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I hereby recommend that the thesis prepared under my supervision by JOSEPH B. STORY

entitled THE STABILITY AND COAGULATION OF SOLS

be accepted as fulfilling this part of the requirements for the degree of DOCTOR OF PHILOSOPHY

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THE STABILITY AND COAGULATION OF SOLS

A dissertation submitted to the
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by

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IN MEMORIAM

DR. LEWIS B. MILLER

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PART I

THE STABILITY OF SULFUR SOLS

Part I Introduction

A considerable number of conflicting theories regarding the cause of the stability of sulfur sols are to be found in the literature. The most important of these theories are:

(1) that the colloidal sulfur is actually a high-sulfur hydrogen persulfide,

(2) that the stability of colloidal sulfur is due to the presence of the thiosulfate ion,

(3) that the stability of colloidal sulfur is due to the presence of the lower polythionate ions (dithionate, trithionate, tetrathionate),

(4) that the stability of colloidal sulfur is due to the presence of pentathionate ions, and

(5) that the stability of colloidal sulfur is due to the presence of hexathionate ions.

It is the object of this investigation to determine which theory is correct.

Part I Theory

Sulfur sols may be either hydrophobic or hydrophilic depending upon their method of preparation. Several examples are as follows.

The Weimarn sulfur sol is prepared by dissolving rhombic sulfur in alcohol and pouring into an excess of water. It is not very stable, and is decidedly hydrophobic. It is irreversibly coagulated by small amounts of electrolytes.

The Selmi sulfur sol is prepared by the reaction between sulfur dioxide and hydrogen sulfide:

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

The Raffo sulfur sol is prepared by the acidification of sodium thiosulfate:

$$Na_2S_2O_3 + H_2SO_4 \longrightarrow S + SO_2 + Na_2SO_4 + H_2O$$

It is convenient to designate both the Selmi and Raffo sols as Oden sols, since Oden has contributed most to their elucidation. These Oden sols are best classified as hydrophilic, for they are coagulated only by large amounts of electrolytes. The precipitates are reversible.

Freundlich and Scholz (4) were the first to suggest that the Oden sulfur sols owe their stability to the presence of pentathionic acid. They demonstrated the

probable presence of pentathionic acid, and determined it by reacting the sol with alkali and titrating the thiosulfate produced iodometrically. Assuming the reaction

$$2Na_2S_5O_6 + 6NaOH \longrightarrow 5Na_2S_2O_3 + 3H_2O$$

they recorded for Selmi and Raffo sols, respectively, values of 0.13 to 0.15 and 0.47 to 0.69 millimols of pentathionic acid per gram of sulfur.

Pentathionic acid is formed in these sols in accord (3) with the equations

$$10SO_2 + 5H_2S \longrightarrow 3H_2S_5O_6 + 2H_2O$$

$$5H_2S_2O_3 \longrightarrow 2H_2S_5O_6 + 3H_2O.$$

The principal evidence Freundlich and Scholz offer for the stabilizing action of the pentathionic acid is the explanation of the coagulation of the Oden sols by alkalies and hydrogen sulfide in terms of the reactions of pentathionic acid. The coagulation of these sols by alkalies can be explained by the reaction

$$2S_5O_6^{--} + 6OH^- \longrightarrow 5S_2O_3^{--} + 3H_2O$$

and the coagulation by hydrogen sulfide by the reaction

$$H_2S_5O_6 + 5H_2S \longrightarrow 10S + 6H_2O.$$

Bassett and Durrant (1) have been quoted (11) as believing that the stabilizing ion is the hexathionate rather than the pentathionate. This is only a half-truth. In the words of Bassett and Durrant

"Our view is that in the 'bound' condition of the

polythionate of the sulfur sols is hexathionate. When it becomes free it is mainly pentathionate, chiefly because the relative force of attraction between the pentathionate and an additional sulfur atom is less than the force of attraction between the latter and the lattice of a sulfur crystal. The irregular structure of the micellar sulfur surface occupies an intermediate position in this respect."

"....From the observed fact that the proportion of 'free' polythionate steadily increases, it may be deduced that the number of positions on the surface of the micelle, where attachment of the polythionate ions is possible, steadily diminishes. The particles of the sol are 'ageing', and we suggest that this is due to the fact that the sulfur particles of the sol have only an imperfect crystal lattice initially.

"Attachment of the polythionate ions only occurs at those parts of the surface where the atomic structure is irregular. As the ions break away in the course of the kinetic equilibrium between the 'free' and the 'bound' polythionate, a few atoms of sulfur are each time removed. This helps to 'smooth down' the irregularities of the sulfur surface until finally a sulfur particle with a completely crystalline structure is obtained, with consequent separation of the particle

in the solid state as a non-colloidal, crystalline sulfur which can be seen under the microscope as octahedra. At the same time that this is happening, some of the 'free' polythionate slowly deposits a part of its sulfur in the non-colloidal, crystalline condition - a process which can be represented by the equation

$$H_2S(x + y)O_6 \longrightarrow H_2S_xO_6 + S_y$$

The $H_2S_xO_6$ subsequently becomes graded up again by attachment to the sulfur micelle. The deposition of sulfur by the 'free' polythionate probably occurs partly on the already crystalline portion of the surface of the sulfur micelles, partly on the crystalline sulfur which has already settled out from the solution, and partly on the non-crystalline areas of the colloidal sulfur particles which are thereby 'smoothed down' and made crystalline by accretion instead of by corrosion.

"This process proceeds steadily until eventually the whole of the colloidal sulfur would become non-colloidal and all of the polythionate would be free."

In the opinion of the writer, there is no essential difference between the views of Freundlich and Scholz and those of Bassett and Durrant, as will be explained later.

It has been also suggested (5) that the lower polythionic acids (dithionic, trithionic, and tetrathionic)

may be stabilizing agents for the sulfur sols.

In recent years Pauli and co-workers (9,10) have challenged the polythionate theory of sulfur sol stabilization. It is suggested that the polythionic acids are a component of the intermicellar fluid, whereas thiosulfurous acid is bound to the particles of the sol and is responsible for the stabilization of the sol.

Dienes (2) believes that colloidal sulfur is actually a high-sulfur hydrogen persulfide. He states that the properties of the sol are actually those of a high-sulfur hydrogen persulfide, and points out that hydrogen sulfide is evolved upon the change of the colloidal sulfur into a carbon disulfide-soluble form. He concedes, however, that similar results were obtained for $K_2S_5O_6$ and H_2S_x.

Part I Procedure

The sodium dithionate used was prepared from barium dithionate by precipitating barium carbonate with carbon dioxide gas, while maintaining neutrality with additions of sodium hydroxide. After enough carbon dioxide was added that no further barium carbonate precipitation occurred, the solution was filtered. Sodium dithionate crystallized out upon evaporation.

The potassium trithionate was prepared by the method of Hertlein (6), wherein sulfur dioxide is bubbled into a saturated potassium thiosulfate solution until a yellow color appears. The solution is allowed to stand until colorless, and the procedure is repeated until no color forms. On standing the salt crystallizes. The reaction is usually formulated

$$2K_2S_2O_3 + 3SO_2 \longrightarrow 2K_2S_3O_6 + S$$

but is actually more complex.

The sodium tetrathionate was prepared in accord with the instructions in Mellor (7) (by the reaction of iodine and sodium thiosulfate).

The sodium pentathionate was prepared by the Raschig method, as given in Mellor (7), wherein concentrated hydrochloric acid acts upon a sodium thiosulfate solution at $-10^{o}C$, in the presence of arsenic trioxide dissolved

in sodium hydroxide.

The methods of preparing the sulfur sols are described in the "Data and Results" section.

Part I Data and Results

It is considered that the ultimate proof of the stabilizing action of a given substance is that of synthesis; that is, this proof should show that the sulfur sol is not formed or is not stable except by the addition of the stabilizing substance.

The greatest task of this investigation was the discovery of a suitable method of preparing the sulfur sol.

In order to be suitable, the sol must meet a number of conditions. These are:

1. The sol must not be inherently stable. Such stability implies the presence of a stabilizing agent. This condition automatically eliminates most of the methods of preparing sulfur sols reported in the literature.

2. The sulfur sol should not contain any substance which could react with the suspected stabilizing substance which is added. Such a reaction could lead to the destruction of the substance being tested or to the formation of a stabilizing substance of unknown composition.

3. The sol should not be formed by the oxidation of a sulfur compound.

4. The sol should not be formed by the reduction of a sulfur compound.

5. The sol should not be formed by the decomposition of a sulfur compound. The oxidation, reduction, and decomposition reactions of sulfur compounds often lead to the formation of a great variety of products.

6. The sol should not be formed by the hot contact of sulfur and water. It has been shown that

there is a reversal of the reaction

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

and that the hydrogen sulfide and sulfur dioxide recombine to form polythionic acids.

An interesting new method of preparing a sulfur sol may be suggested. It involves the use of a solvent for sulfur which is insoluble in water. The sulfur is dissolved in the solvent, and an emulsion of the solvent in water prepared; this emulsion is then dropped into boiling water, and the solvent evaporated. The unique feature of this sol is its uniform and controllable particle size. A given homogenizer may give a relatively uniform emulsion droplet size. By varying the concentration of sulfur in the solvent, the resultant sulfur particle size may be controlled. Since the emulsion droplet is perfectly spherical, its volume can be accurately calculated from a micrometric measurement; and an accurate mass can be calculated for the sulfur particle. This method was investigated only to a small extent, for it fails to meet condition 6.

The first method found which was essentially acceptable for the purpose of this study was that of the hydrolysis of a sodium pentasulfide solution. A few drops of a concentrated sodium sulfide solution saturated with sulfur were dropped into a beaker of water

and the pH of the liquid held at 7 as the hydrolysis of the sodium pentasulfide proceeded and the colloidal sulfur was formed. The presence of hydrogen sulfide was noted by its odor. The formation of the colloidal sulfur is probably due to the reactions

$$2H_2S_5 \rightarrow H_2S_9 + H_2S$$

$$H_2S_5 + H_2S_9 \rightarrow H_2S_{13} + H_2S$$

$$2H_2S_9 \rightarrow H_2S_{17} + H_2S$$

etc.

For a while it was considered that this method was the best that could be found in spite of its failure to meet condition 2. For this reason a certain amount of data was taken using the method.

The method is acceptable for the testing of the theory that the stability of the colloidal sulfur is due to its being actually a high-sulfur hydrogen persulfide. If any method of formation of colloidal sulfur gives rise to high-sulfur hydrogen persulfides, the hydrolysis of sodium pentasulfide is it.

Into 100 ml. of water were dropped 5 drops of the concentrated Na_2S_5 solution, and the pH adjusted to about 6. 50 ml. of this sulfur sol were poured into a graduate and set aside. To the other 50 ml. were added a few small crystals of sodium thiosulfate.

Observation after one day showed that most of the

turbidity had disappeared from the first sol (settled out), and that only a trace of turbidity remained in the sample containing the sodium thiosulfate.

The instability of the first sol indicates that the stability of sulfur sols is not due to the sulfur being in the form of high-sulfur hydrogen persulfides. It is further difficult to explain why hydrogen sulfide should destroy the stability of Oden sols, if they are in reality the high sulfur hydrogen persulfides supposed.

The above method of preparing a sol was used again, except using sodium pentathionate instead of sodium thiosulfate. After one day, no appreciable decrease in turbidity was noted. After three days a small amount of sedimentation was noted, but the sol was still very turbid. After a week a considerable amount of turbidity was still present.

The above data are subject to the criticism that they fail to meet condition 2. Nevertheless they do tend to show that it is the pentathionate ion which stabilizes the sulfur sol rather than the thiosulfate ion. The decrease in the stability of the sol upon the addition of sodium thiosulfate appears to be due to a reaction with the hydrogen persulfide. It is believed, however, that more than a chemically equivalent quantity of sodium thiosulfate was added.

The best method of producing a sulfur sol found was that of grinding rhombic sulfur very finely in an agate mortar and pestle, then adding a few small crystals of the suspected stabilizing substance and grinding some more. The mixture was then moistened and diluted with continued grinding. This method conforms to all six of the conditions for an acceptable method.

When the preceding method was used to test the stabilizing action of sodium pentathionate, it was found that the addition of a little water to the dry mixture when ground produced a creamy slurry of "homogeneous" appearance (i.e., no large particles, or flocs were seen). Further dilution produced a colloidal dispersion. The sample was filtered (the colloidal sulfur passing through the filter paper). After one day there was no appreciable decrease in turbidity, although a film of sulfur had formed on the bottom of the test tube. At the end of three weeks, the sulfur was seen to have completely settled out. The precipitate was reversible, however, for shaking led to the reappearance of turbidity.

When this method was applied using sodium thiosulfate, sodium dithionate, potassium trithionate, and sodium tetrathionate, the moistening of the dry mixture produced a granular rather than creamy appearance.

Further dilution produced large flocs of sulfur in a perfectly clear solution. There was no evidence of a colloidal dispersion.

No attempt was made to make the hexathionate and test its stabilizing action, for according to Bassett and Durrant (1) their product prepared by the method of Weitz and Achterberg (12) (the best method available) was 50% penta- and 50% hexathionate. The similarity of the compounds, their isomorphous nature, and the easy conversion of the hexathionate into pentathionate offers little hope of separating the two compounds, at least without extensive research. It has further been stated (7) that the aqueous solution of hexathionate always contains a little sulfur, but that the amount does not increase with time; and that the sulfur re-appears after the liquid has been filtered. This seems to indicate the equilibrium

$$Na_2S_5O_6 + S \rightleftharpoons Na_2S_6O_6$$

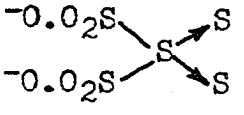
which would make data obtained for the hexathionate by this method inconclusive.

The writer regards the results obtained as direct evidence that it is the pentathionate ion which attaches itself to the sulfur particle to produce the charged and stabilized granule.

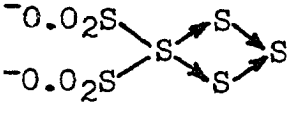
The writer regards this as confirming the view of

Freundlich and Scholz that the stability of the Oden sols is due to pentathionate and that of Bassett and Durrant that the stabilization is due to hexathionate. This apparent contradiction can be explained by noting that Freundlich and Scholz speak of the ion as it exists in the intermicellar fluid, and Bassett and Durrant speak of the ion as it exists on the surface of the sulfur particle. Whether or not a pentathionate ion attached to an exposed sulfur atom of a sulfur particle can be said to be hexathionate is debatable.

The writer believes that the highly specific stabilizing action of the pentathionate ion is due to its structure (8)



which enables it to form a chelate-type compound with an exposed sulfur atom of the sulfur particle to form a structure similar to the hexathionate, which is



There is not, in a sense, a molecule of hexathionate here, for it is not independent of other sulfur atoms. On the other hand, the chemical properties of the complex would be expected to be nearest those of hexathionate. It is upon the kinetic data of a chemical reaction that

Bassett and Durrant base their conclusion.

Part I Summary and Conclusions

The ability to attach itself to a sulfur particle and stabilize the particle as a colloid is highly specific to the pentathionate ion; and is probably due to the structure of that ion, which enables it to form a chelate-type compound with exposed sulfur atoms of the particle. Whether or not this complex should be called hexathionate is debatable.

Although the views of Freundlich and Scholz and of Bassett and Durrant have been quoted respectively as being that the pentathionate and hexathionate ions are the stabilizing ions, their views are not contradictory, and are both supported by the present investigation. Freundlich and Scholz refer to the ion as it exists in solution, while Bassett and Durrant refer to the complex with the sulfur particle.

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PART II

THE COAGULATION OF SULFUR DYE SOLS

Part II Introduction

The study of the coagulation of sulfur dye sols is suggested by the industrial sulfur dye waste disposal problem.

As Geyer and Perry (11) have said:

"The research required for the solution of textile waste disposal problems may be divided into two broad classifications: first, that type of research which is needed for the solution of each local problem; and second, that type of research which will be generally applicable and which will be useful in solving various types of individual problems....past research has related almost entirely to the first type of work.... (and) has been, for the most part, the trial and error type of experimentation. Fundamental research is needed to determine the colloidal and electrical nature of the substances carried in textile wastesand to work out methods for removing the various types of polluting matter."

