THE MECHANISM OF THE MUTUAL
COAGULATION PROCESS

by

Thomas Shelby Chapman

A Dissertation

Presented to the Faculty of

The Rice Institute, Houston, Texas

in Partial Fulfillment of the

Requirements for the

Degree

of

Master of Arts

The Rice Institute

May 1930

Deposited Jan. 1950

*Degree conferred
1931*

TABLE OF CONTENTS

	Page
INTRODUCTION	1
Nature of the Problem	1
Scope of the Investigation.	5
EXPERIMENTAL :	7
Preparation of the Sols	7
Mixing of the Sols.	12
Interaction of Stabilizing Ions	15
Mutual Electrical Neutralization	17
Observations of Biltz	38
Precipitating Ions in the Sols.	38
DISCUSSION OF RESULTS	59
SUMMARY.	64

INTRODUCTION

NATURE OF THE
PROBLEM

When suitable amounts of two sols of opposite sign are mixed, complete mutual coagulation takes place if they are of at all comparable stability.¹ If a suspension of a hydrophylic colloid is added to a less stable sol, the less stable dispersion suffers no change in appearance but becomes more stable toward the usual methods of precipitation. However, several authors report that these protective colloids sometimes do not protect but exert a precipitating action.² This mutual coagulation is ordinarily attributed to the mutual discharge of the electrically charged particles of opposite sign with subsequent agglomeration into clumps that settle out. The observations of Biltz are commonly cited to show that the action

¹ Graham: J. Chem. Soc., 15, 246 (1862); Linder and Picton: 71, 586 (1897); Henri: Compt. rend. Soc. biol., 55, 1666 (1903); Bechold: Z. physik. Chem., 48, 385 (1904); Neiser and Friedman: Munch. Med. Wochenschr., 51, 465, 872 (1904); Biltz: Ber., 37, 1095 (1904); Billitzer: Z. physik. Chem., 51, 148 (1905); Teague and Buxton: 60, 489, (1907).

² Brossa and Freundlich: Z. physik. Chem., 89, 306 (1915); Friedman: Archiv fur Hygiene, 55, 361 (1906); Pauli and Flecker: Biochem. Z., 41, 461 (1912).

is determined only by the charges on the particles and not at all on their nature.¹ Thus a comparison of the precipitating action of a series of sols is said to disclose that while the optimum amount of positive sols required to precipitate negative sols varies, the order is always the same.

Bancroft² pointed out that this deduction from Biltz's data is not justified. Wintgen and Lowenthal³ state the generally accepted view in another way when they say that the mutual precipitation of oppositely charged sols is a maximum when the concentrations of the sols expressed in equivalent aggregates are the same, that is, when equal numbers of charges of opposite sign are mixed. This rule was likewise found not to hold when a highly dispersed sol of one sign is mixed with a coarser sol of opposite sign.

¹ Freundlich: Kapillarchemie, 402 (1909); Thomas: Bogues Colloidal Behavior, 1, 325 (1924).

² J. Phys. Chem., 19, 362 (1915)

³ Z. physik. Chem., 109, 391 (1924)

Lottermoser¹ observed that the most complete coagulation of positively charged AgI containing a slight excess of AgNO₃ and negatively charged AgI containing a slight excess of KI, was obtained when the excess of AgNO₃ in one sol was just equivalent to the excess of KI in the other. This suggests that interaction between the stabilizing ions is the cause of the mutual coagulation of oppositely charged sols. In line with this Freundlich and Nathansohn² found colloidal As₂S₃ sol and Odens sulfur sol to be instable in the presence of each other. Since both sols are negatively charged, this instability cannot be due to mutual electrical neutralization but was found to result from the interaction between the stabilizing electrolytes of the two sols, hydrogen sulfide and pentathionic acid. Following up the above observations, Thomas and Johnson³ attribute mutual coagulation in other cases primarily to chemical interaction of the stabilizing electrolytes in the sols. Thus, the

¹ Kolloid-Z. 6, 78 (1910)

² Kolloid-Z. 28, 258, (1920); 29, 16 (1921)

³ J. Am. Chem. Soc., 45, 2532 (1923)

precipitation of Graham's colloidal ferric oxide, stabilized by hydrogen ion, and colloidal silica, stabilized by hydroxyl ion, was attributed to chemical neutralization. This view was supported by the observation that mutual precipitation was effected over a limited range of purity of sols, when the hydrochloric acid and sodium hydroxide concentration in the sols were approximately equivalent. The variation from equivalence was quite marked in case the sols were fairly pure. thus a silica sol containing 16 SiO_2 to 1 NaOH was precipitated at various dilutions with a sol containing 13 Fe_2O_3 to 1 H_2Cl_3 . At the highest dilution possible for obtaining accurate data, mutual precipitation was observed when an amount of colloidal silica was added corresponding to but 50 percent of the hydrochloric acid. This variation was attributed to the metastability of pure sols, which causes them to precipitate with a subnormal disturbance. This does not seem quite convincing since, in the absence of contamination other than that mentioned, the purity of the sols would scarcely be great enough to make them abnormally sensitive. Erratic results were also obtained when the amount of peptizing agent was too large, say three times as much as

in the case referred to above. Thus, to obtain data to support a purely chemical mechanism involving neutralization of the stabilizing agents, it seems necessary to choose the experimental conditions to fit the case. While everyone will agree that the peptizing agents of two sols may interact under certain conditions, thus affecting the stability of each, such a mechanism of the mutual precipitation process would not account for the repeated observation of mutual precipitation of sols where interaction between the peptizing agents is impossible or improbable.¹

SCOPE OF THE
INVESTIGATION

In an attempt to throw some further light on the several factors which influence the mutual coagulation process, the experiments reported in this paper were carried out. The sols, though mainly of hydrophobic character, were of as varied nature as might be obtained of known purity and stable enough to survive the duration of a series of experiments. Their mutual coagulation was effected with the object of investigating the

¹ Thomas questions whether any such cases exist:

following questions: (1) interaction of stabilizing ions, (2) mutual electrical neutralization, and (3) the effect of electrolytes naturally occurring in the sol. It will be noted that in the discontinuous system Fe_2O_3 (+) and Fe_2O_3 (-) the sols were prepared by methods similar in nature but differing in electrolyte present during the formation, precluding the possibility suggested by the work of Boutaric and Perreau.¹ The latter prepared a positive ferric oxide sol by the usual methods and reversed its charge in a portion through the addition of a polyvalent anion. The mutual coagulating effect of the two sols was then equal to that of a corresponding amount of the polyvalent ion on the resulting total volume of sol. This special case might possibly be explained by dilution of the reversing ion.

¹J. Chem. Phys., 27, 250 (1930)

EXPERIMENTAL

PREPARATION
OF SOLS

Most of the sols used in this investigation were prepared by standard methods which in many cases have been modified by procedures already described in detail. To avoid useless repetition, the sols employed are listed in Table I together with references which give the details of the method of preparation used in each case. In general it may be said that special precautions were taken in the preparation of the sols. Chemicals of a high degree of purity were used and all operations were carried out in pyrex vessels. In every case with the exception of the night blue sol, the preparations were subjected to prolonged dialysis in Neidle¹ dialysers using cellophane bags. The concentrations of the sols were obtained by evaporation of a known volume of the sol to dryness in a platinum dish, and weighing the residue after suitable ignition.

