigation into the quantitative effects of peptising agents on the crystal growth of insoluble metal salts. The final average crystal size of the precipitates of typical silver, copper, and lead salts has been followed, as a function of the concentration of peptising agent and of the stability of the sol from which the crystal growth occurs. Highly supersaturated systems may be stabilised by simple organic acids, ammonia, etc., and the rate of coagulation of the metal salt sol appreciably reduced. When the sol peptisation is due to orientated adsorption of the bulky molecules of a peptiser, the final average crystal size increases inversely as the rate of coagulation and is related to the concentration of peptiser by the exponential relation previously observed for sol stability.² The orderliness of growth (as measured by the standard deviation for crystal weight) also increases with rise in concentration of the peptising agent. The experimental results indicate that the rate of coagulation of the sol is the rate-determining step for the crystal growth of many insoluble metal salts.

Growth by slow ordered fitting of new micelles on a small number of "nuclei" leads to formation of large crystals (of diameter $>50\ \mu$) in solutions of silver, complex copper, and lead salts peptised by organic acids, pyridine, etc.; but slow coagulation of sols peptised by ammonia generally leads to irregular dendritic clusters, unless the complex ammonia salt is present in excess in the solution during the whole period of crystal growth. Coagulation of sols peptised by aqueous suspensions of proteins and polysaccharides leads to precipitation of very small crystallites intimately associated with the peptising sol.

EXPERIMENTAL

Sol Stability.—An aqueous solution of the reacting cation is generally added to an equal volume of the reacting anion solution (in test-tubes or crystallising dishes) containing increasing concentrations of the peptising agent, except where otherwise specified. Before use, the test-tubes, etc., were cleaned with sulphuric acid-dichromate, washed thoroughly several times with distilled water, and dried. The stability of the insoluble metal-salt sol formed has been examined.

Tuller and Fulmer⁷ have measured the rate of coagulation of aqueous sols by observing the critical time at which the direction of the light absorption-time curve for the sol reverses its direction. In a preliminary series of experiments on systems investigated in this work, the plots of light absorption or turbidity (as measured spectrophotometrically) against time showed a similar pattern to those obtained earlier. Typical results are presented in Fig. 1; the origin, *O*

³ Packter, *J. Colloid Sci.*, 1956, **11**, 96.

⁴ LaMer, *J. Amer. Chem. Soc.*, 1951, **73**, 380; Christiansen, *Acta Chem. Scand.*, 1951, **5**, 673

⁵ Reinders, *Z. phys. Chem.*, 1911, **77**, 677.

⁶ Miles, *Proc. Roy. Soc.*, 1931, *A*, **32**, 266.

⁷ Tuller and Fulmer, *J. Phys. Chem.*, 1948, **52**, 787.

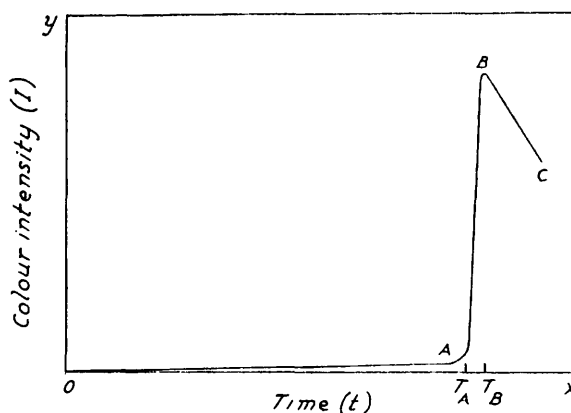
represents the time of mixing of the reacting solutions and $OABC$ is the curve of colour intensity (I) (turbidity for such systems as the silver halides) as measured by the light absorption. Along OA there is a slight increase, followed by a rapid rise in colour intensity (red in silver chromate, green in copper pyridine thiocyanate, and yellow in lead iodide sols) along AB , to a maximum at B . Generally the onset of coagulation (as measured by the change in slope of the $dI/dt-t$ curve) is so abrupt that the point T_A can be observed visually.

Such a procedure has been adopted in these studies. The *sol stability* is defined (after Tuller and Fulmer⁷) as the time of coagulation, $t = OT_B$. Since the coagulation is complete within such a narrow time limit ($T_A T_B$ being only 0.001—0.01 of OT_B), $OT_B = OT_A$; and the coagulation time has been measured in this work as OT_A , the time between the mixing and the onset of coagulation as estimated by visual observation.

The effect of concentrations of peptising agent, $C_p < C_p^*$, on sol stability has also been investigated: C_p is the concentration of peptising agent and C_p^* is the amount required to ensure indefinite stability.

