CCCCVIII.—*Colloidal Sulphur.*

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Experiments referred to in an earlier paper (J., 1927, 1445) indicated that polythionic acids higher than pentathionic might exist. Further study showed that we were actually dealing with solutions containing colloidal sulphur, and this led us to undertake an investigation of this interesting substance. Where we use the term "micelle" in the present communication we mean the negatively charged complex aggregate without the compensating positive ions.

Preparation.—Following Debus (J., 1888, **53**, 278), Odén (*Z.*

Chem. Ind. Koll., 1911, **8**, 186) prepared colloidal sulphur from Wackenroder's solution. Raffo (*ibid.*, 1908, **2**, 354) had prepared it from thiosulphate by the action of sulphuric acid, and Svedberg (*ibid.*, 1909, **4**, 49) from the same sources. " These sols are often called Odén's sols " (Freundlich, " New Conceptions in Colloidal Chemistry," Methuen, 1926, p. 88) in contradistinction to Weimarn's sol (prepared by pouring an alcoholic solution of sulphur into water). We have followed Svedberg's method but have been able to make several useful minor alterations (Expt. A). The distribution of sulphur throughout the process, with other experimental details, is given under Expt. B with Table I, and the results of analysis appear under Expt. C in Table II.

Nature of Stabilising Ion.—Freundlich and Scholz (*Koll.-Chem. Beih.*, 1922, **16**, 234) were the first to suggest that sulphur sols, prepared by the above method, probably owed their stability to the presence of pentathionic acid. They acted on their sols with alkali and estimated the thiosulphate produced iodometrically. Assuming the reaction, $2Na_2S_5O_6 + 6NaOH = 5Na_2S_2O_3 + 3H_2O$, they recorded from 0·47 to 0·67 millimols. of pentathionate per g. of sulphur in their several sols.

The question of the existence of hexathionates arises. Debus (*loc. cit.*, pp. 301—309) claimed to have prepared potassium hexathionate. Weitz and Achterberg (*Ber.*, 1928, **61**, 399) have recently published another method for its preparation. We have followed this method and have satisfied ourselves that it does yield a product containing $K_2S_6O_6$, apparently to the extent of 34% (Expt. D). Partington and Tipler (J., 1929, 1382) found that potassium hexathionate could be obtained in a pure state by this method only when the original thiosulphate had been prepared by Foerster and Mommsen's method (*Ber.*, 1924, **57**, 258), *viz.*, by the interaction of potassium hydrogen sulphide and potassium hydrogen sulphite; otherwise, their products contained less hexathionate than did our specimen obtained from commercial potassium thiosulphate.

Our reason for regarding our specimen as containing hexathionate, and not a mixture of pentathionate with colloidal sulphur, was that the crystals dissolved to form a clear liquid from which no sulphur could be precipitated by addition of concentrated potassium nitrate, whereas 0·06*N*-potassium nitrate was sufficiently concentrated to throw out all colloidal sulphur from our sols.

It seemed likely that, if hexathionates and, possibly, higher polythionates exist, the stabilising ions of the sulphur sols would consist of these rather than of pentathionate. One might expect conditions in the micelle to be particularly favourable for the formation of the highest possible polythionate.

We have studied the action of alkalis on the sols with some care to see whether this point could be decided. We assume that the reaction with alkali can be represented by the equation

$$2Na_2S_{(5+n)}O_6 + 6NaOH = 5Na_2S_2O_3 + 3H_2O + 2nS.$$

It is likely that the sulphur so liberated would be far more reactive than the bulk of the micellar sulphur so that its products of hydrolysis would be formed rapidly enough to be measured along with the thiosulphate. On alkaline hydrolysis, sulphur gives rise to polysulphide and thiosulphate, *via* sulphide and sulphite (Bassett and Durrant, *loc. cit.*, p. 1403). If atmospheric oxidation can occur, the polysulphide might be completely converted into thiosulphate (possibly thus: $Na_2S_2 + 3O = Na_2S_2O_3$), for, whatever the precise mechanism of such oxidation, it occurs readily enough (*idem, ibid.*, p. 1420). Our experimental results (Expts. E.ii and E.iii) show that, although mainly thiosulphate is formed, yet there is, at the same time, a proportion of sulphite and, presumably, sulphide.

At the commencement of the action of alkali there is a very rapid formation of thiosulphate owing to the decomposition of the free and bound polythionate. At the end of the experiments formation of thiosulphate (or of a mixture of this with sulphide and sulphite) is proceeding at a very slow but fairly steady rate owing to hydrolysis of the precipitated sulphur. Complete destruction of the sol and precipitation of ordinary sulphur corresponds more or less to the end of the period of rapid thiosulphate formation, but it is not easy to determine the exact point. The rate at which the stabilising polythionate is decomposed is remarkable. It takes place far more rapidly (Expt. E.i) than does the action of alkali on an aqueous solution of pure potassium tetrathionate (Expt. F). Our results for the rate at which tetrathionate is decomposed agree reasonably well with those of Kurtenacker and Kaufmann (*Z. anorg. Chem.*, 1925, **148**, 369). According to these authors, alkali acts on pentathionate and tetrathionate at about the same rate.

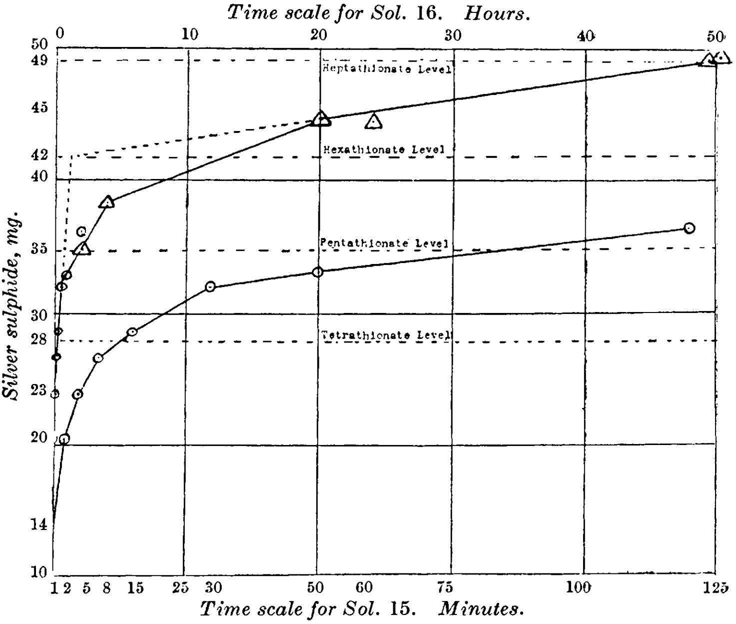
This striking difference suggests that the colloidal sulphur has a marked catalytic effect on the hydrolysis of the polythionate. It seems probable that the " bound " polythionate is hydrolysed much more rapidly than the " free." Although about two-thirds of the total polythionate in the sols used was free, it would be constantly passing into the bound condition owing to the reversible addition to the micelle considered on p. 2925, so that we can assume that the initial rapid production of thiosulphate in the hydrolysis of the sols by alkali is all due to decomposition of " bound " polythionate. On certain assumptions, velocity coefficients can be calculated for the reaction between alkali and sulphur sols which.

on the whole, support the view that the polythionate present in the sols is hexathionate rather than pentathionate. The details are discussed in Expts. E.i and E.ii.

Owing to the very great difference in the rates of hydrolysis of the polythionate and of the precipitated sulphur, it seems justifiable to assume that all production of thiosulphate during the first hour in Expts. E.i and E.ii was due to polythionate, and all which occurred after the first 10 hours was due to the precipitated sulphur

FIG. 1.

△ = *Expts. with Sol.* 16.



⊙ = *Expts. on minute-scale.* ⊙ = *Expts. on hour-scale.*

14 *Mg. of silver sulphide would be produced without treatment with alkali.*

The two portions of the curve of hydrolysis (Fig. 1) from 0 to 1 hour and above 10 hours are approximately straight lines, which, when produced, cut at a level which corresponds to hexathionate, *i.e.*, at a point corresponding to the weight of silver sulphide which could have been obtained if all the polythionate in the sol was hexathionate and if all of it had been converted into thiosulphate in the manner already considered (p. 2921). Although such a procedure is perhaps less convincing than one might wish, the indications it gives make it very probable that the "bound" polythionate in the sulphur sols is essentially hexathionate. It may be that it is hydrolysed so rapidly just because it is hexathionate, but such a view is not supported by the fact that pentathionate and tetrathionate are hydrolysed by alkali at very similar rates (Kurtenacker and Kaufmann, *loc. cit.*).

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

For this reason we think that hexathionate is probably the highest polythionate capable of existence in spite of the views we have previously expressed as to the possible existence of even octathionates (Bassett and Durrant, *loc. cit.*, p. 1445). In the preparation of hexathionate it would appear to be necessary to avoid the presence of colloidal sulphur as far as possible on account of its above-mentioned disruptive action. Even the pentathionate becomes very unstable so soon as the sulphur micelles have been coagulated, and the free polythionate in the filtrates from the sulphur coagulations was never higher than tetrathionate (Expt. G). In all probability this is partly due to the instability of pentathionate in neutral or very faintly acid solution. Under more acid conditions pentathionate might well survive as in the filtrate referred to in Expt. I and in the original " acid filtrates " of Expt. B, Table I.

When a sulphur sol is treated with moderately concentrated sodium hydroxide solution, the formation of an ordinary sodium gel occurs, and the polythionate contained in this appears to be protected from conversion into thiosulphate. This behaviour occurs much less readily with lithium hydroxide (Expt. E.iii).

The phenomena observed when concentrated sulphuric acid acts upon sodium thiosulphate had led us to suppose that polythionic acids even as high as octathionic might be formed (Expt. H). We have found, however, that we were actually dealing with solutions containing a high proportion of the known polythionic acids with a small proportion of colloidal sulphur rendered insensitive to coagulation by the high acidity of the solutions (Expt. I).

The Way in which Colloidal Sulphur originates.—We conclude from the experiments quoted under H and I that in cold concentrated sulphuric acid, thiosulphuric acid is partly converted into polythionic acids.

Polythionates higher than tetra- tend to dissociate rapidly and unless some cause prevented it the sulphur lost would separate in mass. The cause we believe to be coalescence of the molecules at this stage, when the concentration is high, due to mutual attraction of the sulphur atoms in the molecules of polythionic acids and a tendency for crystalline sulphur to be formed. Thus, micelles are formed with an inner nucleus of sulphur partly crystalline in character. The arrangement of sulphur atoms is still partly irregular, however, and on the irregular portions of the micelle polythionate ions still remain attached and impart a negative charge. The rest of the polythionate is rejected when polymerisation occurs, mainly as pentathionate if the aqueous medium is sufficiently acid, otherwise as tetrathionate. The polythionate remaining attached appears to be hexathionate.