The author has discovered in preliminary investigations that sols of sulfur dyes in sodium sulfide solution are best coagulated by sulfurous acid solutions.

It is the object of this investigation to determine the theoretical principles involved in the coagulation, and to elucidate the fundamental chemical and colloidal properties of the reactants and products.

Part II Theory

The Sulfur Dyes

No precise definition of the generic term "sulfur dye" is possible; for, although many examples of this class of tinctorial materials have been known and used for many years, their compositions and structures are unknown (12).

All sulfur dyes are prepared using organic materials. Almost all of them are derived from aromatic compounds of the benzene and naphthalene series (usually from nitrogen-containing derivatives). Aside from the use of mixtures and from the use of dyes of other classes, these aromatic starting materials may be grouped as derivatives of five parent substances: (a) benzene, (b) naphthalene, (c) diphenylamine- nitrated derivatives, (d) diphenylamine- indophenols and indamines, and (e) azines. The substituent groups are usually $-NH_2$, $-NO_2$, $-NO$, $-OH$, $-COOH$, $-SO_3H$, or the smaller alkyl groups; or any combination of these groups.

The preparation of the sulfur dye is carried out by heating the various nitrogenous organic materials described in the preceeding paragraph with sulfur, sodium sulfide, sodium polysulfide, or other sulfurating agents. The products of these processes are mixtures

of sulfur-containing compounds of high molecular weight and low solubility.

Although a great many sulfur dyes are made by varying the starting materials and methods of sulfuration, their properties are very similar, differing in degree rather than in kind.

The most important common property of the members of this class of dyes is their ability to serve as vat dyes for cotton. They may be applied to the fiber from baths containing hydrosulfite or, much more commonly, sodium sulfide. They produce quite fast shades of yellow, brown, blue, violet, and black.

In general these dyestuffs are dark, amorphous powders; many have an almost metallic glint. Most of them are insoluble in water, ether, acetone, the alcohols, aliphatic and aromatic hydrocarbons, dilute mineral acids, concentrated hydrochloric and acetic acids, and the mono- and poly- haloalkanes. Many of the sulfur dyes are soluble in concentrated sulfuric acid, aqueous sodium sulfide, aqueous caustics, hot pyridine, and hot aniline.

Only one sulfur dye, Immedial Reinblau, is known to yield a crystalline bisulfite complex upon treatment with sodium bisulfite. Other dyes are usually converted to water soluble sulfonic, sulfinic, or thiosulfonic

acid derivatives.

Most reagents either do not attack the sulfur dyes at all or else decompose them completely.

X-ray diffraction photographs of a number of the sulfur dyes have shown them to be amorphous.

Because of the insolubility, variability of composition, difficulties of purification, and chemical inertness of the sulfur dyes, they have withstood the majority of attempts to determine their structure. The large amount of work which has been done serves as a basis for a number of well-founded theories, although the exact constitution of no single dye is authoritatively known.

The general nature of the sulfur dyes is fairly well agreed upon; the blacks, blues, and some of the greens and Bordeaux-reds are generally held to be thiazine derivatives, while the majority of the yellows and browns are apparently thiazole derivatives. Some other fundamental ring structures have been proposed for individual dyes, but have not been found to be common among the sulfur colors. Investigations have also been directed toward the manner of combination of sulfur in side chains.

The sulfur dyes form colloidal suspensions rather than true solutions (3).

Belen'kii (1, 2) states that the dispersion of the

leuco suspensions of the sulfur dyes is high. A decrease in the pH of the leuco suspension causes a decrease in the lyophilic properties of the sol. The sulfur and vat dyes form similar hydrosols upon careful oxidation of their leuco suspensions.

In general, the sulfur dyes exhibit hydrophilic properties in alkaline and reducing solutions, and hydrophobic properties in acid and oxidizing solutions. This is indicated in several ways, among the most important of which are structural considerations of the form of the dye under the different conditions. The solubilizing action of alkaline, reducing solutions upon the sulfur dyes is due to the reduction of sulfide linkages to mercaptan groups, and the formation of the sodium salts thereof. This salt is undoubtedly highly ionized. By analogy to the sodium salts of the phenolic -OH groups, it would be expected that the salt would be soluble, as it is. The affinity for water which would be expected from the-SNa group is a typical hydrophilic property. The acidification of the dye produces the slightly ionized mercaptan group which would be expected to show less affinity for water, and hence would tend to be more hydrophobic. The oxidation of the dye converts the mercaptan groups again to sulfide linkages, with the resultant loss of affinity for water and hydrophilic character.

The stability of the colloidal dispersion to electrolytes is an important criterion of colloid character. Hydrophobic colloids are coagulated by small amounts of electrolytes; hydrophylic colloids are not. The reduced, alkaline form of the sulfur dyes is stable in rather concentrated electrolyte solutions.

Another important criterion of colloid character is reversibility of coagulation. If an alkaline, reduced sulfur dye suspension is evaporated to dryness, the residue will readily disperse itself in water to form a new suspension; whereas if a sol of the acid, oxidized form of the sulfur dye is evaporated to dryness, the residue will not go into colloidal dispersion with the addition of water. The former property is characteristic of hydrophilic colloids; the latter, of hydrophobic colloids.

The Mutual Coagulation of Hydrophobic Sols

One of the most important discoveries contributing to the evolution of modern ideas concerning the coagulation of colloids was the discovery by Linder and Picton (15) that sols that precipitate each other migrate oppositely in an electrical field. It was concluded that oppositely charged sols precipitate each other. A number of other investigators have published work

confirming this rule. Wintgen and Lowenthal (21) stated that as a crystalloidal solution is expressed in equivalents, so the concentration of a colloidal solution containing electrically charged particles may be expressed in terms of equivalent-aggregates, an equivalent-aggregate being the weight of a colloidal particle divided by the number of its charges. The normality of a sol is its content expressed in equivalent-aggregate weights. From the investigation of the precipitation of positive Cr_2O_3 and negative SnO_2 sols of varying concentrations, it was found that the point of maximum precipitation took place on mixing equi-normal concentrations of the two sols. For this rule to hold no secondary process, such as interaction between electrolytes in the respective sols, must take place.

Factors besides charge determining mutual precipitation (20) are: (1) mutual adsorption of colloidal particles that is independent of charge, (2) the presence of precipitating ions as impurities and (3) interaction between stabilizing ions.

The best known example of the interaction between stabilizing ions is the discovery by Freundlich and Nathanson (10) that an arsenic trisulfide hydrosol precipitates Oden's sulfur hydrosol (prepared by reacting hydrogen sulfide with a sulfur dioxide solution, precipitating the sulfur with sodium chloride, and

redispersing the sulfur in water). It was deduced that the mutual precipitation of these sols is a result of the reaction

$$5H_2S + H_2S_5O_6 \longrightarrow 10S + 6H_2O$$

in which both stabilizing ions are destroyed.

The Action of a Sulfurous Acid Solution on a Sodium Sulfide Solution (16)

According to Foerster and Kircheisen (6) the mixing of sodium hydrosulfide and sodium bisulfite solutions in the mol ratio 1:2 at room temperature results in instantaneous and almost quantitative sodium thiosulfate formation in accord with the equation

$$2NaHS - 4NaHSO_3 \longrightarrow 3Na_2S_2O_3 - 3H_2O \qquad (B)$$

If, on the other hand, sulfurous acid is allowed to act on sodium sulfide, elementary sulfur is formed in accord with the equation

$$2Na_2S + 3H_2SO_3 \longrightarrow 2Na_2S_2O_3 + 3H_2O + S \qquad (I)$$

Foerster and Mommsen (8) regard this reaction as the result of a number of partial reactions.

It is believed that reaction I proceeds in two principal phases, 1 and 2.

In the first phase (1) sodium sulfide and sulfurous acid form sodium hydrosulfide and sodium bisulfite (A), and later react to form sodium thiosulfate according to equation (B).

$$12Na_2S + 12H_2SO_3 \longrightarrow 12NaSH + 12NaHSO_3 \quad (A)$$

$$6NaSH + 12NaHSO_3 \longrightarrow 9Na_2S_2O_3 + 9H_2O \quad (B)$$

$$12Na_2S + 12H_2SO_3 \longrightarrow 6NaSH + 9Na_2S_2O_3 + 9H_2O \quad (1)$$

Consider the slow addition of a sulfurous acid solution to a sodium sulfide solution. As long as reaction (1) lasts, the sulfurous acid disappears; and Na_2S and NaSH are found in the reaction mixture. The steadily changing ratio of the two causes a steady change in the pH of the solution. When reaction (1) is complete, a further addition of sulfurous acid causes a stepwise change in the pH of the solution, and phase 2 begins.

Up to this point, sodium thiosulfate is produced (equation B) by the reaction of sodium hydrosulfide with the sodium bisulfite cocurrently produced (equation A). After equation (1) has gone to completion, any further sodium bisulfite production must use sodium hydrosulfide. The reactions through which this is brought about lead to the appearance of elemental sulfur.

In the second phase (2)

$$4NaSH + 4H_2SO_3 \longrightarrow 4H_2S + 4NaHSO_3 \quad (C)$$

$$2NaSH + 4NaHSO_3 \longrightarrow 3Na_2S_2O_3 + 3H_2O \quad (B)$$

$$6NaSH + 4H_2SO_3 \longrightarrow 3Na_2S_2O_3 + 3H_2O + 4H_2S \quad (2')$$

$$4H_2S + 2H_2SO_3 \longrightarrow 6H_2O + 6S \quad (D)$$

$$6NaSH + 6H_2SO_3 \longrightarrow 3Na_2S_2O_3 + 9H_2O + 6S \quad (2)$$

After reaction (2) is complete, additional sulfurous acid added remains free, and another stepwise pH change occurs. If 1 and 2 are added, I is obtained

$$12Na_2S + 12H_2SO_3 \longrightarrow 6NaSH + 9Na_2S_2O_3 + 9H_2O \quad (1)$$

$$6NaSH + 6H_2SO_3 \longrightarrow 3Na_2S_2O_3 + 9H_2O + 6S \quad (2)$$

$$12Na_2S + 18H_2SO_3 \longrightarrow 12Na_2S_2O_3 + 18H_2O + 6S \quad (I)$$

Foerster and Mommsen (7) state that the loss of sulfur in the reaction between sulfur dioxide and sodium sulfide can be diminished if a quantity of sodium hydroxide equivalent to the latter is added. The reaction then proceeds according to the equation

$$2Na_2S + 2NaOH + 4H_2SO_3 \longrightarrow 3Na_2S_2O_3 + 5H_2O \quad (II)$$

Mueller and Mehlhorn (16) give data on the action of gaseous sulfur dioxide up to the second step

(a) on dilute (0.217 M.) sodium sulfide solution

Material	Formed (grams)	Theoretical (Eq.I) (grams)
$Na_2S_2O_3$	2.4590	2.5098
Na_2SO_3	0.0378	0.
H_2S	0.0451	0.
S	0.2341	0.2545

(b) on concentrated (1.64 M.) sodium sulfide solution

Material	Formed (grams)	Theoretical (Eq.I) (grams)
$Na_2S_2O_3$	25.66	26.0
Na_2SO_3	0.	0.
H_2S	1.04	0.
S	0.85	2.64

Part II Data and Results

All of the Sulfur Black dye sols used in this investigation, unless otherwise specified, were prepared by weighing out exactly 5.000 grams of T-1636 Sulfogene Carbon HCF Grains (Du Pont) and making up to one liter with a standardized solution of sodium sulfide.

During the course of the investigation it was necessary to prepare two standardized sodium sulfide solutions. In each case, the water used for making up the solutions was deaereated by bubbling steam through the water. This was done in order to prevent air oxidation of the sodium sulfide solution. Each time the bottle containing the solution was opened, the air space above the solution was flushed out with natural gas.

According to "Scott's Standard Methods of Analysis" (19) sodium sulfide can be determined as analkali by titrating with hydrochloric acid. This was done by determining several titration curves (pH vs milliliters of hydrochloric acid) for each solution. According to Brennecke (4) the hydrolysis of sodium sulfide

$$Na_2S + H_2O \longrightarrow NaOH + NaSH$$

is 98.7% complete in 0.05 M solution at 25°C and 91% complete in 1.0 M solution at 25°C. As the titration progresses and the hydroxyl ion is consumed, the

hydrolysis of the sodium sulfide proceeds in accord with the equilibrium relation

$$\frac{[SH^-][OH^-]}{[S^{--}][H_2O]} = K$$

or, since the solution is dilute and the water concentration therefore essentially constant,

$$\frac{[SH^-][OH^-]}{[S^{--}]} = K'$$

It was found that the sharpest end point was produced by titrating only the sodium hydroxide produced by the hydrolysis, for the sodium hydrosulfide end point was dulled by the release of hydrogen sulfide.

The first sodium sulfide solution was found to be 0.02481 M, and the second was 0.02679 M. The dye sols used to obtain the data in experiments 1 - 18, 65, 66, 70 - 73, 75, 78, 79, 81, 83 - 86, and 88 were made up using the first solution, and the dye sols used to obtain the data in experiments 19 - 64, 67 - 69, 74, 76, 77, 80, 82, and 87 were made up using the second solution.

The standard procedure followed in studying the precipitation of the dye sol consisted of pipetting a 49.94 milliliter sample of the dye sol prepared as described above into a 100 milliliter graduate, followed by the addition of the reagent used and by as thorough and rapid a mixing of the reagent and sol as possible. In the case of data involving the changes of pH with

time, the sample was contained in a beaker. Any exceptions to the above procedure are noted with the particular data involved.

The sulfurous acid solution was prepared by bubbling sulfur dioxide gas from a cylinder through distilled water. The sulfurous acid was standardized as 0.514 M. by determining several titration curves (pH vs milliliters of sodium hydroxide solution) for it. The sodium hydroxide solution was standardized against weighed quantities of potassium acid phthalate. The sulfurous acid solution was poured into a number of different bottles and sealed therein in order to prevent the escape of sulfur dioxide or the air oxidation of the sulfurous acid to sulfuric acid. The titration curves obtained in the standardization showed that only a negligible amount of sulfuric acid was present.

The sulfuric acid solution used was standardized by titration with the sodium hydroxide solution.

The sodium sulfite solution was made up to be 0.5000 M by weighing out the proper amount of sodium sulfite.

The effects of rapidly adding varying amounts of sulfurous acid to 49.92 milliliter samples of a sulfur black dye sol made up with sodium sulfide solution are as follows:

Table I

Experiment Number	H_2SO_3 Ml.	Mols SO_2 Mol Na_2S	Time of Settling	Color of Supernatant Liquid (or Filtrate)
1	1.05	0.434	1 day	No sedimentation apparent
2	2.02	0.836	1 day	No sedimentation apparent
3	2.49	1.03	3.5 hrs. 1 day	Turbid dark blue Turbid light blue
4	3.07	1.27	3.5 hrs. 1 day	Clear and colorless Clear and colorless
5	3.54	1.45	3.5 hrs. 1 day	Turbid dark blue Clear and colorless
6	4.04	1.67	1 day	Clear and colorless
7	4.53	1.87	1 day	Light blue
8	5.04	2.08	30 min.	Yellow; blue-black on oxidation
9	5.29	2.18	1 day	Darker blue than Expt. 7
10-17	5.58-9.07	2.30-3.75	30 min.-3.5 hrs.	Yellow; blue-black on oxidation

In shaking the graduates holding the samples in Table I, some of the dye coagulum stuck to the walls of the graduate. During the course of the settling of the coagulum in the graduate, a film of moisture wet the inside of the graduate above the surface of the liquid. This caused particles of dye coagulum stuck to the sides of the graduate for about one centimeter above the surface of the liquid to become dislodged and "settle" into the supernatant liquid. This caused the supernatant liquid to appear slightly darker than it

should have. This effect was discounted in so far as possible in the descriptions given in Table I. It is for this reason that filtrates were described in Table I where the data were available, for these suspended particles were always removed during filtration.