Crystal Growth.—The precipitate is left to grow for 100 hr. in covered beakers in a water-bath kept at 20.0° without stirring. (Where rate of growth is rapid, 1—6 hr. suffice to use up

FIG. 1.



the reacting ions, and complete the precipitation.) The crystals are washed with distilled water to remove adhering reactants, and then with acetone, and dried in warm air at 40°.

The weight of the crop (M_c) is recorded for each addition of peptising agent. Generally $M_c = (M_i - M_{ss})$, where M_i is the initial weight of metal salt in the supersaturated solution, immediately after mixing, and M_{ss} is the saturation solubility at 20°. Values of M_c are expressed in g. per l. of solution.

Average Crystal Diameter.—Small quantities of each crop are transferred to microscope slides as a concentrated slurry in acetone, and the diameters measured on a random batch of 100 crystals against an internal graticule in a Zeiss microscope (magnification $\times 750$). (The diameter is taken as the length of the longest crystal side.) The average diameter for the crop is determined from the results for this random batch.

(1) *The arithmetical mean diameter.* The arithmetical mean diameter on a weight basis (\bar{d}_c) is determined as $\bar{d}_c = \frac{\sum_0^{100} \bar{d}_n^3}{100}$, where \bar{d}_n is the diameter of the n th crystal in the batch.

(2) *The mode diameter.* The mode diameter on a weight basis (\bar{d}_c) represents the size of the type of crystals that are formed from nuclei on which most growth has occurred, and corresponds to the mode on the graph of weight fraction against diameter; \bar{d}_c is determined as follows. Each batch is subdivided into ten groups of diameter $0-0.1\bar{d}_x$, $0.1-0.2\bar{d}_x$, \dots , $0.9-1.0\bar{d}_x$, where \bar{d}_x is the diameter of the largest crystal in the whole batch. The weight fraction (f_n) for each group is determined as

$$f_n = m_n / \sum_{n=0}^{10} m_n$$

($m_n = C_p \sum \bar{d}^3$ is the total weight of the crystals in the n th group; ρ is the specific gravity; and C is a shape factor). \bar{d}_c is taken as the arithmetical mean diameter of that group for which f_n is maximum.

Equation (2) can thus be written as

$$\log_{10} m_c/m_o = FC_p/C_s \dots \dots \dots (2A)$$

or in the form

$$\log_{10} m_c/m_1 = F(C_p - \bar{C}_p)/C_s = -\log_{10} N_c/N_1 \dots \dots \dots (3)$$

Values of F , d_o , and $(d_c)_{max}$. after 100 hours' growth are presented in Table 1 for some typical insoluble metal salts.

FIG. 2. *Crystal growth from citric acid-peptised 0.001M-silver chromate sols (20°; pH 3). Variation in average crystal diameter with acid : silver concentration ratio.*

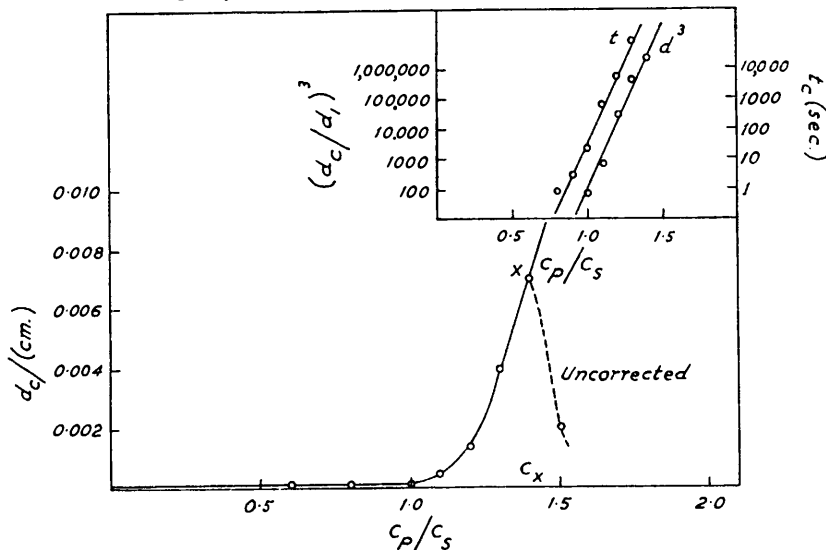


TABLE 1. *Maximum crystal diameter (100 hours' growth from organic acid-peptised sols).*