Ageing of the Sulphur Sols.—In a freshly prepared sulphur sol all the polythionate is in the " bound " condition and attached to the micelles. This was first proved on the small scale by recurding a sol with sodium nitrate, dissolving the curd in water, then curding the new sol immediately with potassium nitrate and testing the filtrate with silver nitrate. No trace of silver sulphide appeared. Sol 18 (200 c.c.) was prepared on these lines, after 11 days had been allowed to elapse for the less stable larger micelles to separate. The test was made a few hours later with the result as tabulated. Here the ratio of " bound " to " free " was 20 to 1; after 159 days it was 59 to 50. This gradual change from bound to free polythionate anion is illustrated by the whole table and is accompanied by a deposition of sulphur which is proportional. This was proved directly by filtering Sol 18 after 159 days and weighing the dried sulphur deposit. These sulphur deposits, after being washed, have been examined repeatedly; they dissolve immediately in carbon disulphide and may be boiled with acidified silver nitrate without showing a trace of silver sulphide. This sulphur, therefore, is non-colloidal. The true curds obtained by coagulating sulphur sols are not soluble in carbon disulphide. The presence of colloidal sulphur seems to have a marked stabilising effect on the polythionate even though it is " free " and unattached to the micelle. The total polythionate in these sols remains practically unchanged for months, though in absence of the colloidal sulphur all the polythionates decompose relatively quickly in aqueous solution (Foerster and Hornig, *Z. anorg. Chem.*, 1922, **125**, 119; Kurtenacker and Kaufmann, *ibid.*, 1925, **148**, 43; Bassett and Durrant, *loc. cit.*, pp. 1421, 1444).

Some important conclusions may be drawn from this. In the normal hydrolysis of pentathionates, tetra- and tri-thionate appear to some extent as intermediate stages. Did degradation to trithionate occur in the sulphur sols, further hydrolysis would inevitably occur to give some sulphate in the practically neutral solution, and gradual disappearance of the polythionate would follow. The fact that this does not happen (see Expt. C, action of barium salt, Sol 17 after 86 days) seems to show conclusively that the polythionate is automatically kept graded up at least to the penta-condition (compare Bassett and Durrant, *loc. cit.*, p. 1432). Such a grading up of the polythionate by the colloidal sulphur could only be effective in resisting decomposition if it were associated with a rapid and continuous interchange between the "free" and the "bound" polythionate due to the existence of a definite equilibrium between the two. That such equilibria occur in sols is well known (Pauli and Valkó, "Elektrochemie der Kolloide," Wien, 1929, p. 103), but it will be hardly possible in many cases to fix the position of equilibrium with any nicety because the whole system is in an essentially unstable condition and is slowly changing. For instance, in the present case, when a sulphur sol is coagulated only the "bound" polythionate goes into the coagulum: the sol obtained by solution (peptisation) of the latter in water will not be in equilibrium so far as its polythionate condition is concerned and some of the "bound" polythionate gradually becomes "free."

A condition of stable equilibrium is not reached, however, because of another change which can be regarded as irreversible, and is one which probably affects the surface of the micelle. 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 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 sulphur particles of the sol have only an imperfect crystal lattice initially.

Attachment of 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 "bound" polythionate, a few atoms of sulphur are each time removed. This helps to "smooth down" the irregularities of the sulphur surface until finally a sulphur particle with completely crystalline structure is obtained, with consequent separation of the particle in the solid state as non-colloidal, crystalline sulphur 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 sulphur 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 sulphur micelle. This deposition of sulphur by the "free" polythionate probably occurs partly on the already crystalline portion of the surface of the sulphur micelles, partly on the crystalline sulphur which has already settled out from the solution, and partly on the non-crystalline areas of the colloidal sulphur particles which are thereby "smoothed down" and made crystalline by accretion instead of by corrosion.

The process proceeds steadily until eventually the whole of the colloidal sulphur would become non-colloidal and crystalline and all the polythionate would become free. (Table II shows that with Sol 15 about two-thirds had become "free" after 100 days, and that with Sol 18 about one-half had become "free" after 159 days; also that the "operating" polythionate of Sol 15 was more than twice as concentrated as that of Sol 18.)

Some time before this point is reached hydrolytic decomposition of the polythionate will become marked, for there will not be sufficient colloidal sulphur present to keep it all graded up (see Expt. I). Throughout its life history, the surface of the particles in the sulphur sol will be kept saturated with polythionate ions in the sense that all the positions where they can become attached will be kept occupied except for the very short intervals of time when positions are vacated owing to the change "bound" polythionate $\rightleftarrows$ "free" polythionate. That the sol particles really are saturated with polythionate seems to be proved by the fact that, if a solution of tetrathionate is added, none of it is carried down in the coagulum. Thus in three cases we mixed equal volumes of Sol 12 with twice as much tetrathionate as the sol contained of polythionate, and then coagulated it by sodium or potassium nitrate. Then we made an analysis for total polythionate carried down by the curd, and obtained 7·9, 8·2, and 8·4 mg. of silver sulphide. In three parallel experiments, with *no* tetrathionate added, we obtained 9·0, 8·5, and 8·3 mg.

In the above way the polythionate plays a very important part in catalysing the change from colloidal to non-colloidal, crystalline sulphur which is of some interest in view of the fact that it also provides a stabilising ion which alone enables the sulphur to exist in the colloidal condition.

This mechanism would not necessarily find a counterpart in other sols, for it depends upon the very peculiar constitution and character of the polythionates. The stability of sulphur sols, prepared as above, is very considerable at ordinary temperatures. Sulphur, soluble in carbon disulphide, separates in moderate amounts soon after the sol has been prepared, but the rate at which the deposition occurs falls off very rapidly (Expt. J). The fresh sol contains particles or micelles of very varying size and containing varying proportions of stabilising polythionate. The proportion of large particles which contain little polythionate is relatively small, and it is these which separate in the early stages. Once they have been eliminated, the further separation of sulphur, though continuous, occurs much more slowly.

It is certain that the separation of ordinary sulphur from the sol is a secondary consequence of the elimination of polythionate from the micelle, and that the latter is not a secondary consequence of the coagulation of the sulphur from some other cause. This is shown by the fact that if a sol is coagulated by an electrolyte immediately after its preparation, no polythionate passes into the filtrate but all is retained in the coagulum (Expt. K). The longer the interval of time which elapses between the formation of the sol and its coagulation, the more polythionate is formed in the filtrate. The polythionate in the filtrate is a measure of the "free" or uncombined polythionate.

It is well known (Pauli and Valkó, *op. cit.*, p. 103) that in most, and probably all, sols there is a definite equilibrium between the stabilising ion of the micelle and the same ion in the free condition. This equilibrium is disturbed by dialysis. In few, if any, cases does the relationship between the free and the bound stabilising ion appear to have been examined hitherto.

Coagulation of the Sulphur Sols by Electrolytes.

It is commonly recognised that the stability of colloidal solutions is determined by the presence of either positive or negative charges upon the particles, and that these charges are due to adsorbed or combined ions—the so-called stabilising ions. Linder and Picton (J., 1895, **67**, 63) (see also Pauli and Valkó, *op. cit.*, p. 180) were the first to give a chemical explanation of the coagulation of sols by electrolytes, and to show that the coagulum carried down that ion of the added electrolyte which was of opposite sign to that carried by the sol particles. The view that colloid coagulation was in this sense very similar to the precipitation of ordinary "insoluble" salts was strongly supported by Duclaux (*J. Chim. physique*, 1907, **5**, 29; 1909, **7**, 405), and during recent years much important work in support of it has been carried out by Pauli and his co-workers (see *op. cit.* for summary). In spite of this, the important part played by the stabilising ion has been almost completely ignored in a very large proportion of the work which has been done on the precipitation of colloids. It is exceptional for the nature of the stabilising ion to be even mentioned, and still less frequently is its amount determined, although the whole quantitative behaviour of sols depends upon this ion. It has become customary to deal with colloidal problems from an almost exclusively physical standpoint—in terms of potential—the more definitely chemical aspects having been largely ignored. It seems likely that the discordant and even contradictory results, sometimes obtained by different investigators in this field, would often be found to be due to differences in the nature or amount of the stabilising ions, had these been determined and recorded.

We have studied the stoicheiometry of the coagulation of sulphur sols by electrolytes in some detail. For work of this nature it is clearly advisable to use sols containing micelles with a relatively high proportion of stabilising ion, since otherwise the quantities one has to estimate are so small that experimental errors become serious. Sols which have been highly " purified " by dialysis contain, as a rule, only a very small proportion of stabilising ion, and are, in consequence, very sensitive to coagulation and quite unsuitable for the purpose we had in view.

The term " coagulating value " as used by Freundlich (*op. cit.*, p. 42) represents the concentration of the coagulating salt in millimols. per litre which is required to cause rapid coagulation. This is referred to as a γ value to distinguish it from the concentration required to produce slow coagulation. We felt sceptical about some of the γ values recorded for sulphur sols by Freundlich and Scholz (*loc. cit.*) and by Freundlich (*op. cit.*, p. 89). Their figures and ours are given side by side [Table VII, Expt. L]; it will be seen that their γ values for barium, calcium, magnesium, and zinc salts are practically identical (1·5 or 1·6), whereas we find Ba = 1·25; Ca = 2·5; Mg = 14; Zn = 24. It may be that our experiments would be called " slow coagulation." In nearly every case the values are those which caused the gel to fall and leave a clear supernatant liquid in 10 minutes. Nevertheless, our values for the five alkali metals are of the same order as those of Freundlich and Scholz, which appear to have been recorded after from 5 to 7·5 seconds.

We conclude from these results, and also from our experiments with thorium hydroxide sols, that there is no sharp distinction between rapid and slow coagulation. Desai (*Koll.-Chem. Beih.*, 1928, **26**, 357) also came to the same conclusion in his work on thorium hydroxide. Coagulation appears to be connected with, at least partial, neutralisation of the colloid particles. In the opinion of some, complete neutralisation is not necessary (see Pennycuick, J., 1930, 1456), but our experiments appear to indicate that it is.

For an electrolyte to be able to cause this neutralisation and coagulation, the ion of opposite sign to the micelle must be capable of forming with the micelle a salt (or, more generally, a product) which is insoluble in the surrounding liquid medium under the prevailing conditions. For this reason, those ions which normally form "insoluble" salts with the stabilising ion of the micelle are usually the most efficient coagulants for that particular sol. But the product formed by the coagulating ion and the micelle is probably always much more insoluble than the product formed by the union of the coagulating ion with the simple stabilising ion of the micelle, and for this reason many ions will coagulate a sol which would not, under similar conditions, give a precipitate with the stabilising ion alone.

We have been able to illustrate this in the case of thorium hydroxide sols and to correlate the solubility of simple thorium salts, basic salts, and the sol-coagulum produced by the corresponding anions. We cannot do so with sulphur sols because the solubility of very few metallic pentathionates (and of no hexathionates) has been determined (see Mellor, "Inorganic and Theoretical Chemistry," Vol. 10, pp. 621—629).

Thus the greater insolubility of most basic salts and of many salts of complex acids as compared with the normal salts of the simple acids is perfectly analogous to the greater insolubility of the sol-coagula. The gel formed by coagulation of a sol by an electrolyte may be looked upon as a special case of a very basic salt or of a salt of a very complicated acid. (In some cases, where coagulation is due to hydrogen ions, the gel *is* a very complex acid.)