Notice that complete coagulation occurs in experiments 4, 5, and 6 with sulfur dioxide to sodium sulfide ratios of 1.27, 1.45, and 1.67 respectively. These values cover a region which lies to an approximately equal extent on either side of a value of 1.5 which corresponds to the theoretical ratio for the reaction

$$2Na_2S + 3H_2SO_3 \longrightarrow 2Na_2S_2O_3 + 3H_2O + S$$

It should be noted, however, that the best coagulation appears to be in experiment 4 in which the value of the sulfur dioxide to sodium sulfide ratio is 1.27. Other data, to be exhibited later, indicate that it is at this value of sulfur dioxide to sodium sulfide ratio that the stabilizing ions are most completely destroyed. The deviation of this value from the theoretical value can be explained by side reactions, such as

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

If this reaction occurs, a greater amount of hydrogen sulfide will be consumed by a given amount of sulfur dioxide than indicated by the equation in which sodium

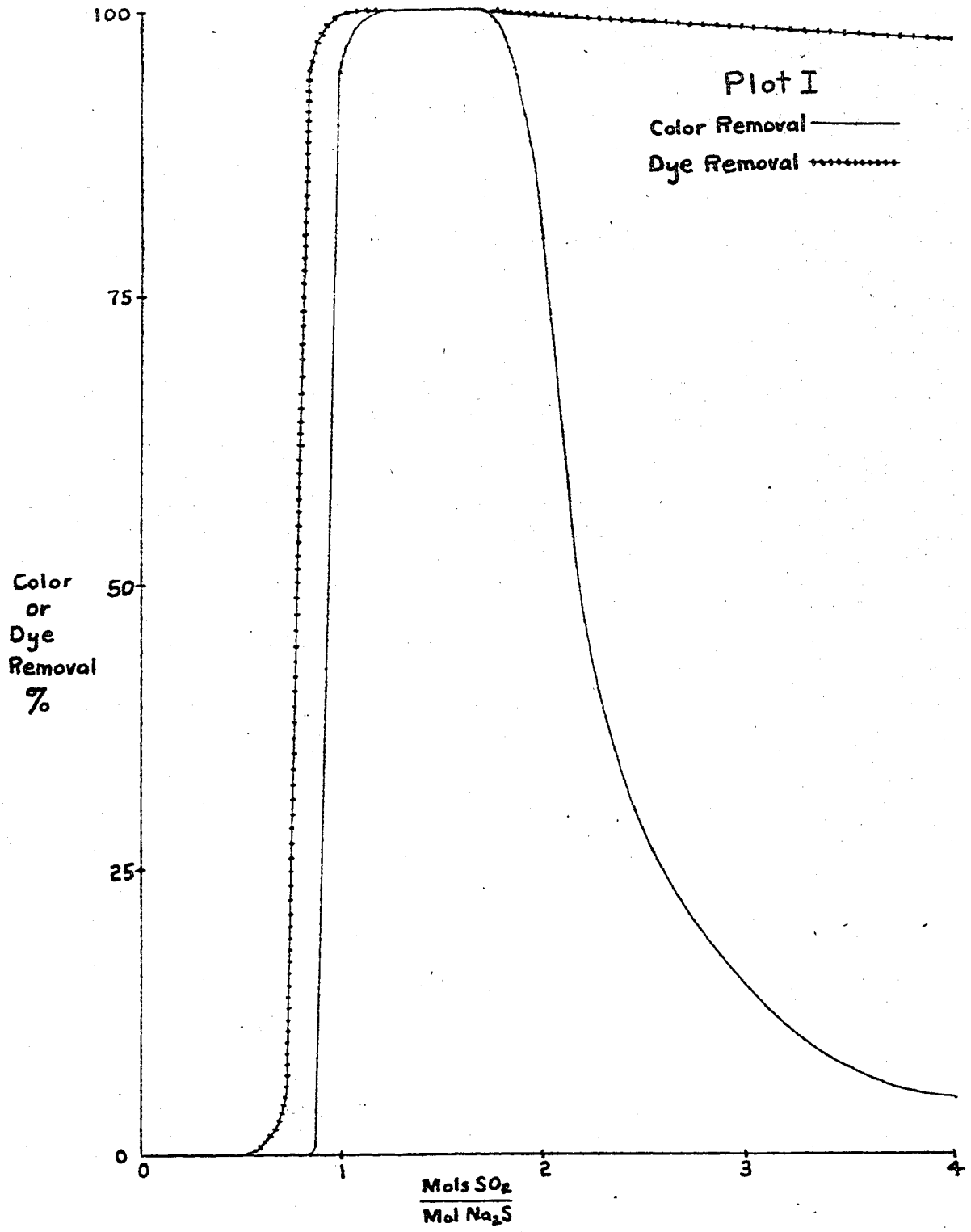
thiosulfate is formed, and a smaller total amount of sulfur dioxide will be required.

It is not surprising that some of the sodium sulfide should react as hydrogen sulfide, for later results will show that the reaction occurs largely in the pH range below 7.0.

The supernatant liquids of the samples of Table I containing excess sulfurous acid were a clear, golden yellow color. When these liquids were exposed to oxidation, either by standing with the mouth of the graduate unstoppered or by filtration, the yellow color changed to a blue-black color. The intensity of the color increased with increasing sulfur dioxide to sodium sulfide. The excess sulfurous acid apparently reacts with some of the leuco-Sulfur Black compound to form a bisulfite addition product, or a sulfonic, sulfinic, or thiosulfonic acid derivative; from which the Sulfur Black dye is regenerated by oxidation.

In Plot I is shown an estimate of the dye removal and color removal from the supernatant liquid of a Sulfur Black dye sol coagulated by sulfurous acid as a function of the ratio of sulfur dioxide to sodium sulfide.

Two curves are given in Plot I. The curve of "Per cent Color Removal" refers to the appearance of the supernatant liquid, and corresponds roughly to the per cent light transmission of the supernatant liquid. The



other curve "Per Cent Dye Removal" is an estimate of the percentage of the total dye which is precipitated. The two curves differ because only a small part of the sulfur dye originally present in the Sulfur Black dye sol is sufficient to render the sol completely opaque. This results in the fact that at a sulfur dioxide to sodium sulfide ratio of about 1.0 (experiment 3) the supernatant liquid is still highly colored, whereas almost all of the dye has been removed. Again, at a sulfur dioxide to sodium sulfide ratio of about 2.0 (experiments 7 and 8) an appreciable color is apparent in the supernatant liquid, but dye removal is still essentially complete.

The pH values of the filtrates from the indicated samples as a function of the amount of sulfurous acid added are recorded below:

Table II

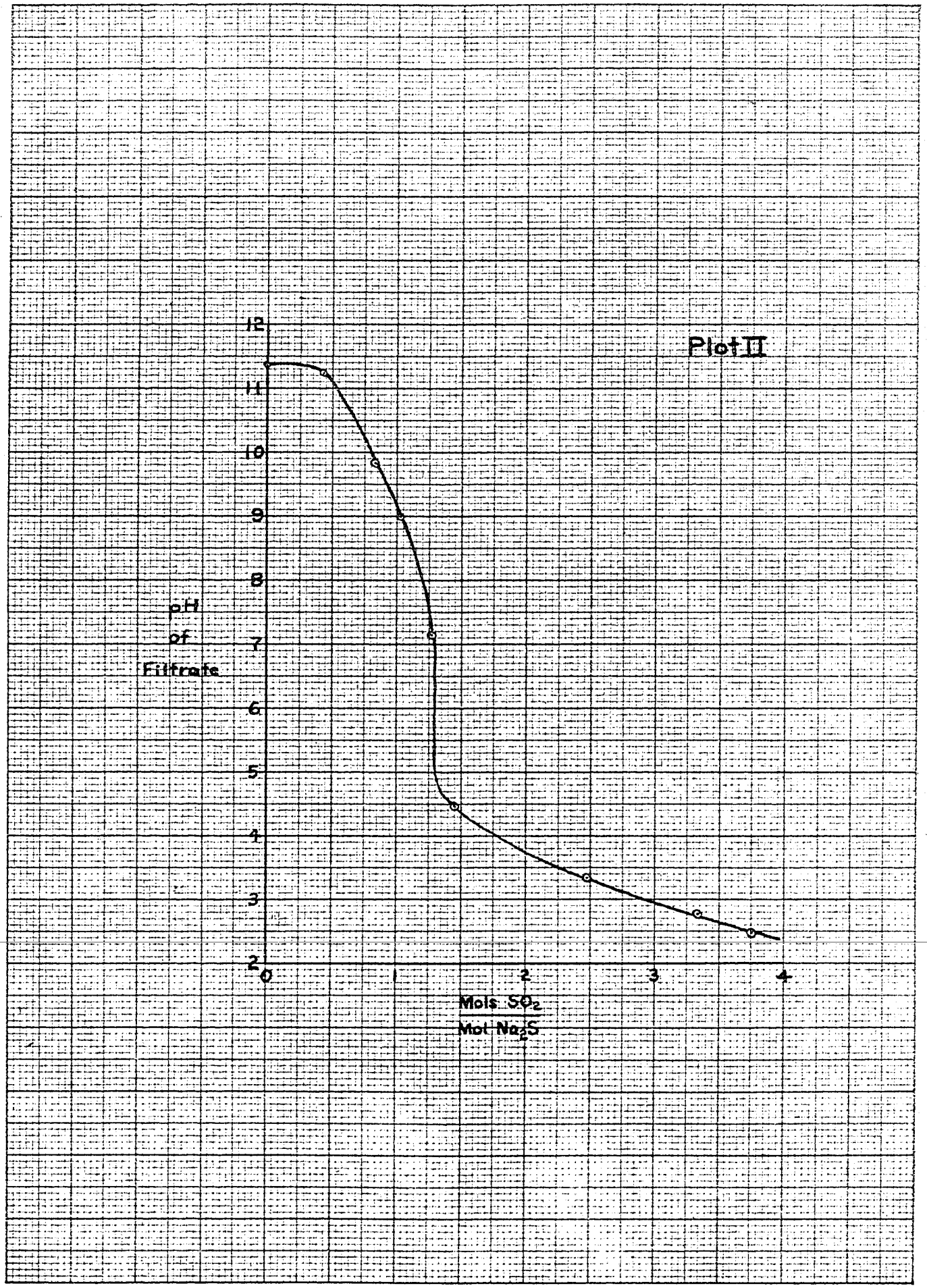
Experiment Number	H_2SO_3 Ml.	Mols SO_2 / Mol Na_2S	Appr. Reaction Time, Hours 16.5 pH	18.5 pH	75 pH	96 pH
18	0.00	0.00	11.37	11.37	11.37	11.37
1	1.05	.434			11.22	
2	2.02	.836			9.82	
3	2.49	1.03			9.00	
4	3.07	1.27			7.15	
5	3.54	1.45			4.48	
6	4.04	1.67		3.61		
7	4.53	1.87		3.49		
8	5.04	2.08	3.02			
9	5.29	2.18		3.29		
10	5.58	2.30	2.95			
11	5.83	2.41				3.26
12	5.99	2.48			3.33	
13	6.09	2.52	2.69			
14	6.52	2.70				3.20
15	7.00	2.89				3.16
16	8.09	3.34			2.79	
17	9.07	3.75			2.49	

Table I indicated that the quickest and most complete coagulation of the sulfur black dye sol occurred in experiment 4, which is seen in Table II to have a filtrate of pH = 7.15. This value represents the nearest approach of any sample in Table II to complete neutrality. Again evidence is seen that in this sample the most complete mutual destruction of sodium sulfide and sulfurous acid occurs.

Plot II shows the pH of the filtrates of coagulated sulfur black dye sols after approximately 75 hours reaction time as a function of the ratio of sulfur dioxide to sodium sulfide.

The point lying on the steepest part of the plot corresponds to experiment 4 (sulfur dioxide to sodium sulfide ratio = 1.27, pH = 7.15), in which the quickest and most complete coagulation was observed.

There is a rather sharp bend in the curve in Plot II at the upper end. This bend occurs approximately at the point representing experiment 1 (sulfur dioxide to sodium sulfide ratio = 0.434, pH = 11.22). There was no apparent change during experiment 1, except for a film of sulfur which formed on the surface of the sample due to air oxidation. There was no coagulation of dye in this sample, for when the sample was filtered, no coagulated dye was retained by the filter paper. Other



samples with a greater sulfur dioxide to sodium sulfide ratio, but not enough to produce any visible coagulation, did leave residues upon filtration. The existence of this region of non-coagulation and its coinciding with the part of the curve above the sharp bend suggests a considerable change in the nature of the reaction at the bend.

As previously stated, the sodium sulfide is largely hydrolyzed according to the equation

$$Na_2S + H_2O \longrightarrow NaOH + NaSH$$

Since the hydroxyl ion is a stronger base than the hydrosulfide ion, the first drop of sulfurous acid solution added will tend to ionize and act as an acid to neutralize the sodium hydroxide; i.e., remove the hydroxyl ion,

$$2NaOH + H_2SO_3 \longrightarrow Na_2SO_3 + H_2O$$

As the hydroxyl ion is consumed, the hydrolysis of the sodium sulfide proceeds as previously explained. If this is the only reaction occurring, it is seen that at a sulfur dioxide to sodium sulfide ratio of 0.5 all of the sodium hydroxide is consumed. The break in the curve occurs at approximately this value.

It seems unlikely that any appreciable amount of sulfur is produced by the reaction during the period indicated above, for it would have to be absorbed by

the sodium sulfide to prevent the precipitation of the dye.

$$Na_2S + (1,2,3,4)S \longrightarrow Na_2S(2,3,4,5)$$

This seems unlikely, since the film of sulfur produced by the air oxidation was not absorbed. Also, even if only one atom of sulfur is absorbed by each atom of sodium sulfide, and the reaction went entirely according to the equation

$$2Na_2S + 3H_2SO_3 \longrightarrow 2Na_2S_2O_3 + 3H_2O + S$$

sulfur would be absorbed until two thirds of the sodium sulfide had been reacted, and no coagulation would occur until the sulfur dioxide to sodium sulfide ratio exceeded 1.0. This corresponds approximately to experiment 3 in which coagulation was found to be almost complete.

The bottom part of the curve is such as would be expected in the titration of a base by a weak acid. The addition of excess sulfurous acid beyond the amount required to reach the steep portion of the curve seems to remain as free acid, excepting the relatively small amount combining with the leuco-Sulfur Black, as previously explained. The presence of excess sulfurous acid in all four of the samples corresponding to the bottom portion of the curve was noted by the odor of the samples.

The colloidal-eEectrical nature of the coagulum

produced by the interaction of sulfur dye sols and sulfurous acid solutions is of fundamental importance. The coagulum, however, does not by its nature lend itself to study by cataphoretic methods.

Fortunately, it was found that the electrical properties of the colloid during the course of its coagulation could be studied through sedimentation data.

This is possible because the principal factor acting to prevent the coalescence of particles is the charge on the particles. The smaller the charge upon the particles, the more readily they agglomerate and the larger will be the particle-aggregates.

It is a well known fact that in unhindered sedimentation large particles settle more rapidly than small particles, in conformity with Stokes' Law.

In Tables III - VIII are recorded data which express the rate of sedimentation (as given by the volume) of the coagulated dye as a function of the sulfur dioxide to sodium sulfide ratio for the sedimentation (or reaction) periods indicated. The milliliter readings could be converted into a height in centimeters using the measurement of the graduate used. A reading of 90.0 milliliters on the graduate corresponds to a height of 17.0 centimeters.