	F	d_o (μ)	$(d_c)_{max}$ (μ)		F	d_o (μ)	$(d_c)_{max}$ (μ)
				Silver chromate			
Citric acid				Glutamic acid			
0.0010M-sol	9.2	<0.2	65	0.0010M-sol	25.0	<0.2	80
0.0025 "	6.2	<0.2	40	0.0025 "	5.0	<0.2	45
0.0050 "	2.5	0.3	25				
				Copper pyridine thiocyanate			
Citric acid				Citric acid			
0.0050M-sol	1.8	1.2	55	0.0100M-sol	0.5	0.5	30
				Lead iodide			
Ammonium acetate				Ammonium gluconate			
0.0050M-sol	1.5	1.2	100	0.0050M-sol	1.0	1.2	55
0.0100 "	0.1	0.5	40	0.0100 "	0.4	0.5	20

The maximum crystal size (after 100 hours' growth) for a particular salt decreases with rise in sol concentration, and, like F and \bar{C}_p/C_s , is determined by the structure of the adsorbed peptising agent.

Organic acids also peptise the sols of simple copper salts,² but the precipitates obtained on slow coagulation still consist of gelatinous aggregates of small crystallites (of $d < 0.1 \mu$) which readily re-peptise by simple stirring.

(iii) Orderliness of growth. The orderliness of growth also increases continuously with increasing C_p/C_s , and the values of σ_d and f_n for some typical systems are presented in Table 2.

(B) *Sols peptised by ammonia and organic bases.* (i) Sol stability. The peptising effect of ammonia and organic bases has been studied on a series of insoluble silver and copper salts, and

FIG. 3. Crystal growth from citric acid-peptised 0.005M-copper dipyridine thiocyanate sols (20°; pH 6). Variation in average crystal diameter with acid : copper concentration ratio.

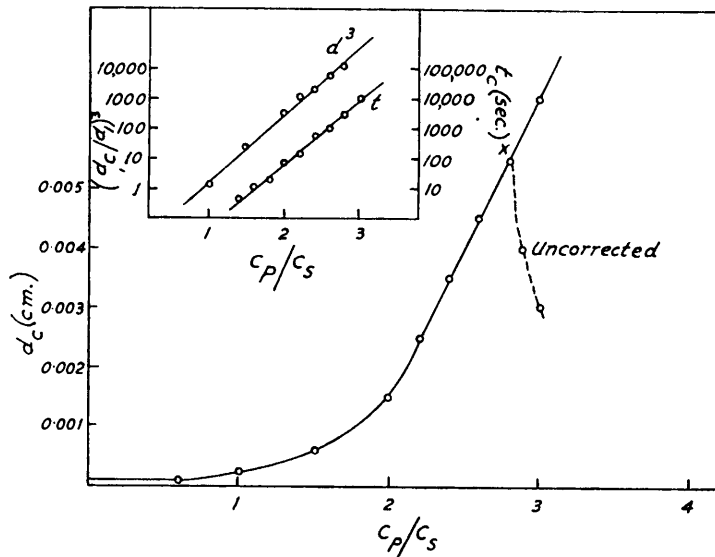


FIG. 4. Crystal growth from ammonium acetate-peptised lead iodide sols (20°; pH 7). Variation in average crystal diameter with anion : lead concentration ratio.