Ions, such as sodium, which usually give soluble salts are not generally such efficient coagulants for negative sols as other positive ions such as potassium, barium, or thorium, which form less soluble salts (Expt. M.i). The precipitation of simple electrolytes is governed by the law of mass action, which enables the qualitative and, in many cases, the quantitative behaviour of many compounds to be predicted. It seems certain that the same or a similar law applies to the electrolytic coagulation of colloidal solutions. Qualitatively it evidently does, and it is found that with weaker sols or with weaker coagulating solutions relatively greater excesses of the coagulating electrolyte have to be used to cause coagulation (Expts. M. ii and iii). Any attempt to apply the law of mass action quantitatively to the precipitation of colloidal solutions is difficult, if not impossible, partly owing to the uncertainty as to how to express the active mass of the micelle. There are two other reasons, however. One is that the transition between complete precipitation and no precipitation is very sudden in the case of a sol, although it is quite gradual in the case of ordinary precipitations which involve only simple ions. This makes it difficult to obtain partial precipitation of a sol; for example, although addition of barium ion equivalent to the polythionate ion of the micelle may precipitate a sulphur sol completely, one-half or three-quarters of that amount may produce no coagulum. This peculiar difference between the two classes of precipitation appears to be connected with the fact that each micelle of the sol carries a large number of stabilising ions. On addition of a coagulating electrolyte, in amount insufficient for complete coagulation, one does not get complete neutralisation and consequent precipitation of an equivalent proportion of the sol micelles, but all the micelles become partly neutralised. Thus all the micelles remain charged to some extent—practically up to the point where the full amount of electrolyte required for complete coagulation has been added—and for this reason little, if any, precipitation occurs.

The partially discharged micelles may, however, coalesce to produce larger particles still in suspension (see last two results, Expt. O). In sulphur sols we have very heterogeneous micelles (Expt. N).

Since all the micelles in a sol tend to be discharged at a similar rate, coagulation, brought about by the addition of electrolytes, would be absolutely sharp and sudden in the case of a sol in which all the micelles were of the same size and carried the same number of charges. With a very heterogeneous sol, however, it seems clear that this will no longer be quite true, and micelles with the larger mass/charge ratio will tend to be completely discharged and coagulated before the others, so that coagulation will tend to occur gradually. The more heterogeneous the sol the greater the range over which coagulation will take place, although this range will probably be small in all cases. With a given sol, the range appears to be greater the more concentrated the sol, so that in practice partial coagulation can only be satisfactorily achieved with concentrated sols. The second reason why quantitative application of the law of mass action to colloidal precipitation is difficult, is that secondary changes seem to occur in the coagulum after it has been formed which are irreversible or, more probably, only slowly reversible. That such must be the case is shown, for instance, by the fact that, whereas a very considerable excess of potassium ion is needed to precipitate a sulphur sol, the coagulum which is produced only redissolves very slowly and with difficulty in cold water (Expt. M. iii). There are strong indications that these secondary changes are connected with the elimination of combined water from the coagulum, for they are found to be less marked with coagula produced by ions such as sodium, magnesium, nickel, cobalt, iron, and copper, which have a strong tendency to remain hydrated, and these coagula readily redissolve in cold water; still more rapidly do those produced by lithium nitrate or by mineral acids. Freundlich (*op. cit.*, p. 75) remarks that " hydration in hydrophilic sols plays a rôle similar to hydration in true solutions." This is true, and in our view the amount of hydration is directly connected with the coagulant ion, and thus sulphur sols (Odén's) are " hydrophilic " simply because they happen to be sodium salts rather than because they contain pentathionic acid, which is Freundlich's view (*op. cit.*, p. 89).

The secondary changes may set in before complete neutralisation of the micelles has occurred, and may be partly responsible for the coarsening of the micelles and the increased turbidity of the sols produced by electrolyte additions which are insufficient to cause actual coagulation. They may also enable complete coagulation to occur after a long time from mixtures which are too dilute to allow of immediate curding (Expt. R).

In the reaction-velocity experiments (Expt. D) the active mass of the micelle was taken as proportional to that of the stabilising ion regarded as evenly distributed throughout the sol, and there seems to be some justification for this.

In examining the question as to whether a " solubility product " can be calculated for the gels obtained from colloidal sulphur, we have proceeded similarly, using the molar concentration of the bound polythionate. Both with barium and with potassium gels we have obtained a remarkable approximation to constancy of the expressions $[Ba^{\cdot\cdot}][S_xO_6'']$ and $[K^{\cdot}]^2[S_xO_6'']$, respectively, using the value of the barium and potassium concentrations which caused coagulations reasonably soon. These values are very difficult to determine with any consistency and accuracy, owing very largely, we consider, to the different rate at which the secondary dehydration or other processes occur in sols of different strength. It is noteworthy that, since the precipitation of many substances, such as silver chloride—and, possibly, of most—passes through a colloidal phase, and is eventually the coagulation of a sol, it would be rather remarkable if a solubility-product law did not apply to this stage if it applies to the precipitation as a whole.

Sulphur sols are made less sensitive to coagulation by other electrolytes in a remarkable way by acids, and to a less extent by sodium salts (Expt. O). Such a marked protective action of hydrogen ions on a negative sol appears to be very unusual. It seems to us that this " antagonistic action " can be explained in a similar way to that offered above for the suddenness with which practically complete coagulation of a sol occurs.

In spite of much work on the problem of solubility, we still have to accept the solubility of any substance as being more or less a specific property, although some general empirical rules can be applied to groups of compounds. Acids are frequently much more soluble than their sodium salts, which, in turn, are more soluble than salts of most other metals. Again, with increase of concentration, something happens to the ions of an electrolyte which is variously ascribed to formation of un-ionised molecules or to decrease of activity. In this kind of way the polyvalent micelles of the sulphur sol, if in presence of hydrogen or sodium ions, become extensively occupied by these, so that coagulation of the sols by other ions forming less soluble products is largely prevented.

The antagonistic action of the hydrogen, lithium, or sodium ions is due to the fact that micellar salts are formed which are largely acid, lithium, or sodium salts and only partly salts of the other precipitating kation under test. They have the greater specific solubility characteristic of acids or of lithium or sodium salts, and so are much less readily precipitated. Hydrogen, lithium, or sodium ions, in sufficiently high concentration, can, however, themselves cause coagulation.

Freundlich and Scholz (*loc. cit.*) consider that the antagonistic action is connected with hydration effects, but in what way they could not say. Odén (" Der Kolloide Schwefel," *Nova Acta Upsala*, 1912, IV, **3**, 66; see Pauli and Valko, *op. cit.*, p. 195) and others assume that adsorption of the contra-ion is the cause of the antagonistic action. The assumption of any such adsorption seems to us unnecessary to account for ordinary ion-antagonism of the kind referred to above. Occasionally we have tested for it in washed gels of sulphur, but with negative results (Expt. P). The anions of the coagulating electrolytes are not present in the coagula. There are other types of interference, however, where it does seem necessary to assume it, and especially in the case of the coagulation of sulphur sols by thorium nitrate. In very low or in high concentrations, thorium nitrate is an effective coagulant for colloidal sulphur, though at intermediate concentrations it has no action (Expt. Q). This is most easily accounted for by supposing that the insoluble thorium–sulphur–polythionate product, which is formed by low concentrations of thorium nitrate, takes up additional thorium ions when larger amounts are added, so that a much higher thorium nitrate concentration is required to enable the nitrate ion to precipitate the much more soluble nitrate of the new complex so produced. This complex might be regarded as a double salt

$$2[S_xS_6O_6]'' + Th^{\cdot\cdot\cdot\cdot} \longrightarrow \{[S_xS_6O_6]_2Th\} \xrightarrow{Th^{\cdot\cdot\cdot\cdot}}$$

$$\{[S_xS_6O_6]_2Th\}Th^{\cdot\cdot\cdot\cdot} \xrightarrow{4NO_3'} \{[S_xS_6O_6]_2Th\}Th(NO_3)_4.$$

Thorium nitrate is the only salt which we have observed to behave in this way towards sulphur sols. This case would correspond to the two types of silver chloride sol $[(AgCl)_xCl]'$ and $[(AgCl)_xAg]^{\bullet}$ and the known double salts $[AgCl_2]Na$ and $[Ag_2I]NO_3$. Behaviour analogous to that of thorium nitrate is well known in the precipitation of sols by multivalent ions (see, *e.g.*, Ostwald, " Practical Colloid Chemistry," 4th ed., p. 146).

Coagulation of Sulphur Sols by Positive Ions in Amount Equivalent to the Stabilising Polythionate Ion.—Since the stabilising ion of the sulphur sols is a polythionate, and since the metallic polythionates are as a rule moderately soluble, the amount of electrolyte necessary for coagulation is generally greater than that equivalent to the polythionate of the micelle. We have, however, obtained complete coagulation with barium, neodymium, and thorium salts added in amount equivalent to this " bound " polythionate. There is a minimum sol concentration below which an excess of barium salt, at any rate, is required, and at very low sol concentrations we have shown that thorium nitrate, in equivalent concentration, causes coagulation to proceed very slowly. Whether excess of coagulant is required or only an amount equivalent to the stabilising ion, the sulphur coagulum always contains an equivalent amount of the precipitating positive ion (experiments illustrating this are given under Expt. R).

EXPERIMENTAL.

Experiment A (*Theory, p.* 2920).

Preparation of Sulphur Sols.—A solution of 83·6 g. of sodium thiosulphate crystals in 50 c.c. of water is slowly added to 65·5 c.c. of concentrated sulphuric acid, the temperature being kept below 25°. (This need not take more than ½ hour.) After addition of 50 c.c. of water, the beaker containing the mixture is placed into a previously heated water-bath, and the temperature of the mixture raised to 85°. In about ¼ hour practically all the sulphur dioxide has been driven off and the yellow mixture is almost clear, only a very small amount of solid non-colloidal sulphur being present.

It is unnecessary to filter at this stage; nearly all the non-colloidal sulphur can be removed by decantation before cooling. It is very important not to heat the mixture above about 90°, and not to prolong the heating in the bath; otherwise, the bulk of the sulphur separates in the non-colloidal state. This is due to hydrolytic decomposition of the stabilising polythionate in the hot acid solution.

The yellow solution deposits practically all its colloidal sulphur on cooling to room temperature, and after standing for 3 hours this is collected on a Buchner funnel. This we find more satisfactory than centrifuging. The first filtration removes the bulk of the sulphate and acid. The sulphur is next dissolved in cold water and reprecipitated by an electrolyte in amount sufficient to cause curding. For this purpose we used $5N$-sodium nitrate, since chloride would have interfered with our subsequent analyses. When large volumes of liquid are used, two precipitations with sodium nitrate and two more Buchner filtrations are sufficient to remove all sulphate, but sols so prepared contain a small amount of sodium nitrate derived from the mother-liquor retained by the last curd. This can be almost entirely avoided in the following way, which we actually applied to the case of sol 9*a*.

After the second precipitation with sodium nitrate, the curd is separated and dissolved in a small amount of water, and about one-fifth of the solution so obtained is retained. The other four-fifths are curded with sodium nitrate, and the curd is collected, washed with the remaining fifth of the sulphur solution, and dissolved in water.

Experiment B (*Theory, p.* 2920).

Distribution of Sulphur during the Preparation of Sols 14, 15, *and* 17.—Each sol was prepared from 83·6 g. of crystalline sodium thiosulphate and should contain 21·56 g. of sulphur. No attempt has been made to include sulphur escaping as dioxide, whether formed by the primary reaction $H_2S_2O_3 \longrightarrow H_2SO_3 + S$ or by oxidation brought about by the hot, concentrated sulphuric acid. The values of $r = [S_1]/[S_3O_6'']$ (molar ratio) found for the *acid filtrates* are in parentheses.

Notes on Experiment B.—The weights of sulphur deposits are approximate; all other weights, and also the other volumes in Table I, are fairly accurate.

The sulphur deposits were usually obtained in two portions, (*a*) that decanted from the original solution after digestion on the water-bath, and (*b*) that filtered from the final sol when the last sodium curd was dissolved in water.

