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A Dissertation

Presented to the Faculty of The Rice Institute for
the degree of
Doctor of Philosophy.

by

Jacob Leighty Sherrick.

1919?

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ADSORPTION BY PRECIPITATES.

The Adsorption of Anions by Precipitated Barium Sulphate.

by

Jacob Leighty Sherrick.

One of the great drawbacks in gravimetric analysis is the tendency of precipitates to carry extraneous materials out of solution with them. This fact has been recognized for quite a long time and a large part of the work which has been done upon analytical procedures has had for its object the correction of errors introduced in this way.

Particularly, for very accurate work such as molecular weight determinations, is it necessary to guard against the errors caused by the phenomenon of adsorption. On the other hand, many of the analytical procedures used in industrial analyses, where rapidity of manipulation takes precedence over extreme accuracy, would not be possible if it were not for this property of precipitates of adsorbing material from solution. We are familiar with the fact that it is possible to so remove a peptizing agent by continued washing as to cause the otherwise coarse grained precipitate to be peptized and run through the filtering media. However, in some cases where extreme accuracy is not essential from a commercial standpoint, the contamination of precipitated materials is so great that the ordinary processes must be so modified as to eliminate the relatively large errors otherwise introduced. As an example of this we may take the determination of sulphates as barium sulphate. In a large number of cases where this procedure is used in commercial analysis, although it would not give results accurate enough for molecular weight determinations, nevertheless, it is sufficiently accurate for the purpose at hand. On the contrary, in the case of the determination of the sulphur content of iron pyrite, the contamination of the barium sulphate by the iron would be so great that the results would be valueless, if some change in the method were not made.¹

A great deal of work has been done on the contamination of precipitated barium sulphate by the adsorption of substances dissolved in the solution from which the salt separates. For the most part, these investigations have dealt with the influence of different metallic ions on the purity of the precipitated salt. However, as early as 1842, Mendeli^{jeff} carried out experiments which would seem to indicate that nitrate ion is adsorbed more readily than chloride ion. "In a few precipitations a part of one of the dissolved salts is so attracted that it comes down with the precipitate. The author dissolved barium nitrate in ten parts of water, precipitated approximately one half of it with sulphuric acid and allowed the barium sulphate to settle. The clear supernatant liquid was poured off and evaporated and the barium nitrate content was determined. The precipitate and the remaining liquid was weighed and finally the weight of the precipitate was determined. The latter was filtered, washed and ignited and hence consisted of pure barium sulphate. The solution obtained by filtering and washing the precipitate was evaporated and the barium nitrate obtained was weighed. If the weight of the barium nitrate and of the barium sulphate is subtracted from the weight of the precipitate and the solution contained in it, one obtains the weight of the water which was present in the solution. If one calculates from these experiments how much barium nitrate there was present in the supernatant solution and from this how much there was in the solution which was mixed with the precipitate, one finds that this contains only two thirds as much barium nitrate as was obtained by the evaporation of the wash water; so that one third of this adheres to the barium sulphate on account of the surface attraction of the barium sulphate for the barium nitrate. If barium chloride is precipitated in the same way with sulphuric acid, no barium chloride is carried down with the barium sulphate. If, on the other hand, a solution of nitric acid and sodium sulphate is precipitated with barium nitrate and the precipitate washed until a drop on a platinum foil leaves no residue, the barium sulphate contains as much as two percent of sodium nitrate. If this is ignited so that the sodium nitrate is decomposed, it can then be extracted with water. Barium sulphate has such a slight attraction for barium chloride that it can not take it up from an aqueous solution of the same; for the barium nitrate the attraction is so great that a great deal of water is necessary in order to wash it out; for the sodium nitrate the attraction is so great that it can not be removed even though the water possesses a marked

solvent power for sodium nitrate."

In 1871, Teschemacher and Smith³ mention the contamination of barium sulphate by barium chloride used in the precipitation and even at that time they recognized the fact that the chloride contamination depended in amount on whether the sulphate or the barium chloride was present in excess. Various other investigators observed this chloride contamination from time to time and it was made the subject for rather extended investigations by Richards and Parker⁴ and by Hulett and Duschak.⁵

The contamination of barium sulphate by iron salts was noted by many workers, since it was particularly apparent on account of the color imparted to the precipitate upon ignition. Glendinning and Edger⁶ call attention to the fact as do also, Sloane,⁷ Schneider,⁸ Gladding,⁹ Gyzander¹⁰, Knorre¹¹, and others. As a matter of interest, in connection with the consideration of the tendency of a polyvalent ion to be adsorbed more than an ion of lower valence, we should note the method used for the prevention of the contamination by ferric iron in solution. Thus, Gyzander¹⁰ adds hydroxylamine hydrochloride to reduce the iron to the ferrous state and says that the barium sulphate precipitated from the resulting solution is free from iron.

The various text books of Quantitative Analysis have much to say as to the necessity for the absence of certain ions from the solutions in which sulphates are to be determined as barium sulphate. Thus, Ireadwell¹² states, - "The determination of sulphuric acid is theoretically very simple; the acid is precipitated with barium chloride and weighed as barium sulphate. Practically, however, there are often a great many difficulties arising from the fact that barium sulphate possesses a great tendency of dragging down other substances with it. The impurity usually causes high results, but occasionally the opposite effect is produced, particularly when the solution contains considerable iron in the ferric form. In that case the precipitated barium sulphate contains ferric sulphate and the latter on ignition loses SO_3 , so that ferric oxide is weighed instead of the corresponding amount of barium sulphate. Aluminum and chromium behave in the same way.

"When nitric or chloric acid is present, the

precipitate will contain barium nitrate or chlorate and these substances can not be removed by washing. Furthermore, if the precipitation is effected by the rapid addition of a large excess of barium chloride, the precipitate will contain considerable amounts of the reagent. If, on the other hand, the latter is added drop by drop until the precipitation is complete, a considerable excess may be added without influencing the purity of the precipitate. The presence of considerable amounts of potassium salts is especially disadvantageous; the precipitated barium sulphate will then always contain potassium sulphate. Sodium salts, however, do not seem to have any disturbing action."

As a further indication of the quite generally recognized contamination of precipitated barium sulphate, the following discussion is taken from Fresenius¹³, -"It (barium sulphate) has a great tendency, upon precipitation, to carry down with it other substances contained in the solution from which it separates, more particularly barium nitrate, nitrates and chlorates of the alkali metals, ferric oxide, etc. ----- Even the precipitate obtained from the solution of barium chloride by means of sulphuric acid in excess contains traces of barium chloride, which it is impossible to remove even by washing with boiling water, but which are dissolved by nitric acid (Siegle). ----- If a fluid contains metaphosphoric acid, barium can not be precipitated out of it by means of sulphuric acid; the resulting precipitate too contains phosphoric acid (Scheerer, Rube)¹⁴."