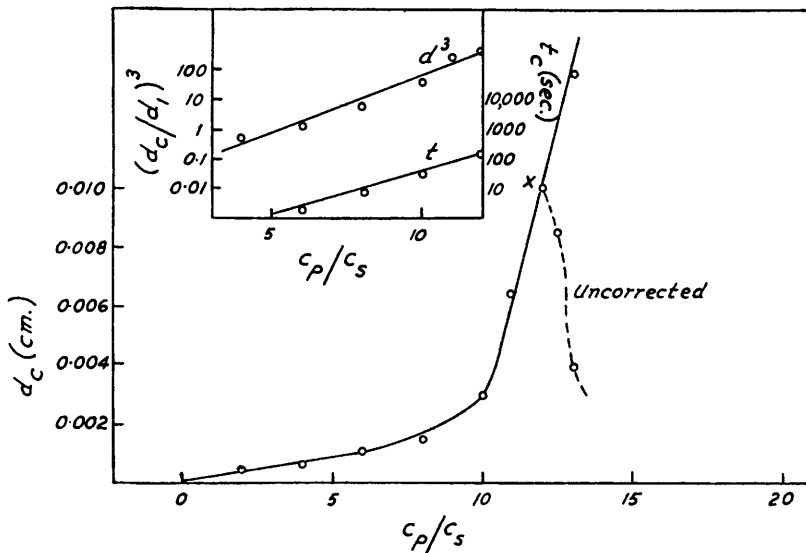
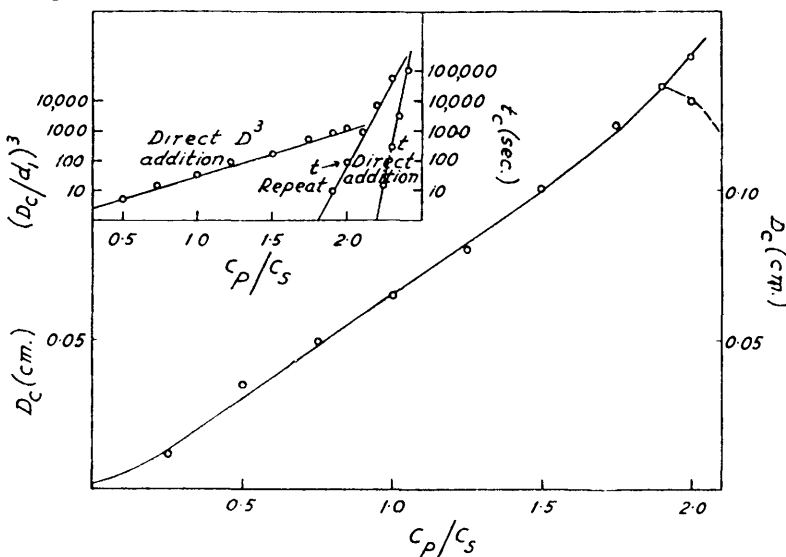


TABLE 2. Orderliness of growth: variation of $(f_n)_{max}$ and σ_d with concentration of peptising agent (citric acid).

(A) 0.001M-Silver chromate sols			(B) 0.005M-Copper pyridine thiocyanate sols		
c_p/c_s	$(f_n)_{max}$	σ_d	c_p/c_s	$(f_n)_{max}$	σ_d
0	0.10	0.78	0	0.10	0.80
1.0	0.18	0.65	1.0	0.15	0.75
1.1	0.26	0.56	1.6	0.18	0.65
1.2	0.35	0.49	2.0	0.24	0.55
1.3	0.61	0.30	2.2	0.35	0.45
1.4	0.80	0.15	2.4	0.51	0.39
			2.6	0.68	0.28
			2.8	0.90	0.15

the results for typical systems are presented in Fig. 5 (inset). The stability varies with the ammonia-metal salt concentration ratio, according to equation (1), and t_c reaches 24 hr. at the peptisation ratio. High stability is generally observed only at C_p/C_s values greater than 70–80% of the peptisation ratio.

FIG. 5. Crystal growth from ammonia-peptised 0.0025M-silver chromate sols (20°; pH 11). Variation of average diameter of dendritic clusters with ammonia: silver concentration ratio.



The ammonia-metal salt concentration ratio may also be varied by addition of acetic acid to equivalent sols completely peptised by ammonia. The stability of such sols also decreases markedly with fall in the free ammonia concentration, $C_p = (C_p^* - C_{HOAc})$. It is seen, however, from Fig. 5 (inset) that, at values of C_p/C_s of about 60–80% of the peptisation ratio, the stability of the acetic acid-treated sols is still very much higher than that observed for the salt peptised by direct addition of ammonia. This result follows from the formation of the stable ammonia-complexed metal salt sol.³

(ii) Crystal growth. (a) Silver salts. Coagulation of the ammonia-peptised equivalent sols (in covered vessels to prevent loss of ammonia by evaporation) leads to growth of large, well-formed crystals only in systems of the insoluble silver salts of organic acids. Slow coagulation of the ammoniacal solutions of such salts as the chloride, chromate, or oxalate does not lead to precipitation, while over the range of more rapid coagulation, *i.e.*, $C_p/C_s = 0.5-0.8C_p^*/C_s$, these solutions deposit dendritic clusters of small crystals of particle size 0.5–2 μ , similar to those obtained by surface evaporation.⁵

The average diameter D_c of the dendritic cluster increases, however, with rise in the concentration (C_p) of protecting agent to a maximum at $C_p = 0.8-0.9C_p^*/C_s$ and (see Fig. 5)

$$\log_{10} [D_c/d_0]^3 = F' C_p/C_s \dots \dots \dots (4)$$

Values of F' , F , d_0 and $(D_c)_{\max}$ for typical insoluble silver salt systems are presented in Table 3.