By analysis, the acid filtrate for Sol 17 gave normalities : $H = 8{\cdot}33$, $SO_4 = 12{\cdot}4$, Na (by diff.) $= 4{\cdot}07$, and the value of r, after 2 days, $= 1{\cdot}45$. The acid filtrate for Sol 14 gave $r = 2{\cdot}03$ immediately, and 1·51 after 5 months; Sol 15 gave $r = 1{\cdot}62$ after 15 hours and 1·07 after 20 days. All these acid filtrates slowly deposited sulphur, partly colloidal, and the high r values are due to a small content of colloidal sulphur. When the original acid solutions are cooled, most of the pentathionic acid remains in the acid filtrate and most of the colloidal sulphur is left in the curd which separates.

TABLE I.

	Original acid filtrate.	Filtrates from successive curds. Produced by sodium nitrate.			The sol itself.	Sulphur deposited in the operations.
Sol No. 14.						
Volume	110 c.c.	225 c.c.	265 c.c.	190 c.c.	200 c.c.	
Solution containing						
S	0·497 g.	0·092 g.	0·042 g.	0·027 g.	1·556 g.	
S as S_3O_6	0·747 ,,	0·005 ,,	0·007 ,,	0·002 ,,	0·028 ,,	
Total S	1·244 ,,	0·097 ,,	0·049 ,,	0·029 ,,	1·584 ,,	6·95 g.
		(r = 2·03.) Grand total = 9·960 g.				
Sol No. 15.						
Volume	182 c.c.	500 c.c.	270 c.c.		200 c.c.	
Solution containing						
S	0·592 g.	1·994 g.	0·214 g.		4·530 g.	
S as S_3O_6	1·127 ,,	0·290 ,,	0·011 ,,		0·317 ,,	
Total S	1·719 ,,	2·284 ,,	0·225 ,,		4·847 ,,	3·52 g.
		(r = 1·62.) Grand total = 12·59 g.				
Sol No. 17.						
Volume	200 c.c.	370 c.c.	200 c.c.		200 c.c.	
Solution containing						
S	0·86 g.	0·659 g.	0·099 g.		3·928 g.	
S as S_3O_6	1·76 ,,	0·081 ,,	0·026 ,,		0·302 ,,	
Total S	2·62 ,,	0·740 ,,	0·125 ,,		4·230 ,,	3·20 g.
		(r = 1·45.) Grand total = 10·52 g.*				

* A small amount of "Sol 17. *b*" was made containing sulphur not here shown.

The weights of silver sulphide found correspond with polythionate here expressed as S_3O_6''.

It being assumed that the Buchner funnel retained 2 c.c. of liquor, then calculation from the volumes of curd filtrates for Sol 17 indicates that the acidity of this sol was $8·33 \times 2 \times 2/370 \times 200 = 0·0004N$, the normality of the "acid filtrate" being $8·33N$. The other sols were less acid.

Experiment C (*Theory, p.* 2920).

Analyses of Sulphur Sols.—Table II gives the analyses of the numerous sulphur sols we have prepared, with references to the experiments made with the sols. All of the sols were analysed as soon as they reached a fairly stable condition, and most of them were re-analysed at intervals (sulphur separates out rather rapidly for the first two days).

From the figures in the column "ρ," an empirical formula for the average micelle can be deduced which will alter according to the age of the sol (also quoted). Thus for Sol 8 after 45 days the formula, if S_3O_6'' is the stabiliser, would be $Na_2S_3O_6,80S$, whereas if S_5O_6'' is the stabiliser it would be $Na_2S_5O_6,78S$, etc. The method of arriving at the ρ values was to coagulate the sol by potassium nitrate, then to determine the polythionate in the filtrate and the potassium in the coagulum. These should agree with the *total* polythionate deduced from the weight of silver sulphide produced when the sol is boiled with acidified silver nitrate.

For example, taking the analysis of Sol 17 after 86 days: 5 c.c. of sol yielded 0·0192 g. of silver sulphide, and another 5 c.c. yielded 0·0063 g. of potassium sulphate from the potassium curd, which is equivalent to 0·0090 g. of silver sulphide. The filtrate from the potassium curd yielded 0·0102 g. of silver sulphide. Here the agreement was exact. In the same analysis the filtrate from the 0·0192 g. of silver sulphide yielded 0·0354 g. of barium sulphate, and calculation shows that this corresponds to 0·0192 × 2 g. of silver sulphide (2 mols. of $BaSO_4$ for each mol. of Ag_2S as required). This result with a sol which was 86 days old is important, because it shows that ageing does not cause the polythionate to decompose with formation of sulphate. Inspection of the table makes it evident that very little decomposition of any sort occurs. The only changes of importance are the separation of polythionate from the micelles into the surrounding medium and the slow deposition of sulphur—both changes become slower and slower with advancing age and (see p. 2924) doubtless are interdependent.

One method of analysis, with silver nitrate, was described in our previous paper (*loc. cit.*, p. 1451). The use of a weighed filter paper is not, however, necessary, for after detachment of the bulk of the dried precipitate of silver sulphide and sulphur, which is then heated in the ignition tube as described, the small quantity remaining on the paper is burnt with it and weighed as metallic silver. For accurate work this procedure is preferable.

We have only used the weighed paper method for determining weights of sulphur, *e.g.*, the sulphur deposits in Table I.

It is very important to acidify silver nitrate before boiling it with the sols. We acidified it with nitric acid so that the concentration of acid was not less than $0{\cdot}13N$ and not more than $0{\cdot}2N$ in the mixture. Below $0{\cdot}13N$, sulphur reacts slowly with silver nitrate, and above it, nitric acid oxidises silver sulphide after prolonged boiling. Five minutes' boiling, with intermediate acid concentration, is sufficient to complete the conversion of silver polythionates and also of silver thiosulphate into silver sulphide and sulphuric acid.

The subsequent treatment (before drying and weighing) is to wash well with water, then with cold dilute aqueous ammonia, and finally with hot water. This removes all traces of adsorbed sulphuric acid.

TABLE II.

Composition of Colloidal Sulphur Sols.

(The last column in the table indicates the experiments in which the several sols are specifically referred to. The same sols and also the first six sols were also used in numerous other experiments of which no detailed account has been given.)

Sol. No.	Mg. from 10 c.c. of sol, Ag$_2$S.	S.	Molecular ratios, S$_1$/total S_3O_6'' = r.	S$_1$/micellar S_3O_6'' = ρ.	Milli-equivs. per litre of polythionate as S_3O_6''. Total.	Bound.	Free.	Age of sol, days.	Used in Expts.
1	22·2	149·0	52·3		17·9			1	
1	22·6	150·0	51·5		18·2			1	
2	13·4	97·2	56·2		10·8			1	
2	13·0	96·9	57·6		10·5			1	
2	12·9	88·1	52·9		10·4			22	
3	3·1	36·9	92·2		2·5			1	
4	9·8	62·0	49·6		7·9			1	
5	13·1	50·8	30·0		10·6			8	
6	17·4	103·8	46·3		14·0			2	
6	17·0	100·8	45·9		13·7			10	
7	26·2	145·4	43·0		21·1			2	L
8	21·8	116·0	41·2	80·2	17·6	9·0	8·6	45	O, P
9a	17·8	88·2	38·4	69·7	14·3	7·9	6·4	2	M, R
9b	23·6	96·0	31·5		19·0			2	M
9b	21·6	73·8	26·5	55·0	17·4	8·4	9·0	26	
10	20·8	112·6	41·7		16·8			3	G, J, N, R
10	19·6	102·4	40·5		15·8			11	
10	18·7	93·2	38·9		15·1			82	
10	19·0	92·0	37·5	84·8	15·3	6·8	8·5	102	
11a	15·5	108·5	54·2		12·5			3	N, R
11a	16·5	108·7	51·1	90·6	13·3	7·5	5·8	6	
11b	24·0	129·8	41·9		19·3			16	
12	21·8	147·0	52·5		17·6			3	K
12	22·0	128·6	45·1	93·1	17·8	8·6	9·2	8	
12	22·4	130·8	45·2		18·0			17	
13	20·2	104·9	40·2	64·0	16·3	10·2	6·1	12	M, R
13	20·2	107·4	41·2	63·5	16·3	10·3	6·0	26	
13	21·4	114·6	41·5	76·5	17·2	9·3	7·9	32	
14	5·5	77·8	109·5		4·4			11	B
14	6·3	84·4	102·9	155·7	5·1	3·4	1·7	33	
15	41·0	226·5	42·8	60·5	33·0	23·4	9·6	6	B, E, I, R
15	41·0	194·2	36·7		33·0			57	
15	42·0	198·2	36·6	63·5	33·8	19·5	14·3	65	
15	39·6	165·6	32·5	90·5	31·9	11·4	20·5	100	
16	12·9	54·8	32·9		10·4			124	E
16	14·0	53·6	29·2		11·4			134	
16	13·6	57·5	32·7		10·9			144	
17	39·0	196·4	39·2	55·9	31·4	21·9	9·5	2	B, C, R
17	38·8	176·6	37·2	52·6	31·3	21·0	10·3	10	
17	38·4	147·0	29·7	63·3	31·0	14·5	16·5	86	
18	15·6	146·0	72·5	76·4	12·6	12·0	0·6	< 1	E, J, K, P, R
18	16·0	151·2	73·5	88·8	12·9	10·6	2·3	10	
18	13·5	128·4	73·7	136·3	10·9	5·9	5·9	159	

Experiment D (*Theory, p.* 2920).

Confirmation of the Existence of Hexathionate.—We followed Weitz and Achterberg's method (*loc. cit.*) in every particular and obtained crystals of which 31·4% was potassium chloride, 5·6% water, and the rest a mixture, giving the following results on treatment with silver nitrate:

	Wt. of mixture, mg.	Ag_2S, mg.	S, mg.	*r*.
i	107·4	47·6	15·2	2·46
ii	162·1	80·3	25·0	2·51
iii	140·9	60·9	20·1	2·56

If we take $r = 2{\cdot}50$, the mixture, excluding potassium chloride, contained 50% of penta- and 50% of hexa-thionate. There was no indication of turbidity in the crystals or in the solution. When the latter was mixed with potassium nitrate, there was no sign of any precipitate, although the concentration of potassium nitrate was higher than that which had always curded colloidal sulphur.

Experiment E.i (*Theory, pp.* 2921, 2922).

Nature of Stabilising Polythionate.—Rapid action of alkali on Sol 15 at 22°; 20 c.c. of 0·05*N*-sodium hydroxide acting on 2 c.c. of Sol 15. Results summarised in Table III. Col. 1 gives the time in minutes for which the alkali acted. Col. 2 gives the weight of silver sulphide obtained. Col. 3 gives the percentage conversion to thiosulphate on the assumption that pentathionate is the stabilising polythionate, and that it reacts with alkali according to the equation $2Na_2S_5O_6 + 6NaOH = 5Na_2S_2O_3 + 3H_2O$. Col. 5 gives the percentage conversion to thiosulphate on the assumption that hexathionate is the stabilising polythionate, and that the reaction with alkali follows the course $2Na_2S_6O_6 + 8NaOH + O_2 = 6Na_2S_2O_3 + 4H_2O$, which indicates some atmospheric oxidation occurring at the same time as the hydrolysis.

In col. 4 are given the coefficients calculated for a bimolecular reaction from the figures in col. 3, the formula used being $k = 1/t \,.\, x/a(a - x)$, where $a = 100$.