Table III

Sedimentation Time = 30 minutes

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
1	0.434	51.1	51.1	100.
2	0.836	52.0	52.0	100.
3	1.03	52.5	52.5	100.
4	1.27	53.1	51.9	97.5
5	1.45	53.5	53.0	90.0
6	1.67	54.0	52.9	97.9
7	1.87	54.5	53.0	97.1
8	2.08	55.0	51.3	93.2
9	2.18	55.3	47.0	85.0
10	2.30	55.6	38.2	68.6
11	2.41	55.8	31.0	55.6
12	2.48	56.0	36.8	65.6
13	2.52	56.1	35.0	62.4
14	2.70	56.5	35.5	62.8
15	2.89	57.0	41.9	73.5
16	3.34	58.1	43.1	74.2
17	3.75	59.1	57.0	96.4

Table IV

Sedimentation Time = 3.0 hours

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
6	1.67	54.0	45.8	84.9
7	1.87	54.5	43.2	79.2
9	2.18	55.3	31.3	56.6
11	2.41	55.8	25.7	46.1
14	2.70	56.5	23.4	41.4
15	2.89	57.0	25.0	43.9

Table V

Sedimentation Time = 3.5 hours

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
1	0.434	51.1	51.1	100.
2	0.836	52.0	52.0	100.
3	1.03	52.5	50.0	95.2
4	1.27	53.1	38.3	72.0
5	1.45	53.5	47.5	88.9
6	1.67	54.0	44.8	83.0
7	1.87	54.5	42.0	77.0
8	2.08	55.0	36.0	65.5
9	2.18	55.3	31.0	56.0
10	2.30	55.6	22.6	40.6

Table V (Continued)

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
11	2.41	55.8	25.3	45.4
12	2.48	56.0	25.1	44.9
13	2.52	56.1	22.5	40.1
14	2.70	56.5	23.2	41.0
15	2.89	57.0	24.8	43.5
16	3.34	58.1	27.8	47.8
17	3.75	59.1	36.1	61.0

Table VI

Sedimentation Time = 20.5 hours

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
1	0.434	51.1	51.1	100.
2	0.836	52.0	52.0	100.
3	1.03	52.5	36.0	68.5
4	1.27	53.1	34.4	64.7
5	1.45	53.5	38.3	71.6
12	2.48	56.0	23.1	41.2
16	3.34	58.1	24.6	42.3
17	3.75	59.1	25.3	42.7

Table VII

Sedimentation Time = 73.5 hours

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
1	0.434	51.1	51.1	100.
2	0.836	52.0	52.0	100.
3	1.03	52.5	27.2	51.9
4	1.27	53.1	32.8	61.7
5	1.45	53.5	34.4	64.4
12	2.48	56.0	22.7	40.5
16	3.34	58.1	23.5	40.5
17	3.75	59.1	20.9	35.4

Table VIII

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Time hours	Coagulum Volume ml.	Coagulum, % of Total Volume
6	1.67	54.0	17.5	38.0	70.4
7	1.87	54.5	17.3	34.6	63.5
8	2.08	55.0	16.3	30.5	55.5
9	2.18	55.3	17.3	28.0	50.6
10	2.30	55.6	16.3	21.5	38.6
11	2.41	55.8	17.3	24.1	43.2
			42.	23.7	42.5
			95.	23.0	41.2
12	2.48	56.0	20.5	23.1	41.2
			73.5	22.7	40.5

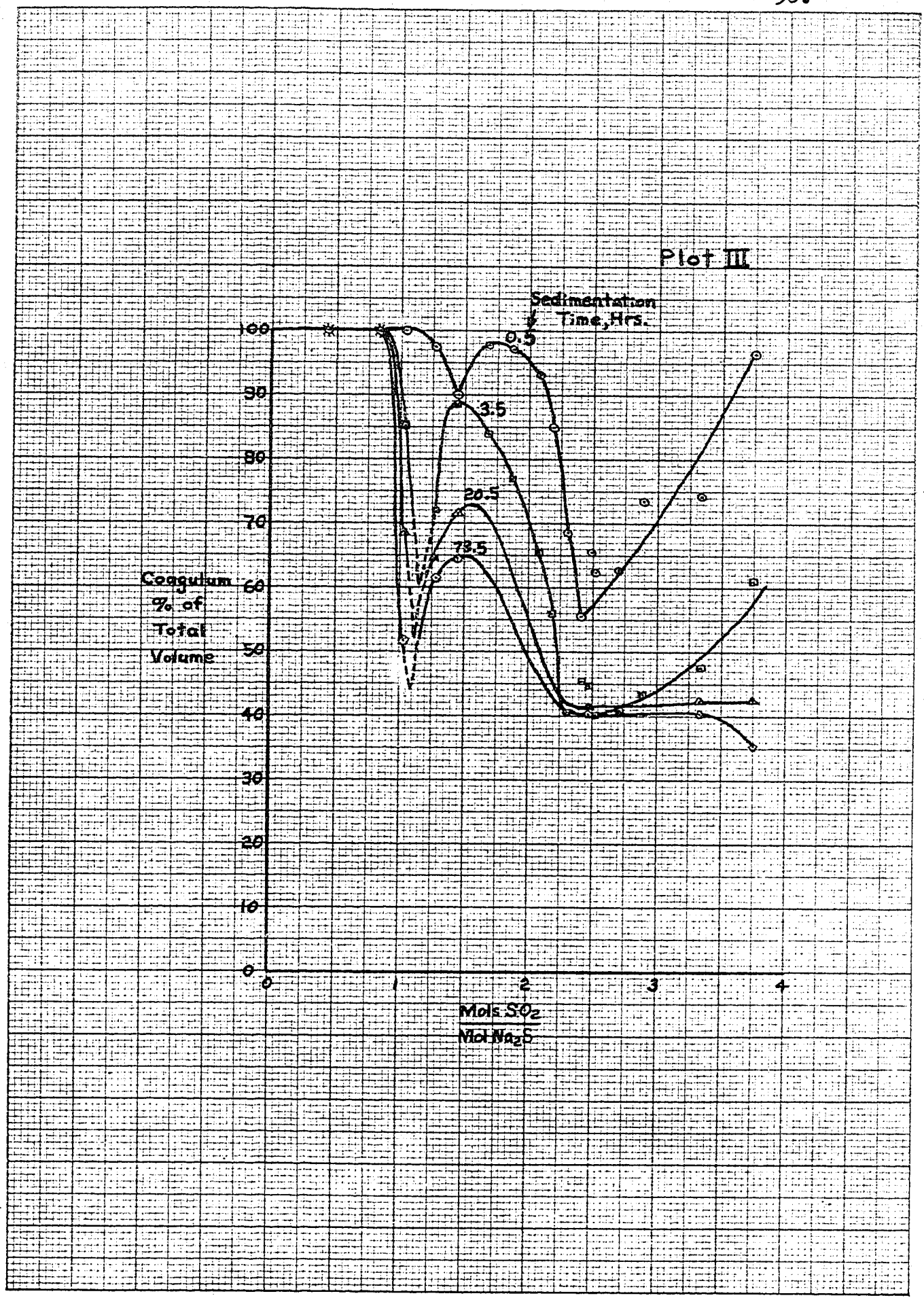
Table VIII (Continued)

Experiment Number	Mols SO_2 / Mol Na_2S	Total Volume ml.	Time hours	Coagulum Volume ml.	Coagulum, % of Total Volume
13	2.52	56.1	16.3	21.5	38.3
14	2.70	56.5	17.	22.2	39.3
			42.	19.4	34.3
			95.	19.0	33.6
15	2.89	57.0	17.	23.0	40.7
			42.	20.4	35.8
			95.	19.9	34.9
16	3.34	58.1	20.5	24.6	42.3
			73.3	23.5	40.5
17	3.75	59.1	20.5	25.3	42.7
			73.3	20.9	35.4

The data of Tables III, V, VI, and VII are represented graphically in Plot III.

The most striking feature of Plot III is the existence of two minima in the coagulum volumes, corresponding to two maxima in the rates of sedimentation.

In Tables IX and X these maxima of rates of sedimentation as represented by the data are tabulated. Table IX contains the experiments corresponding to the "first" maxima of the sedimentation rates; i.e.,



the value of the maxima of sedimentation rates for the sedimentation times indicated for the smaller sulfur dioxide to sodium sulfide ratio; and Table X contains the experiments corresponding to the "second" maxima of sedimentation rates; i.e., the value of the maxima of sedimentation rates for the sedimentation times indicated for the larger sulfur dioxide to sodium sulfide ratio.

Table IX

First Maxima of Sedimentation Rates

Experiment Number	Sedimentation Time hours	Mols SO_2 / Mol Na_2S	Coagulum, % of Total Volume
5	0.5	1.45	90.0
4	3.5	1.27	72.0
4	20.5	1.27	64.7
3	73.5	1.03	51.9

Note that Plot III indicates that the first minima of sedimentation rate for 20.5 and 73.5 hours lie between the values for which data are available. This represents only a small difference in sulfur dioxide to sodium sulfide ratio, but probably represents a large difference in sedimentation rate.

Table X

Second Maxima of Sedimentation Rates

Experiment Number	Sedimentation Time hours	Mols SO_2 / Mol Na_2S	Coagulum, % of Total Volume
13	0.5	2.54	62.4
10	3.5	2.30	40.6
10	16.3	2.30	38.6

A comparison of Tables IX and X with Table I shows that the region of the first maxima of rates of sedimentation of Table IX corresponds to the region of maximum rate and completeness of coagulation of Table I. A similar comparison shows that all of the samples of the second maxima of rate of sedimentation (Table X) produce yellow supernatant liquids which turn blue-black on oxidation.

The so-called sedimentation rates do not actually represent particles in unhindered sedimentation during the latter periods of time, but represent a compression of the coagulum.

The explanation of the maxima of sedimentation rates is that they are an indirect, but definite, result of a minimum charge upon the particles, as previously explained.

A maximum in the rate of sedimentation of the

coagulum then, indicates a minimum charge on the particles of the coagulum. The explanation of the two maxima of rates of sedimentation seems to be that the first maxima correspond to the most complete mutual destruction of the stabilizing ions of the sulfur dye and sulfur sols, while the second maxima correspond to the isoelectric point.

It is believed that the isoelectric point of the coagulum is quite low, perhaps at a value of about pH = 3. As Plot V will show, the pH of the reacting mixtures does not reach this value in the region of the first maxima of rate of sedimentation. It is apparent that the coagulum, at the first maxima of sedimentation rates, is negatively charged by adsorption of hydroxyl ions. On either side of these maxima, however, the charge is considerably greater due to the presence of excess of the stabilizing ion. At a smaller sulfur dioxide to sodium sulfide ratio, the hydrosulfide ion, which is the stabilizing ion of the sulfur dye sol, is present in excess and gives the sulfur dye a strong negative charge. For a larger sulfur dioxide to sodium sulfide ratio, the increase in the negative charge of the coagulum is probably due to two phenomena. First, it seems that in the reaction between sulfur dioxide and sodium sulfide some polythionates are always produced.

If excess hydrosulfide ions are present, the polythionate ions will be destroyed by reaction, e.g.,

$$HS_5O_6^- + 5HS^- \longrightarrow 10S + 6OH^-$$

If there is not enough hydrosulfide ion completely to destroy the polythionate ions, the excess polythionate ions will be strongly absorbed by the sulfur (they are the stabilizing ions of sulfur sols), and produce a strong negative charge on the sulfur particles. The second probable contributing factor to the increase in charge on the coagulum with greater sulfur dioxide to sodium sulfide ratios than necessary for complete coagulation is that excess sulfur dioxide forms a compound with the sulfur dye, as previously discussed. If this compound is a bisulfite addition product, or a sulfonic, sulfinic, or thiosulfonic acid derivative, then it would be the equivalent of introducing an ionic group into the dye molecule. This would, of course, make the dye highly negatively charged.

The latter factor does not seem to be as important as the first, for the sample in experiment 6 had a larger sulfur dioxide to sodium sulfide ratio than any of the samples corresponding to first maxima of the sedimentation rate, but produced a clear and colorless filtrate (indicating a negligible amount of compound formation with the sulfur dye).

The behavior of the coagulum in the presence of polythionate ion is in itself evidence that it is the polythionate ion and not the thiosulfate ion which stabilizes sulfur sols. There is already present at the first maxima of the sedimentation rates a considerable amount of thiosulfate ion. The small additional amount which might be caused by the use of a larger sulfur dioxide to sodium sulfide ratio would have no appreciable additional effect on the charge on the sulfur particles.

Table XI is a composite of Tables III - VIII, retabulated for the purpose of showing the sedimentation of individual samples as a function of time.

Table XI

Experiment Number	Mols SO_2 / Mol Na_2S	Sedimentation Time hours	Coagulum, % of Total Volume
1	0.434	0.5	100.
		3.5	100.
		20.5	100.
		73.8	100.
2	0.836	0.5	100.
		3.5	100.
		20.5	100.
		73.8	100.

Table XI (Continued)

Experiment Number	Mols SO_2 / Mol Na_2S	Sedimentation Time hours	Coagulum, % of Total Volume
3	1.03	0.5	100.
		3.5	95.2
		20.5	68.5
		73.5	51.9
4	1.27	0.5	97.5
		3.5	72.0
		20.5	64.7
		73.5	61.7
5	1.45	0.5	90.0
		3.5	88.9
		20.5	71.6
		73.5	64.4
6	1.67	0.5	97.9
		3.0	84.9
		3.5	83.0
		17.5	70.4
7	1.87	0.5	97.1
		3.0	79.2
		3.5	77.0
		17.3	63.5
8	2.08	0.5	93.2
		3.5	65.5
		16.3	55.5

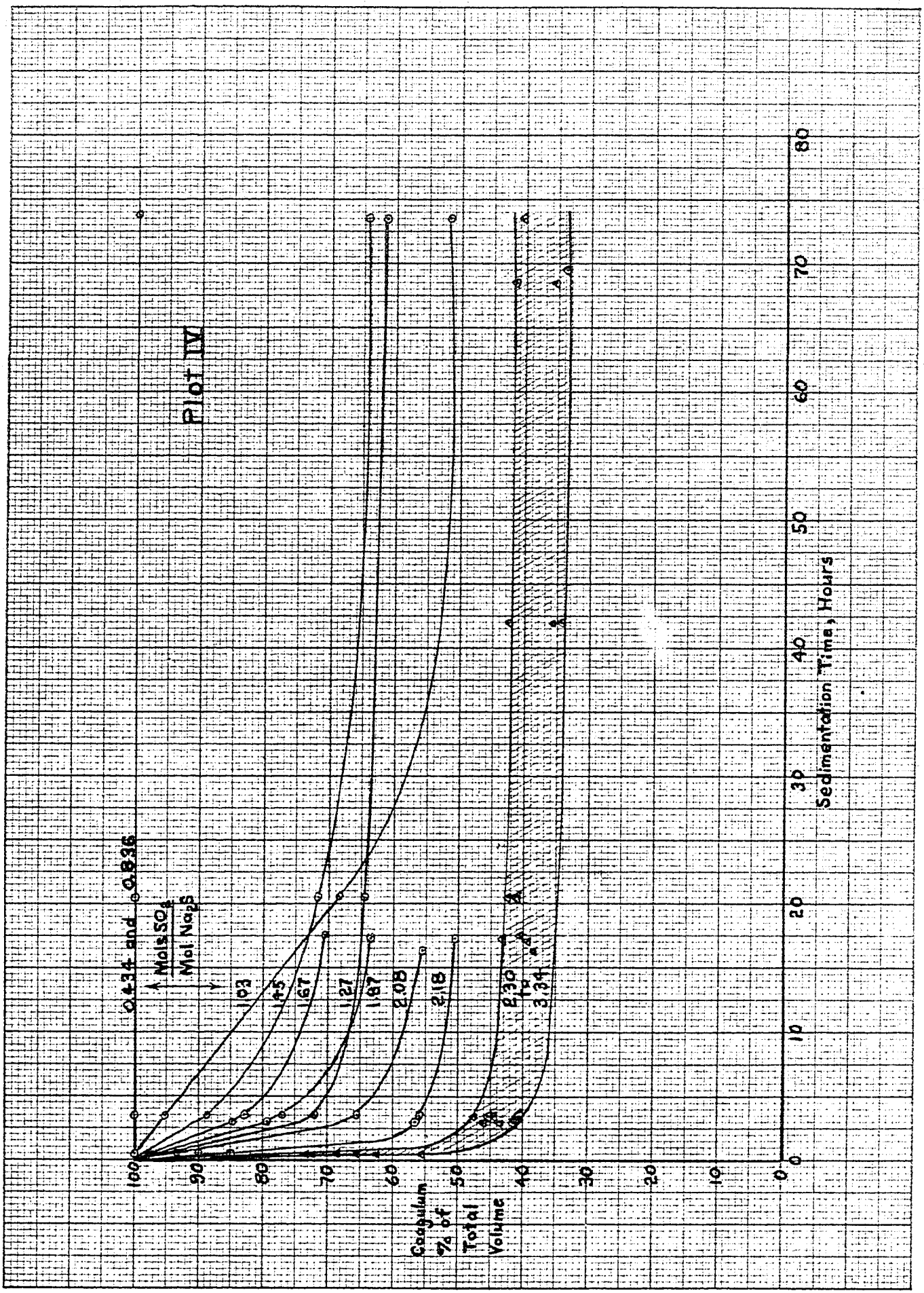
Table XI (Continued)

Experiment Number	Mols SO_2 / Mol Na_2S	Sedimentation Time hours	Coagulum, % of Total Volume
9	2.18	0.5	85.0
		3.0	56.6
		3.5	56.0
		17.3	50.6
10	2.30	0.5	68.6
		3.5	40.6
		16.3	38.6
11	2.41	0.5	55.6
		3.0	46.1
		3.5	45.4
		17.3	43.2
		42.0	42.5
		95.0	41.2
12	2.48	0.5	65.6
		3.5	44.9
		20.5	41.2
		73.5	40.5
13	2.52	0.5	62.4
		3.5	40.1
		16.3	38.3

Table XI (Continued)

Experiment Number	Mols SO_2 / Mol Na_2S	Sedimentation Time hours	Coagulum, % of Total Volume
14	2.70	0.5	62.8
		3.0	41.4
		3.5	41.0
		17.0	39.3
		42.0	34.3
		95.0	33.6
15	2.89	0.5	73.5
		3.0	43.9
		3.5	43.5
		17.0	40.7
		42.0	35.8
		95.0	34.9
16	3.34	0.5	74.2
		3.5	47.8
		20.5	42.3
		73.3	40.5
17	3.75	0.5	96.4
		3.5	61.0
		20.5	42.7
		73.3	35.4

The data of Table XI are represented graphically in Plot IV.