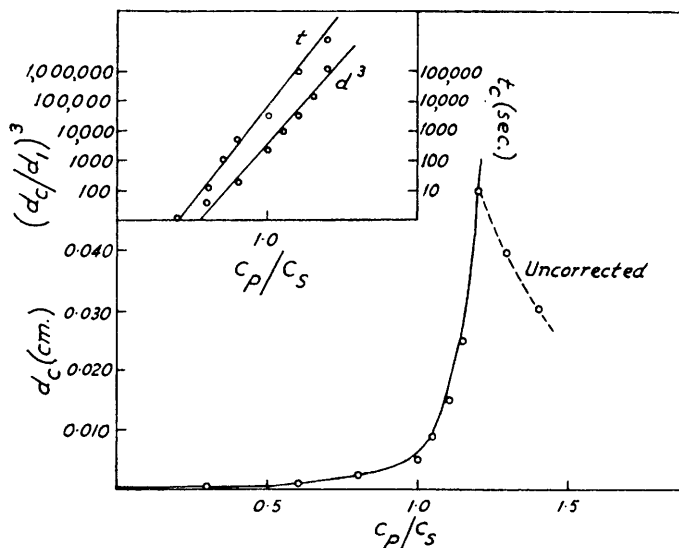
There is no correlation between the F and F' values for these systems.

(b) Copper salts. Rapid coagulation of ammoniacal solutions of the simple copper salts at $C_p/C_s = 0-0.7C_p^*/C_s$ leads to formation of a highly hydrated gelatinous precipitate of the basic salt, but slow coagulation of the highly peptised sols does not lead to precipitation. Slow coagulation of the sols peptised by pyridine, ethylenediamine, and other organic bases, however,

TABLE 3. Maximum crystal diameter (100 hours' growth from ammonia-peptised sols).

	F	F'	d_0 (μ)	$(D_c)_{\max}$ (μ)
0.005M-Silver chloride	1.2	0.2	<0.2	25
,, chromate	17.0	0.6	<0.2	140
,, oxalate	12.0	1.8	0.3	180
0.05M-Silver benzoate	3.0	2.0	18.0	160

FIG. 6. Crystal growth from pyridine-peptised 0.25M-copper chromate sols (20°; pH 11). Variation in average crystal diameter with pyridine : copper concentration ratio.



leads to formation of large, well-formed crystals. The average crystal diameter and weight vary with the concentration of peptising agent according to the relations (3) observed for growth from organic acid peptised sols (see Fig. 6).

(iii) Addition of acetic acid to fully peptised sols. Coagulation of the ammonia-peptised sols, partially neutralised by acetic acid to give sol stabilities of $t = 1-10,000$ sec., also leads to formation of dendritic clusters for most silver and copper salt systems.

(C) Sols peptised by proteins and polysaccharides (in fluid suspension). The growth of crystals from sols peptised by dilute fluid suspensions of various protein and polysaccharide gel media has also been examined. The rate of crystal growth from such a "supersaturated" system will depend on two main factors, the rate of transfer of material from the bulk of the system to the environment of the growing "nucleus" or crystal, and the rate of deposition of material from this region on to the faces of growth. In the first part of this work we have kept the viscosity of the systems examined constant at 1.00-1.10 centipoises, and under these conditions the rate of crystal growth is mainly determined by the second interface reaction.

(i) Sol stability. The peptising properties of gelatin, agar, etc., for silver, copper, and lead salts are determined by the free glutamic and gluconic acid residues of the protein and polysaccharide molecule respectively.² The variation of sol stability with concentration of these additives therefore follows a similar pattern to that observed with the simple amino- and hydroxy-organic acids, *i.e.*, equation (1).

(ii) Crystal growth. The slow coagulation of the metal salt sols peptised by such materials

in *fluid suspension* does not, however, lead to formation of large crystals. Silver chromate and lead iodide are precipitated in dilute gelatine and agar suspensions as small crystallites of particle size 0.1–1.0 μ , intimately associated with the macromolecule. The precipitate can indeed only be separated from the liquid phase by prolonged centrifugation (2–4 hr. at 1000 g).