In cols. 6 and 7 are given coefficients calculated from the figures in col. 5 for a bi- and a ter-molecular reaction respectively, again taking $a = 100$, and using the expression $k = 1/t.\ x(2a - x)/2a^2(a - x)^2$ in calculating the third-order constant. In making these calculations we assume (1) that the alkali concentration remains constant throughout the reaction, and (2) that the concentration of the polythionate is inversely proportional to the volume of the solution in spite of the fact that a large proportion of it is concentrated on the micelles. The figures show that *k* calculated for a bimolecular reaction on the pentathionate basis is reasonably constant, whilst k calculated on the hexathionate basis for a termolecular reaction also approximates to a constant. We attach especial significance to this last result in view of the fact that a third-order constant was obtained for the action of alkali on tetrathionate (Experiment F). Without attempting to explain the full meaning of these figures, it does seem to us that, if tetrathionate gives a third-order constant, it is more likely that polythionates higher than tetra- would give a third-order constant rather than a second. We conclude, therefore, that the behaviour with alkali indicates that the polythionate of the colloidal sulphur micelles is hexathionate rather than pentathionate although, of course, the proof is not absolute.

TABLE III.

1. Time, t (mins.).	2. Ag_2S, mg.	3. % Conversion for $S_5O_6''=x$.	4. 2nd order for S_5O_6'', $k \times 10^4$.	5. % Conversion for $S_6O_6''=x$.	6. 2nd order for S_6O_6'', $k \times 10^4$.	7. 3rd order for S_6O_6'', $k \times 10^6$.
1	11·5	29·1	41·0	21·9	28·9	31·96
2	11·7	30·8	22·3	23·1	14·8	17·28
4	13·6	46·6	21·8	35·0	13·6	17·08
8	15·4	61·7	20·1	46·2	10·7	15·34
15	16·3	69·2	15·0	51·9	7·2	11·08
30	18·4	86·6	21·9	65·0	6·2	11·93
50	19·2	93·3	25·8	70·0	4·7	10·11
120	20·9			80·7	3·5	10·77
360	21·8			86·2	1·7	7·16

Initial normalities : $OH' = 0{\cdot}045N$; polythionate $= 0{\cdot}003N$.

Limiting weight of Ag_2S = 20 mg. on the basis of pentathionate, and 24 mg. on the basis of hexathionate. The original polythionate before the action of alkali gave 8 mg. of Ag_2S. The percentage conversion is readily calculated from the figures given in col. 2 of Table III. This experiment was carried out when Sol 15 was over 100 days old (see Table II) and when the free polythionate was practically two-thirds of the total polythionate. As stated on p. 2921, it is considered that the reaction with alkali occurs when the polythionate is in the bound condition.

Experiment E.ii (*Theory, pp.* 2921, 2922).

The experiments summarised in Table IV were made in order to examine the nature of the products formed after long-continued action of alkali on the sulphur sol. A fresh sol had to be used since none of Sol 15 remained. The reaction, except during the first few hours, was essentially hydrolysis of the sulphur separated from the micelle owing to destruction of the polythionate by the alkali in the first stage of the experiment. Sulphate was estimated in the filtrate from the silver sulphide and, as the table shows, the ratio $Ag_2S/BaSO_4$ was very close to unity, which would correspond to formation of nothing but thiosulphate during the reaction. This appears to show that practically complete oxidation of the products of hydrolysis had occurred: $S_2 + 2NaOH + O_2 = Na_2S_2O_3 + H_2O$. It must, however, be mentioned that in Expt. E.ii the silver sulphide was not examined for the possible presence of free silver due to the presence of unaltered sulphite in the alkaline solutions. In Expt. E.iii, such examination was made, and a small proportion of silver was found. It is thus likely that the silver sulphide of Expt. E.ii may have also contained a little free silver, but the excellent agreement between the total sulphur of col. 8 and that calculated from the composition of the sol suggests that there was very little.

TABLE IV.

Action of 50 *c.c. of* 0·05N-NaOH *on* 10 *c.c. of Sol* 16 *at* 22°.

	Ag_2S, g.	$BaSO_4$, g.	Sulphur, in Ag_2S, g.	Sulphur, in $BaSO_4$, g.	Sulphur, free, g.	Sulphur, total, g.	Ratio $Ag_2S/BaSO_4$. Found.	Ratio $Ag_2S/BaSO_4$. Calc.	Temp.
Sol analysis	0·0136	0·0258	0·0017	0·0035	0·0536	0·0588	1 : 2	1 : 2	
Period with NaOH, hrs.									
2	0·0335	0·0359	0·0044	0·0049	0·0494	0·0587	1 : 1·11	1 : 1	19°
4	0·0377	0·0389	0·0048	0·0053	0·0485	0·0586	1 : 1·10	1 : 1	21
20	0·0443	0·0431	0·0057	0·0059	0·0472	0·0588	1 : 1·04	1 : 1	21
24	0·0444	0·0467	0·0058	0·0064	0·0467	0·0589	1 : 1·10	1 : 1	22
49¼	0·0485	0·0495	0·0063	0·0068	0·0459	0·0590	1 : 1·08	1 : 1	21
50½	0·0495	0·0510	0·0064	0·0066	0·0458	0·0588	1 : 1·03	1 : 1	22

In Fig. 1 the results of Experiments E.i and E.ii have been plotted on a common scale, mg. of silver sulphide produced by 10 c.c. of sol being plotted against time. Since Sol 15 contained 31·9 milli-equivs. of polythionate per litre, and Sol 16 only 10·9, the weights of silver sulphide obtained in the Sol 15 experiments (in which only 2 c.c. of sol were used) have been multiplied by 5 × 10·9/31·9 to bring them into line with the Sol 16 experiments. Some of Experiments E.ii were carried out at temperatures differing somewhat from 22°. In order to plot the results in Fig. 1, the weight of silver sulphide was increased or decreased by 1·9% for each degree below or above 22° as the result of a special experiment to determine the influence of temperature.

Experiment E.iii (*Theory, pp.* 2921, 2923).

The results shown in Table V illustrate the effect of much stronger alkali on sulphur sols. We included lithium hydroxide in the investigation so as to be sure that no coagulation of the sol had occurred before actual destruction of the polythionate. With sodium hydroxide solutions above about 0·1*N*, the curding effect can be seen, and curding probably occurs in the latter stages of the action if the sodium hydroxide has a greater concentration than 0·05*N*. If such curding occurs, polythionate may remain protected in the gel. This is probably the reason why 0·182*N*-sodium hydroxide acts at about the same rate as 0·091*N*.

Lithium hydroxide shows no sign of curding at any stage up to 0·18*N*, and for this reason causes more hydrolysis than does sodium hydroxide in the same time. The difference between the (Ag_2S + Ag) obtained in Experiment 3 with sodium hydroxide and Experiment 2 with lithia is 107 — 76 = 31 mg., whilst the bound hexathionate contained in 5 c.c. of Sol 18 could yield after conversion to thiosulphate 23 mg. of silver sulphide. This suggests that with the strong sodium hydroxide practically all the polythionate had remained unacted upon in the curd, and that the hydroxide had been simply slowly hydrolysing the sulphur of a gel; whereas the lithium hydroxide had first acted upon the hexathionate and then been slowly acting upon ordinary sulphur, not a gel.

These experiments with Sol 18 were carried out when hardly any of the polythionate was in the free condition, and were started soon after the first analysis shown in Table II.

Slow action of alkali on the sulphur in 5 *c.c. of Sol* 18 *following the rapid action on* S_6O_6''. (*Total volume after mixing,* 55 *c.c.*)

TABLE V.

				Sulphur,					
Conc., milli-equivs. per l.	Ag_2S, mg.	Ag,* mg.	$BaSO_4$, mg.	in Ag_2S, mg.	in $BaSO_4$, mg.	free, mg.	total, mg.	Period, hrs.	Temp.
1 NaOH, 45·5	71·2	19·6	84·4	9·2	11·6	53·2	74·0	184	17°
2 ,, 91	59·2	8·5	69·7	7·6	9·5			161	17
3 ,, 182	59·8	16·3	72·3	7·7	9·9	51·5	69·1	137	17
1 LiOH, 45·5	79·3	9·7	88·5	10·2	12·2	50·8	73·2	184	17
2 ,, 182	87·0	20·5	99·0	11·2	13·6	49·0	73·8	113	17
3 ,, 182	140·0	19·1	170·0	18·1	23·4	32·8	74·3	216	16
Analysis, no alkali	7·8		13·8	1·0	1·9	73·0	75·9		

* The proportions of silver sulphide and silver present were determined by heating a weighed amount with sulphur and noting the increase in weight.

In the last experiment with lithia, 55% of the sulphur, other than polythionate sulphur, had been converted in 216 hours, as compared with 50% conversion of the polythionate sulphur in 15 minutes in Experiment E.i. This is justification for treating the initial rapid reaction and the final slow reaction with alkali as though independent, and extrapolating the corresponding portions of the curve until they cut in the manner considered on p. 2922.

Experiment F (*Theory, p.* 2921).

Slow Action of Alkali on Tetrathionate.—We prepared a pure specimen of potassium tetrathionate. The reaction with alkali can be written $2K_2S_4O_6 + 6NaOH = 3Na_2S_2O_3 + 2K_2SO_3 + 3H_2O$, and with silver nitrate we get a mixture, $3Ag_2S + 2Ag_2$. With concentrations after mixing: $NaOH = 0{\cdot}16N$, $K_2S_4O_6 = 0{\cdot}02N$, at $t = 18°$, we obtained 118·4 mg. of mixture after 28 hours, and 129·9 mg. after 88 hours. The maximum being 147·0, and the weight in absence of alkali being 62·0 mg., we could calculate percentage change to be 66 for 28 hours and 80 for 88 hours. With $a = 100$, we found $k = 1{\cdot}36 \times 10^{-5}$ *for each result* if the action is of the third order.

Now, substituting $1{\cdot}36 \times 10^{-5}$ for k in the third-order equation we found 50% conversion should take 6 hours almost exactly. Actually we left the action for 6½ hours and obtained 105·9 mg. of the mixture (= 51% conversion), in agreement with theory. Next, we repeated the experiment with the same tetrathionate concentration and final sodium hydroxide concentration of $0{\cdot}32N$ (instead of $0{\cdot}16N$). We acidified the mixture to stop the action precisely after 1 hr. 37 mins. (exactly one-quarter of 6 hrs. 30 mins.) and obtained 105·8 mg. of the mixture. Thus the action behaves as though of second order with respect to alkali. Since 50% conversion took 6 hrs. here and only 15 mins. with the hexathionate in Sol 15, this rate was 24 times as slow as the other.

Experiment G (*Theory, p.* 2923).

Filtrates from Coagulations of Sulphur Sols.—These filtrates have never been found to contain " free " polythionate higher than the tetrathionate (*i.e.*, $r = 1$). The experiment with Sol 10 quoted under Experiment N, where silver nitrate was the coagulant, gave $r = 0$, corresponding with trithionate. In nearly every other case r was between 0 and 1. Once or twice it reached 1. As a rule we did not carry out a test, because the weights usually are very small and this makes it difficult to transfer enough of the dry mixture of silver sulphide and sulphur to the tube from which the sulphur is to be distilled. Unless the sol is comparatively " old," there is not much " free " polythionate to deal with.

Experiment H (*Theory, p.* 2923).