The zinc and copper ferrocyanide sols used in the first series of experiments were prepared

¹
J. Am. Chem. Soc., 38, 1270 (1916)

Table I

Sols Used in Mutual Coagulation Experiments

Sol	Reference to method of preparation
As_2S_3	Freundlich and Nathansohn: Kolloid-Z., <u>28</u> , 258 (1928)
SnO_2	Weiser: J. Phy. Chem., <u>26</u> , 682 (1922)
Congo red acid	Weiser and Radcliffe: J. Phys. Chem., <u>32</u> , 1878 (1928)
$\text{Cu}_2\text{Fe}(\text{CN})_6$	Weiser: J. Phys. Chem., <u>30</u> , 1530 (1926)
$\text{Zn}_2\text{Fe}(\text{CN})_6$	Same procedure as for $\text{Cu}_2\text{Fe}(\text{CN})_6$ sol
Sulfur	Weiser and Cunningham: Colloid Symposium Monograph, <u>6</u> , 326 (1928)
Molybdenum blue	Biltz: Ber., <u>35</u> , 4431 (1902)
Night blue	Addition to water
Fe_2O_3 (-)	Hazel and Sorum: J. Am. Chem. Soc., <u>52</u> , 1337 (1930)
Fe_2O_3 (+)	Sorum: J. Am. Chem. Soc., <u>50</u> , 1263 (1928)
Cr_2O_3	Neidle: J. Am. Chem. Soc., <u>39</u> , 71 (1917)
CeO_2	Biltz: Ber., <u>35</u> , 4431 (1902)
BaSO_4	Modification of Kato's method.
BaCO_3	Buzagh: Kolloid-Z., <u>38</u> , 222; <u>39</u> , 218 (1926)
Sb_2S_3	Biltz: Ber., <u>37</u> , 1097 (1904)
$\text{Cu}_3(\text{FeC}_6\text{N}_8)_2$	See below
AgI (-)	Lottermoser: J. prakt. Chem., (2) <u>68</u> , 340 (1903)
TiI (+)	Ostwald: Die wissenschaftlichen Grundlagen der analytischen Chemie, 209 (1904)

by the interaction of hydroferrocyanic acid and copper salt while in the later experiments potassium ferrocyanide was employed. The use of hydroferrocyanic acid to obtain the salt is advantageous since the precipitate is almost pure $\text{Cu}_3\text{Fe}(\text{CN})_6$.¹

Copper ferricyanide sol prepared by mixing equivalent amounts of dilute solutions of potassium ferricyanide and copper sulfate, followed by washing the precipitated gel in the centrifuge until peptization was complete and dialyzing.

The colloidal barium sulfate used in the first series of experiments was prepared by the method of Kato² which consists in diluting a one molar solution of sulfuric acid with twice its volume of alcohol and adding to it an equivalent amount of a molar solution of barium acetate diluted with 5 times its volume of alcohol. The resulting gelatinous precipitate and milky sol were evaporated to dryness under

¹ Cf. Weiser: J. Phys. Chem., 34, 343 (1930)

² Mem. Coll. Sci. Kyoto Imp. Univ., 2, 187 (1909-10)

reduced pressure below 40° and the precipitate was dispersed by shaking with water. Due to the difficulty of removing the acetic acid by this method as well as the complications introduced by low temperature, low pressure distillation of a frothing liquid, the procedure was modified to some extent. It was found that if a slight excess of barium acetate was employed in the mixing of the solutions described that the gelatinous precipitate would be peptized entirely to a milky sol on stirring vigorously about half an hour after the mixing. A large excess of barium acetate produced no precipitate while an excess of sulfuric acid resulted in the complete precipitation of the sol leaving a clear supernatant layer. The alcosol, either from slight or large excess of barium acetate, was subjected to dialysis. About a week of continuous dialysis served to replace the alcohol with water and to remove the acetic acid giving a sol comparable with Kato's in stability. When an alcosol containing the gelatinous precipitate, either from insufficient barium acetate or insufficient stirring, was dialyzed the precipitate

lost its gelatinous character and was left as a slimy deposit on the bottom of the dialyzer. Since the barium acetate is so susceptible to hydrolysis, rather than determine the excess necessary it was found more convenient to prepare small test samples after the solutions were made up. Attempts to prepare a negative sol through the use of other barium salts were negative.

In the study of the effect of the concentration of stabilizing electrolyte the sols were prepared in the following manner. A large volume of the sol (8 or 10 liters) was made up and divided into a number of equal portions which were dialyzed simultaneously and continuously in the hot. From time to time samples were removed for analysis until the analysis showed the desired ratio of sol to electrolyte, when the sol was removed and stored in pyrex ballon flasks. The chloride content of these sols was determined by dissolving in nitric acid after the addition of a suitable amount of silver nitrate.

METHOD OF
MIXING SOLS

The procedure employed in the first series of experiments was as follows: A suitable volume of one sol was taken and varying amounts of a second sol of opposite sign was added until the approximate range of complete mutual coagulation was located. The zone of complete mutual coagulation was then determined more sharply by making a series of mixtures in the boundary region using a constant volume of one sol and slightly varying the amounts of the second. The mixtures, after shaking well, were allowed to stand 30 minutes, shaken again and centrifuged for one minute at 3000 r. p. m. in a No. 1 International-Equipment-Company centrifuge and examined for complete mutual coagulation. When the presence of a small amount of colloid was not readily determined by visual observation as in the case of stannic oxide sol, a portion of the supernatant liquid after centrifuging was pipetted off and treated with an electrolyte containing a multivalent precipitating ion. The absence of a precipitate or a floc on standing two hours was taken as an indication

that no sol was present. The results are given in Tables III, IV, V, and VI.

The method of the first series suffered only a little refinement in the later experiments. In these the sols were mixed in such amount that the total volume of the mixture was always 10 cc. and allowed to stand for an hour before centrifuging, shaking at fifteen minute intervals.

INTERACTION OF
STABILIZING IONS

If the stabilizing ions of two oppositely charged sols are capable of interaction to form an insoluble or a slightly dissociated compound it is altogether likely that such interaction will influence the mutual coagulation process. Thus interaction between the stabilizing hydrogen and ferric ions in a Graham ferric oxide sol and the hydroxyl ions in a silicon dioxide sol will influence the mutual coagulation of the two sols as emphasized by Thomas and Johnson.¹ But mutual coagulation in general is not dependant on the removal of the respective stabilizing ions by such an interaction. This may be shown by the fact that often the stabilizing ion of one sol, for instance ferrocyanide, may be found in the supernatant liquid after complete mutual coagulation, in this case with ferric oxide. If the precipitation is due to interaction of the stabilizing ions they should be removed from ionic solution. Weiser² has shown the mechanism by which

¹ Loc. cit.