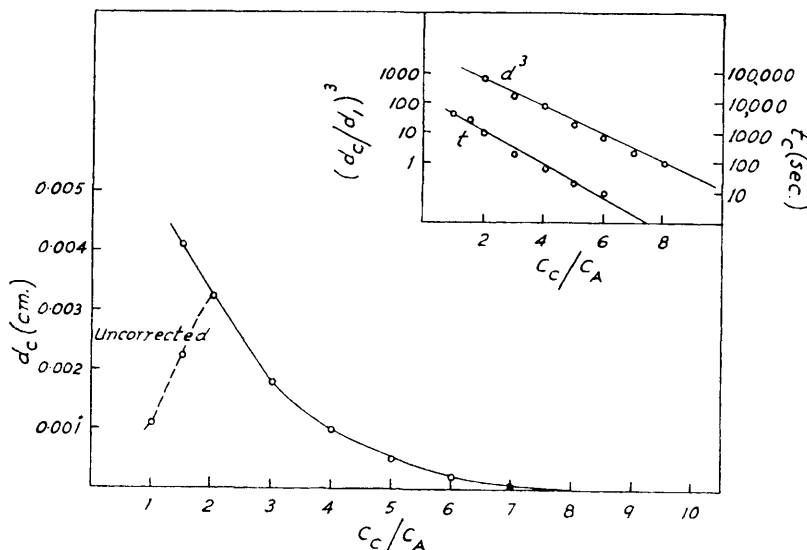
(II) *Coagulation of Peptised Equivalent Sols by Excess of Ion.*—The equivalent sols of insoluble metal salts peptised by organic acids, ammonia, etc., can in turn be coagulated by addition of excess of one of the reacting ions.³ Crystal growth from such systems has been studied.

(A) *Organic acid-peptised sols.*—(i) Sol stability. The stability of organic acid- and anion-peptised sols of insoluble metal salts is reduced by excess of cation according to Tuller and Fulmer's relationship,⁷ viz.,

$$\log_{10} t_c = \log_{10} t_e - bC_c/C_s \quad \dots \quad (5)$$

where t_c is the stability in presence of excess of cation concentration C_c , and t_e is the stability of the *equivalent sol* (for which $C_c = 0$). Results for typical metal salt systems are presented in

FIG. 7. Crystal growth from citric acid-peptised 0.005M-silver chromate sols, in presence of excess of cation (20°): $C_p/C_s = 0.8 \times$ peptisation ratio. Variation in average crystal diameter with excess cation: anion concentration ratio.



the earlier work on sol stability; C_s is the sol stability, and b represents the fall in stability, as measured by $\log t_e/t_c$, at unit value of C_c/C_s .

The coagulating effect of the excess of cation increases with fall in the peptising agent sol concentration ratio below the peptisation ratio according to the relation $b = \beta(C_p/C_s)^m$. Rapid coagulation (at $t = 1$ sec.) occurs at some particular value of C_c , viz., ($C_c = \bar{C}_c$), i.e.,

$$\log t_c = -b(C_c - \bar{C}_c)/C_s \quad \dots \quad (6)$$

where \bar{C}_c is mainly determined by the value of $1/b$.

(ii) Crystal growth. Slow coagulation of the fully peptised citric acid sols by moderate amounts of excess of cation lead to formation of well-formed crystals. The average diameter (d_c) decreases with excess of cation concentration according to the relation (see Fig. 7).

$$\log_{10} m_c/m_1 = \log_{10} d_c^3/d_1^3 = -b'(C_c - \bar{C}_c)/C_s \quad \dots \quad (7)$$

The d_c^3 line runs parallel with the sol stability line, and $b' = b$, i.e., equation (6) can be written

$$\log m_c/m_1 = -b(C_c - \bar{C}_c)/C_s = -\log N_c/N_1 \quad \dots \quad (7A)$$

(B) *Ammonia-peptised sols.* (i) Sol stability. The coagulation of the equivalent sols by excess of reacting ion has been discussed by the author.³ Whereas the fully peptised silver

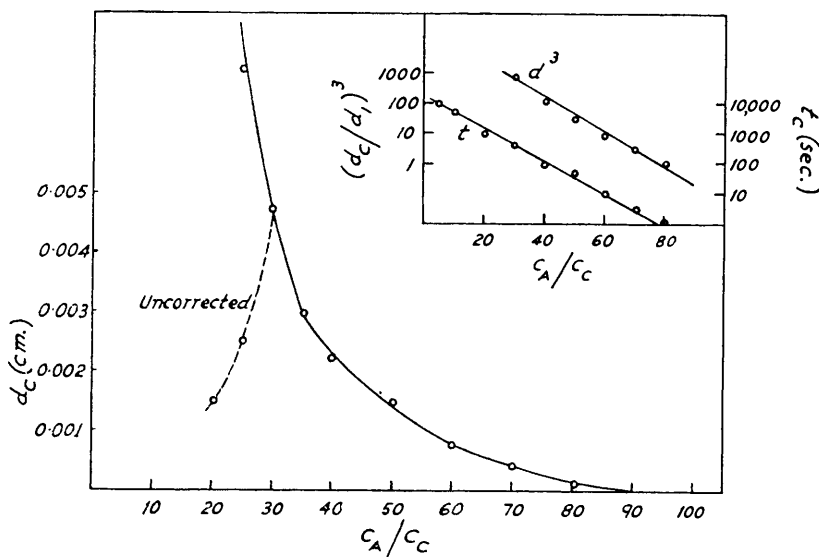
salt sols, for example, can be flocculated by an excess of silver ion of about 1.2—1.3, they are much less sensitive to excess of anion. At any ammonia-sol concentration ratio (C_p/C_s), the stability decreases with excess of anion concentration, according to the Tuller-Fulmer relation (5), so that