During the first period of the sedimentation, the rate of sedimentation is more or less constant, and is represented in Plot IV by the initial straight line portions of the curves. During this period the particles of the coagulum are in unhindered sedimentation.

Note the maximum in rate of sedimentation shown during this period in experiment 4 (sulfur dioxide to sodium sulfide ratio = 1.27). As previously explained, this probably is a result of the formation of particle aggregates of a maximum size at this sulfur dioxide to sodium sulfide ratio because of there being a minimum charge on the particles.

In all samples previously discussed, the mixing of the sulfurous acid solution with the sulfur dye sol was brought about as rapidly as possible. Even so, there was an interval of time taken during which the required amount of sulfurous acid solution was being run from the buret into the graduate. There was undoubtedly mixing in the upper portion of the graduate during this time. Another second or two elapsed while the buret was being read and the reading recorded. (It was necessary to read and record at this point because of tendency of the buret to leak due to attack of the sulfurous acid upon the stopcock grease. Several

kinds of stopcock grease were tried, but all failed.) The graduate was then shaken. Since it was at this time that most of the mixing occurred, most of the sample can be said to have been mixed instantaneously with the sulfurous acid solution.

In previous experiments it was noted that the pH of samples of sulfur dye sols to which a sulfurous acid solution had been added did not remain constant. This indicates that the reactions involved are not instantaneous.

It was believed that the coagulation might be influenced by the rate of mixing of the reagents. To investigate this possibility, varying amounts of sulfurous acid solution were added to several samples of sulfur dye sols. The sulfur dye samples were placed in beakers and the sulfurous acid solutions added slowly with stirring. The results are as follows

Table XII

Slow Addition of Sulfurous Acid Solution

Experiment Number	Mols SO_2 / Mol Na_2S	Initial pH*	Coagulum Volume after 3 hours	Filtrate pH	Appearance of Filtrate
19	1.03	7.00	no sedimentation	9.40	dark green
20	1.05	10.00	no sedimentation	10.87	as dark as original solution
21	1.26	8.40	no sedimentation	10.30	as dark as original solution

* the pH reading of the sample immediately after the sulfurous acid solution addition was completed

From Table XII it is apparent that the slow addition of the sulfurous acid solution decreases the degree of coagulation of the sulfur dye sols. Experiment 21, for example, used a sulfur dioxide to sodium sulfide ratio of 1.26, which is almost identical with the ratio of 1.27 for experiment 4. Practically complete coagulation was noted in experiment 4, whereas very little coagulation was observed in experiment 21. The pH of the filtrate in experiment 21 was 10.30, as compared with 7.15 in experiment 4. It was not possible to add the sulfurous acid solution to all samples at exactly the same rate. It is presumed that this accounts for the irregularity of the data in Table XII.

The principal reason for the decreased degree of coagulation in the case of the slow addition of sulfurous

acid is that a large part of the sulfur is formed and given time to coagulate in the presence of excess hydrosulfide ions. This amount of sulfur is consequently ineffective in causing the coagulation of the sulfur dye. Evidence presented later indicates that no fundamental change in the nature of the reactions taking place is involved.

Tables XIII, XIV, XV, XVI, and XVII give data on the variation of pH with time for rapid additions of various amounts of sulfurous acid solution. The samples were contained in beakers during the course of the observations, and agitated at the times of the pH readings to prevent settling.

Table XIII

Rapid Addition of Sulfurous Acid Solution
Experiment 22
Sulfur Dioxide to Sodium Sulfide Ratio = 1.17

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	7.00	90.5	8.80
--	< 7.00	91.	8.90
37.	7.10	93.	8.90
63.	7.40	117.	8.93
73.	7.60	199.	9.20
85.	7.90	266.	9.29
86.	8.10	327.	9.21

Table XIII (Continued)

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
87.	8.25	349.	9.26
88.	8.31	1046.	8.90
89.	8.55	1353.	8.83
89.5	8.66	1752.	8.65
90.	8.70		

Table XIV

Rapid Addition of Sulfurous Acid Solution
Experiment 23
Sulfur Dioxide to Sodium Sulfide Ratio = 1.56

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	6.40	50.	3.41
4.	6.12	56.	3.41
5.	5.90	61.	3.38
6.	5.60	63.	3.41
7.	5.47	68.	3.43
9.	5.10	80.	3.46
10.	4.87	85.	3.49
12.	4.55	96.	3.52
13.	4.25	104.	3.44
15.	4.10	125.	3.67
17.	3.95	248.	3.80
18.	3.80	311.	3.84

Table XIV (Continued)

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
24.	3.53	1043.	5.29
28.	3.45	1334.	5.99
33.	3.41	1560.	6.80
43.	3.41		

Table XV

Rapid Addition of Sulfurous Acid Solution
Experiment 24
Sulfur Dioxide to Sodium Sulfide Ratio = 1.93

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	5.10	104.	2.79
24.	3.61	124.	2.85
26.	3.40	125.	2.85
29.	3.25	154.	2.83
31.	3.11	174.	2.85
61.	2.83	861.	3.50
71.	2.85	1152.	3.60
90.	2.80	1557.	4.24

Table XVI

Rapid Addition of Sulfurous Acid Solution
Experiment 25
Sulfur Dioxide to Sodium Sulfide Ratio = 2.12

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	3.35	33.	2.80
1.	3.22	54.	2.75
2.	3.10	64.	2.70
4.	3.03	101.	2.80
5.	3.00	117.	2.70
9.	2.85	811.	3.35
21.	2.80	1101.	3.67

Table XVII

Rapid Addition of Sulfurous Acid Solution
Experiment 26
Sulfur Dioxide to Sodium Sulfide Ratio = 2.32

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	2.99	64.	2.75
2.	2.90	78.	2.72
6.	2.90	112.	2.79
7.	2.81	131.	2.78
20.	2.81	821.	3.33
31.	2.75	1111.	3.57
46.	2.71		

The samples noted in Tables XIII, XIV, XV, XVI and XVII settled overnight in their beakers during the gaps in time apparent in the tables of data. After this sedimentation period of approximately 12 hours, the supernatant liquids were observed as noted in Table XVIII

Table XVIII

Sedimentation Time = 12 hours

Experiment Number	Mols SO_2 / Mol Na_2S	Supernatant Liquid
22	1.17	blue tint
23	1.56	light blue tint
24	1.93	light blue tint
25	2.12	no sedimentation apparent
26	2.32	no sedimentation apparent

The samples were transferred to graduates so that the supernatant liquids could be observed under conditions comparable with those for the samples of Table I. The samples were observed after they had settled for approximately three and a half hours and the observations noted in Table XIX

Table XIX

Experiment Number	Mols SO_2 / Mol Na_2S	Supernatant Liquid
22	1.17	very faint blue tint
23	1.56	blue
24	1.93	light blue

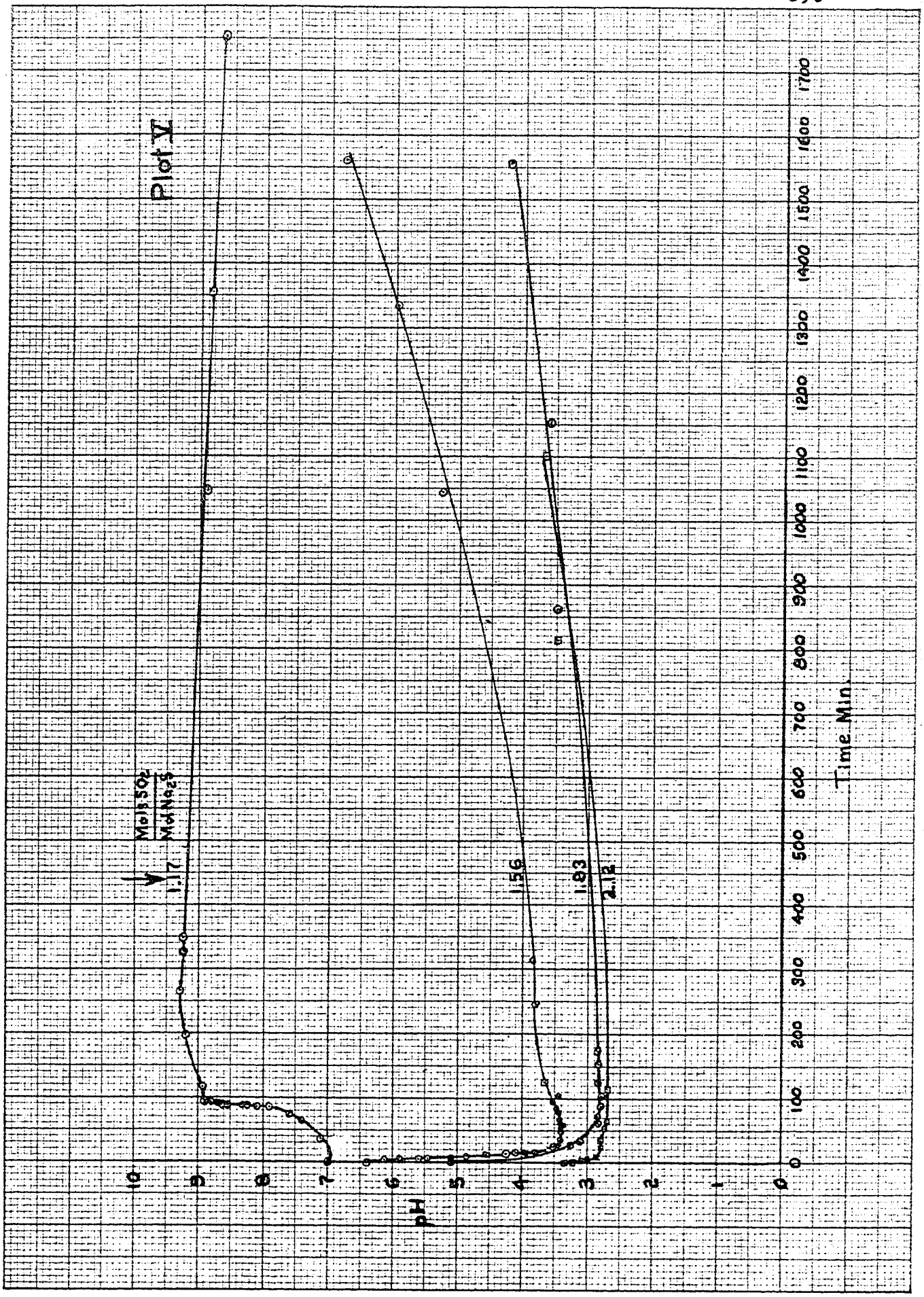
The samples in Table XIX were filtered and the quality of the filtrates noted in Table XX

Table XX

Experiment Number	Mols SO_2 / Mol Na_2S	Filtrate
22	1.17	clear and colorless
23	1.56	blue green tint
24	1.93	very faint blue green tint

The data of Tables XIII through XVI are represented graphically in Plot V. The curve for Table XVII is almost identical with that for Table XVI, except that it begins with a slightly lower initial value of pH.

Table XIX indicates that experiments 22, 23 and 24, corresponding to sulfur dioxide to sodium sulfide ratios of 1.17, 1.56, and 1.93, respectively, correspond to essentially complete coagulation. Comparison shows that the samples in Table I representing substantially complete



coagulation fall within this range. Experiment 2, in which no sedimentation was apparent, had a sulfur dioxide to sodium sulfide ratio of 0.836, and experiment 8, which was yellow at first and was oxidized to a blue-black color, had a sulfur dioxide to sodium sulfide ratio of 2.08.

Both sets of data seem to indicate, then, that almost complete coagulation occurs approximately between sulfur dioxide to sodium sulfide ratios of 1.0 and 2.0, with complete coagulation occurring over a somewhat narrower range approximately between ratios of 1.1 and 1.7.

To a number of sulfur dye sol samples contained in beakers were added slowly with stirring varying amounts of sulfurous acid solution. The data are recorded in the following tables.

Table XXI

Slow Additions of Sulfurous Acid Solution
Experiment 27
Sulfur Dioxide to Sodium Sulfide Ratio = 0.95

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0*	6.66	23.	6.62
3.	6.65	261.	6.99
9.	6.64	1266.	9.50
14.	6.64		

* Zero time in this and subsequent tables refers to zero time after the end of the slow sulfurous acid addition.

Table XXII

Slow Additions of Sulfurous Acid Solution
Experiment 28
Sulfur Dioxide to Sodium Sulfide Ratio = 1.10

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	6.88	16.	8.70
5.	7.10	17.	8.89
10.	7.27	19.	9.17
11.	7.58	20.	9.20
12.	7.80	36.	9.63
14.	8.40	1139.	9.88
15.	8.62		

Table XXIII

Slow Addition of Sulfurous Acid Solution
Experiment 29
Sulfur Dioxide to Sodium Sulfide Ratio = 1.38

Time after Mixing Minutes	pH
0.	6.37
41.	6.19
202.	6.03

Table XXIV

Slow Addition of Sulfurous Acid Solution
Experiment 30
Sulfur Dioxide to Sodium Sulfide Ratio = 1.45

Time after Mixing Minutes	pH
0.	6.20
27.	6.19
187.	6.07

Table XXV

Slow Addition of Sulfurous Acid Solution
Experiment 31
Sulfur Dioxide to Sodium Sulfide Ratio = 1.60

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	5.90	37.	4.89
2.	5.80	55.	4.81
4.	5.65	59.	4.67
5.	5.60	64.	4.63
10.	5.43	92.	4.61
17.	5.24	237.	4.53
27.	5.10	1242.	5.21
32.	5.00		

Table XXVI

Slow Addition of Sulfurous Acid Solution
Experiment 32
Sulfur Dioxide to Sodium Sulfide Ratio = 1.70

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	5.51	18.	5.03
4.	5.40	24.	4.90
6.	5.25	988.	4.40

Table XXVII

Slow Addition of Sulfurous Acid Solution
Experiment 33
Sulfur Dioxide to Sodium Sulfide Ratio = 1.76

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
0.	5.10	20.	3.03
1.	4.60	22.	3.01
2.	4.30	26.	2.98
3.	4.00	29.	2.92
4.	3.78	36.	2.91
5.	3.60	40.	2.90
6.	3.49	47.	2.87
7.	3.37	49.	2.86
8.	3.29	53.	2.81
9.	3.25	56.	2.81
10.	3.23	67.	2.81
11.	3.22	100.	2.74

Table XXVII (Continued)

Time after Mixing Minutes	pH	Time after Mixing Minutes	pH
12.	3.20	105.	2.78
13.	3.14	113.	2.79
14.	3.13	1215.	3.20
18.	3.09		

The degree of coagulation observed in the preceeding samples is indicated in Table XXVIII