Under the discussion of the determination of sulphuric acid, the same author gives the following: "The exact estimation of sulphuric acid as barium sulphate is by no means so simple as it was formerly believed to be, but requires, on the contrary, great care and attention. This arises from three causes: - First, the barium sulphate is found to be far more soluble than was imagined in solutions of free acids and of many salts; second, it is extremely liable to carry down with it foreign salts, which are of themselves soluble in water; thirdly, when the precipitate has once separated in the impure state, it is often very difficult to purify it completely.

"The solution should contain but little free hydrochloric acid, and no nitric or chloric acid. ---"

¹⁵
Gooch states: - "When barium is precipitated as sulphate the tendency of the precipitate to include

foreign matter, if present, is very marked. It has been the custom to attempt the purification of barium sulphate contaminated by alkali salts by digesting, in hydrochloric acid, the washed precipitate. Phinney¹⁶ has shown, however, that dilute hydrochloric acid alone dissolves barium sulphate itself, while mixtures of hydrochloric acid with enough sulphuric acid to prevent such solvent action do not completely remove the impurity; and Mar¹⁷ has shown that the presence of hydrochloric acid even in large excess, does not prevent contamination by alkali salts."

The various methods for the correction of errors due to such contamination, has usually taken the form of the elimination of those substances which cause undue adsorption, or the treatment of the precipitates for purification. Thus Fresenius fuses the precipitate with sodium carbonate, extracts the melt with water and reprecipitates. Mar dissolves the precipitate in concentrated sulphuric acid; evaporates this solution to dryness; boils with hot water and then proceeds to filter, wash, ignite and weigh. Others dissolve the precipitate in concentrated sulphuric acid and reprecipitate by dilution.

The recognition of some of the principles applying to the phenomenon of adsorption and the importance of the state of subdivision or extent of surface, has lead to still a further method. This method consists of the addition of substances, to the solution, which having a slight solvent action on the precipitate, cause a growth of crystal size. In the process of recrystallization and growth of crystals taking place in the presence of a medium having a slight solvent action, the extent of surface being diminished, the adsorption of extraneous materials is decreased. A number of authors recommend the use of various amounts of hydrochloric acid in the precipitation of barium sulphate and they apparently believe that the solubility of barium sulphate in hydrochloric acid is insufficient to interfere with correct results. Richards and Parker¹⁸, and Allen and Johnson¹⁹, believe that any correct results obtained, under these conditions of precipitation, are due to the compensation of the two errors of solution and adsorption. Johnson and Adams²⁰, although they recommend the presence of a large excess of hydrochloric acid, apply corrections obtained from experiments on pure sodium sulphate. From another standpoint, this increase of crystal size in the presence of a medium having a slight solvent action, is taken advantage of in order to make precipitates more easily filterable. Thus, Osborn²¹ treats his barium sulphate precipitates with a solution of ammonium acetate before throwing them on the filter paper. In this connection it is interesting,

in the light of the results later obtained by us with nitrates and the warning usually given in text books regarding the necessity for the absence of nitrates, to note that Browning²² states that an excess of nitric acid or nitro-hydrochloric acid, up to ten percent by volume is not only not to be avoided, but is actually to be recommended in the precipitation of the sulphate radicle as barium sulphate. He states that the precipitate is more coarsely crystalline and contains less impurities.

As regards the mechanism of the contamination of barium sulphate by foreign substances, the views are many and divergent. Hulett and Duschak⁵ consider, as a possible explanation of chloride contamination, the formation of such complex salts as $\text{BaCl} \cdot \text{HSCl}_4$ and $\text{BaCl}_2 \cdot \text{SCl}_4$. Silberberger²³, for the contamination by potassium nitrate claims the formation of a complex $\text{KCl} \cdot \text{BaSO}_4 \cdot \text{BaSO}_4 \cdot \text{K}$; and for potassium chloride $\text{Cl} \cdot \text{BaSO}_4 \cdot \text{BaSO}_4 \cdot \text{BaSO}_4 \cdot \text{K}$. He states, further, that sodium salts are not retained by barium sulphate in the form of complexes. Johnson and Adams²⁰ conclude that it is a phenomenon of adsorption. Richards²⁴ compares the contamination by ferric sulphate to the occlusion of hydrogen by palladium which probably involves both solid solution and adsorption. Schneider³ looks upon it as a case of solid solution; but Huster and Thiel²⁵ and also Horte²⁶ conclude that the contamination is an adsorption phenomenon. Smith²⁷ states that it is neither a case of solid solution nor adsorption; but is the result of the formation of a complex of the composition $\text{Ba}(\text{Fe}(\text{SO}_4)_2)_2$. Weiser²⁸ attributes the contamination to adsorption and has shown the influence of the preferential adsorption of ions on the size of the crystals of barium sulphate.

The adsorption theory offers the only explanation of the well-known fact that barium sulphate takes up all manner of substances. Thus, not only do we have records of the contamination of barium sulphate by the sulphates of iron, chromium, aluminum, calcium and the alkali metals and by the chlorides of sodium, potassium and barium, but barium sulphate when added to both true and colloidal solutions, has been found to serve as an excellent adsorbing agent. Vanino and Hartl²⁹ find that, when barium sulphate is added to a colloidal gold solution, the solution is decolorized and destroyed. Patten³⁰ finds that, when barium sulphate is boiled with solutions of the chlorides of iron, manganese, and chromium, some of the metal passes into the barium sulphate in each case. Hulett and Duschak⁵ find that pure barium sulphate takes up chlorides upon standing in contact with a chloride solution.

Since a systematic study of the adsorption of different anions by barium sulphate has not been made, it was thought desirable to conduct a series of experiments along these lines for the purpose of determining the order of adsorption of the ions under identical conditions of precipitation. In the first place it was hoped that such an order of adsorption of ions might enable us to trace out some of the factors influencing adsorption in general. Furthermore, it was thought that such a series of experiments would enable us to determine the validity of conclusions previously reached concerning the relative effect of certain anions on the purity of precipitated barium sulphate.

Two general methods have been used for determining the relative adsorption of ions. One method consists in determining the effect of various ions of one charge on the precipitation of a colloid that owes its stability to the preferential adsorption of an ion of opposite charge. The precipitating power in such cases depends on the degree of adsorption. This method was first used by Schulze⁵¹; and from the results of his experiments we have what is known as Schulze's law, namely, that the power of an active ion to precipitate colloidal solutions is a function of its valence or the number of electrical charges which it carries. There are two general methods of conducting experiments on the precipitating power of electrolytes. One method consists in allowing a drop of the colloid to flow into a large volume of the electrolyte. In this way a series of determinations are made until that concentration of electrolyte is found that will just cause a coagulation of the drop. A second method consists in adding the electrolyte a drop at a time to a given amount of the colloidal solution until precipitation takes place.