$$\log_{10} t_e = \log_{10} t_c - bC_A/C_c \quad \dots \quad (5A)$$

where C_A now represents the excess of anion concentration; here b varies inversely as the ease of destabilisation of the ammonia-peptised sol and increases rapidly with fall in C_p/C_s .

(ii) Crystal growth. Slow coagulation by excess of anions of silver-salt sols peptised by ammonia at $C_p/C_s = 0.7-1.0C_p^*/C_s$, i.e., from systems containing the complex metal salt, leads to formation of well-shaped crystals of appreciable size, similar in character to those prepared from the ammoniacal solution by internal evaporation.⁸ The average crystal size decreases with the excess of anion concentration, according to equations (7) and (7A), and typical results for silver chromate systems are presented in Fig. 8.

FIG. 8. Crystal growth from ammonia-peptised 0.005M-silver chromate sols, in presence of excess of anion (20°): $C_p/C_s = 0.8 \times$ peptisation ratio. Variation in average crystal diameter with excess anion concentration ratio.



DISCUSSION

Generally, during any precipitation process resulting from a double decomposition, nuclei of colloidal dimensions are first formed, and the crystal growth thereafter depends upon a competition between the growth of these nuclei from the metal salt in supersaturated solution, and its utilisation in the formation of fresh nuclei. It is evident that for a given amount of material which is ultimately to appear as precipitate, the average particle size will be small when the formation of fresh nuclei is the predominating factor, but that, as this formation of new nuclei is retarded, the final particle size will increase. This work has demonstrated that the *crystallinity* of insoluble metal salts (as measured by the average crystal diameter on a weight basis) may indeed be improved by addition of peptising agents that reduce the rate of coagulation of the sol from which the precipitate is grown.

The enhanced stability of insoluble metal-salt systems in solutions of organic acids, gelatin, and agar is in turn due to peptisation of the sol by adsorption of the undissociated acid molecule on the surface of the sol micelles,² while peptisation with ammonia occurs by adsorption of this reagent on the sol of the complex metal-ammonia salt.³ The rate

⁸ Cf. Walker, Bray, and Johnson, *J. Amer. Chem. Soc.*, 1927, **49**, 1250; Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954, p. 152.

of coagulation becomes appreciably reduced after adsorption of some definite amount of peptising agent (C_p), and varies with concentration of the additive according to the relation $-\log_{10} k_c/k_1 = F(C_p - \bar{C}_p)/C_s$. Slow coagulation leads to good crystallinity, however, only in those systems where peptisation is due to an *orientated* adsorption of a bulky organic molecule on the surface of the sol micelles; this in turn may regulate the fitting of the coagulated (and dehydrated) micelle on an existent crystal lattice. The slow coagulation of simple copper salts in solution of organic acids (which is not caused by such a mechanism) still leads to formation of a highly hydrated gelatinous precipitate, *i.e.*, a disordered structure with many free valency bonds.

Slow coagulation from ammonia-peptised systems, where the simple metal salt is still the main constituent, leads to a disordered dendritic growth; but coagulation, by excess of anion, of systems containing the complex metal ammonia salt, results in larger, well-formed crystals.

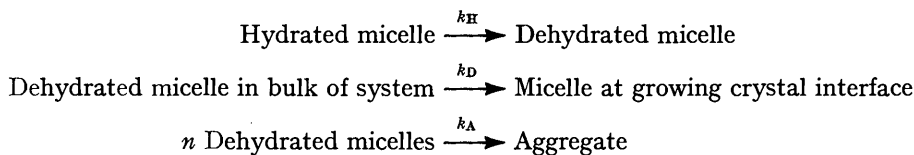
Similarly, whereas lead iodide and silver chromate show good crystallinity when grown from sols peptised by hydroxy- and amino-acids, respectively, slow coagulation of the sols peptised by long polypeptide and polysaccharide chains does not lead to formation of large crystals. The chains tend to "intermesh" and prevent the diffusing micelles from fitting in an ordered manner on a small number of nuclei: instead, a large number of small crystallites intimately associated with the peptiser are produced.