² J. Phys. Chem., 25,1 (1931)

Table II

Mutual Coagulation of Oppositely Charged Sols

Positive Sol	Stabilizing Ion	Negative Sol	Stabilizing Ion
1 Fe_2O_3	H^+	$\text{Zn}_2\text{Fe}(\text{CN})_6$	$\text{Fe}(\text{CN})_6^{4-}$
2 BaCO_3	Ba^{++}	$\text{Zn}_2\text{Fe}(\text{CN})_6$	$\text{Fe}(\text{CN})_6^{4-}$
3 BaSO_4	Ba^{++} and H^+	$\text{Cu}_2\text{Fe}(\text{CN})_6$	$\text{Fe}(\text{CN})_6^{4-}$
4 BaCO_3	Ba^{++}	SnO_2	OH^-
5 BaCO_3	Ba^{++}	As_2S_3	HS^-
6 Fe_2O_3	H^+	$\text{Cu}_3(\text{FeC}_6\text{N}_6)_2$	$\text{Fe}(\text{CN})_6^{4-}$
7 Fe_2O_3	H^+	Congo red acid	Congo red anion
8 BaSO_4	Ba^{++} and H^+	$\text{Cu}_3(\text{FeC}_6\text{N}_6)_2$	$\text{Fe}(\text{CN})_6^{4-}$
9 TlI	Tl^+	SnO_2	OH^-
10 BaCO_3	Ba^{++}	AgI	I^-

Remarks

- (1) $\text{H}_4\text{Fe}(\text{CN})_6$ soluble and highly ionized.
 (2) $\text{Ba}_2\text{Fe}(\text{CN})_6$ quite soluble. (3) $\text{Ba}_2\text{Fe}(\text{CN})_6$ and $\text{H}_4\text{Fe}(\text{CN})_6$ soluble. (4) $\text{Ba}(\text{OH})_2$ soluble.
 (5) BaHS soluble. (6) $\text{H}_3\text{Fe}(\text{CN})_6$ and $\text{Fe}(\text{FeC}_6\text{N}_6)$ soluble. (7) pH of Fe_2O_3 sol = 6.8
 (8) $\text{Ba}_3\text{Fe}(\text{C}_6\text{N}_6)_2$ and $\text{H}_4\text{Fe}(\text{CN})_6$ soluble.
 (9) TlOH soluble. (10) BaI_2 soluble.

electrolytes are displaced in the coagulation of sols by electrolytes. The same condition may also obtain in the precipitation of sols by sols.

That chemical interaction of stabilizing ions is not in general necessary for the mutual coagulation of sols is illustrated by the results of some observations on the mutual coagulation of oppositely charged sols where there is no interaction between the stabilizing ions with the formation of an insoluble or slightly dissociated compound. In these experiments a 10 cc portion of one sol was taken and the other sol added quite slowly until a point of complete mutual coagulation was found. A few combinations are recorded in Table II. The list may be extended by anyone who desires.

MUTUAL ELECTRICAL
NEUTRALIZATION

Since coagulation takes place when the charge on the particles of a sol is reduced to a critical value below which the particles will agglomerate sufficiently large to settle, it would seem to follow that, if no other factor comes in, mutual coagulation

would result when amounts of sols bearing equal numbers of opposite charges are mixed. Moreover, if electrostatic neutralization were the only factor, one would expect the range of mutual coagulation to be relatively narrow and that a given series of sol of one sign would always arrange themselves in the same order regardless of what sol of opposite sign is precipitated. From the experimental results it is obvious that the precipitating power of sols of one sign for sols of opposite sign is not determined exclusively by the charge on the colloidal particles.

The results recorded in Tables III to VI are represented in a diagram, Fig. 1. The right hand side of the diagram corresponds to 100 per cent by weight of Cr_2O_3 , CeO_2 , Fe_2O_3 , and BaSO_4 , respectively, and 0 percent of As_2S_3 , $\text{Cu}_2\text{Fe}(\text{CN})_6$, Congo red acid, SnO_2 , and $\text{Zn}_2\text{Fe}(\text{CN})_6$; while the left hand side corresponds to 100 per cent of the latter compounds and zero per cent of the former. The shaded portions

Table III

Mutual Coagulation of Fe_2O_3 Sol and Negative Sols

cc Fe_2O_3	Observations	cc SnO_2	Range of mutual coagulation % Fe_2O_3 by weight
2.59 gm/l		2.37 gm/l	
10	excess Fe_2O_3	1.6	
10	complete mutual	1.8	86.0 to 84.5
10	coagulation	2.0	
10	excess SnO_2	2.2	
		$\text{Zn}_3\text{Fe}(\text{CN})_6$	
		2.10 gm/l	
10	excess Fe_2O_3	1.2	
10	complete mutual	1.4	90.0 to 75.5
10	coagulation	4.0	
10	excess $\text{Zn}_3\text{Fe}(\text{CN})_6$	4.2	
		$\text{Cu}_2\text{Fe}(\text{CN})_6$	
		3.28 gm/l	
5	excess Fe_2O_3	1.0	
5	complete mutual	1.25	76.0 to 66.5
5	coagulation	2.0	
5	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	2.25	
		Congo red acid	
		1.95 gm/l	
5	excess Fe_2O_3	1.5	
5	complete mutual	1.75	79.0 to 58.0
5	coagulation	4.75	
5	excess C R A		

Table III
(continued)

cc	Observations	cc	Range of mutual
Fe_2O_3		As_2S_3	coagulation
2.59 gm/l		2.22 gm/l	% Fe_2O_3 by weight
5	excess Fe_2O_3	5.0	
5	complete mutual	5.25	57.5 to 49.0
5	coagulation	6.0	
5	excess As_2S_3	6.25	

Table IV

Mutual Coagulation of Cr_2O_3 Sol and Negative Sols

cc	Observations	cc	Range of mutual
Cr_2O_3		$\text{Zn}_2\text{Fe}(\text{CN})_6$	coagulation
2.17 gm/l		2.10 gm/l	% Cr_2O_3 by weight
5	excess Cr_2O_3	6.0	
2	complete mutual	2.5	45.5 to 24.0
2	coagulation	6.5	
2	excess $\text{Zn}_2\text{Fe}(\text{CN})_6$	6.75	
		SnO_2	
		2.37 gm/l	
2	excess Cr_2O_3	3.75	
2	complete mutual	4.0	31.5 to 23.5
2	coagulation	6.0	
2	excess SnO_2	6.25	

Table IV
(continued)

cc	Observations	cc	Range of mutual
Cr_2O_3		Congo red acid	coagulation
2.17 gm/l		1.95 gm/l	% Cr_2O_3 by weight
1	excess Cr_2O_3	5.75	
1	complete mutual	6.0	15.5 to 14.0
1	coagulation	6.75	
1	excess CRA	7.0	
		$\text{Cu}_2\text{Fe}(\text{CN})_6$	
		3.28 gm/l	
1	excess Cr_2O_3	5.0	
1	complete mutual	5.25	11.0 to 7.5
1	coagulation	7.75	
1	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	8.0	
		As_2S_3	
		2.22 gm/l	
1	excess Cr_2O_3	11.5	
1	complete mutual	11.75	7.5 to 6.0
1	coagulation	15.0	
1	excess As_2S_3	15.25	

Table V

Mutual Coagulation of CeO_2 Sol and Negative Sols

cc	Observations	cc	Range of mutual
CeO_2		$\text{Zn}_2\text{Fe}(\text{CN})_6$	coagulation
2.50 gm/l		2.10 gm/l	% CeO_2 by weight
5	excess CeO_2	3.50	
5	complete mutual	3.75	61.0 to 54.5
5	coagulation	5.0	
5	excess $\text{Zn}_2\text{Fe}(\text{CN})_6$	5.25	
		SnO_2	
		2.37 gm/l	
5	excess CeO_2	4.0	
5	complete mutual	4.25	55.0 to 51.5
5	coagulation	5.0	
4.75	excess SnO_2	5.0	
		As_2S_3	
		2.22 gm/l	
3	excess CeO_2	1.5	
3	complete mutual	1.75	66.0 to 23.5
3	coagulation	11.0	
3	excess As_2S_3	12.0	
		Congo red acid	
		1.95 gm/l	
3	excess CeO_2	5.25	
3	complete mutual	5.5	41.0 to 30.0
3	coagulation	9.0	
3	excess CRA	9.25	