Many determinations made in this way are of doubtful accuracy because of the experimental difficulties involved. The time factor may influence these determinations to quite a large extent since the adsorption of different ions may require different lengths of time for attaining equilibrium. Furthermore, although agitation usually has very little effect on the more stable colloidal solutions, nevertheless, when electrolytes are added in amount slightly less than that necessary to cause precipitation, the stability of the colloid is interfered with to such an extent that agitation will cause precipitation.⁵² In view of these facts it is hard to see how the solutions may be mixed uniformly so as to give true measures of concentration effects, and prevent local effects, without at the same time affecting the

precipitation by agitation. These and other sources of error were recognized by Schulze³³ : "The beginning of precipitation is dependent on a few factors other than the degree of dilution of the solution and the influence of these must be kept constant if strictly comparable results are to be obtained. The effect of these factors may be shown best by an example. Dilute sulphuric acid (9.8 grams per liter) immediately precipitates arsenic sulphide solution dropped into it. On the other hand, a solution one-third as strong, that is 3.267 grams per liter of H_2SO_4 , remains clear after the addition of the yellow solution even on long standing. By very vigorous shaking, however, it becomes slightly turbid and a like change is brought about by boiling. If the hot liquid is thoroughly shaken, the turbidity increases until finally the sulphide agglomerates and sinks to the bottom, the solution becoming clear as water. If, however, the solution is nearer the critical dilution, namely 3.6 grams of H_2SO_4 per liter, the resulting solution which is clear yellow at the start becomes turbid on standing. The phenomenon takes place in such a way that the yellow color changes into a reddish-yellow and this in turn into a yellowish-red while the solution which was quite transparent at the start decreases in clearness and finally becomes quite cloudy. By shaking this solution which is on the verge of a change, insoluble sulphide very quickly precipitates.

"In the precipitation of soluble arsenious sulphide, therefore, temperature, mechanical agitation and time are of very great importance even if of lesser influence than the dilution of the liquid which effects the precipitation. In order to keep all these factors constant in the observations it is necessary to work under the same external conditions."

Kato³⁴ found that the usual difficulties in determining the concentration of electrolyte that would just cause coagulation, were magnified in the case of colloidal barium sulphate. The degree of turbidity of the colloidal solution caused by adding an electrolyte varied continuously with the concentration of the latter, within certain limits. This made it difficult to determine at what concentration the turbidity really took place. The attempt to use Richards'³⁵ nephelometer for determining the critical concentration failed and viscosity measurements proved valueless³⁶. The concentration of electrolyte necessary for coagulation, that was finally adopted, was the concentration in which the colloid settled within twenty four hours. "In this way quite definite results were obtained since there was no difficulty in judging whether the settling was complete. It must be added here, however, that by complete settling it is not meant that the colloid was completely coagulated."

But the concentration determined by measuring the time required for the settling will serve safely as a measure of comparison of the coagulative power of electrolytes".

The results of Kato's investigations are of doubtful value for deducing the order of adsorption of anions. Thus he finds little difference in the precipitating concentration for potassium chloride, potassium bromide, potassium iodide, potassium chlorate and potassium nitrate; as nearly as can be determined hydrochloric acid and nitric acid behave the same, as do barium chloride and barium nitrate. This would mean that the anions concerned are adsorbed by positively charged colloidal barium sulphate to approximately the same degree. This can not be true, particularly in view of the results reported in this paper. The difficulty lies in the experimental method which is necessarily limited in accuracy and hence, figures representing the relative amounts of the various ions adsorbed are only approximate.

It is usually assumed, as Hardy⁵⁷ did, that the effect of the cation is negligible in the precipitation of a positive colloid, and the anion in the precipitation of a negative colloid; but this can not be strictly true. For example, if a positive colloid is precipitated by means of a representative series of sodium salts, it will be found that the critical concentration of the electrolyte necessary to produce precipitation will vary within wide limits. Now, if the concentration of the anion is the only thing that counts, it must be assumed either that the sodium ions are not adsorbed at all by the disperse phase or that the adsorption is the same at all concentrations. In view of what is known of the specific nature of adsorption it is questionable whether this is strictly true with any disperse phase; and it certainly would not be true with all. It seems more probable that the relatively slight effect of the ion with the same charge as the colloid under consideration may, in certain cases, be lost sight of altogether because of the errors inherent in the experimental method.

Kato found a wide variation from Hardy's rule in a number of cases. Among others, he found that sodium tetraborate, mercuric chloride, acetic acid, sodium citrate, phosphoric acid, barium chloride, barium nitrate, ferrous chloride, ferric sulphate, calcium chloride, and aluminum sulphate have a particularly weak coagulative power; while sodium thiosulphate, citric acid and solutions of sodium and potassium hydroxide have a particularly strong coagulative power. Even in the light of all these exceptions, he considers that his results are in accord with Hardy's rule. However, he rightly attributes the

the abnormally weak coagulative power of certain electrolytes to the protective action of the cation.

A second method of determining adsorption consists in shaking a solution of known concentration with a known weight of solid and pipetting off some of the supernatant liquid which is subsequently analyzed. The amount of adsorption is then calculated from the change in the concentration. Leighton³⁸, working in Bancroft's laboratory on the adsorption of alkali and acids by cellulose, pointed out that such a calculation was accurate only in case no liquid was taken up by the solid. Since cotton does take up water, results for cotton obtained in this way are wrong. The method of determination adopted by Leighton consisted in centrifuging the cotton and then analyzing the cotton direct. This method would give too high results unless the treatment with the centrifuge removes all the liquid. It seems to us that the latter is altogether improbable, particularly, in view of the difficulty experienced by Leighton in getting cotton even approximately free from water.

In the case of a crystalline precipitate, for example barium sulphate precipitated from chloride solution, it is possible by washing to remove the solution held among the crystals so that the wash water gives no test for chlorides. Adsorbed chloride is not removed by this process. It would be interesting to know in Leighton's experiments to what extent the alkali would be removed by washing with water.

Osaka³⁹ carried out some experiments on the adsorption of salts by charcoal, analyzing the solution before and after the treatment. He recognized, as did Leighton, that correct results could not be obtained without taking into account the amount of solution taken up by the solid adsorbing agent: "Since the amount of the salt in a given quantity of solution has been determined, the total amount of salt remaining in solution after adsorption may easily be found if the total amount of solution after adsorption or that of water in it be known. In order to obtain the amount of the water remaining in solution after adsorption that adsorbed by charcoal must be estimated, but as there is no direct means for its determination, the following procedure was adopted: "Some water was put in the bottom of a small glass vessel of desiccator form about nine centimeters high, a small glass basin with a given quantity of blood charcoal was placed over it and the cover was water tightly sealed with picetin. The whole apparatus was dipped completely into a thermostat at 25° and the basin with charcoal was weighed at intervals of about a week until it became constant in weight, being kept during the weighing between a pair of watch glasses. This required about one month and as a mean of five determinations it was

ascertained that animal charcoal, treated as above stated, adsorbed water to 85% of its weight. As the solutions used in the experiments were about one-tenth normal or less, it was assumed that the amount of water adsorbed by charcoal from solution does not differ much from that adsorbed from pure water."