The final average weight of the crystals that grow from the peptised sol—by slow ordered fitting on a small number of nuclei—increases exponentially with the concentration of peptiser and thus varies inversely as the rate of coagulation of the sol. This result is to be expected if we assume that the main growth occurs on the small number (N) of nuclei of sufficiently large surface area, that are formed during the short time interval (T) immediately after mixing.⁹ At this early stage of the precipitation process, we may further assume that the rate of formation of nuclei will vary as the rate of coagulation; whence for any particular concentration (C_p) of peptiser, $dN/dt = \alpha kc$ (where α is a constant), *i.e.*, $N_c/T = \alpha kc$ and

$$m_c/m_0 = N_0/N_c = (N_0/T)/(N_c/T) = k_0/k_c$$

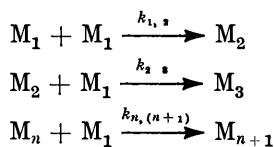
More detailed analysis of the crystal growth is a far more complex problem, since the rate of growth at any instant depends on the surface area and the "supersaturation," both of which may vary continuously throughout the period of growth.¹⁰

The *overall* mechanism of such a sol micelle aggregation, may, however, be examined by application of statistical methods to the kinetics of the following process:



In the solutions investigated in this work, the rate (k_D) of diffusion of the dehydrated micelles from the bulk of the system to the region of growing crystal face is rapid compared with the rate of aggregation (k_A), and k_D will not be a rate-determining factor.

We assume that growth occurs from units of approximately the same initial particle size, and that intermediate products cannot interact with each other, but only with further monomer: *i.e.*,



⁹ Davies and Jones, *Discuss. Faraday Soc.*, 1949, 5, 103.

¹⁰ Branson, Dunning, and Millard, *ibid.*, p. 83; Davies and Jones, *Trans. Faraday Soc.*, 1955, 51, 812.

where M_n represents an aggregate of n units. If $k_{1,2} = k_{2,3} = k_{n,(n+1)} = k_A$, then the molecular composition of the final product can be derived from statistical theory, developed for such reactions by Flory and Kierle.¹¹

At any time, the extent of the reaction, p , is determined by k_A according to the relation $(1 - p) = 2/k_A t$, while the distribution curve for the weight fraction has its maximum at the n -mer, where

$$n = \frac{(1 - p)^2}{\log p} \exp [-(1 + \log p)]$$

and as p approaches unity,

$$n = (1 - p)/e = 2/ek_A t$$

(e is the base of the natural logarithms). If the weight of the dehydrated micelle is W , then the final average crystal weight, $m = C_p d^3 = nW = 2W/ek_A t$. We have, in fact, found experimentally that m varies inversely as the rate of coagulation, and the results thus demonstrate that this coagulation may well be the rate-determining step in the process of crystal growth from a peptised sol. Since $k_c/k_0 = -F(C_p - \bar{C}_p)/C_s$, it follows that m_c/m_0 will vary directly as $F(C_p - \bar{C}_p)/C_s$, as has been observed experimentally.

At high rates of coagulation (corresponding to $t < 1$ sec.), a very large number of highly hydrated small crystallites are formed instantaneously on mixing, and no further growth can occur from a solution that is exhausted of reacting ions. As k is reduced, however, fewer aggregates of micelles are formed during the first period after mixing; and these grow further by slow ordered fitting of new micelles; whereas rapid rate of growth leads to a wide distribution of crystal sizes, addition of peptiser agents favours the formation of a crop of larger crystals with a narrow size distribution.

Conclusions.—The experimental results for crystal growth from highly supersaturated metal salt solutions support Balarev and Traube's hypothesis that the basic unit from which crystals grow is the micelle of the peptised sol. Aggregation occurs after slow coagulation of this sol, and the crystal growth follows a step-like reaction of the second order.

The crystallinity (as measured by the average crystal diameter on a weight basis) may be improved by addition of peptising agents that reduce the rate of coagulation of the sol, from which the metal salt precipitate is grown.

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KING'S COLLEGE (LONDON UNIVERSITY), STRAND, W.C.2.

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¹¹ Flory and Kierle, *ibid.*, 1936, 32, 54.