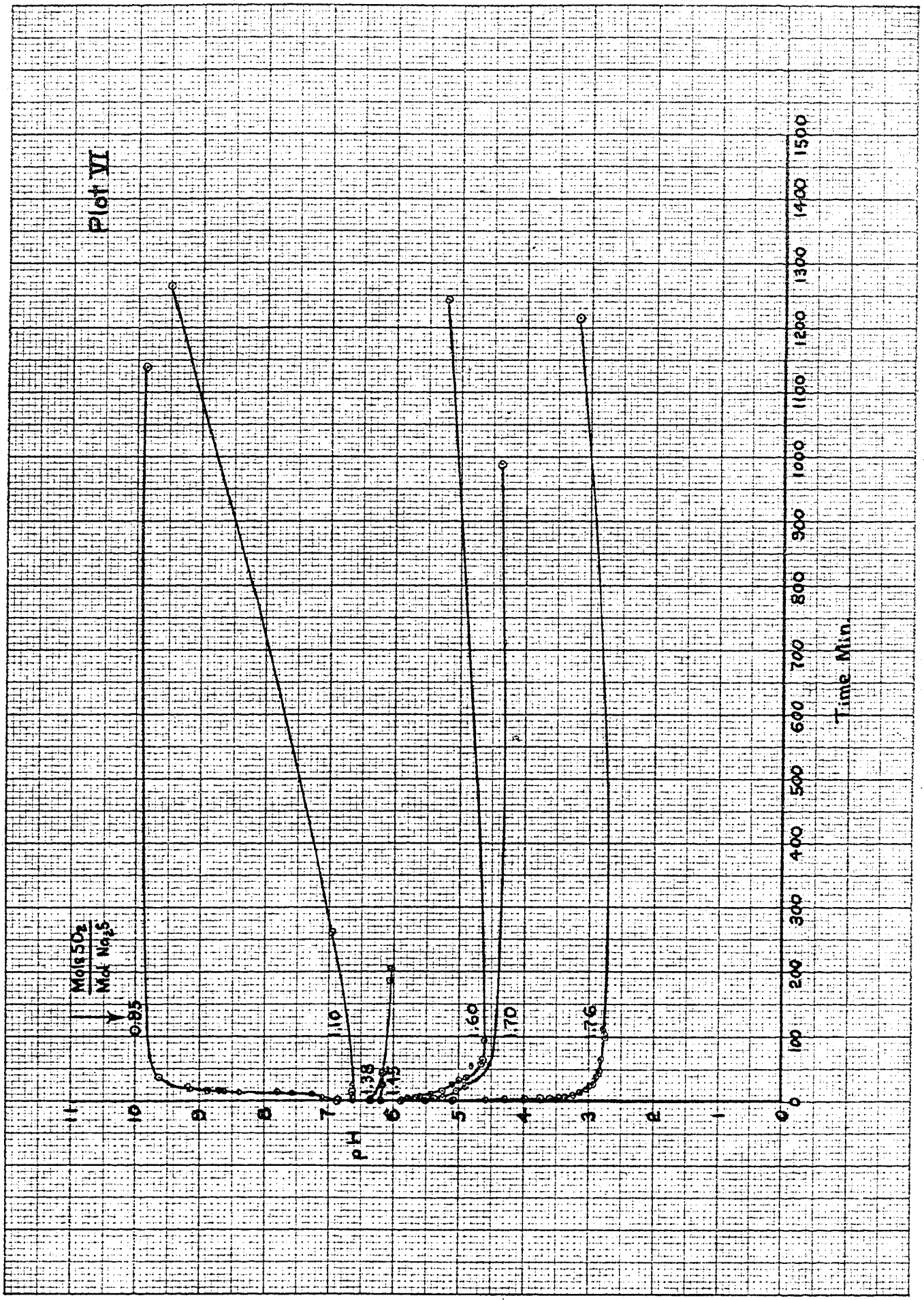
Table XXVIII

Experiment Number	Mols SO_2 / Mol Na_2S	Filtrates (or Supernatant Liquid)
27	0.95	Jet Black (Left no residue)
28	1.10	(No evidence of sedimentation)
31	1.60	Jet Black (Left a residue)
32	1.70	Jet Black
33	1.76	(Yellow; blue-black on oxidation)

The data in Table XXVIII confirm the conclusion drawn from Table XII that the slow addition of the sulfurous acid solution to the sulfur dye sol decreases the degree of coagulation.

The data of Tables XXI through XXVII are represented graphically in Plot VI.

The shapes of the curves in Plots V and VI are essentially the same, except that the abrupt changes



apparent in the curves in Plot V appear rounded in Plot VI.

This indicates that the decreased degree of coagulation observed upon slow addition of the sulfurous acid solution is not due to a change in the nature of the reactions involved.

From Plot V it can be seen that the pH of the solution immediately after mixing varies considerably with the sulfur dioxide to sodium sulfide ratio.

It would be very desirable to be able to use this "immediate" pH value to predict the future course of the coagulation. It is for this purpose that the following study of the coagulation of sulfur dye as a function of the "immediate" pH has been made.

The sulfur dioxide solution was run into one beaker, and the sulfur dye sol was contained in another. The two were mixed rapidly (more nearly instantaneously than before) and immediately poured into graduates. The data are given in Tables XXIX and XXX. The volumes of sulfurous acid given are only approximate.

Table XXIX

Experiment Number	Approximate Volume H_2SO_3 ml.	Immediate pH	Time Min.	"Final" pH Supernatant liquid and sludge	"Final" pH Supernatant liquid
34	2.0	8.90	1261	10.80	
35	2.5	7.85	1260	9.58	
36	3.0	7.30	1263	7.98	
37	3.5	7.00	1272	6.98	8.90
38	4.0	6.70	1270	4.90	6.52
39	4.5	6.60	1268	4.01	4.40
40	5.0	6.30	1266	3.30	3.43
41	5.5	6.00	1264	3.19	3.25
42	6.0	6.00	1270	3.00	3.00

Table XXX

Experiment Number	Immediate pH	Supernatant Liquid
34	8.90	No evidence of settling
35	7.85	No evidence of settling
36	7.30	No evidence of settling
37	7.00	Turbid, intense blue color
38	6.70	Clear, slight blue tint
39	6.60	Blue tint
40-42	6.30-6.00	Yellow (dark blue on oxidation)

The most complete coagulation was observed in experiment 38. Judging from past experience, the samples

from experiments 38 and 39 would filter to give a clear and colorless filtrate. The best "immediate" pH for coagulation would seem to be about 6.70. The supernatant liquid in this sample is seen, from Table XXIX, to have the "final" pH nearest 7.00; i.e., 6.52.

The "intense blue color" described in Table XXX for the supernatant liquid in experiment 37 was of about the appearance of a concentrated copper sulfate solution. From experience it is known that this appearance indicates a very small deficiency of sulfur dioxide, compared with the amount necessary for the most complete coagulation of the sulfur dye sol. The best value of "immediate" pH may well be slightly greater than 6.70.

Sedimentation data for the samples as a function of "immediate" pH is given in the following tables.

Table XXXI

Sedimentation Time = 2.5 hours

Experiment Number	Immediate pH	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
34-36	8.90-7.30	No sedimentation evident		100.
37	7.00	53.0	50.5	95.4
38	6.70	53.5	38.0	71.0
39	6.60	54.0	42.0	77.8

Table XXXI (Continued)

Experiment Number	Immediate pH	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
40	6.30	54.1	47.3	87.4
41	6.00	54.8	48.1	88.0
42	6.00	55.1	46.1	83.5

In Table XXXI it is seen that the coagulum volume is a minimum in experiment 38, which shows the most complete coagulation. The coagulum volumes increase to a maximum, then decrease again. The minimum coagulum volume means a maximum sedimentation rate.

Table XXXII

Sedimentation Time = 18.0 hours

Experiment Number	Immediate pH	Total Volume ml.	Coagulum Volume ml.	Coagulum, % of Total Volume
34-36	8.90-7.30	No sedimentation apparent		100.
37	7.00	53.0	34.2	64.5
38	6.70	53.5	32.2	60.2
39	6.60	54.0	35.1	65.0
40	6.30	54.1	36.0	66.5
41	6.00	54.8	34.7	63.4
42	6.00	55.1	30.3	55.0

Again it is seen that a maximum sedimentation rate occurs in experiment 38, followed by a decrease in rate,

then an increase. This is the same behavior noted in Tables III-VIII.

The data in Tables XXXI and XXXII are represented graphically in Plot VII.

The extrapolation of the data in Tables XXXI and XXXII in Plot VII shows the minimum coagulum volumes (maximum sedimentation rates) to occur at ~~an~~ "immediate" pH values of 6.8 and 6.9. This confirms the conjecture made from the observation of the colors of the samples.

It is desired to study the effect of dilution upon the coagulation of sulfur dye sols. In order to do this a dilute dye sol was prepared by the dilution of 25.00 ml. of the standard dye sol to one liter. To samples of this sol were added quickly varying amounts of sulfurous acid solution and the pH immediately attained was measured. The dilute dye sol is 2.5% of the concentration of the standard sulfur dye sol. The data obtained are given in Table XXXIII.

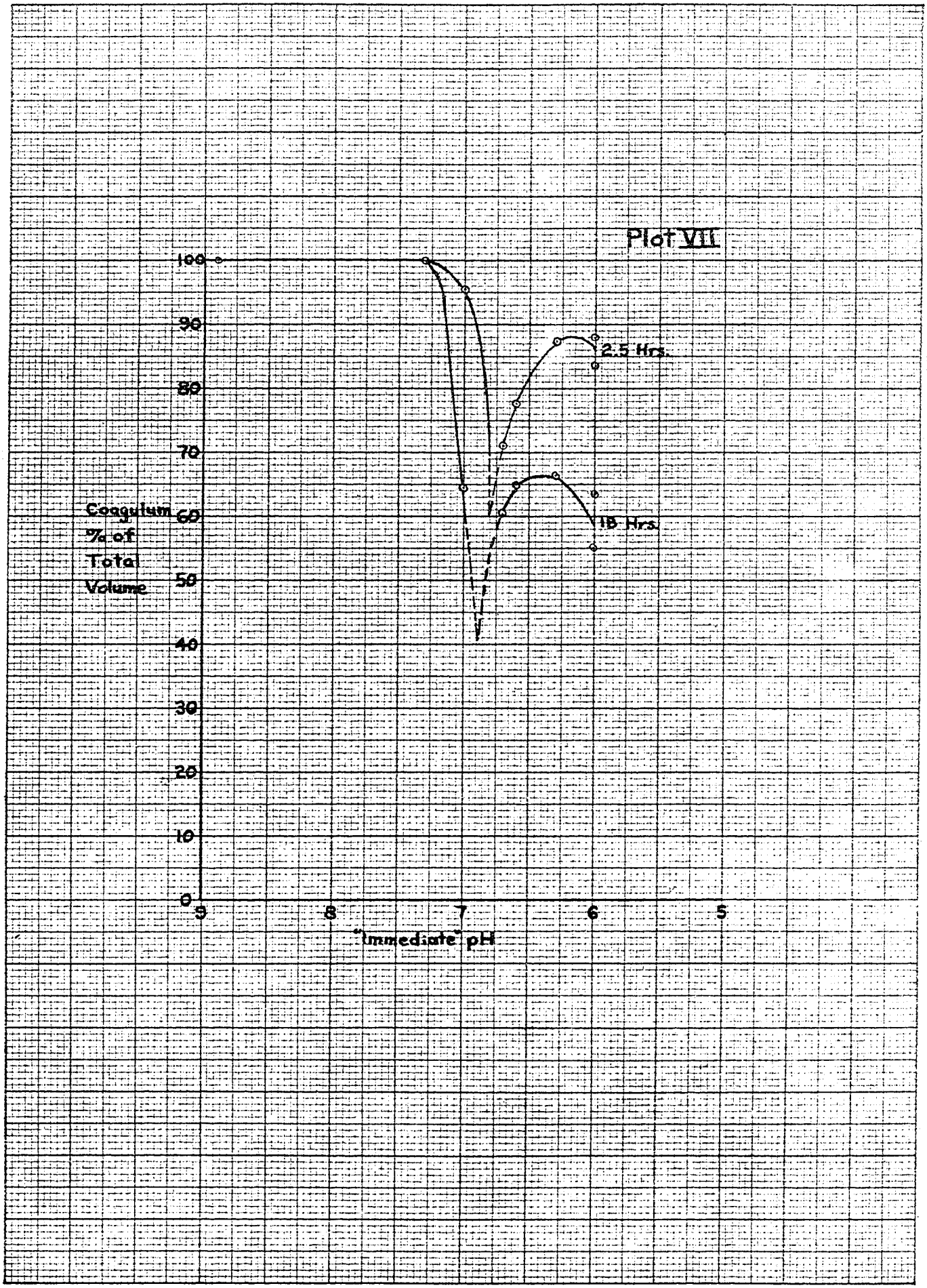


Table XXXIII

Coagulation of Dilute (2.5%) Sulfur Dye Sols

Experiment Number	Immediate pH	pH after Four Hours	Observations Immediate	Filtrate
43	2.49	3.47	large flocs	clear and colorless
44	2.53	3.39	large flocs	very faint blue tint
45	2.60	3.70	large flocs	very faint blue tint
46	2.65	3.65	large flocs	clear and colorless
47	2.90	- --	no flocs	----------
48	3.40	- --	no flocs	----------
49	4.40	3.19	large flocs	clear and colorless
50	6.03	- --	a few small flocs	----------

In no case above was complete sedimentation observed, although there was an increasing tendency to sedimentation with decreasing pH values.

The quantity of sulfurous acid required for the coagulation of the dilute (2.5%) sulfur dye sol was determined. At first a slow addition was attempted, but it was found that after adding sulfurous acid solution to a pH of 2.65, still no coagulation was observed. Again it is seen that the addition of the sulfurous acid should be rapid. Approximately 5 ml. of the sulfurous acid solution were added rapidly to

500 ml. of the dilute dye sol. A very coarse floc was almost immediately apparent, and the pH of the solution was 2.90 (it sank within perhaps a minute to 2.75). The amount of sulfurous acid solution used here corresponds to the use of 20 ml. for a 50 ml. sample of the standard dye sol. The volume of the sulfurous acid solution used in experiment 38, in which a maximum of coagulation was observed, was about 4 ml. This corresponds to a 500% increase in sulfurous acid consumption.

Although the floc settled quickly, there remained in the solution a considerable amount of "colloidal" sulfur. It was possible, however, to remove the floc and sulfur by filtration. It was further noted that the solution smelled of sulfur dioxide, whereas the most completely coagulated standard sulfur dye sol was odorless and nearly tasteless.

Approximately 4 ml. of sulfurous acid solution were added to another sample of the dilute sulfur dye sol. Large flocs were observed, and the pH sank within a few minutes to 2.80. Again the supernatant liquid was colored and contained colloidal sulfur. This corresponds to a 400% increase in the sulfurous acid consumption over that required for an equivalent standard sulfur dye sol.

Another dilution of Sulfur Black dye sol was

prepared by diluting 15 ml. of the standard dye sol to one liter. To this dilute (1.5%) sulfur dye sol were added varying amounts of sulfurous acid solution. The data are tabulated in Table XXXIV

Table XXXIV

Coagulation of Dilute (1.5%) Sulfur Dye Sols

Experiment Number	Immediate pH	Observations
51	2.27	small flocs
52	2.50	no flocs
53	2.60	no flocs
54	2.60	small flocs
55	2.67	no flocs
56	2.70	no flocs
57	2.70	very small flocs
58	2.87	small flocs
59-62	2.90-3.45	no flocs

The 1.1 ml. of sulfurous acid solution required for the 50 ml. of sample corresponds approximately to a sulfurous acid consumption of 73 ml. for experiment 38, or almost a twenty-fold increase.

Another dilute Sulfur Black dye sol was prepared by diluting 10 ml. of the standard sulfur dye sol to one liter. This made a sol 1% of the original con-

centration. One milliliter of the sulfurous acid solution brought the pH of 50 ml. of this dilute (1%) sulfur dye sol down to 2.40, but no flocs appeared.

From the above data it is apparent that the ease of coagulation of Sulfur Black dye sols by sulfurous acid solutions decreases with decreasing concentration of dye and sodium sulfide. In addition to the effect of the concentration of the sulfur dye sol itself, there is the effect of the increasing degree of ionization of the sulfurous acid with increasing dilution.

In order to study the coagulating effect of mixed sulfurous and sulfuric acids upon Sulfur Black dye sols, a sulfuric acid solution was prepared, and found to be 1.093 Molar by titration with a standardized sodium hydroxide solution using a pH meter to determine the end point. A 0.5000 Molar sodium sulfite solution was made up by weighing out the calculated amount of sodium sulfite.