The results obtained in this way assume that charcoal takes up the same amount of water from the saturated vapors as it does when placed in the liquid. It is a question whether this is true⁴⁰ and if not, Osaka's results are necessarily incorrect, so far as absolute amounts adsorbed are concerned.

It is evident that the determination of the order of adsorption of ions is open to considerable experimental difficulty. From what has just been said it is probable that the most accurate results may be obtained by choosing a suitable adsorbing material and analyzing for the ions direct. It so happens that precipitated barium sulphate furnishes a very satisfactory adsorbing medium for the determination of a number of adsorbed anions. In the first place, it has a marked tendency to adsorb most ions; in the next place, it may be precipitated directly in the presence of anions that do not form insoluble barium salts and the adhering solution may be removed by washing the crystals; finally, it has been found possible to analyze the precipitated salt for a number of adsorbed anions without unduly complicated and time consuming procedures.

It was, of course, particularly important to maintain uniform conditions in the experiments if comparable results were to be obtained. The general method of procedure was to precipitate a constant amount of barium sulphate by mixing a solution of a given sulphate with a solution of a barium salt. By this procedure three ions were kept constant throughout the series of experiments and the fourth was varied. The concentration of the ions were maintained as uniform as possible by working with fairly dilute solutions. The adsorbed ion was determined directly in the precipitated salt.

It was found necessary to devote considerable attention to the determination of conditions which would yield uniform results since small variations in the conditions of precipitation and the subsequent treatment of the salt had a marked influence on the amount of a given anion adsorbed. The conditions of precipitation and treatment finally adopted were followed throughout all the experiments.

Special methods of analysis were required to determine the ions adsorbed by barium sulphate since such small quantities of material were involved. Hulett and Buschak⁵ determined the adsorbed chloride in barium sulphate by dissolving the latter in sulphuric acid and estimating the hydrochloric acid evolved. With this as a start, methods were applied or evolved for the determination of a number of ions. In making determinations which involve the estimation of such small quantities of the various elements, it was realized that volumetric analysis should be used as far as possible if the procedures were not to be excessively time-consuming and complicated. Although some of the methods used for the determination of the ions adsorbed were not brought to such a degree of accuracy as might be possible, we felt that they were sufficient for our purposes and we did not wish to become involved in tedious analytical work and lose sight of our main purpose, by attempting to refine methods beyond our immediate needs. We are certain that some of the methods used were capable of much greater accuracy than was indicated by the preliminary applications of them to the estimation of known weights of material; and we expect at some later date to take them up systematically for the purpose of determining their limitations. However, there was manifestly no use in our trying at this time to refine a method of analysis beyond the point where the error of the determination fell within the variation in adsorption incident to our inability to control conditions affecting adsorption itself. Furthermore the determinations of ions adsorbed by barium sulphate were made under particularly favorable conditions and were in most cases unquestionably more accurate than the determinations made on known weights of material. The reason for this will be pointed out in the subsequent experiments.

Determinations were made on the following anions adsorbed by barium sulphate: chloride, chlorate, permanganate, nitrate, nitrite, cyanide, sulphocyanate, ferrocyanide and ferricyanide. In the interest of accuracy a number of determinations were made in every case and the average taken. The determination of the various ions will be taken up separately.

The Adsorption of Chloride Ion

As before mentioned Hulett and Buschak determined directly the amount of chloride ion taken up by barium sulphate under widely varying conditions of precipitation. The method was essentially as follows: The precipitated salt contained in a closed vessel was dis-

solved in concentrated sulphuric acid. In this process any chloride was converted into hydrochloric acid which was carried into a standard silver nitrate solution by aspirating air through the system. The rate of the solution of the barium sulphate was hastened by heating in a hot water bath. Allen and Johnson⁴¹ shortened the process of solution of the salt by direct heating with a small flame. Furthermore they determined the silver chloride gravimetrically instead of by the more accurate volumetric method.

Apparatus and general method.- In our experiments on adsorbed chloride ion, an apparatus was employed similar to that recommended by Hulett and Duschak. The apparatus is shown in Figure 1. The precipitate together with the asbestos mat from the Gooch crucible into which it was filtered, was placed in the reaction vessel of approximately 100 cc. capacity; and 50 cc. of concentrated sulphuric acid was poured onto it. The ground-glass stopper, with the delivery tube *g*, was attached as quickly as possible and air aspirated slowly through the apparatus. The wash bottle *a* contained a 20% solution of potassium hydroxide and *b* contained concentrated sulphuric acid. In addition to these precautions for obtaining pure air, the source of supply was outside the laboratory. The two tubes *d* and *e* contained N/100 silver nitrate solution. To prevent leaking, the ground-glass joint was moistened with concentrated sulphuric acid. After the aspiration of the air had been started, the water in the beaker *g* was heated to boiling. Under these conditions the barium sulphate dissolved slowly in the acid and any adsorbed chloride was converted into hydrochloric acid which was carried along in the stream of air and reacted with the silver nitrate in tube *d*. Under the conditions of our experiments, no hydrochloric acid escaped the first tube but the tube *e* was always retained as a safeguard against loss. When all of the hydrochloric acid had been evolved- usually four hours were sufficient- the excess of silver nitrate was determined by titration and the adsorption computed from this data.

The titrations were made under carefully controlled conditions using potassium chromate as an indicator. The process was carried out in a dark room lighted by an electric light; the solution was contained in a porcelain dish and yellow glasses were worn to aid in distinguishing the end point. Using these precautions, a sharp end-point was possible and check results were readily obtained.