Action of Cold 20N-*Sulphuric Acid on Sodium Thiosulphate.*—10 C.c. of $20{\cdot}2N$-sulphuric acid were delivered rapidly into tubes containing weighed quantities of thiosulphate previously dissolved in the minimum amount of water. The mixture was shaken immediately. Phenomena invariably were as follows: (i) Cloudiness for a few minutes, (ii) quite clear for an hour or more, the solution becoming first pale and later strongly yellow in tint, while sulphur dioxide was slowly being evolved, (iii) renewed cloudiness followed by sedimentation of sulphur.

After this strongly acid mixture had been left for various periods, given in Table VI, the top liquid was drained off or filtered and diluted with ten times its volume of water. This was either boiled or else mixed cold with hydrogen peroxide. In either case a considerable deposit of sulphur resulted, most of which was due to dilution alone. Then either lanthanum or thorium nitrate was added until further addition caused no further precipitate. (Neither of them caused much further deposit.) The clear liquid, obtained by final filtration, was precipitated by silver nitrate, then boiled, and the weights of silver sulphide and of sulphur were determined in the usual way (see Table VI). The value in the last column is a molar ratio.

TABLE VI.

	Weight of dissolved $Na_2S_2O_3,5H_2O$, g.	Period before dilution, hrs.	Ag_2S obtained, mg.,		Sulphur obtained, mg.	Value of r or S_1/Ag_2S.
			actual.	for 1 g. of salt.		
a. 1	0·25	0·5	13·7	54·8	3·3	1·86
,, 2	0·5	0·5	27·5	55·0	8·7	1·86
,, 3	0·25	1·0	14·9	59·6	4·2	2·19
,, 4	0·25	2·0	16·0	64·0	4·7	2·28
,, 5	0·25	4·5	13·8	55·2	4·4	2·47
,, 6	0·25	16·0	18·4	73·6	6·0	2·52
b. 1	1·0	2·0	37·2	37·2	13·2	2·75
,, 2	1·5	2·0	17·3	11·6	8·1	3·60
,, 3	1·5	5·2	13·0	8·7	5·9	3·50
,, 4	1·0	16·0	15·2	15·2	8·7	4·48
,, 5	1·0	19·0	13·9	13·9	10·3	5·74
,, 6	1·6	41·0	9·4	5·9	4·0	3·03
c. 1	1·0	2·5		77·2	22·5	2·15
,, 2	1·0	6·6		50·9	20·7	3·15
,, 3	1·0	14·0		35·6	9·2	2·19
,, 4	1·0	19·0		28·1	16·4	4·54
,, 5	1·0	24·0		27·6	18·9	5·26

Notes.—The "*c*" experiments were after treatment with H_2O_2.

The values for "r" are 0 for tri-, 1 for tetra-, 2 for penta-, 3 for hexa-, 4 for hepta-, and 5 for octa-thionic acid.

Deductions from Table VI.—The weights of silver sulphide give the relative amounts of polythionate $H_2S_{(3+r)}O_6$ present, independently of their nature. The "*a*" results, calculated for 1 g. of thiosulphate, give higher figures for silver sulphide than do the "*b*" results, probably because residual sulphur dioxide was removed more rapidly on boiling since less was actually present; in the "*c*" experiments the sulphur dioxide was removed (by hydrogen peroxide) before boiling, and the silver sulphide is seen to be similar in amount to that in the "*a*" series.

In *a*, the nature of polythionate changed gradually with period of action with the cold, concentrated acid, rising, on the average, from penta- to half way between penta- and hexa-thionate in 16 hours.

In *b* also, the value of *r* rose steadily with period of action, appearing to exceed octathionate after 19 hours but to fall to hexa- during the last 22 hours in Experiment *b*. 6.

In *c* (with the exception of *c*. 3), the value of *r* rose in the same way from penta- to just over octa-thionic acid in 24 hours.

Experiment I (*Theory*, *p*. 2923).

4 G. of thiosulphate crystals were treated with 40 c.c. of 20·2*N*-sulphuric acid. The phenomena were the same as before, but *r* rose to 8·2 after 22 hours' action, followed by dilution up to 440 c.c. and removal of sulphur dioxide by hydrogen peroxide. Though higher than the previous maximum, this value is very much lower than that of any sol recorded in Table II. The explanation is readily seen by taking Sol 15 (Tables I and II) as an example. The hot yellow solution in the water-bath was approximately 8*N* for hydrogen-ion and 4*N* for sodium-ion concentration, and on cooling, the latter concentration was sufficiently high to throw out a sodium curd, leaving behind 78% of the total polythionate in the acid filtrate. If this 78% had been retained, then the value of *r* for Sol 15 would have been 8·8 instead of just about 40 as recorded. Comparing this with the present case, where we have $H^{\bullet} = 18N$, $Na^{\bullet} = 0{\cdot}36N$, we find that the far lower $Na^{\bullet}$ concentration in presence of higher $H^{\bullet}$ concentration admits of no curd in the cold and no rejection of free polythionic acid from the mixture. The hydrogen-ion concentration was so high that no thorium curd could be obtained even with high concentration of thorium nitrate. We then nearly neutralised a portion of the diluted mixture by means of sodium hydroxide and did obtain a potassium curd, though we had to add potassium nitrate so that it was finally above *N*. Here the sodium concentration (replacing $H^{\bullet}$) was very high. From this curd and its filtrate we found that just about five-sixths of the total polythionate was "free" and the value of ρ came to just about 48. Next, we nearly neutralised two other portions of the mixture with ammonia instead of sodium hydroxide, because the ammonium ion is not so "antagonistic" as the sodium, and found that curds could be obtained by thorium nitrate and by potassium nitrate when added in much lower concentration. Three days elapsed between the last two experiments, and the analyses carried out in each case showed that about 10% of the total polythionate had decomposed in this interval, probably owing to the large

proportion of polythionate in the free condition. The filtrate from the potassium curd gave $r = 1{\cdot}79$, which approaches the value for pentathionate. The acidity of the sol previous to curding with potassium nitrate was $0{\cdot}06N$.

The phenomena observed in Expts. H and I indicate—by appearance, disappearance, and reappearance of sulphur—the reactions successively obtaining in the process of polythionate formation, whilst the gradual deepening of the yellow tint indicates that increasing amounts of colloidal sulphur are being stored up in the micelles.

The first appearance of sulphur indicates the reaction $H_2S_2O_3 \longrightarrow H_2SO_3 + S$. This sulphur, together with that produced by the reaction between hydrogen sulphide and sulphurous acid, is gradually taken up by trithionic acid produced in the reaction $2H_2S_2O_3 \longrightarrow H_2S_3O_6 + H_2S$. Formation of anhydrothiosulphuric acid, $H_2S_4O_5$ (Bassett and Durrant, *loc. cit.*, p. 1434), prevents either of these reactions occurring too quickly. Visible sulphur, formed in the initial stages of the mixing, disappears. This disappearance continues (for 2 hours in the last experiment mentioned in Experiment H) whilst higher polythionates and micelles of colloidal sulphur are being built up, and until the now yellow liquid has reached a stage of sulphur saturation.

The reappearance of sulphur in the concentrated acid indicates that maximum saturation has been exceeded. The considerable deposit of pure sulphur (carefully examined) which occurred on large dilution indicates that the larger micelles had separated owing to loss of charge due to bound polythionate becoming free in the manner discussed on p. 2925.

Experiment J (*Theory, p.* 2926).

Rate of Deposit of Sulphur in the Process of Ageing.—The rate was so rapid during the first day after preparation that it was not worth while to make the first analysis of each sol until the second day at earliest. With Sol 18 we surmounted this difficulty by waiting 10 days between the two final curdings with sodium nitrate. After the final curding, we carried out an analysis as soon as possible (a few hours after dilution to 200 c.c.), as recorded in Table II. The table also shows, as a rule with any one sol, a diminution of colloidal sulphur with time: where it does not do so, the sol was not refiltered between analyses, but had been thoroughly mixed by shaking before withdrawal of samples for analysis. Sol 10 was analysed after the 3rd, 11th, 82nd, and 102nd day, from which a regular curve was constructed tending towards a straight line eventually. The mean deposit *per diem* between the 3rd and the 11th day was 11 times as great as the mean daily deposit during the remaining period. The deposit *prior* to the third day was much greater than the total subsequent amount.

Experiment K (*Theory, p.* 2927).

These experiments show that in freshly made sols the whole of the polythionate is " bound."

i. 10 C.c. of Sol 12, which, at the time, contained 9·2 milli-equivs. of " free " polythionate per litre, was re-curded by *N*-sodium nitrate, and the curd washed with sodium nitrate solution. It was then dissolved in water *to produce a new sol.* This sol was *immediately* curded by 0·2*N*-potassium nitrate, and washed with potassium nitrate solution. The filtrate (and washings) was then boiled with silver nitrate. *No trace of any darkening could be detected.*

ii. In another experiment similar to the above, the curd itself was analysed and gave silver sulphide corresponding to 99·2% of the total polythionate, *i.e.*, for what *had been* the " bound " polythionate in Sol 12.

iii. Sol 18 was prepared as noted in Experiment J. The first analysis was made a few hours after making up the sol to 200 c.c., and indicated (see Table II) that only 0·6 milli-equiv. per litre of " free " polythionate was present.

Experiment L (*Theory, p.* 2928).

TABLE VII.

The coagulation of colloidal sulphur by electrolytes (*expressed in millimols. per litre*).

F. and S.		F.	B. & D. (i).		B. & D. (ii).	No. of Expts.
LiCl	>1500	640	$LiNO_3$	>2000		4
NaCl	750	220	$NaNO_3$	>1000		2
$\frac{1}{2}Na_2SO_4$			$\frac{1}{2}Na_2SO_4$	>1300		4
KCl	85	95	KNO_3	96		4
$\frac{1}{2}K_2SO_4$	100		$\frac{1}{2}K_2SO_4$	105		3
RbCl	80	80				
$\frac{1}{2}Rb_2SO_4$			$\frac{1}{2}Rb_2SO_4$	89		6
CsCl	95	95				
$\frac{1}{2}Cs_2SO_4$			$\frac{1}{2}Cs_2SO_4$	72		5
HCl	850	650	HCl	$>$ 800	>1000	7
$\frac{1}{2}H_2SO_4$	900		$\frac{1}{2}H_2SO_4$	$>$ 900	>2000	8
$BaCl_2$	1·5					
$Ba(NO_3)_2$	1·5		$Ba(NO_3)_2$		1·25	3
$CaCl_2$	1·5	1·6	$Ca(NO_3)_2$		2·5	5
$MgCl_2$	1·5		$Mg(NO_3)_2$		14	9
$MgSO_4$	1·6					
$ZnSO_4$	1·5		$ZnSO_4$		24	8
$CeCl_3$		0·05				
$Th(NO_3)_4$			$Th(NO_3)_4$	0·128	0·40	8

TABLE VII (*contd.*).

Composition of Sols.			
F. & S.	F.	B. & D. (i).	B. & D. (ii).
S = 364 mg./l.	(Not stated)	S = 342 mg./l.	S = 646 mg./l.
$H_2S_5O_6$ = between 0·17 and 0·25 millimol./l.*		S_5O_6 = 0·146 millimol./l.	S_5O_6 = 0·46 millimol./l.
NaCl = 0·44 millimol./l.		$NaNO_3$ = 1·24 millimols./l.	$NaNO_3$ = 1·54 millimols./l.
(Acidity not stated.)		$H^{\cdot}$ = 0·12 milliatom/l.	$H^{\cdot}$ = 0·145 milliatom/l.