Table V
(continued)

cc	Observations	cc	Range of mutual
CeO_2		$\text{Cu}_2\text{Fe}(\text{CN})_6$	coagulation
2.50 gm/l		3.28 gm/l	% CeO_2 by weight
3	excess CeO_2	4.25	
3	complete mutual	4.5	39.0 to 25.0
3	coagulation	6.75	
3	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	7.0	

Table VI

Mutual Coagulation of BaSO_4 Sol and Negative Sols

cc	Observations	cc	Range of mutual
BaSO_4		Congo red acid	coagulation
14.79 gm/l		1.95 gm/l	% BaSO_4 by weight
5	excess BaSO_4	1.5	
5	complete mutual	1.75	95.5 to 86.5
5	coagulation	6.0	
5	excess CRA	6.25	
		As_2S_3	
		2.22 gm/l	
5	excess BaSO_4	3.0	
5	complete mutual	3.25	91.0 to 89.0
5	coagulation	4.25	
5	excess As_2S_3	4.5	

Table VI
(continued)

cc	Observations	cc	Range of mutual
BaSO_4		$\text{Cu}_2\text{Fe}(\text{CN})_6$	coagulation
14.79 gm/l		3.28 gm/l	% BaSO_4 by weight
5	excess BaSO_4	1.25	
5	complete mutual	1.5	94.0 to 86.0
5	coagulation	3.75	
5	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	4.0	
		$\text{Zn}_2\text{Fe}(\text{CN})_6$	
		2.10 gm/l	
5	excess BaSO_4	4.0	
5	complete mutual	4.25	89.0 to 85.5
5	coagulation	6.0	
5	excess $\text{Zn}_2\text{Fe}(\text{CN})_6$	6.25	
		SnO_2	
		2.37 gm/l	
5	excess BaSO_4	3.0	
5	complete mutual	3.25	90.5 to 79.5
5	coagulation	8.0	
5	excess SnO_2	8.25

FIG. I
Range of mutual coagulation of oppositely charged sols. Series I.

of the diagram thus represents the composition of the coagulum in the range of mutual coagulation in weight per cent of the dry constituents.

The composition of the precipitates using each positive sol with the several negative sols is represented in the order of increasing amounts of the negatively charged constituent, assuming that the mid point of the range of complete mutual coagulation is the optimum point, It will be noted that the order in which the negative sols arrange themselves is not the same even for the hydrous oxide sols, which may be assumed to have very similar physical characteristics, and is quite different with a different type of sol such as barium sulfate.

The results recorded above were extended in a second series of experiments with different sols. The method of procedure differed only as described previously, the changes being made only for convenience in observation and calculation. The results are tabulated in Tables VII to X inclusive and are represented similar to the first series in the diagram Fig. 2.

Table VII

Mutual Coagulation of Fe_2O_3 Sol and Negative Sols

cc. Fe_2O_3	Observations	cc Molybdenum blue	Range of mutual coagulation
1.72 gm/l		0.18 gm/l	% Fe_2O_3 by weight
4.8	excess MB	5.2	
4.9	complete mutual	5.1	94.2 to 90.2
6.3	coagulation	3.7	
6.4	excess Fe_2O_3	3.6	
		Fe_2O_3 (-)	
		0.30 gm/l	
2.8	excess Fe_2O_3 (-)	7.2	
2.9	complete mutual	7.1	82.5 to 70.0
4.5	coagulation	5.5	
4.6	excess Fe_2O_3	5.4	
		As_2S_3	
		1.64 gm/l	
5.1	excess As_2S_3	4.9	
5.2	complete mutual	4.8	59.1 to 53.2
5.8	coagulation	4.2	
5.9	excess Fe_2O_3	4.1	
		Congo red acid	
		0.61 gm/l	
2.2	excess CRA	7.8	
2.3	complete mutual	7.7	49.8 to 45.8
2.6	coagulation	7.4	
2.7	excess Fe_2O_3	7.3	

Table VII
(continued)

cc	Observations	cc	Range of mutual
Fe_2O_3		$\text{Cu}_2\text{Fe}(\text{CN})_6$	coagulation
1.72		3.23	% Fe_2O_3 by weight
gm/l		gm/l	
4.7	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	5.3	
4.8	complete mutual	5.2	46.5 to 32.9
6.2	coagulation	3.8	
6.3	excess Fe_2O_3	3.7	
		Sulfur	
		0.30	
		gm/l	
0.5	excess Sulfur	9.5	
0.6	complete mutual	9.4	39.0 to 27.0
1.0	coagulation	9.0	
1.1	excess Fe_2O_3	8.9	
		SnO_2	
		1.73	
		gm/l	
0.5	excess SnO_2	9.5	
0.6	complete mutual	9.4	18.0 to 6.0
1.8	coagulation	8.2	
1.9	excess Fe_2O_3	8.1	

Table VIII

Mutual Coagulation of Cr_2O_3 Sol and Negative Sols

cc Cr_2O_3	Observations	cc Molybdenum blue	Range of mutual coagulation
0.82 gm/l		0.18 gm/l	% Cr_2O_3 by weight
2.4	excess MB	7.6	
2.5	complete mutual	7.5	73.6 to 60.3
3.8	coagulation	6.2	
3.9	excess Cr_2O_3	6.1	
		Fe_2O_3 (-)	
		0.30 gm/l	
1.9	excess Fe_2O_3 (-)	8.1	
2.0	complete mutual	8.0	61.6 to 40.5
3.7	coagulation	6.3	
3.8	excess Cr_2O_3	6.2	
		$\text{Cu}_2\text{Fe}(\text{CN})_6$	
		3.23 gm/l	
4.4	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	5.6	
4.5	complete mutual	5.5	21.6 to 17.2
5.2	coagulation	4.8	
5.3	excess Cr_2O_3	4.7	
		Congo red acid	
		0.61 gm/l	
0.7	excess CRA	9.3	
0.8	complete mutual	9.2	11.7 to 10.5
0.9	coagulation	9.1	
1.0	excess Cr_2O_3	9.0	

Table VIII

(continued)

cc	Observations	cc	Range of mutual
Cr_2O_3		As_2S_3	coagulation
0.82 gm/l		1.64 gm/l	% Cr_2O_3 by weight
1.5	excess As_2S_3	8.5	
1.6	complete mutual	8.4	9.4 to 8.7
1.7	coagulation	8.3	
1.8	excess Cr_2O_3	8.2	
		SnO_2	
		1.73 gm/l	
1.5	excess SnO_2	8.5	
1.6	complete mutual	8.4	9.4 to 8.2
1.8	coagulation	8.2	
1.9	excess Cr_2O_3	8.1	
		Sulfur	
		0.30 gm/l	
0.1	excess Sulfur	9.9	
0.2	complete mutual	9.8	7.8 to 5.3
0.3	coagulation	9.7	
0.35	excess Cr_2O_3	9.65	

Table IX

Mutual Coagulation of Night Blue Sol with Negative Sols

cc	Observations	cc	Range of mutual
Night blue		Molybdenum blue	coagulation
0.72 gm/l		0.18 gm/l	% NB by weight
2.8	excess MB	7.2	
2.9	complete mutual	7.1	63.0 to 62.0
3.0	coagulation	7.0	
3.1	excess NB	6.9	
		Fe ₂ O ₃ (-)	
		0.30 gm/l	
0.6	excess Fe ₂ O ₃ (-)	9.4	
0.7	complete mutual	9.3	67.2 to 15.3
4.6	coagulation	5.4	
4.7	excess NB	5.3	
		Cu ₂ Fe(CN) ₆	
		3.23 gm/l	
5.3	excess Cu ₂ Fe(CN) ₆	4.7	
5.4	complete mutual	4.6	23.5 to 20.7
5.8	coagulation	4.2	
5.9	excess NB	4.1	
		Sulfur	
		0.30 gm/l	
0.3	excess Sulfur	9.7	
0.4	complete mutual	9.6	19.2 to 9.1
0.9	coagulation	9.1	
1.0	excess NB	9.0	