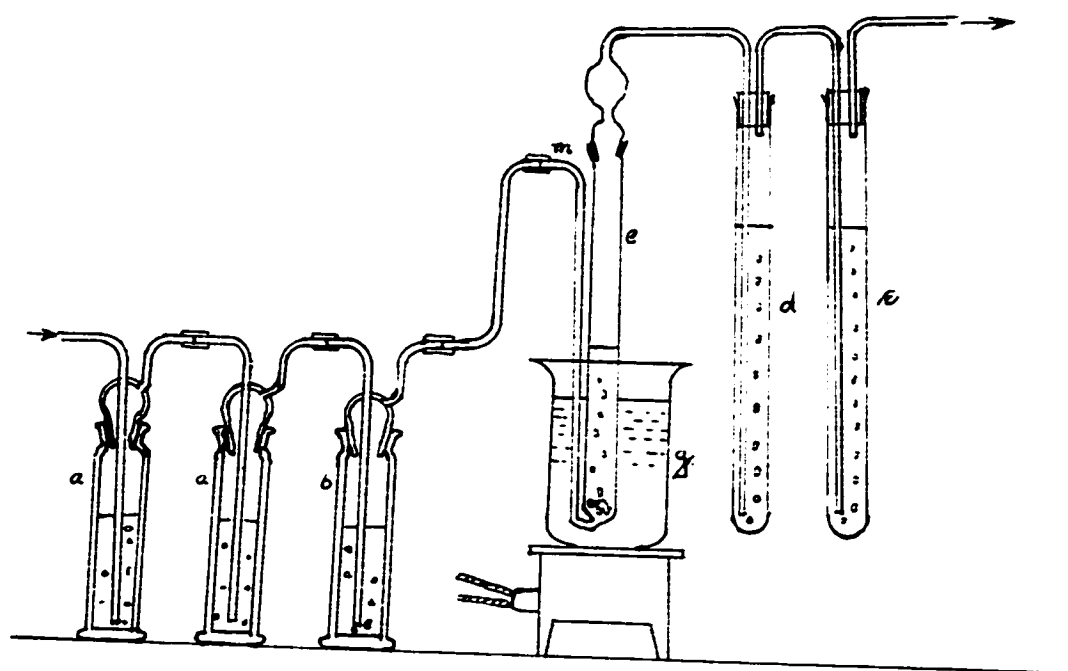


Figure 1

Determination of "blank". As we were not sure of the purity of the sulphuric acid, and as chlorides might be adsorbed by the asbestos mat during the filtration process, a number of "blank" determinations were run. The mat was prepared and through it was filtered a solution corresponding to the mother liquor resulting from the precipitation of barium sulphate from barium chloride solution in the regular determination of adsorbed chloride ion. After washing until the wash water gave no test for chlorides, the asbestos was placed in the apparatus and the determinations were made as before described. The results of a series of determinations are given in Table I. The correction was applied in subsequent determinations.

Table I.

Time as- pirated Hours	Conc. H_2SO_4 cc.	N/100 $AgNO_3$ cc.	N/100 $NaCl$ cc.	Blank N/100 solution, cc.	Average.
6	50	50	49.5	0.5	
6	50	50	49.6	0.4	
10	40	50	49.7	0.4	
24	50	50	49.5	0.5	
24	50	50	49.5	0.5	
24	40	50	49.6	0.5	
24	40	50	49.6	0.5	
24	50	50	49.5	0.5	0.5

Determination of chlorine in $BaCl_2 \cdot 2H_2O$. In order to test the accuracy of the method a determination was made on a known weight of barium chloride. A sample of the pure salt labeled "For Analysis" was weighed in a weighing bottle. From this was removed a crystal, the weight of which was determined by difference. The crystal was placed in the apparatus and the chlorine determined as before described. The crystal disappeared slowly in the concentrated acid due to the immediate formation around it of a film of barium sulphate, which dissolves but slowly. The result of the determination, given in Table II shows that the method is very accurate indeed.

Table II.

Determination of chlorine in $BaCl_2 \cdot 2H_2O$.

Weight of barium chloride taken found		Percent Chlorine taken found		Difference expressed in cc. N/100 solution.
0.03580	0.03573	29.03	28.97	0.05

In order to get some idea as to the best conditions for obtaining comparable data, a number of determinations were made of chloride ion adsorbed in barium sulphate, precipitated under different conditions.

It is a well known fact that barium sulphate precipitated from sodium sulphate solution by an excess of barium chloride is in a finer state of division than that precipitated by an excess of sodium sulphate. This is due to the fact that, other conditions being the same, barium ion is much more strongly adsorbed than is sulphate ion, and hence peptization is greater in the former case than in the latter.⁴² It was of interest to know to what extent the adsorption of chloride ion was affected by the two conditions. Accordingly a series of experiments were carried out as follows:

Adsorption of chloride ion in the presence of an excess of sodium sulphate : On account of the great amount of work already done on barium sulphate it was thought best to take such concentrations of solutions and amounts of materials as would correspond with usual analytical procedures for the determination of barium or sulphate. Our results might serve, then, for application to analytical methods and would throw some light on the various statements found as to the contamination of barium sulphate precipitates by different materials in solution. In these experiments 50 cc. of $M/10$ sodium sulphate solution were added to 160 cc. of water in a 400 cc. beaker; and the solution brought to boiling. While stirring the solution vigorously with a platinum gauze stirrer driven by an electric motor, 40 cc. of an $M/10$ solution of barium chloride solution were added from a burette, thus precipitating 4 millimols of barium sulphate. The time of addition was 30 seconds; the total time of stirring 4 minutes. The precipitate was allowed to stand in its mother liquor on a hot plate at 60°C . for 23 hours, after which it was filtered through a Gooch crucible and washed six times with hot water, the 30 cc. crucible being filled each time. After this treatment tests showed the absence of chlorides in the wash water. The precipitate, together with the asbestos mat, was transferred to the apparatus above described and the amount of the adsorbed chloride ion was determined. The results of a series of determinations are given in Table III. In the first column is given the number of cubic centimeters of $M/100 \text{ AgNO}_3$ solution corresponding to the amount of hydrochloric acid evolved from the precipitate. From this, the other values given in the table were calculated.

Table III.

Adsorption of chloride ion
(Na_2SO_4 in excess)

N/100 AgNO_3 cc.	Chloride ion adsorbed by barium sulphate			Average
	grams	grams per 100 mols	gram equivalents per 100 mols	
0.50	0.00018	4.44	0.125	0.125
0.60	0.00021	5.33	0.150	
0.50	0.00018	4.44	0.125	
0.43	0.00015	3.82	0.108	
0.48	0.00017	4.26	0.120	
0.48	0.00017	4.26	0.120	

Adsorption of chloride ion, in the presence of excess barium chloride: The same procedure was followed in this series of experiments as in the preceding, except that 40 cc. of M/10 sodium sulphate were added to 50 cc. of M/10 barium chloride diluted with 160 cc. of water. Thus an equivalent excess of barium chloride was employed as there was excess of sodium sulphate in the preceding experiments. The results are given in Table IV.

Table IV.

Adsorption of Chloride Ion
(BaCl_2 in excess)

N/100 AgNO_3 cc.	Chloride ion adsorbed by barium sulphate.			Average
	grams	grams per 100 mols	gram equivalents per 100 mols	
5.48	0.00195	48.64	1.370	1.578
5.68	0.00202	50.04	1.420	
6.19	0.00230	57.45	1.547	
6.39	0.00245	61.20	1.732	
6.79	0.00241	60.26	1.697	
6.84	0.00244	60.95	1.710	

As was to be expected, the amount of chloride ion adsorbed in the presence of excess barium chloride was more than 12 times greater than with sodium sulphate in excess. Since the absolute amount of adsorbed material is very small in any case, if a convenient quantity of precipitated material is used, it was decided to adopt for all subsequent determinations that condition in which the adsorption would be the larger, that is, the precipitation in the presence of an excess of barium salt.