One set of data was taken by adding varying amounts of the sodium sulfite solution to 49.92 ml. samples of the standard sulfur dye sol in 100 ml. graduates, followed by adding varying amounts of the sulfuric acid.

Another set of data was taken in which the sodium sulfite solution was mixed with the sulfuric acid before the addition of the mixture to the sulfur dye sol samples.

A third set of data was taken in which the sulfur dye was acidified, followed quickly by the addition of the sodium sulfite.

A close study of the data taken for the three different methods of mixing the reagents reveals no apparent difference. The three sets will be combined into a composite table. The arrangement will be made according to the total amount of sulfuric acid added.

Table XXXV

Mixed Acid Coagulation of Sulfur Dye Sols
Composite Table - Total Acid Correlation

Experiment Number	Mols H_2SO_4 Added / Mol Na_2S	Mols Na_2SO_3 Added / Mol Na_2S	Odor	Supernatant Liquid	Filtrate
63	0.407	0.372	None	No sedimentation	*
64	0.825	0.372	Slight H_2S	No sedimentation	*
65	0.879	0.804	*	No sedimentation	*
66	0.959	0.397	*	No sedimentation	Very dark blue
67	1.20	0.372	H_2S	Turbid, greenish blue	Very dark blue
68	1.24	0.745	H_2S	Turbid blue	*
69	1.25	1.12	H_2S	Turbid blue	*
70	1.31	2.01	H_2S	No sedimentation	*
71	1.33	2.01	H_2S	No sedimentation	*
72	1.34	0.397	H_2S	No dye, but S turbidity	Slight blue tint
73	1.35	0.804	H_2S	No dye, but S turbidity	Clear and Colorless

Table XXXV (Continued)

Experiment Number	Mols H_2SO_4 Added / Mol Na_2S	Mols Na_2SO_3 Added / Mol Na_2S	Odor	Supernatant Liquid	Filtrate
74	1.42	1.16	H_2S	Dark blue-black	*
75	1.53	0.397	H_2S	No dye, less turbid than 72	Clear and colorless
76	1.65	1.86	H_2S	No dye, but S turbidity	*
77	1.66	0.372	H_2S	No dye, but S turbidity	Clear and colorless
78	1.78	0.397	*	No dye, less turbid than 75	Clear and colorless
79	1.78	0.804	H_2S	Clear and colorless	Clear and colorless
80	1.85	1.51	H_2S	No dye, but S turbidity	*
81	1.98	2.01	H_2S	Clear and colorless	*
82	2.06	1.68	H_2S	Clear and colorless	*
83	2.34	0.804	H_2S	Colorless, but S turbidity	Clear and colorless
84	4.40	2.01	SO_2	Faint yellow tint	*
85	4.43	2.80	SO_2	Yellow	*
86	4.44	2.42	SO_2	Yellow tint	*
87	4.19	1.86	SO_2	Yellow tint	*
88	5.41	4.05	SO_2	Yellow	*

* Not recorded

Observation of the arrangement of the data shown in Table XXXV reveals that the data correlate best on a basis of the total acid (sulfuric plus sulfurous) used. The acid actually added was sulfuric, but in the presence of sodium sulfite is the equivalent of the total acid then present.

Note that in general total sulfur dye coagulation is found with mols acid to mols sodium sulfide ratios of greater than 1.35. The yellow color appears in the supernatant liquid where the sulfurous acid in the solution is detectable by its odor.

Previous work has indicated that the sulfurous acid to sodium sulfide ratio for the most complete coagulation of the sulfur dye sol should be 1.27. It is noted from Table XXXV that all samples except one having a total acid to sodium sulfide ratio greater than this value, and an excess of acid over sodium sulfite, show complete dye coagulation. Two samples having a slightly larger acid to sulfide ratio, 1.31 and 1.33, but an excess of sodium sulfite, did not coagulate. It is to be noted that the filtrates from these two samples had pH values of 9.82 and 9.28, respectively; whereas experiments 68 and 69, having smaller acid to sulfide ratios but better coagulation, had filtrates with pH values of 6.60 and 6.90.

Experiment 74, in which coagulation was not complete, had a considerably greater proportion of sulfurous acid for approximately the same total acid to sulfide ratio.

The conclusion to be drawn from the above is that for use of a minimum amount of total acid for the coagulation of a sulfur dye sol, a minimum proportion of sulfurous acid to sulfuric acid should be used. This is to be expected, for where sulfuric acid is present it serves as an acid only, and the hydrogen sulfide is driven from the solution; where sulfurous acid is present, it must react with the hydrogen sulfide as well as serve as an acid.

It is to be noted that with the use of mixed acids there frequently appears in the supernatant liquids a sulfur turbidity. This was not the case when the sulfur dye sols were coagulated by sulfurous acid alone. The intensity of this turbidity appears to diminish with increasing total acid to sulfide ratio for a constant sulfurous acid to sulfide ratio, and to diminish with increasing sulfurous acid to sulfide ratio for a constant total acid to sulfide ratio.

One of the major differences between the coagulation of the sulfur dye sols with sulfurous acid and with sulfuric acid-sulfurous acid mixtures is the appearance of considerable quantities of hydrogen sulfide

when the mixed acids are used. The odor of hydrogen sulfide was scarcely noticeable even at the instant of mixing the sulfurous acid with the sulfur dye sols, and disappeared entirely after a fraction of a minute had elapsed.

Notice that for a given amount of sodium sulfite solution, it is possible to have either hydrogen sulfide or sulfur dioxide evolved from the coagulated sample, depending upon the amount of sulfurous acid added (cf. experiments 81 and 84).

With regard to a correlation of the pH of the filtrates with color, it can be stated that all filtrates having a pH less than 5.5 are colorless (with regard to sulfur dye). At very low pH values a yellow color does appear.

For purposes of comparison, sulfuric acid was added to a sulfur dye sol to a pH of 2.81. Upon allowing sedimentation to occur, it was noted that the supernatant liquid was light blue in color and moderately turbid with colloidal sulfur. After approximately 15 hours the sample was filtered, and the pH of the filtrate found to be 4.29.

Tests have shown that sols of most other sulfur dyes besides Sulfur Black are coagulated by sulfurous acid solutions. Good results were obtained in coagulating sols of the following dyes: National Sulfur

Brown 2 G (Color Index No. 949), Sulfogen Brown (Du Pont), Sulfogen Bordeaux Brown (Du Pont), Sulphogen Yellow D (Du Pont, Color Index No. 948), Pyrogen Pure Blue 2 RL (Color Index No. 961), and Sulfogene Navy Blue (Du Pont).

The only dye which was not entirely successfully coagulated was National Sulfur Green T (Color Index No. 1006). Although a coagulum was produced, the supernatant liquid remained highly colored.

The incomplete coagulation of the Sulfur Green is believed to be a result of the presence of sulfonic acid groups in the molecule. These groups exert a solubilizing influence not found in the other dyes. The greater charge on the Sulfur Green micelle was demonstrated by cataphoretic velocity measurements.

The measured velocities in $\frac{\text{cm.}}{\text{sec. volt/cm.}}$ are as follows:

Sulfur Black $= 1.9 \times 10^{-5}$

Sulfur Yellow $= 2.0 \times 10^{-5}$

Sulfur Green $= 3.5 \times 10^{-5}$

It was found that indigo sols (in hydrosulfite solution) could be coagulated by the introduction of hydrogen sulfide into the strongly acidified sol. The reactions involved are

$$H_2S_2O_4 + H_2S \longrightarrow H_2S_2O_3 + H_2O + S$$

$$H_2S_2O_3 \longrightarrow SO_2 + H_2O + S$$

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

The mechanism of the coagulation here is not the same as with the sulfur dyes. The strongly acid condition causes the indigo sol to be positively charged, and it is coagulated by the negatively charged sulfur sol formed by the reactions.

Part II Summary and Conclusions

It has been discovered that almost all sulfur dye sols (in sodium sulfide solution) can be completely coagulated by the addition of sulfurous acid. Under proper conditions, no hydrogen sulfide is evolved.

The sulfurous acid reacts with the sodium sulfide substantially in accord with the equation

$$2Na_2S + 3H_2SO_3 \longrightarrow 2Na_2S_2O_3 + 3H_2O + S$$

A mutual coagulation occurs between the sulfur dye sol and the sulfur sol so produced. The coagulation is due, not to a mutual neutralization of electrical charge, but to a reaction between the hydrosulfide ions stabilizing the sulfur dye sol and the pentathionate ions stabilizing the sulfur sol according to the equation

$$HS_5O_6^- + 5SH^- \longrightarrow 10S + 6OH^-$$

Almost complete coagulation of a Sulfur Black dye sol occurs between sulfur dioxide to sodium sulfide ratios of 1.0 and 2.0, with complete coagulation occurring over a somewhat narrower range approximately between ratios of 1.1 and 1.7.

Best results were obtained when the sulfur dye sol and sulfurous acid solution were mixed instantaneously.

The reactions involved in the coagulation occur

over a period of time, rather than instantaneously. The future course of these reactions, with respect to ultimate degree of coagulation, can be predicted from the pH of the sulfur dye sol immediately after the sulfurous acid solution has been added. The most complete coagulation of a Sulfur Black sol was found to occur at an "immediate" pH of about 6.8. Small increases in "immediate" pH had a very deleterious effect upon the degree of coagulation, whereas small decreases had relatively little effect.

The dilution of a sulfur dye sol beyond a certain point was found to decrease the degree of coagulation which could be brought about. Up to this point, however, the principal effect of dilution was that a larger sulfur dioxide to sodium sulfide ratio was required for coagulation.

No hydrogen sulfide is evolved if sulfuric acid is added to a sulfur dye sol until the sodium hydroxide formed by the hydrolysis

$$Na_2S + H_2O \longrightarrow NaOH + NaSH$$

is neutralized. The subsequent addition of sulfurous acid solution causes the precipitation of a greater proportion of sulfur. If a mixture of sulfuric and sulfurous acid solutions is added to a sulfur dye sol, varying degrees of coagulation can be obtained, with

varying amounts of hydrogen sulfide evolution.

Indigo sols (in hydrosulfite solutions) may be coagulated by the addition of acid and hydrogen sulfide. The sulfur formed by the reactions

$$H_2S_2O_4 + H_2S \longrightarrow H_2S_2O_3 + H_2O + S$$

$$H_2S_2O_3 \longrightarrow SO_2 + H_2O + S$$

$$SO_2 + 2H_2S \longrightarrow H_2O + 3S$$

and the indigo sol coagulate by a mutual neutralization of electrical charge.

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PART III

THE MECHANISM OF THE COAGULATION OF SOLS AND SUSPENSIONS BY ALUMINUM HYDROXIDE

Part III Introduction

In studying the coagulation of dilute sulfur dye sols by aluminum hydroxide, the author discovered that the coagulation of the sol was dependent upon the direction of approach to the pH of flocculation.

Attempts to explain this led to the formulation of a new theory (supplemental to the present theory) of the aluminum hydroxide coagulation of suspensions.

The following investigation concerns itself with the refinement and proof of that theory.

Part III Theory

Colloids may be divided into two major classes, depending upon the relation between the colloidal particles (the dispersed phase) and the continuous phase. If there is little interaction between the particles and the continuous phase, the particles go into suspension only with relative difficulty, and when in suspension are easily coagulated. The sol is said to lyophobic. If there is a considerable interaction between the particles and the continuous phase, the particles show an affinity for the continuous phase and as a result go easily into suspension. Once in suspension, the particles are coagulated only with considerably more difficulty than in the case of the lyophobic colloids. The sol is said to be lyophilic.

The principle stabilizing factor of the lyophobic sols, and one of the two stabilizing factors of the lyophilic sols, is the electrical charge on the particle. The excellent discussion of the electrical nature of colloidal particles by Hartman (7) is summarized here.

The explanation of the charge on the colloidal particle is a composite of several facts associated with the chemical and physical equilibrium at the interface between two phases. The factors involved in the

explanation of the origin and nature of the charge on the granule (the colloidal particle without the outer layer of charges adjacent to the surface) are: (1) the charge inherent with the internal phase of certain colloidal systems as a result of the tendency for that phase to be transformed from the atomic to the ionic state, and (2) the establishment of a new charge or the modification of the existing charge on the internal phase as a result of adsorption.

According to Nernst (10), a solid possesses a tendency to pass from the atomic to the ionic state (pass into solution) when brought into contact with a liquid. This concept has met with considerable opposition, but it expresses, at least qualitatively, the charge acquired by the particle in contact with liquids. This tendency of the particle to go into solution results in the particle assuming a charge opposite in sign to that of the ion which is produced. The electrostatic forces thus formed will be sufficiently great to hold a layer of the ions to the surface of the particle. In addition to these electrostatic attractive forces which oppose the transformation of the solid into ions, the effect of the osmotic pressure is to cause the ions in solution to be deposited on the particle, thus further increasing the charge on the particle.

If, for a metal, the electrolytic solution tension effect is greater than the osmotic pressure effect plus the effect of electrostatic attractive forces, the inherent charge on the internal phase particle is negative. On the other hand, if the electrolytic solution tension effect is less than the osmotic pressure effect plus the effect of electrostatic attractive forces, the charge is positive. Analogous reasoning can be used for non-metals.

The view of Freundlich that the origin and nature of the electrostatic charge possessed by a colloidal particle is a result of adsorption has been supported and expanded by Bancroft (1). According to this view, colloidal particles in suspension may have the property of adsorbing ions of a definite charge. The sign of the charge will depend upon the selective adsorption properties of the suspended particles; it will be positive if cations are adsorbed to a greater extent than anions, and negative if the anions are selectively adsorbed.

In general, the hydroxyl ion is more strongly adsorbed than the hydrogen ion, as evidenced by the large number of rather inert substances (e.g., silver, gold, platinum, charcoal) possessing a negative charge in neutral solution (in which the hydroxyl and hydrogen

ion concentrations are equal).

There is no doubt that the adsorptive capacity possessed by the colloidal particles is a controlling factor in the establishment of the charge.

Helmholtz (8) suggested the existence of an electrical double layer adjacent to the surface of the colloidal particle. He considered the inner layer of charges to be immediately adjacent and fixed to the colloidal particle. He considered the outer layer of charges to be movable, opposite in sign to those of the inner layer, (such that the net charge is zero) and separated from them by a distance of the order of atomic dimensions. The modern modification of this concept (6,3,11) changes it to the extent that the outer layer is considered diffuse, with the concentration of the counter ions decreasing with increasing distance from the particle according to an exponential law.

The charge on a colloidal particle will be decreased by the adsorption of oppositely charged ions. Since the charge on the particle is the principal stabilizing factor in the lyophobic sols, its removal results in coagulation. This is brought about by a relatively small ionic concentration as compared with that necessary for the coagulation of lyophilic sols (which are also stabilized by solvation). The coagulating effects of

univalent, divalent, and trivalent ions are in the approximate ratios 1:100:1000.

The mutual coagulation observed upon mixing two oppositely charged hydrophobic sols is due to the mutual neutralization of electrical charge (9). It has been found (13) that maximum precipitation takes place on mixing electrically equivalent quantities of the sols (assuming no secondary process, such as the interaction of stabilizing ions).

Factors besides charge determining mutual precipitation are: (1) mutual adsorption of colloidal particles that is independent of charge, (2) the presence of precipitating ions as impurities and (3) interaction between stabilizing ions.

The best interpretation of the mechanism of the coagulation of suspensions by aluminum hydroxide which the writer has found in the literature is given by Dorr and Lasseter (4):

"The flocculation of dilute suspensions and others carrying relatively large individual particles is best accomplished by subjecting them to the enveloping action of a gel-like substance. This enveloping action supplements the attracting forces between partially or totally discharged particles and increases the probability of coalescence upon collision. Aluminum salts, so widely employed in practice, combine these factors. The

application of aluminum sulfate, for example, to the flocculation of suspensions is usually conducted within a pH range permitting the precipitation of aluminum hydroxide, but without regard to the isoelectric point of the suspended solids.

"Three functions are performed by the salt upon addition to a dispersed suspension: (1) the dissolved aluminum ions reduce the surface charges sufficiently to permit the flocculation of the particles; (2) the aluminum hydroxide precipitate formed may carry a positive potential and neutralize some of the negatively charged particles, resulting in mutual coagulation; (3) the gel-like precipitate envelops and cements the particles together in clumps. The first and third functions are the predominant factors controlling coalescence. Their relative importance probably depends respectively upon whether the particle charge is nearly completely destroyed or just reduced to a value permitting some coalescence upon contact. The adjustment of pH is necessarily a part of the first function.