Table IX
(continued)

cc	Observations	cc	Range of mutual
Night blue		Congo red acid	coagulation
0.72 gm/l		0.61 gm/l	% NB by weight
1.0	excess CRA	9.0	
1.1	complete mutual	8.9	13.8 to 12.7
1.2	coagulation	8.8	
1.3	excess NB	8.7	
		As ₂ S ₃	
		1.64 gm/l	
1.4	excess As ₂ S ₃	8.6	
1.5	complete mutual	8.5	8.8 to 7.2
1.8	coagulation	8.2	
1.9	excess NB	8.1	
		SnO ₂	
		1.73 gm/l	
1.2	excess SnO ₂	8.8	
1.3	complete mutual	8.7	8.4 to 5.9
1.8	coagulation	8.2	
1.9	excess NB	8.1	

Table X

Mutual Coagulation of BaSO_4 Sol and Negative Sols

cc BaSO_4	Observations	cc Molybdenum blue	Range of mutual coagulation
5.60 gm/l		0.18 gm/l	% BaSO_4 by weight
6.3	excess MB	3.7	
6.4	complete mutual	3.6	99.1 to 98.2
7.8	coagulation	2.2	
7.9	excess BaSO_4	2.1	
		Congo red acid	
		0.61 gm/l	
4.3	excess CRA	5.7	
4.4	complete mutual	5.6	94.8 to 87.8
6.6	coagulation	3.4	
6.7	excess BaSO_4	3.3	
		As_2S_3	
		1.64 gm/l	
6.2	excess As_2S_3	3.8	
6.3	complete mutual	3.7	89.3 to 85.3
7.1	coagulation	2.9	
7.2	excess BaSO_4	2.8	
		Sulfur	
		0.30 gm/l	
1.3	excess Sulfur	8.7	
1.4	complete mutual	8.6	86.7 to 75.3
2.6	coagulation	7.4	
2.7	excess BaSO_4	7.3	

Table X
(continued)

cc	Observations	cc	Range of mutual
BaSO_4		$\text{Cu}_2\text{Fe}(\text{CN})_6$	coagulation
5.60 gm/l		3.23 gm/l	% BaSO_4 by weight
6.2	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	3.8	
6.3	complete mutual	3.7	81.7 to 74.8
7.2	coagulation	2.8	
7.3	excess BaSO_4	2.7	
		Fe_2O_3 (-)	
		0.30 gm/l	
0.5	excess Fe_2O_3 (-)	9.5	
0.6	complete mutual	9.4	99.2 to 54.4
8.7	coagulation	1.3	
8.8	excess BaSO_4	1.2	
		SnO_2	
		1.73 gm/l	
2.1	excess SnO_2	7.9	
2.2	complete mutual	7.8	89.6 to 47.6
7.3	coagulation	2.7	
7.4	excess BaSO_4	2.6

FIG. 2
Range of mutual coagulation of oppositely charged sols. Series 2.

Table XI

Mutual Coagulation Data of Biltz

Milligrams of constituents in coagulum in the zone of mutual coagulation			Range of mutual coagulation % by weight	
Au	1.4 CeO ₂	4.8 to 1.8	CeO ₂	77.5 to 56.0
Au	1.4 ThO ₂	3.2 to 2.3	ThO ₂	70.0 to 62.0
Au	1.4 Fe ₂ O ₃	4.0 to 1.8	Fe ₂ O ₃	74.0 to 56.0
Au	1.4 ZrO ₂	2.2 to 1.2	ZrO ₂	63.0 to 46.0
Au	1.4 Cr ₂ O ₃	0.4 to 0.55	Cr ₂ O ₃	22.0 to 4.0
Au	1.4 Al ₂ O ₃	0.2 to 0.15	Al ₂ O ₃	12.5 to 9.5
Sb ₂ S ₃	5.6 Fe ₂ O ₃	8.0 to 5.2	Fe ₂ O ₃	50.0 to 48.0
Sb ₂ S ₃	28.0 ThO ₂	5.5 to 3.0	ThO ₂	50.0 to 35.0
Sb ₂ S ₃	28.0 CeO ₂	13.5 to 9.6	CeO ₂	32.5 to 25.5
Sb ₂ S ₃	28.0 ZrO ₂	9.1 to 4.5	ZrO ₂	24.5 to 14.0
Sb ₂ S ₃	28.0 Al ₂ O ₃	9.0 to 1.5	Al ₂ O ₃	24.0 to 5.0
Sb ₂ S ₃	28.0 Cr ₂ O ₃	4.0 to 2.0	Cr ₂ O ₃	12.5 to 6.5
As ₂ S ₃	12.0 Fe ₂ O ₃	7.0 to 4.8	Fe ₂ O ₃	37.0 to 28.5
As ₂ S ₃	12.0 ThO ₂	3.5 to 2.5	ThO ₂	22.5 to 17.0
As ₂ S ₃	24.0 Al ₂ O ₃	9.0 to 1.5	Al ₂ O ₃	27.0 to 6.0
As ₂ S ₃	24.0 CeO ₂	4.0 to 3.5	CeO ₂	15.0 to 12.5
As ₂ S ₃	24.0 ZrO ₂	2.7 to 1.3	ZrO ₂	10.0 to 5.0
As ₂ S ₃	12.0 Cr ₂ O ₃	2.7 to 0.4	Cr ₂ O ₃	5.5 to 3.0

FIG. 3

Range of mutual coagulation of oppositely charged sols (Biltz).

OBSERVATIONS
OF BILTZ

From the mutual coagulation observations of Biltz¹, the zone of complete mutual coagulation was estimated. These data are shown in Table XI and are plotted in Fig. 3. The hydrous oxides, which give positive sols, are arranged in order of decreasing amount in mixtures with Au, Sb_2S_3 , and As_2S_3 , respectively, assuming that the optimum point of mutual coagulation is the midpoint of the range. In this series of experiments also it will be seen that the order of oxides is by no means the same, as is usually assumed.

PRECIPITATING IONS
IN THE SOLS

Since it is practically impossible to prepare a sol without the presence of at least a slight amount of electrolyte, it is unthinkable to consider the action of such a colloid without taking into consideration the effect due to this electrolyte, either free in solution or adsorbed as a peptizing agent on the surface of the particles. If this electrolyte

¹ Ber., 37, 1104 (1904)

contains a multivalent ion then its effect can certainly not be disregarded for, according to the Schulze-Hardy rule¹, the greater the valence of a precipitating ion the lower the concentration necessary for the precipitation of a sol. The effect of the presence of unadsorbed multivalent ions in the sols as a factor in the mutual coagulation process has not been taken into account by any one. For example, if the excess alkali ferricyanide used in the preparation of a negatively charged ferricyanide sol is not removed completely and this sol is employed to coagulate positive sols, the ferricyanide ion in the intermicellar solution will exert a precipitating action on the positive sol that is independent of the mutual coagulation of the oppositely charged particles. In such a case one would expect the range of coagulation to be relatively wide. In the previous experiments an attempt was made to avoid this complication by working with well dialyzed sols.