In the previous determination of the adsorbed chloride ion in barium sulphate precipitated in the presence of an excess of barium chloride, the variation in the individual results was rather large, amounting to the equivalent of 1.4 cc. of N/100 solution for the four millimols of barium sulphate precipitated. Since the method used was much more accurate than this, it was evident that we were not controlling sufficiently the conditions under which the precipitation and consequently the adsorption, took place. The greatest chance for variation of conditions seemed to be in the digestion of the precipitate on the hot plate as there was no regulating device on the plate and hence its temperature probably fluctuated considerably. Hulett and Duschak have shown that the amount of adsorption changes during prolonged standing of the precipitate in contact with its mother liquor. A further chance for variation seemed to exist in the local temperature effects which might result from the addition of a cold (25°C.) solution of sodium sulphate to a boiling hot solution of barium chloride. Further determinations were accordingly made in order to determine whether a change in conditions of precipitation along the lines indicated would result in more constant values for the adsorption.

Adsorption of chloride ion in barium sulphate precipitated from sodium sulphate solution. The method of precipitation and treatment of the salt was modified in the following respects: Instead of adding a cold solution of sodium sulphate to the boiling hot solution of the barium salt, the following procedure was adopted. A 100 cc. burette was filled to the 40 cc. mark with an N/10 solution of sodium sulphate; this solution was then allowed to run from the burette into a clean beaker until the burette had emptied itself down to the glass stopcock; the solution in the beaker was then brought to boiling and evaporated to about one-half its original volume; the boiling hot solution was now poured back into the burette and, after washing in any of the solution that was clinging to the side of the beaker, the liquid in the burette was made up to the 40 cc. mark by the addition of boiling water. This solution was now mixed thoroughly by turning the burette over and over after it had been stoppered. Forty cubic centimeters of this solution were then used for precipitating the barium sulphate. As a further change, instead of allowing the precipitate to stand for twenty three hours on the hot plate, as previously, it was filtered immediately after precipitation. The time of stirring was decreased from four minutes to one minute. These changes in the procedure should tend to increase the total amount of adsorption. The results of a series of determinations are given in Table V.

Table V.

Table V.

Adsorption of Chloride Ion.
(barium chloride in excess)

N/100 AgNO_3 cc.	Chloride Ion adsorbed by barium sulphate.			Average
	grams	grams per 100 mols	gram equivalents per 100 mols	
7.00	0.00249	62.13	1.750	-----
6.80	0.00241	60.35	1.700	
7.20	0.00256	63.93	1.800	
7.10	0.00252	63.01	1.775	
7.10	0.00252	63.01	1.775	
				1.760

Adsorption of chloride ion in barium sulphate precipitated from sulphuric acid solution. Since barium ion is strongly adsorbed by barium sulphate and since hydrogen ion is much more strongly adsorbed than most univalent⁴³ cations, it follows that greater peptization of barium sulphate should result when the precipitation was effected from sulphuric acid solution than from sodium sulphate solution.²⁸ It follows further that, other conditions remaining constant, one would expect to get a greater anion adsorption when the precipitation was effected in the presence of hydrogen ion than in the presence of the sodium ion. A series of experiments were carried out to verify this point. The conditions of precipitation and the procedure followed are the same as given in the preceding paragraph with the exception that an M/10 solution of sulphuric acid was used instead of an M/10 solution of sodium sulphate. The results are given in Table VI.

Table VI.

Adsorption of Chloride Ion

(Barium sulphate from sulphuric acid with excess barium chloride)

N/100 AgNO_3 cc.	Chloride ion adsorbed by barium sulphate			Average
	grams	grams per 100 mols	gram equivalents per 100 mols	
9.0	0.00319	79.33	2.250	-----
9.0	0.00319	79.88	2.250	
9.4	0.00333	83.43	2.350	
9.3	0.00330	83.54	2.325	
				2.294

By comparing the results in Table V with those in Table VI it will be seen that the conclusion

namely that greater chloride ion adsorption results in the presence of hydrogen ion than in the presence of sodium ion.

Since in both sets of experiments the results of the different determinations agreed closely enough among themselves it was felt that the conditions of precipitation, filtration and washing were controlled sufficiently; hence these same conditions were used in all subsequent determinations. In all cases hereafter the precipitation was effected from sodium sulphate solution as dilute sulphuric acid would have an undesirable effect on certain of the salts, for instance the cyanides. In every case was used the barium salt of the ion whose adsorption was to be determined. These conditions will hereafter be alluded to as regular.

Adsorption of Bromide ion

Determination of bromine in bromides. (Fine powder)

Table VII.

Salt	weight		Percent found	Cc. of N/100 solution		Diff.
	taken	found		required	taken	
BaBr ₂ ·2H ₂ O	0.0509	0.0463	91.9	30.55	28.10	2.45
BaBr ₂ ·2H ₂ O	0.0400	0.0353	88.0	24.01	21.19	2.82
BaBr ₂ ·2H ₂ O	0.0342	0.0775	92.0	50.54	46.52	4.02
BaBr ₂ ·2H ₂ O	0.0386	0.0349	90.4	25.17	20.97	2.20
BaBr ₂ ·2H ₂ O	0.0439	0.0404	92.0	26.35	24.25	2.10
BaBr ₂ ·2H ₂ O	0.0644	0.0595	92.3	38.72	35.70	3.02
KBr	0.0134	0.0114	35.1	11.26	9.56	1.70

Determination of bromine in bromides. It seemed probable that the same general method of procedure could be used for the determination of bromide ion adsorbed in barium sulphate, as was used for chloride ion. It was planned to treat the precipitate with 50 cc. of concentrated sulphuric acid to which had been added a small amount of potassium dichromate. The bromine liberated could then be swept along in the air stream; absorbed in a solution of potassium iodide; and finally titrated with an N/100 solution of sodium thiosulphate. In order to test this method, small weighed portions of bromides were placed in the apparatus and subjected to the procedure. The results are given in Table VII above.

These results were disappointing to say the least, as in no case did we obtain more than 92.3% of the theoretical amount of bromine. It was noticed, however, that there was a brisk evolution of gas when the acid was first thrown upon the bromide ans, as in the first few cases, the acid was added through the ground-glass joint at the top of the apparatus, it was thought that some of the gas may have escaped before the apparatus could be closed. In the last four determinations of the series the bromide was placed in the apparatus and, after closing the ground-glass joint and disconnecting the two wash bottles, the acid was run in through the tube e, Fig. I, while a stream of air was being aspirated through the system. In this way there would be no chance of losing any of the gas evolved. The results, however, were no better than before. In the last case, where potassium bromide was used instead of barium bromide, only 85% of the theoretical amount of bromine was obtained. It seemed altogether probable that the low values resulted from one or both of the following causes: In the first place a very rapid reaction resulted at the moment the acid struck the crystals and it is altogether likely that some of the hydrobromic acid formed escaped oxidation by the chromic acid and hence escaped detection. In the last few determinations which were run in order to find out, if possible, the reason for the low results, it was noted that the gas first evolved was not colored and fumed; while the gas evolved after the crystals were completely covered with the acid mixture, was the color of bromine and was given off slowly. The slow evolution of bromine following the first reaction was due to the fact, that the particles of barium bromide were coated with a layer of barium sulphate which dissolved slowly, slowed down the action on the crystal to such an extent that no hydrobromic acid escaped oxidation. In the experiment with potassium bromide, on which the action was rapid from start to finish, the result was lower than with barium bromide. This would be expected since more hydrobromic acid would escape oxidation in the former than in the latter case.