F. & S. = Freundlich and Scholz (*loc. cit.*, 1922).
F. = Freundlich (*loc. cit.*, 1926, p. 89).
B. & D. (i) = Present authors, Sol. No. i.
B. & D. (ii) = ,, ,, ,, ii.

* Calculated from data recorded per g. of sulphur.

Notes on Table VII.

Our experiments were made with the earlier sols diluted to suitable strength for comparison with Freundlich and Scholz's work. In these we did not know the ratio of "bound" and "free" polythionate.

The figures given in millimols./l. for S_5O_6 represent the *total* polythionate. We now know that coagulation is determined by the "bound" polythionate.

The sol used as No. ii was one-tenth of the concentration of a sol (No. 7) after restandardising. We then used the undiluted sol and found concentrations (in millimols./l.) required were very different. Thorium nitrate (since shown to act stoicheiometrically) was 4·0 (very closely) instead of 0·40. Barium nitrate was 8·8 instead of 1·25. Potassium chloride was 192 instead of 96. Thus thorium nitrate (and also silver nitrate after heating) had to be ten times as concentrated when acting on the original sol, which also was ten times as concentrated as No. ii sol.

In all these experiments (except with $AgNO_3$) 10 minutes were allowed at room temperature to *just* get precipitation with clear liquid above, thus involving several trials with varying salt concentration.

All the concentrations in the above table, both of the added electrolytes and of the sol constituents, are those prevailing immediately after mixing. In our experiments 5 c.c. of suitably diluted electrolyte were always added to 5 c.c. of the sol.

Experiment M (*Theory, p.* 2929).

(i) *The Solubility of Sulphur Gels in Relation to the Solubility of Simple Salts having the Same Kation.*—Table VII shows great differences among many of the kations required to produce gels. We believe this is largely due to great differences in the solubility of the gels produced. The following figures, obtained with Sol 13, indicate the relative concentrations of potassium and sodium nitrates and sulphuric acid required to curd this sol.

	Final normalities.		Normality-ratio. $\frac{\text{Salt normality}}{\text{“Bound” } S_xO_6 \text{ normality}}$.
	Salt.	"Bound" S_xO_6.	
KNO_3	0·123	0·0087	14
$NaNO_3$	1·51	0·0071	212
H_2SO_4	10·0	0·0050	>2000
$Ba(NO_3)_2$	0·005	0·005	1 (from other sols)

TABLE VIII.

(ii) *Solubility product of barium–sulphur gels.*

2 C.c. of Sol 13 were used in each of the following experiments, with barium nitrate as coagulant.

Order of expt.	Total vol. after mixing, c.c.	Ratio $\frac{Ba^{\cdot\cdot}}{S_xO_6''}$.	Molarity after mixing.		Solubility product, $[S_xO_6''][Ba^{\cdot\cdot}] \times 10^6$.	Remarks.
			S_xO_6'' (bound).	$Ba^{\cdot\cdot}$.		
1	4	1·6	0·0025	0·004	10	Immediate curd.
2	4	1	0·0025	0·0025	6·2	,, ,,
3	8	1	0·00125	0·00125	1·6	No immediate curd. Thick milky liquid.
4	10	2	0·001	0·002	2	Thick milky liquid.
5	6	1	0·00165	0·00165	2·7	Curd forms rapidly.
6	14	3·2	0·0008	0·00256	2·0	Immediate curd.
7	18	8·3	0·00055	0·0046	2·5	,, ,,
8	17	5·5	0·000585	0·00324	1·6	,, ,,
9	10	1	0·001	0·001	1	Milky liquid, gradually curded.
10	16	2·5	0·000625	0·0016	1	Immediate curd.
11	12	1	0·000825	0·000825	0·68	Very slight clouding. No curd after 24 hrs.
12	16	1·7	0·000625	0·00109	0·68	Milky at once, soon curds.
13	40	10·9	0·00025	0·00272	0·68	Curds more rapidly than the last.
14	40	8·2	0·00025	0·00205	0·525	Curds similarly to the last.

(iii) *Solubility product of potassium–sulphur gels.*

5 C.c. of Sol 9*a* or 9*b* used in each experiment, with potassium nitrate as coagulant.

Order of expt.	Total vol. after mixing, c.c.	Ratio $\frac{2K^{\cdot}}{S_xO_6''}$.	Molarity after mixing.		Solubility product, $[S_xO_6''][K^{\cdot}]^2 \times 10^6$.	Remarks.
			S_xO_6'' (bound).	$K^{\cdot}$.		
Sol 9*a*						
1	5·1	0·93	0·0043	0·002	17·2	Partial curding.
2	218	1640	0·000101	0·082	6·7	Distinct cloud formed.
3	108·5	777	0·000203	0·079	1·26	Slow curding.
Sol 9*b*	50	190	0·00042	0·08	2·7	Milky initially. Curded over-night.

Sol 9*a*, in addition to the figures recorded in Table II, contained 15·5 milli-equivs. of sodium nitrate per litre, whereas Sol 9*b* contained practically none. The presence of sodium nitrate tends to increase the solubility of the gel.

It was found impossible to obtain any values for the solubility of the potassium gel by direct determination in the usual way. After the gel from 5 c.c. of Sol 9*b* in 500 c.c. of water had been shaken at 25° for 18 hours, the bulk of the bound polythionate appeared to have become free, with little, if any, corresponding solution of colloidal sulphur. Experiments in which the potassium gel was boiled with potassium nitrate of different concentrations led to the same conclusions.

The solubility of these simple electrolytes follows the same order. Nitric acid cannot be compared, as it oxidises the sulphur. Barium nitrate in more dilute solution (see Table VII) must be in concentration higher than that of the bound polythionate [in terms of normality the figures given in Table VII become $Ba(NO_3)_2 =$ 0·0025, *Total* $S_xO_6 =$ 0·00092].

Experiment N (Theory, p. 2930).

Heterogeneity of Sulphur Sol Micelles.—To 10 c.c. of the Sol 11*a*, *half* the volume of 0·01*N*-silver nitrate equivalent to the total polythionate was added, the mixture was well shaken in the cold, and left for 18 hours. Most of the sulphur was precipitated and was filtered cold. Filtrate and washings were then boiled after acidification with nitric acid. The mixture became very dark and was filtered. The filtrate was boiled with 12 c.c. of 0·01*N*-silver nitrate, giving a black precipitate. Each filter-paper, after being dried at 100°, and weighed in the case of Nos. 1 and 2, was burnt, and the content reduced to metallic silver.

Results.

	S, g.	Ag, g.		Ag_2S, g.		$r = S/Ag_2S$.
No. 1 gave	0·0723	0·0023	=	0·0030	hence	186·7
No. 2 ,,	0·0288	0·0040	=	0·0053	,,	42·3
No. 3 ,,		0·0065	=	0·0086	(⟶ due to " free " S_xO_6)	
Totals	0·1011			0·0169		
Original analysis of sol	0·1087			0·0165		$r = 51·1$ $\rho = 90·6$

In another experiment, Sol 10 was divided into *four* portions. Here the ratios of sulphur to silver sulphide (r values) in the successive precipitates were 434, 98, 34, and 0, and the analysis (Table II) gave $r = 37·5$ ($\rho = 84·8$). The last precipitate represented the " free " polythionate, and this, since $r = 0$, appeared as trithionate (the third addition of silver nitrate had stripped off all other sulphur). The first three values (434, 98, and 34) should be compared with the ρ value (84·8) since that also is independent of " free " polythionate.

Hence the first S/S_3O_6 ratio was five times ρ (the average), the second was slightly higher, and the third was less than half the average ratio for the whole sol.

These results show that the micelles were very heterogeneous; the larger ones, being the less highly charged by polythionate ions, were the first to be coagulated.

Experiment O (Theory, p. 2931).

Antagonistic Action of Acids and of Sodium Salts.—A large number of experiments were made in which, with a constant concentration of colloidal sulphur, coagulation was effected with potassium chloride, nitrate, or sulphate in the presence of various amounts of acid. These experiments, and others using nitric and phosphoric acids, showed that the increased amount of potassium salt required to produce coagulation bore a rough proportionality to the hydrogen-ion concentration rather than to the absolute amount of acid present—for which reason acetic acid has very little "antagonistic" action.

This antagonistic action of hydrogen ions was demonstrated roughly in a different way by shaking, for a short time, a potassium–sulphur gel containing 1·6 mg. of potassium and 5·3 mg. of polythionate (calculated as S_5O_6) with 10 c.c. of $0{\cdot}01N$-nitric, sulphuric, or phosphoric acid ($0{\cdot}01N$ in regard to first hydrogen). In each case the curd was partially dissolved, 77% by nitric, 51·5% by sulphuric, and 32·8% by phosphoric acid. (For strict proportionality to the hydrogen-ion concentrations, the figures should have been 77, 64, and 53.)

The "antagonistic" action of sodium salts, which is precisely analogous to that of acids, can also be demonstrated by solubility experiments. 5 C.c. of Sol 8 were curded with 10 c.c. of N-potassium nitrate. The washed curd was mixed with sodium nitrate so that we finally had 25 c.c. of $0{\cdot}4N$-sodium nitrate. When the temperature of the mixture was raised to 55° the curd entirely disappeared, and reappeared on cooling. In parallel circumstances, water being used instead of $0{\cdot}4N$-sodium nitrate, the curd is practically insoluble.

We have shown that the gels of copper, nickel, and cobalt can be dissolved completely by dilute solutions of sulphuric and nitric acids. If the acid is first mixed with the sulphur sol, then these gels fail to appear on addition of these metallic salts in concentration which otherwise would cause coagulation.

Many investigators have regarded all sulphur gels (and other gels) as if they were the same thing produced by various means. This is not correct. *Each gel is the salt of the ion which produced it.*

Our sulphur sols have all been solutions of the sodium salt. The inverse or solubility method of demonstrating the antagonistic action of hydrogen, sodium, or other ions is perhaps useful as showing more clearly than does the ordinary coagulation method of colloid chemistry that the antagonistic action is quite analogous to the increased solubility of an ordinary crystalline salt in an acid or salt not having an ion in common with it. Thus potassium–sulphur gel is more soluble in hydrochloric acid or sodium acetate solutions than in pure water, just as is lead sulphate.

Experiment P (Theory, p. 2932).

Absence of Anions of Coagulating Electrolytes from Washed Sulphur Gels.—The fact that we have repeatedly found that the kations present in the sulphur gels are equivalent to the bound polythionate (Expt. R) has made it hardly necessary to show that the anions are absent. We tested a thorium gel from Sol 8, produced by thorium nitrate, for nitrate by Devarda's method (with a blank experiment also) and could find no trace. Recently, with Sol 18 curded by neodymium chloride, we tested as follows for chloride : The washed curd was boiled with excess of silver nitrate acidified by nitric acid. The precipitate was washed and then digested with ammonia (which, if silver chloride were present, would dissolve it and leave the silver sulphide and sulphur unaffected). We then filtered the liquid and acidified the filtrate by nitric acid. There was not the faintest trace of chloride.

Experiment Q (Theory, p. 2932).

Behaviour of Thorium Nitrate, of Various Concentrations, in coagulating a Sulphur Sol.—Table VII shows that the sulphur sol containing 0·146 millimol. per litre of polythionate required thorium nitrate of concentration 0·128 millimol. per litre to produce a gel. The actual experiments which led to that conclusion are as follows :

In each experiment ten minutes were allowed. Observations of what happened after shorter periods and, in the later experiments, after longer periods are recorded.