¹ J. prakt. Chem., (2) 25, 431 (1882); 27, 320 (1883)

Too, if an electrolyte be added stepwise to a sol it is found that a larger quantity of electrolyte is required to obtain complete precipitation than if the electrolyte be added all at one time. This phenomenon, known as acclimatization, is ascribed in part to adsorption of the precipitating ion by the coagulated particles of the sol, these particles thus taking up more electrolyte than is necessary to effect their precipitation if the electrolyte be added all at once.¹ Similarly, it was found that, for instance, if just enough congo red acid sol was added to coagulate a quantity of barium sulfate sol and the complete coagulation of this mixture demonstrated, several times this amount of barium sulfate sol might then be added before it remained suspended in the supernatant liquid. Likewise if the maximum amount of congo red acid sol was added to the barium sulfate sol, after coagulation a much greater amount could be added and precipitated than had previously been used in coagulation.

¹ Weiser: J. Phys. Chem., 25, 404 (1921)

However, if the coagulum was washed well in the centrifuge, a much smaller excess of either sol was required in order that it might remain in suspension, showing that electrolyte freed from the precipitated sol in the coagulation produces a very much more marked effect than that of adsorption of the excess precipitating sol by the coagulum. In all the experiments this condition was minimized by complete and immediate mixing but the effect of electrolytes present in excess cannot be disregarded.

Accordingly precipitation was carried out using sols of ferric oxide and alumina containing varying amounts of electrolyte toward negative sols of different character. This excess quantity of electrolyte was obtained by incomplete dialysis, a large quantity of sol being prepared and portions dialyzed for different periods of time until an analysis showed a suitable ratio of Cl ion to Fe_2O_3 or Al_2O_3 . The results of these experiments are tabulated in Tables XII to XVII inclusive, and are shown diagrammatically in Figs. 4 and 5.

Table XII

Mutual Coagulation of Fe_2O_3 Sols and $\text{Cu}_2\text{Fe}(\text{CN})_6$ Sol

cc Fe_2O_3	Observations	cc $\text{Cu}_2\text{Fe}(\text{CN})_6$	Range of mutual coagulation
2.77 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0615	4.18 gm/l	% Fe_2O_3 by weight
3.2	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	6.8	
3.3	complete mutual	6.7	24.6 to 39.9
5.0	coagulation	5.0	
5.1	excess Fe_2O_3	4.9	
2.83 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0402		
3.1	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	6.9	
3.2	complete mutual	6.8	24.2 to 39.5
4.9	coagulation	5.1	
5.0	excess Fe_2O_3	5.0	
3.01 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0480		
3.2	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	6.8	
3.3	complete mutual	6.7	26.2 to 42.0
5.0	coagulation	5.0	
5.1	excess Fe_2O_3	4.9	
3.04 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0169		
3.7	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	6.3	
3.8	complete mutual	6.2	30.8 to 45.2
5.3	coagulation	4.7	
5.4	excess Fe_2O_3	4.6	
3.03 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0071		
4.3	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	5.7	
4.4	complete mutual	5.6	36.4 to 55.1
6.3	coagulation	3.7	
6.4	excess Fe_2O_3	3.6	

Table XII

(continued)

cc Fe_2O_3	Observations	cc $\text{Cu}_2\text{Fe}(\text{CN})_6$	Range of mutual coagulation
2.94 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0027	4.18 gm/l	% Fe_2O_3 by weight
5.2	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	4.8	
5.3	complete mutual	4.7	44.3 to 75.0
8.1	coagulation	1.9	
8.2	excess Fe_2O_3	1.8	

Table XIII

Mutual Coagulation of Al_2O_3 Sols and $\text{Cu}_2\text{Fe}(\text{CN})_6$ Sol

cc Fe_2O_3	Observations	cc $\text{Cu}_2\text{Fe}(\text{CN})_6$	Range of mutual coagulation
0.391 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.152	4.18 gm/l	% Al_2O_3 by weight
3.2	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	6.8	
3.3	complete mutual	6.7	4.4 to 6.83
4.5	coagulation	5.5	
4.6	excess Al_2O_3	5.4	
0.446 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0865		
4.1	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	5.9	
4.2	complete mutual	5.8	7.16 to 11.95
5.6	coagulation	4.4	
5.7	excess Al_2O_3	4.3	
0.408 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0490		
5.4	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	4.6	
5.5	complete mutual	4.5	10.6 to 25.7
7.8	coagulation	2.2	
7.9	excess Al_2O_3	2.1	

Table XIII

(continued)

cc	Observations	cc	Range of mutual
Al_2O_3		$\text{Cu}_2\text{Fe}(\text{CN})_6$	coagulation
0.454 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0740	4.18 gm/l	% Al_2O_3 by weight
4.4	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	5.6	
4.5	complete mutual	5.4	8.15 to 14.5
6.1	coagulation	3.9	
6.2	excess Al_2O_3	3.8	
0.505 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0647		
5.3	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	4.7	
5.4	complete mutual	4.6	8.8 to 28.8
7.7	coagulation	2.3	
7.8	excess Al_2O_3	2.2	
0.381 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.134		
3.4	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	6.6	
3.5	complete mutual	6.5	4.68 to 7.46
4.7	coagulation	5.3	
4.8	excess Al_2O_3	5.2	

Table XIV

Mutual Coagulation of Fe_2O_3 Sol and As_2S_3 Sol

cc	Observations	cc	Range of mutual
Fe_2O_3		As_2S_3	coagulation
2.77 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0615	3.80 gm/l	% Fe_2O_3 by weight
5.6	excess As_2S_3	4.4	
5.7	complete mutual	4.3	51.5 to 58.5
6.6	coagulation	3.4	
6.7	excess Fe_2O_3	3.3	

Table XIV
(continued)

cc Fe_2O_3	Observations	cc As_2S_3	Range of mutual coagulation % Fe_2O_3 by weight
2.83 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0402	3.80 gm/l	
5.8	excess As_2S_3	4.2	
5.9	complete mutual	4.1	51.7 to 56.0
6.3	coagulation	3.7	
6.4	excess Fe_2O_3	3.6	
3.01 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0480		
5.7	excess As_2S_3	4.3	
5.8	complete mutual	4.2	52.3 to 56.1
6.2	coagulation	3.8	
6.3	excess Fe_2O_3	3.7	
3.04 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0169		
5.5	excess As_2S_3	4.5	
5.6	complete mutual	4.4	50.5 to 57.4
6.3	coagulation	3.7	
6.4	excess Fe_2O_3	3.6	
3.03 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0071		
5.6	excess As_2S_3	4.4	
5.7	complete mutual	4.3	50.9 to 61.0
6.6	coagulation	3.4	
6.7	excess Fe_2O_3	3.3	
2.94 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0027		
6.0	excess As_2S_3	4.0	
6.1	complete mutual	3.9	54.9 to 93.5
9.5	coagulation	0.5	
9.6	excess Fe_2O_3	0.4	