A second factor is the following: In so far as the hydrobromic acid was oxidized by the sulphuric acid, sulphur dioxide was produced which might escape oxidation and be carried along with the bromine into the potassium iodide solution. There the sulphur dioxide would act on the iodine liberated by the bromine reducing it to hydroiodic acid. This would give low results. In order to get accurate results by this method, it would seem that it was necessary to have the action on the bromide proceed very slowly so that sufficient time was allowed for complete oxidation by the chromic acid mixture. Since the samples used in the above experiments had been ground in an agate mortar,

they were in a rather fine state of division and hence were acted on more rapidly than larger particles would be. Accordingly a number of determinations were made on $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$, in which the weighed sample consisted of a single crystal of the salt. As the samples were of the same average weight as in the previous experiments, the surface of contact and hence the rate at which they were attacked was correspondingly decreased. The results of these experiments are given in Table VIII.

Table VIII.

Determination of Bromine in $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$.
(Single crystal)

Weight taken	$\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ found	Percent found	Cc. of N/100 solution		
			Theoret- ical	taken	Difference
0.0350	0.0341	97.4	21.01	20.47	0.54
0.0435	0.0424	97.6	26.11	25.47	0.64
0.0502	0.0484	96.4	30.13	29.05	1.08
0.0313	0.0307	98.0	13.95	13.41	0.44

In the above series of experiments, the lowest result obtained was 96.4% of the theoretical, while the highest was 98.0%. These values were much more satisfactory than those previously obtained because of the slower action. On account of the slow rate at which precipitated barium sulphate dissolves in sulphuric acid, the method is entirely satisfactory for the estimation of bromide ion adsorbed in barium sulphate.

Adsorption of bromide ion. Four millimols of barium sulphate were precipitated in the regular way by adding 40 cc. of an N/10 solution of sodium sulphate to 50 cc. of N/10 barium bromide solution diluted with 160 cc. of water. The precipitate was treated as previously described and the amount of the bromide ion adsorbed was estimated. The results of a series of determinations are given in Table IX.

Table IX.

Adsorption of bromide ion.

N/100 $\text{Na}_2\text{S}_2\text{O}_3$ cc.	grams	Bromide ion adsorbed by BaSO_4	
		grams per 100 mols	gram equivalents per 100 mols.
3.63	0.00294	73.51	Average 0.920 0.763 0.813 0.793 0.813 0.970
3.07	0.00245	61.32	
3.27	0.00261	65.32	
3.17	0.00243	60.92	
3.27	0.00261	63.32	
3.43	0.00273	69.52	
			0.831

Adsorption of Iodide ion.

Determination of iodine in potassium iodide. It was thought that the same method, for determining adsorbed bromide ion, might be applied to the determination of adsorbed iodide. In order to test this, weighed amounts of potassium iodide were taken and subjected to the same treatment as the barium bromide in the preceding experiments. The use of barium iodide was impracticable for the preliminary tests because of the highly deliquescent nature of the salt. The first difficulty encountered was that the iodine, liberated from the sulphuric acid-dichromate mixture, condensed in the upper part of the reaction chamber around the ground-glass joint; and after aspirating air through the system for twenty four hours, only 21% of the theoretical amount of iodine was obtained, although all color of the element had disappeared from the reaction chamber. It was thought that the low results might be due to the loss of iodine through the ground glass joint. To determine whether or not this was the case, experiments were carried out in an apparatus without the ground glass joint. The weighed sample was placed in a reaction vessel, the same size as that previously used, and the exit tube was sealed on. This apparatus was surrounded by a steam jacket to facilitate the sweeping over of the iodine into the potassium iodide solution. The experiments with apparatus were as unsatisfactory as those preceding them. It was noted however, that a considerable quantity of iodine vapor was swept into the potassium iodide solution but relatively little of it remained, indicating that a later reduction had taken place. In view of our experi-

ments with bromides these results might have been expected. Since hydriodic acid is a much stronger reducing agent than hydrobromic acid, it reduces sulphuric acid very rapidly with the formation of sulphur dioxide and hydrogen sulphide. Under the conditions of the experiment, these gases were in part swept over into the potassium iodide solution and subsequently reduced the iodine that was carried over. It is altogether probable that the method would work much more satisfactorily with barium bromide than with potassium iodide for the action would be slower under these conditions and oxidation by the chromic acid much more nearly complete. However, it was decided to adopt a different method altogether. The sample of iodide was placed in the reaction vessel to which the outlet tube was subsequently sealed. This was surrounded by a steam jacket as in the previous experiments. Instead of catching the gases, liberated by the chromic acid mixture, in potassium iodide solution they were absorbed in a ten percent solution of sodium hydroxide. Under these conditions, the iodine would exist as iodide and iodate while sulphur dioxide and hydrogen sulphide would go to sulphite and sulphide respectively. After aspirating air through the system for twenty four hours, in order to make sure that all the iodine was washed over, the sodium hydroxide solution was placed in a distilling flask; acidified with sulphuric acid; and an excess of ferric ammonium alum added. It was then distilled, and the distillate caught in a solution of potassium iodide.⁴⁴ All the iodine was obtained in this way and was subsequently titrated with an N/100 sodium thiosulphate solution in the usual way. The results are given in Table X.

Table X.

Weight of KI		Percent found	Cc. of N/100 Solution.		
Taken	found		Theoretical	Taken	Difference
0.0147	0.0143	97.3	3.35	3.62	0.27
0.0130	0.0126	97.0	7.33	7.57	0.25
0.0250	0.0252	100.9	15.06	15.20	0.14

It may be seen from the above table that the method, as finally modified, gives quite satisfactory results.

Adsorption of iodide ion. Four millimols of barium sulphate were precipitated in the regular way and the amount of adsorbed iodide ion determined. On dissolving the sulphate in the acid, no color of iodine vapor was observed at any time, whereas in the case of known weights of iodides the violet vapor of iodine could be distinguished for a full hour while air was being aspirated through the system. When the final titrations were made, they showed that but very little iodide ion had been adsorbed. The results of a series of experiments are given in Table XI.

Table XI.

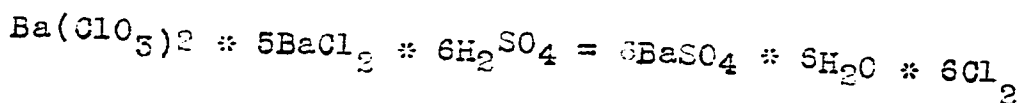
Adsorption of iodide ion.