$Th(NO_3)_4$, millimols./l.	Percentage of total sulphur deposited.	Observations.
110	96	Opaque in 30 seconds, coagulates slowly.
11·0	0	Remains translucent, no deposit.
1·1	0	Remains translucent, slightly clouded.
0·132	89·2	Opaque in 30 seconds, deposits sulphur.
0·128	96·0*	,, 20 ,, ,, ,,
0·119	93·4	,, 30 ,, ,, ,,
0·110	93·3	,, 30 ,, ,, ,,
0·096	0	Milky, no deposit in 48 hours.†
0·055	0	Translucent, no deposit after 3 days, or even after a week.‡

* The other 4% of total sulphur remained in the liquid. We now know that this was contained in the "free" polythionate then present.

† Ultramicroscope showed sulphur particles to be 19 times the diameter of those present in the sol.

‡ Here the diameters had been enlarged to only 1·27 times as great as those present in the sol.

Experiment R (Theory, p. 2933).

Presence in Coagula from Sodium–Sulphur Sols of the Positive Ion of the Coagulant in Amount Equivalent to the Bound Polythionate of the Micelle.—The discovery of "free" and "bound" polythionate already described made us realise that we were dealing with micelles constantly, though slowly, changing in composition. Hence it was evident that re-analyses of the sol were required from time to time; also that when analyses of coagula were made at intermediate times, especially with the " younger " sols, we should allow for the rate of change in amount of bound polythionate. We did this in many instances, and our results agreed with theory within the bounds of legitimate experimental error.

Two general methods of arriving at the composition of gels were possible, (i) direct analysis, (ii) differential analysis. The latter demands a knowledge of the exact amount and composition of the coagulating solution and also of the composition of the filtrate from the gel.

In some cases both methods could be employed and in those cases our results were confirmed. In no case had we any evidence running contrary to the statement implied in the heading to this experiment.

We give some examples of analyses—more particularly those where the amount of coagulant necessary to cause curding was equivalent to the " bound " polythionate.

Potassium. (i) The curd produced by 2 c.c. of *N*-potassium nitrate acting on 5 c.c. of Sol 17, 20 *days old* and diluted to 25 c.c., was washed, dried, ignited, and re-ignited after addition of sulphuric acid; this gave 7·7 mg. of potassium sulphate which corresponds with 11·0 mg. of silver sulphide. From figures quoted in Table II, 5 c.c. of Sol 17 gave 13·6, 12·3, and 9·0 mg. of Ag_2S after 2, 10, and 86 days, whence, after 20 days (by curve), it should give 11·0 mg. almost exactly. Silver sulphide, in all cases, represented the " bound " polythionate.

(ii) Analysis of the curd from Sol 17, 86 *days old*, is recorded (Experiment C) where exact equivalence was found between $K^{\cdot}$ and S_xO_6'' and also between them and the sulphate generated in the filtrate from " free " polythionate.

(iii) The method explained in Experiment C was adopted in the other 18 determinations of " free " and " bound " which appear in Table II, thus involving the potassium curd. The main object was to determine " bound " polythionate. When this was known we were able to proceed with electrolytes other than potassium salts.

Sodium. The final sodium curd produced by sodium nitrate in the preparation of Sol 9*a* was washed on the Buchner funnel with a portion of solution from the previous curd. The final curd was thus almost free from adhering nitrate. Its sol was analysed at once, giving

14·4 milli-equivs. per l. of S_xO_6'' and (*via* ignited Na_2SO_4)
14·6 ,, ,, ,, Na.

Since all polythionate is " bound " at the early stage (Experiment K), the result shows equivalence of sodium and bound polythionate in the sodium curd.

(Other sols, see Table VII, contain excess of sodium.)

Silver. The silver curd decomposes slowly in the cold, rapidly on heating, but the silver contained is equivalent to the original " bound " polythionate. This appears in Experiment N, and otherwise by adding the minimum of acidified silver nitrate necessary to react with a *known* amount of " bound " polythionate. After boiling, the silver sulphide formed corresponded with this; and addition of fresh silver nitrate to the filtrate gave sulphide corresponding with the " free " polythionate.

Nickel, cobalt. The curds from these metals, like that from sodium, are dissolved by washing. We could not use the method recorded for sodium and had to be content with showing that the " free " polythionate of the filtrate corresponded with that found from the potassium curd. Sol 11 was curded by nickel and by cobalt sulphate, and the free polythionate agreed with that from potassium.

Aluminium. This finely divided curd, though practically insoluble in water, gave some trouble in filtering and washing. Sol 10 (5 c.c.) was curded by excess of 0·032*N*-aluminium nitrate. The curds were washed, dried at 100°, weighed, and then ignited. Their filtrates were treated with silver nitrate as usual.

	Weight of curd.	Weight of Al_2O_3.	Weight of Ag from filtrate.
i	54·8 mg.	1·0 mg.	2·7 mg.
ii....................	55·1 ,,	1·0 ,,	3·0 ,,
iii....................	54·7 ,,	1·0 ,,	3·3 ,,

Twelve days later the analysis of Sol 10 (102 days old) was made. By proportion (see Table II), 2·7 mg. of silver should be obtained from filtrate and 0·8 mg. of alumina in the curd (corresponding with " bound " S_xO_6). (We had reason to believe that some hydrolysis of aluminium nitrate, during washing, accounted for the alumina being rather high.)

Neodymium (the salts of this metal are practically not hydrolysed, and the equivalent is 5·3 times that of aluminium).

	Normalities after mixing.		
Total vol.	Bound polythionate.	$Nd^{\cdot\cdot\cdot}$.	Nd_2O_3 in curd.
5 *C.c. of Sol* 15 *used.*			
15 c.c.	0·0065	0·0077	5·4 mg.
50 ,,	0·00194	0·00198	5·4 ,,
10 *C.c. Sol* 18 *used.*			
70 c.c.	0·0015	0·0015	6·3 ,,

The weight of neodymia theoretically equivalent to the bound polythionate in the case of Sol 15 is 5·6 mg., and in the case of Sol 18, 5·9 mg. Owing to the nature of the neodymium and thorium gels, they are exceedingly difficult to wash thoroughly, and the oxides obtained by very strong ignition must be washed to remove a small amount of sodium sulphate (amounting to about 0·5—0·9 mg. in the above experiments).

Thorium. 5 C.c. of Sol 13 were curded by thorium nitrate equivalent to bound S_xO_6, where final normalities of each were 0·00436*N*. Found: ThO_2 in curd, 2·9 mg.; Ag_2S from filtrate, 4·9 mg., in exact agreement with theory for replacement of "bound" polythionate and for "free" polythionate in filtrate. Sol 18 (170 days old), with bound polythionate 0·0059*N* : 10 c.c. were curded completely by 5·9 c.c. of 0·01*N*-thorium nitrate.

Found: ThO_2 in curd $=$ 4·1 mg. Calc.: 3·9 mg.
,, Ag_2S (filtrate) $=$ 6·5 mg. ,, 6·2 ,,

from last analysis (159 days old). (See further thorium results in still more dilute solution, where it appears that stoicheiometric coagulation is completed in 48 days when the final dilution is 0·00024*N*.)

Barium. Sol 13 was treated with barium nitrate at various dilutions in 14 experiments. Those which gave immediate curds are tabulated; those in lower concentration gave milkiness only.

Experiments i—vi were with 2 c.c. of Sol. 13.
Experiment vii was with 10 c.c. of Sol 13.

	Normalities.			
	Bound S_xO_6.	$Ba^{\cdot\cdot}$ ion.	$BaSO_4$ of curd.	Ag_2S of filtrate.
Expt. i	0·008	0·008	1·9 mg.	(not weighed)
,, ii	0·0033	0·0033	1·8 ,,	1·5 mg.
,, iii	0·0016	0·0051	2·2 ,,	1·4 ,,
,, iv	0·0011	0·0092	2·3 ,,	1·4 ,,
,, v	0·00117	0·00627	2·3 ,,	1·5 ,,
,, vi	0·00125	0·0032	2·3 ,,	1·7 ,,
Sum of ii—vi (for 10 c.c.)			10·9 ,,	7·5 ,,
Calc., from analysis of sol *preceding* i			12·0 ,,	7·4 ,,
Expt. vii	0·008	0·008	10·6 ,,	9·2 ,,
Calc., from analysis of sol *just after* vii			10·1 ,,	9·3 ,,

Results show rapid stoicheiometric coagulation if the sol concentration is such that the polythionate is not less than 0·0033*N*. The analyses quoted are tabulated (Table II) for 26 and for 32 days.

Comparison of Slow Reactions with Barium Nitrate and Thorium Nitrate on Large Dilution of Sol 13.—The final concentration was 0·24 milli-equiv. per litre (0·00024*N*) for $Ba^{\cdot\cdot}$ or for $Th^{\cdot\cdot\cdot\cdot}$ in each mixture, and for bound polythionate in both.

Observations recorded.

(Solutions in corked flasks.)

	Barium mixture.	Thorium mixture.
After 38 days.	Discrete particles, clear liquid, no deposit.	Cloudy liquid, fine deposit.
After 48 days.	Same particles, less clear liquid, no deposit.	Clear liquid, increased deposit.
Inference.	Reaction incomplete.	Reaction complete.

Summary.

1. Odén's colloidal sulphur is to be regarded as the soluble sodium salt of a sulphur–polythionate complex.

2. The nature of the polythionate present in the complex has been examined, and, although the results are not considered to be conclusive, they indicate that it is probably hexathionate.

3. Reasons are given for considering that hexathionate is probably the highest definite polythionate capable of existence, *i.e.*, there is nothing between it and " colloidal sulphur."

4. In a freshly prepared sulphur sol all the polythionate is in the " bound " condition and attached to the micelle.

5. As the sulphur sol ages, more and more of the polythionate becomes free.

6. This gradual liberation of the polythionate is considered to run parallel with the production of a crystalline lattice in the sulphur of the micelle.

7. The polythionate in the sols is protected from hydrolysis in a remarkable way by the colloidal sulphur.

8. The polythionate provides the stabilising ion for the sulphur sol, but it also provides the mechanism by which the latter is ultimately destroyed, with separation of crystalline sulphur.

9. The coagulation of sulphur sols by salts has been shown to depend entirely upon the precipitation of curds which are to be considered as salts of the sulphur–polythionate complex with the kation of the electrolyte.

10. Coagulation is determined by solubility and other factors, which are very similar to those governing the precipitation of simple salts. For this reason, the coagulating efficiency of a metal ion depends much more upon whether it tends to form insoluble salts than upon its valency.

11. Owing, probably, to the large number of charges on one micelle, there are differences between the behaviour on precipitation of simple salts and of colloids.

12. In spite of this it has been shown that a sort of " solubility product " can be determined for the gels obtained from sulphur sols.

13. The coagulation of sulphur sols is always an exact chemical

process. The curds contain the precipitating kation in amount exactly equivalent to the " bound " polythionate.

14. In favourable cases, *i.e.*, when the curd is sufficiently insoluble and the sol not too dilute, a sulphur sol can be quantitatively coagulated by an amount of the precipitating electrolyte which is stoicheiometrically equivalent to the " bound " polythionate.

15. In other cases, the weaker the sol and the more soluble the curd, the greater the excess of coagulant which must be added.

16. The " antagonistic " action of hydrogen and some other ions, such as sodium, can be satisfactorily accounted for in terms of the high solubility of the sulphur–polythionic acid or salt.

17. The coagulating action of thorium nitrate is peculiar, and necessitates the assumption of a double compound of thorium nitrate with the thorium salt of the sulphur–polythionate complex.

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