Table XV

Mutual Coagulation of Al_2O_3 Sols and As_2S_3 Sol

cc	Observations	cc	Range of mutual coagulation
Al_2O_3		As_2S_3	% Al_2O_3 by weight
0.391 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.152	3.80 gm/l	
2.7	excess As_2S_3	7.3	
2.8	complete mutual	7.2	2.9 to 6.43
4.0	coagulation	5.0	
4.1	excess Al_2O_3	5.9	
0.446 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0865		
4.1	excess As_2S_3	5.9	
4.2	complete mutual	5.8	7.83 to 14.05
5.3	coagulation	4.7	
5.4	excess Al_2O_3	4.6	
0.408 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0490		
5.3	excess As_2S_3	4.7	
5.4	complete mutual	4.6	11.58 to 14.9
6.2	coagulation	3.8	
6.3	excess Al_2O_3	3.7	
0.454 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0740		
4.2	excess As_2S_3	5.8	
4.3	complete mutual	5.7	8.25 to 17.5
6.4	coagulation	3.6	
6.5	excess Al_2O_3	3.5	
0.505 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0647		
4.4	excess As_2S_3	5.6	
4.5	complete mutual	5.5	9.83 to 19.8
6.5	coagulation	3.5	
6.6	excess Al_2O_3	6.4	

Table XV
(continued)

cc	Observations	cc	Range of mutual
Al_2O_3		As_2S_3	coagulation
0.381 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.134	3.80 gm/l	% Al_2O_3 by weight
3.3	excess As_2S_3	6.7	4.94 to 6.86
3.4	complete mutual	6.6	
4.1	coagulation	5.9	
4.2	excess Al_2O_3	5.8	

Table XVI

Mutual Coagulation of Fe_2O_3 Sols and SnO_2 Sol

cc	Observations	cc	Range of mutual
Fe_2O_3		SnO_2	coagulation
2.77 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0615	3.51 gm/l	% Fe_2O_3 by weight
1.8	excess SnO_2	8.2	
1.9	complete mutual	8.1	15.6 to 28.2
2.9	coagulation	7.1	
3.0	excess Fe_2O_3	7.0	
2.83 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0402		
1.9	excess SnO_2	8.1	
2.0	complete mutual	8.0	16.77 to 33.15
3.8	coagulation	6.2	
3.9	excess Fe_2O_3	6.1	
3.01 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3}$ 0.0480		
1.5	excess SnO_2	8.5	
1.6	complete mutual	8.4	14.32 to 29.63
3.3	coagulation	6.7	
3.4	excess Fe_2O_3	6.6	

Table XVI

(continued)

cc	Observations	cc	Range of mutual
Fe_2O_3		SnO_2	coagulation
3.04 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3} 0.0169$	3.51 gm/l	% Fe_2O_3 by weight
2.7	excess SnO_2	7.3	
2.8	complete mutual	7.2	34.75 to 51.4
5.5	coagulation	4.5	
5.6	excess Fe_2O_3	4.4	
3.03 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3} 0.0071$		
5.8	excess SnO_2	4.2	
5.9	complete mutual	4.1	55.4 to 62.7
6.6	coagulation	3.4	
6.7	excess Fe_2O_3	3.3	
2.94 gm/l	$\frac{\text{Cl}}{\text{Fe}_2\text{O}_3} 0.0027$		
7.8	excess SnO_2	2.2	
7.9	complete mutual	2.1	76.0 to 77.0
8.0	coagulation	2.0	
8.1	excess Fe_2O_3	1.9	

Table XVII

Mutual Coagulation of Al_2O_3 Sols and SnO_2 Sol

cc	Observations	cc	Range of mutual
Al_2O_3		SnO_2	coagulation
0.391 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3} 0.152$	3.51 gm/l	% Al_2O_3 by weight
3.6	excess SnO_2	6.4	
3.7	complete mutual	6.3	6.3 to 9.65
4.9	coagulation	5.1	
5.0	excess Al_2O_3	5.0	

Table XVII
(continued)

cc	Observations	cc	Range of mutual coagulation
Al_2O_3		SnO_2	% Al_2O_3 by weight
0.446 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0865	3.51 gm/l	
5.0	excess SnO_2	5.0	
5.1	complete mutual	4.9	11.7 to 16.6
6.1	coagulation	3.9	
6.2	excess Al_2O_3	3.8	
0.408 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0490		
6.5	excess SnO_2	3.5	
6.6	complete mutual	3.4	18.42 to 25.87
7.5	coagulation	2.5	
7.6	excess Al_2O_3	2.4	
0.454 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0740		
5.5	excess SnO_2	4.5	
5.6	complete mutual	4.4	14.6 to 19.45
6.4	coagulation	3.6	
6.5	excess Al_2O_3	3.5	
0.505 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.0647		
5.4	excess SnO_2	4.6	
5.5	complete mutual	4.5	14.9 to 22.4
6.4	coagulation	3.6	
6.5	excess Al_2O_3	3.5	
0.381 gm/l	$\frac{\text{Cl}}{\text{Al}_2\text{O}_3}$ 0.134		
4.1	excess SnO_2	5.9	
4.2	complete mutual	5.8	6.85 to 18.26
5.8	coagulation	4.2	
5.9	excess Al_2O_3	4.1

Fig 4

These data demonstrate that as the electrolyte in one sol is diminished, the precipitating action of the other becomes more predominant, i.e., a copper ferrocyanide sol containing an excess of ferrocyanide ion with a pure ferric oxide sol produces a wide range of complete mutual coagulation while the range of a stannic oxide sol which requires only a slight amount of hydroxyl ion to produce a very stable sol is remarkably narrow, in fact, if it were not for the fact that the stability of the mixed sol decreases visibly as one approaches the region of mutual coagulation it would be exceedingly difficult to obtain a value. It is noteworthy that at the point at which distortion appears in the curves, the ultrafiltrate of the ferric oxide sol no longer showed a test for chlorides. The ultrafiltrate of all alumina sols gave a positive test.

These observations are extended in Table XVIII and diagram Fig. 6, which represent experiments on mutual coagulation in which the period of dialysis of both the negative and positive sols were varied.

Table XVIII

Mutual Coagulation of Relatively Pure and Impure Sols

cc	Observations	cc	Range of mutual
Fe_2O_3 impure		$\text{Cu}_2\text{Fe}(\text{CN})_6$ impure	coagulation
1.38 gm/l		2.85 gm/l	% Fe_2O_3 by weight
4.6	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	5.4	
4.7	complete mutual	5.3	30.0 to 43.1
6.1	coagulation	3.9	
6.2	excess Fe_2O_3	3.8	
		$\text{Cu}_2\text{Fe}(\text{CN})_6$ pure	
		2.50 gm/l	
4.1	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	5.9	
4.2	complete mutual	5.8	28.6 to 42.4
5.6	coagulation	4.4	
5.7	excess Fe_2O_3	4.3	
		SnO_2 impure	
		3.23 gm/l	
2.7	excess SnO_2	7.3	
2.8	complete mutual	7.2	14.2 to 30.0
5.0	coagulation	5.0	
5.1	excess Fe_2O_3	4.9	
		SnO_2 pure	
		2.11 gm/l	
0.3	excess SnO_2	9.7	
0.4	complete mutual	9.6	2.62 to 3.12
4.1	coagulation	5.9	
4.2	excess Fe_2O_3	5.8	

Table XVIII

(continued)

cc	Observations	cc	Range of mutual
Fe_2O_3 pure		$\text{Cu}_2\text{Fe}(\text{CN})_6$ impure	coagulation
1.52 gm/l		2.85 gm/l	% Fe_2O_3 by weight
5.6	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	4.4	
5.7	complete mutual	4.3	30.1 to 66.0
7.6	coagulation	2.4	
7.7	excess Fe_2O_3	2.3	
		$\text{Cu}_2\text{Fe}(\text{CN})_6$ pure	
		2.50 gm/l	
5.2	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	4.8	
5.3	complete mutual	4.7	40.6 to 58.7
7.0	coagulation	3.0	
7.1	excess Fe_2O_3	2.9	
		SnO_2 impure	
		3.23 gm/l	
7.9	excess SnO_2	2.1	
8.0	complete mutual	2.0	65.4
	coagulation		
8.1	excess Fe_2O_3	7.9	
		SnO_2 pure	
		2.11 gm/l	
4.0	excess SnO_2	6.0	
4.1	complete mutual	5.9	33.4 to 55.2
6.3	coagulation	3.7	
6.4	excess Fe_2O_3	3.6	