"In general, the principles and practice involved in the flocculation of suspended particles by aluminum salts apply in the use of ferric salts."

The structure of the aluminum hydroxide gel formed in the cold is usually said to be amorphous (2), but

Weiser (12) does not believe this to be the case. He says that if it is amorphous when first formed, it goes to γ-$Al_2O_3.H_2O$ (boehmite) in a short time (as indicated by X-ray patterns).

Part III Procedure

The procedure followed in this investigation was very simple.

In all cases 50 ml. samples of the sols to be flocculated were used. Each sample was pipetted into a beaker, and the glass and calomel electrodes of a pH meter immersed therein. The sol was then made very acid (pH < 3.0) or very alkaline (pH > 11.0), as desired. (In the case of the sulfur dye sol the acid pH used was <4.0 and the alkaline pH >10.0). To this acid or alkaline sol was then added a measured amount of an aluminum sulfate solution. The sol was adjusted to a pH of 7, and the sample immediately poured into a 100 ml. graduate and set aside.

The aluminum sulfate solution was made up by weighing out 5.00 grams of $Al_2(SO_4)_3.18H_2O$, diluting to 500 ml., and acidifying with H_2SO_4 to prevent hydrolysis.

The aluminum sulfate solution was measured out by dropping from an eyedropper, calibrated to deliver 0.0419 ml. per drop. Smaller additions of less than one drop of the original solution were made by preparing new solutions by dilution.

Since the data are used comparatively, there is no point in converting the number of drops used into weight

or mols of aluminum ion used. Furthermore, the numbers of drops used will usually have the convenience of being small integers.

The dilute sulfur dye sol was prepared by the dilution to one liter of 10.00 ml. of a sulfur black dye sol 0.02679 molar in sodium sulfide and containing 5.000 grams of Sulfogen Carbon HCF grains (Du Pont) per liter.

A Pontacyl Green (Color Index No. 1102) sol was prepared by making 0.2567 grams of the dye up to one liter with distilled water.

The platinum sols used were prepared by the Bredig method; i.e., by striking a direct current arc between two platinum wires beneath the surface of distilled water in a beaker. The voltage was about 110 v., and the amperage about 4 amps.

Two types of sulfur sols were prepared. The first was a Selmi sol prepared by bubbling hydrogen sulfide gas into an excess of sulfurous acid solution. A portion of this was withdrawn for use, and the rest was "boiled" under vacuum to remove most of the excess sulfurous acid. The second was a Weimarn sol prepared by pipetting into almost a liter of water 10.00 ml. of 95% alcohol saturated with sulfur and making up to one liter with water. 0.0473 grams of Roccal were

weighed out and made up to 500 ml. with the Weimarn sulfur sol.

An Indian Blue sol was prepared by making 0.1954 grams of Indian Blue (Badische)(Color Index No. 1106) up to one liter with water (the Indian Blue spontaneously went into suspension).

The Roccal-containing Indian Blue suspension was prepared by making 0.0541 grams of Roccal up to 500 ml. with some of the above Indian Blue sol.

Part III Data and Results

The writer suggests that the mechanism of the flocculation of colloidal and suspended particles by aluminum hydroxide is dependent upon the interaction of six factors; namely,

(1) the sign of the charge on the particles,

(2) the magnitude of the charge on the particles,

(3) the extent of adsorption of the aluminum-containing ion by the particles,

(4) the nature of the aluminum-containing ion, especially with regard to the sign of the charge on the ion,

(5) the concentration of the aluminum-containing ion in the intermicellar fluid, and

(6) the specific adsorption of the particles by the aluminum hydroxide.

It is apparent that these factors are not entirely independent. If, for example, the concentration of the aluminum-containing ion is increased, the extent of adsorption of the ion is increased, the magnitude of charge on the particle is changed, and under proper conditions the sign of the charge is changed.

These factors determine the mechanism of the coagulation by determining the concentration of the aluminum-containing ion in the immediate neighborhood of the particle. These ions may be either held as adsorbed ions or as counter ions.

The counter ions are concentrated around the particle as a result of the electrostatic attraction of these ions to the oppositely charged adsorbed ions. The charge on the particle, then determines the composition of the counter layer (in a given ionic atmosphere). Specifically, a negatively charged particle will concentrate positive ions in its double layer. If the intermicellar fluid is acid, the aluminum-containing ion will be positive, and will be found in the double layer in a greater concentration than in the intermicellar fluid. An increase in the pH of the suspension will bring about the hydrolysis of the aluminum ion and the precipitation of aluminum hydroxide. Since the greatest concentration of the ion is to be found in the counter layer surrounding the particle, it is in this layer that the precipitation of the aluminum hydroxide will begin. The particle will then be coated with a layer of aluminum hydroxide. This coated particle will behave as a particle of aluminum hydroxide and will coalesce with others as aluminum hydroxide particles coalesce.

If the negatively charged particle is in a strongly alkaline solution, the aluminum-containing ion will be negative; and will be expelled from the counter layer. The greatest concentration of the aluminate ion will be found in the intermicellar fluid, and when hydrolysis

occurs upon the lowering of the pH of the suspension the precipitation of the aluminum hydroxide will occur in the intermicellar fluid. If the pH is below the isoelectric point of the aluminum hydroxide, the colloidal aluminum hydroxide precipitated will be positively charged and will mutually coagulate with the negative particles. If the pH of the suspension is such that the charge on the colloidal aluminum hydroxide particle is negative, no coagulation of the suspended particles is expected, except as a result of a specific absorption of the particle by the aluminum hydroxide (e.g., lake formation). This is of little importance, for Fricke and Keefer (5) have found that the isoelectric points of amorphous aluminum hydroxide and boehmite (γ-AlOOH) are pH values of 9.45 and 9.40 to 9.45 respectively. Flocculations are almost universally carried out at lower pH values.

Similarly, when the particle is positively charged, the aluminum-containing ion is to be found concentrated in the counter layer in alkaline solution, and expelled from the counter layer in acid solution. A decrease in the pH of the alkaline suspension will lead to the coating of the particle by aluminum hydroxide. If the flocculation is approached from the acid side, positively charged aluminum hydroxide will be formed. Coagulation

is not expected unless there is a specific adsorption of the particle by the aluminum hydroxide.

The aluminum-containing ion will be adsorbed by the particle to a greater or less extent. The principal effect of this adsorption follows as a result of the change in the charge of the particle.

As long as the adsorption does not change the sign of the charge, the mechanism will not be altered. If the adsorbed ion decreases the charge on the particle, it will to that extent decrease the concentration of its kind in the counter layer. Since, however, the adsorbed ion is itself subject to hydrolysis, the net effect of the adsorption on the flocculation of the particle will be small.

If the adsorption does change the sign of the charge on the particle, the mechanism will be altered. The ionic species adsorbed will then be expelled from the counter layer, and since its concentration will be greatest in the intermicellar fluid, precipitation of aluminum hydroxide will begin in the intermicellar fluid, and the mechanism will be that of the mutual coagulation of oppositely charged particles.

There exists the possibility that the adsorbed ions may hydrolyze to form a film of hydrous alumina over the surface of the particle. This condition is

probably seldom realized, for the concentration of the adsorbed ion on the surface of the particle must be great enough that the aluminum hydroxide molecules formed by the hydrolysis of the ions are close enough for water to be eliminated between adjacent molecules to form the hydrous alumina film.

All of the above discussion concerning the decrease in the charge on the particle and the change of the sign of the charge implies that the adsorbed ion and the original particle are oppositely charged. The adsorption of an ion of similar charge by the particle will not change the mechanism of the coagulation (that of mutual coagulation). Since the similar charges hinder the adsorption of the ion there is even less chance here than in the case of oppositely charged ions and particles that there will be a film of hydrous alumina formed about the particle by the hydrolysis of the adsorbed ions.

The evolution of the theory just discussed began with an investigation of the use of the aluminum hydroxide floc for the coagulation of dilute sulfur dye sols.

The results of the investigation may be summarized as follows:

When the acid Sulfur Black dye sol contained 3 or

more drops of the aluminum sulfate solution, a floc was immediately produced by the neutralization of the sol (to a pH of 7). When the sol contained 2 or less drops, no floc was produced.

When the alkaline Sulfur Black dye sol contained 13 or more drops of the aluminum sulfate solution, a floc was immediately produced by the neutralization of the sol (to a pH of 7). When the sol contained 12 or less drops, no floc was produced.

It is surprising to find that there is a four-fold increase in aluminum sulfate required for coagulation on neutralizing from the alkaline side as compared with that required for coagulation on neutralizing from the acid side. In this particular case, a part of the difference observed may be due to a difference in the lake-forming properties of the aluminum hydroxide, depending upon whether it was formed from alkaline or acid solution.

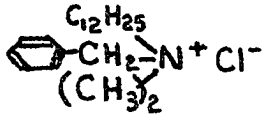
The first important point which must be established by further investigation is whether or not the observations made for the sulfur dye sol are general for all negative sols.

Only a small part of the data actually taken will be presented, for they are to a considerable extent repetitious.

The result of an investigation on a Pontacyl Green dye sol is as follows:

Experiment Number	$Al_2(SO_4)_3$ Solution, Drops	Side from which Coagulation Approached	Immediate Observation	Sedimentation Time, Hours	Observation after Sedimentation
1	10	Alkaline	Solution clear	4.0	Solution clear no flocs
2	10	Acid	Turbid, no flocs	4.0	Turbid, a few flocs settled
3	15	Alkaline	Turbid, no flocs	3.5	Completely settled
4	15	Acid	Flocs	3.5	Completely settled; supernatant liquid slightly lighter than in Expt. 3
5	30	Alkaline	Flocs	2.0	Completely settled
6	30	Acid	Flocs; settled more rapidly than those of Expt. 5	2.0	Completely settled; supernatant liquid slightly lighter than in Expt.5

The Pontacyl Green sol was clear. When shaken, it foamed indicating the presence of a dispersing agent. The negative charge on the floc particles was demonstrated by the coagulation of the sol by "Roccal", a cationic surface active agent having the formula



An examination of the preceeding table of data shows that the Pontacyl Green sol is best coagulated by approaching the pH of flocculation from the acid side.

The generality of the phenomenon observed in the coagulation of Sulfur Black and Pontacyl Green sols is further demonstrated by the following investigation on a Bredig platinum sol. The fact that the platinum sol is negatively charged is given in the literature, and was verified by Roccal coagulation.

Experiment Number	$Al_2(SO_4)_3$ Solution, Drops	Side from which Coagulation Approached	Immediate Observation	Sedimentation Time, Hours	Observation after Sedimentation
7	0.01	Alkaline	Flocs questionable	2.0	Practically no sediment
8	0.01	Acid	Flocs	2.5	A small amount of sediment
9	0.1	Alkaline	-----	1.0	No flocs
				1.5	Very fine flocs, no sediment
				3.0	Small flocs, but no sediment
				6.5	Almost no sediment
10	0.1	Acid	-----	1.0	Flocs
				1.5	Sedimentation present
				3.0	Flocs and sedimentation
				6.5	Considerable amounts of sediment
11	1.	Alkaline	No flocs apparent	0.25	No flocs settled out
				1.25	No flocs settled out

Experiment Number	$Al_2(SO_4)_3$ Solution, Drops	Side from which Coagulation Approached	Immediate Observation	Sedimentation Time, Hours	Observation after Sedimentation
12	1.	Acid	Flocs	1.0	Some sedimentation
				1.5	Some sedimentation
13	2.	Alkaline	Flocs	0.25	No flocs settled out
				1.25	Only a small amount of flocs settled out
14	2.	Acid	Flocs	1.0	Some sedimentation
				2.0	Sedimentation largely complete

Similar results were obtained in investigations of a sulfur sol prepared by the action of hydrogen sulfide on a sulfurous acid solution, an indigo sol prepared by the dilution and oxidation of a leuco-indigo suspension, and an Indian Blue sol. All of these sols are known to be negatively charged. (Negative charges are reported in the literature for the sulfur sol (7) and for indigo sol (14). The Indian Blue sol was coagulated by Roccal.)

From the preceeding results it may be regarded as established that, in general, a negatively charged particle is best coagulated by aluminum hydroxide when the pH of flocculation is approached from the acid side.

The second important point which must be established is whether or not positively charged particles are best coagulated by approaching the pH of flocculation from the alkaline side.

This proof presented one of the greatest difficulties of the investigation. The difficulty arises because the hydroxyl ion has a greater affinity for surfaces than has the hydrogen ion. The result is that most hydrophobic particles are negative in neutral solution. The aluminate ion, which must exist in the presence of the positively charged particle in order to fulfill

the conditions necessary to test the theory, is stable only in strongly alkaline solution. In strongly alkaline solution the tendency for the particle to be negative is almost overwhelming.

The quest for a pure substance which would form a positively charged hydrophobic colloid in strongly alkaline solution was unsuccessful. It was found possible, however, to force a positive charge on the hydrophobic particles by using the cationic surface active agent Roccal.

Typical data obtained for the positive sulfur sol so formed is as follows

Experiment Number	$Al_2(SO_4)_3$ Solution, Drops	Side from which Coagulation Approached	Immediate Observation	Sedimentation Time, Hours	Observation after Sedimentation
15	5	Acid	------	1.0	Flocs settling out
				1.5	Flocs settling out
16	5	Alkaline	------	1.0	Flocs larger than in Expt. 15
				1.5	Flocs considerably larger than in Expt. 15
17	7	Acid	Very small flocs	1.0	Flocs settling out
				1.5	Flocs settling out
18	7	Alkaline	A considerably heavier floc than in Expt. 17	1.0	Flocs larger than in Expt. 17, and more are settled
				1.5	Flocs considerably larger than in Expt. 17

In taking data on the coagulation of dyes positively charged by Roccal, there was a complicating factor in that the dyes were coagulated into small flocs by the Roccal. Platinum sols were also coagulated by Roccal. It was found, however, by pouring the dye slowly into the Roccal-containing solution, the effect could be minimized. Data taken in this way for the positive Indian Blue sol confirmed the results obtained for the positive sulfur sol.

From the preceeding results it may be regarded as established that a positively charged particle is best coagulated by aluminum hydroxide when the pH of flocculation is approached from the alkaline side.

The generality of the results using negative sols, and the confirmation of the predicted behavior of the positive sols are strong evidence for the acceptance of the proposed theory. In order to clinch the proof, it was shown that the individual particles, when the pH of 7 was approached from the proper direction, actually were coated with aluminum hydroxide.

This was done by using a sulfur sol prepared by bubbling hydrogen sulfide gas into an excess of sulfurous acid solution. When the sol was made neutral, the excess sulfurous acid was converted into sodium sulfite. This should react with the colloidal sulfur present according

to the equation

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

This was found to be the case when the pH of 7 was approached from either direction. The observed phenomenon was, of course, the disappearance of the sulfur turbidity.

If, however, a small amount of aluminum sulfate solution be added, there is a difference in the behavior of the sulfur sol (negatively charged). When the sol is made neutral from the alkaline side, the sulfur turbidity disappears within an hour, just as it does when no aluminum sulfate has been added. When another sample of the sol containing the same amount of aluminum sulfate is made neutral from the acid side, there is no apparent decrease in turbidity after an hour. When the sample stands overnight, the sulfur still does not dissolve, but settles to the bottom.

The only apparent explanation of the above observations is that the aluminum hydroxide has indeed in the one case completely coated each sulfur particle, protecting it from attack by the sodium sulfite; and in the other case has not coated any of the particles.

Part III Summary and Conclusions

The mechanism of the coagulation of a charged particle by aluminum hydroxide flocculation is determined by the charge on the particle and the charge on the aluminum-containing ion.

If the charges on the particle and on the ion are opposite, the ion will occur in greater concentration in the counter layer of the particle than in the intermicellar fluid, and hydrolysis of the ion will coat the particle with aluminum hydroxide.

If the charges on the particle and on the ion are the same, the ion will be expelled from the counter layer of the particle, and hydrolysis of the ion will cause the precipitation of aluminum hydroxide in the intermicellar fluid. If this aluminum hydroxide has a charge opposite to that of the particle, mutual coagulation will occur.

Part III Bibliography

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