Table XVIII

(continued)

cc	Observations	cc	Range of mutual
BaSO_4 impure		$\text{Cu}_2\text{Fe}(\text{CN})_6$ impure	coagulation
10.61 gm/l		2.85 gm/l	% BaSO_4 by weight
3.0	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	7.0	
3.1	complete mutual	6.9	62.5 to 88.8
6.8	coagulation	3.2	
6.9	excess BaSO_4	3.1	
		$\text{Cu}_2\text{Fe}(\text{CN})_6$ pure	
		2.50 gm/l	
2.5	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	7.5	
2.6	complete mutual	7.4	59.8 to 88.4
6.4	coagulation	3.6	
6.5	excess BaSO_4	3.5	
		SnO_2 impure	
		3.23 gm/l	
1.8	excess SnO_2	8.2	
1.9	complete mutual	8.1	43.5 to 82.4
5.9	coagulation	4.1	
6.0	excess BaSO_4	4.0	
		SnO_2 pure	
		2.11 gm/l	
0.1	excess SnO_2	9.9	
0.2	complete mutual	9.8	9.5 to 81.8
4.7	coagulation	5.3	
4.8	excess BaSO_4	5.2	

Table XVIII

(continued)

cc	Observations	cc	Range of mutual
BaSO_4 pure		$\text{Cu}_2\text{Fe}(\text{CN})_6$ impure	coagulation
10.47 gm/l		2.85 gm/l	% BaSO_4 by weight
3.1	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	6.9	
3.2	complete mutual	6.8	52.2 to 94.4
8.2	coagulation	1.8	
8.3	excess BaSO_4	1.7	
		$\text{Cu}_2\text{Fe}(\text{CN})_6$ pure	
		2.50 gm/l	
2.7	excess $\text{Cu}_2\text{Fe}(\text{CN})_6$	7.3	
2.8	complete mutual	7.2	62.2 to 92.4
7.4	coagulation	2.6	
7.5	excess BaSO_4	2.5	
		SnO_2 impure	
		3.23 gm/l	
0.1	excess SnO_2	9.9	
0.2	complete mutual	9.8	6.19 to 74.1
4.7	coagulation	5.3	
4.8	excess BaSO_4	5.2	
		SnO_2 pure	
		2.11 gm/l	
0.1	excess SnO_2	9.9	
0.2	complete mutual	9.8	9.1 to 92.7
7.2	coagulation	2.8	
7.3	excess BaSO_4	2.7

Fig. 6

One might conclude therefore that in two impure and relatively unstable sols of opposite charge, the range of coagulation would be rather broad, increasing with the precipitating power of the electrolytes present as impurity and that in two very stable and pure sols it should be comparatively narrow. The complete mutual precipitation of hydrophylic colloids is difficult of attainment. This is no doubt due to the fact that both the above conditions obtain, namely, there is little excess electrolyte present and second the sols are of very stable character. It probably means that the range is so narrow as to escape observation. The significance of the hydrogen ion concentration (electrolyte) in the mutual coagulation of protein has been demonstrated by Michaelis and Davidsohn¹.

¹ Biochem. Z., 32, 496 (1912)

DISCUSSION OF RESULTS

From the observations summarized in Figs. 1 to 6 of the preceding section, the following facts in connection with the mutual coagulation process are brought out: First, the complete mutual coagulation of two sols of opposite charge may take place over a narrow range of concentrations or over quite a wide range of concentrations. Second, purification of one sol may increase or decrease this range depending on the sol of opposite charge. Third, when, for example, a given series of positive sols is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols.

These results indicate that the mutual coagulation process may be determined by a number of factors that are effective to different degrees with different sols. The more important of these will be considered in a general way in the following paragraphs.

1. Mutual Electrical Neutralization

If mutual coagulation is due to mutual electrical neutralization the conditions which must obtain are very much more definite than those observed in actual cases. Hence, while such neutralization may be the ultimate determining factor in general, it is ordinarily so modified by other important considerations that its effect is more or less concealed. It is evident that if it were the only factor the range of mutual coagulation would be narrow and a given series of sols of one sign would always arrange themselves in the same order regardless of what sol of opposite charge is precipitated. It may be, however, that this is the precominating factor when the range of coagulation is quite narrow as in the case of pure, stable sols.

2. Mutual Adsorption of Colloidal Particles

Since the mutual coagulation process is not independent of the nature of the colloidal particles, it is altogether probable that a specific adsorption occurs between the two kinds of particles

that is not determined by their electric charge, and will have an important effect in determining the range of mutual coagulation. Thus, if the mutual attraction is relatively great between two electrically neutral particles which yield sols of opposite sign, one would expect this force of attraction to supplement the electrostatic attraction between the oppositely charged colloidal particles and thereby extend the range of mutual coagulation. Fifteen years ago Bancroft¹ called attention to the importance of adsorption of the particles of one colloid by those of another in the mutual coagulation process, but his paper has been overlooked or has not been taken seriously by most people. Unfortunately, the magnitude of the effect on the mutual coagulation process of mutual adsorption of particles which is independent of their charge, cannot be evaluated quantitatively until the magnitude of the mutual adsorption force is known.

¹ J. Phys. Chem., 19, 362 (1915)

3. Precipitating Ions in the Sols

Excess precipitating ions in the sols certainly exert a precipitating action that is independent of the mutual coagulation of the oppositely charged particles. This independent action depends on the relative concentration of the excess electrolytes in the sols. Thus a wide range of precipitation may be caused either by instability of a sol and, in consequence, the increased action of the oppositely charged sol and electrolyte or by an excess of electrolyte and its precipitating power. Such factors should be taken into account in any consideration of the mutual coagulation process since with the exception of the hydrophylic sols their influence never becomes small enough to be negligible.

4. Interaction Between Stabilizing Ions

Attention has been called to the observations of Lottermoser and of Thomas and Johnson, which show that interaction between stabilizing ions with the formation of an insoluble or slightly

ionized compound may sometimes play an important role in the mutual coagulation process. However, even in cases where such an interaction is possible, it is altogether unlikely that the effect is independent of the electrostatic attraction and the specific adsorption between particles. Certainly, one gets mutual coagulation where removal of stabilizing ions by neutralization or precipitation is a remote possibility (Table 1.)

SUMMARY

The results of this investigation are as follows:

1. The zone of complete mutual coagulation of two sols of opposite sign may be very narrow or quite broad.

2. When a given series of positive sols, for example, is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols.

3. The behavior noted in 1 and 2 is accounted for by the fact that the precipitating power of positive sols for negative sols is not determined exclusively by the charge on the colloidal particles. Other factors which influence the mutual coagulation process are (1) mutual adsorption of colloidal particles, that is independent of their charge, (2) the presence of precipitating ions as impurities in the sols, and (3) interaction between stabilizing ions.

4. Complete mutual coagulation is not due in general to interaction and consequent removal of the stabilizing electrolytes of oppositely charged sols, but this factor may be important in certain cases.