N/100 Na ₂ S ₂ O ₃ cc.	grams	Iodide ion adsorbed by BaSO ₄		*
		grams per 100 mols	gram equivalents per 100 mols	
0.3	0.00038	9.52	0.075	Average
0.2	0.00025	6.55	0.050	
0.1	0.00013	3.17	0.025	
0.3	0.00038	9.52	0.075	
				0.056

Indeed the quantity adsorbed was so minute that the values can be only approximately accurate. The results show conclusively that iodide ion is adsorbed by barium sulphate the least of any of the ions considered.

Adsorption of Chlorate Ion.

Determinations on known weights of Ba(ClO₃)₂·H₂O.-- The attempt was made to use a method for the determination of chlorate ion which depends on the oxidizing power of chlorate to liberate chlorine from hydrochloric acid, so that advantage could be taken of the accurate iodine-thiosulphate titration. The procedure was as follows: A weighed amount of barium chlorate was mixed with 0.2000 grams of barium chloride and placed in the reaction vessel. Onto this was poured fifty cubic centimeters of concentrated sulphuric acid to which had been added three drops of concentrated hydrochloric acid. The evolved gas was drawn through potassium iodide solution as previously and the liberated iodine was titrated with N/100 sodium thiosulphate solution. The following reaction was expected to take place between the chloric acid and the hydrochloric acid:



The results are given in Table XII.

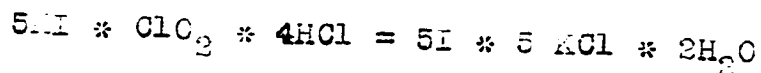
Table XII.

Determinations on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$

(In the light)

Weight of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$		Percent found.	Cc. of N/100 Solution.		
Taken	Found		Theoret- ical.	Taken	Difference
0.0105	0.0079	75.2	39.03	29.56	9.72
0.0110	0.0086	77.9	40.49	31.92	9.03
0.0114	0.0089	87.0	42.45	36.97	5.50
0.0135	0.0111	82.5	50.25	41.45	3.32
0.0139	0.0104	75.1	51.74	39.83	12.91

The results obtained show only from 75% to 87% of the theoretical and are evidently unsatisfactory from any point of view. In the previous experiments with bromides and iodides, tests were made to determine whether it was possible to pour in the sulphuric acid at the ground glass joint or whether the gas evolution was so rapid that some of the gas escaped before the joint could be closed. It was found that in no case was there any loss in this way since the results were the same whether the acid was poured into the inlet tube after the joint had been connected or whether it was added at the joint. Since the latter procedure was the more convenient, the above experiments were carried out in this manner. Furthermore, since we had been mistaken in attributing the low results in previous experiments to losses at the joint, we were inclined to look for some other explanation. In view of our previous experiments, the most probable source of error seemed to be the escape of some ClO_2 before it had a chance to be reduced by the hydrochloric acid. This would cause no error providing the ClO_2 reached the acidified solution of potassium iodide as such, for the following reaction would then take place:



On the other hand, if some of this ClO_2 were decomposed by the light before reaching the potassium iodide solution, low results would be obtained. To test this point a series of experiments were carried out in the dark room. The results are given in Table XIII.

Table XIII.
Determinations on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ (In the dark).

Weight of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$		Percent found.	Cc. of N/100 Solution.		
Taken	Found		Theoret- ical	Taken	Difference.
0.0114	0.0092	80.2	42.43	54.07	3.56
0.0130	0.0079	60.9	42.39	39.46	13.93
0.0108	0.0074	69.0	40.20	27.72	12.48

As may be seen, the results were not so good as those previously obtained in the light. The wide variation in the values pointed to a loss of gas, which must have happened before the joint was fitted in place after the addition of the acid. This seemed not unlikely for the conditions were quite different than in the experiments with bromides and iodides. Not only was the total amount of gas liberated in the experiments with chlorates very much greater, but the gas was lighter. Accordingly a series of determinations were made in the dark, adding the acid through the inlet tube after the ground glass joint was closed tightly and sealed with concentrated sulphuric acid. A blank was run in each experiment in order to make sure that the quantity of hydrochloric acid evolved and passing into the potassium iodide solution, did not itself liberate iodine from the solution due to the presence of iodates or a too high acid concentration. The results are given in Table XIV.

Table XIV.
Determinations on $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$

Weight of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$		Percent found	Cc. of N/100 Solution.		
Taken	Found		Theoret- ical	Taken	Difference
0.0150	0.01283	93.7	48.39	47.72	0.61
0.0137	0.01336	100.4	49.54	49.72	0.18
0.0150	0.01520	101.5	48.39	49.51	0.92

The above results were very satisfactory compared with the previous determinations. Accordingly, in all subsequent experiments, where a rapid reaction was likely to take place, the acid was added at the inlet tube of the apparatus instead of at the joint.

Adsorption of chlorate ion. Barium sulphate was precipitated in the regular way in the presence of excess barium chlorate and the adsorbed chlorate ion determined. The results are tabulated in Table XV.

Table XV.

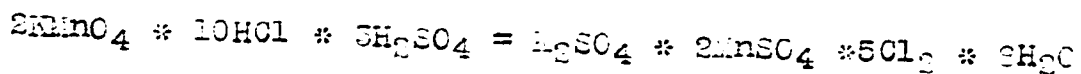
Adsorption of Chlorate Ion.

M/100 MgSO ₄ cc.	grams	Chlorate ion adsorbed by BaSO ₄		
		grams per 100 mols	Gram equivalents per 100 mols.	
133.41	0.01925	481.52	5.767	<u>Average</u> 5.857
135.45	0.01984	471.02	5.644	
146.39	0.02056	509.07	6.099	

Adsorption of Permanganate Ion.

Advantage was taken of the same general procedure, for determining permanganate ion, as was found successful for determining chlorate ion.

Determinations on known weights of KMnO₄. A weighed amount of potassium permanganate was mixed with 0.2 gram of barium chloride in the reaction vessel and 50 cc. of sulphuric acid to which had been added three drops of concentrated hydrochloric acid was allowed to flow in at the inlet tube. The evolved chlorine was conducted into potassium iodide solution and the liberated iodine titrated in the usual way. The following reaction was expected to take place:



The results of the preliminary experiments were quite satisfactory as shown in the Table XVI.

Table XVI.

Determinations on KMnO_4 .

Weight of KMnO_4		Percent found	Cc. of N/100 solution.		
Taken	Found		Theoretical	Taken	Difference
0.0100	0.0098	98.0	31.64	31.01	0.63
0.0103	0.0103	99.7	32.59	32.50	0.09
0.0156	0.0157	100.5	49.37	49.60	0.23

Adsorption of permanganate ion. Since the results on known weights of permanganate proved satisfactory, experiments were made on permanganate ion adsorbed by precipitated barium sulphate in the regular way, excess of barium permanganate. The results are given in Table XVII.

Table XVII.

Adsorption of Permanganate Ion.

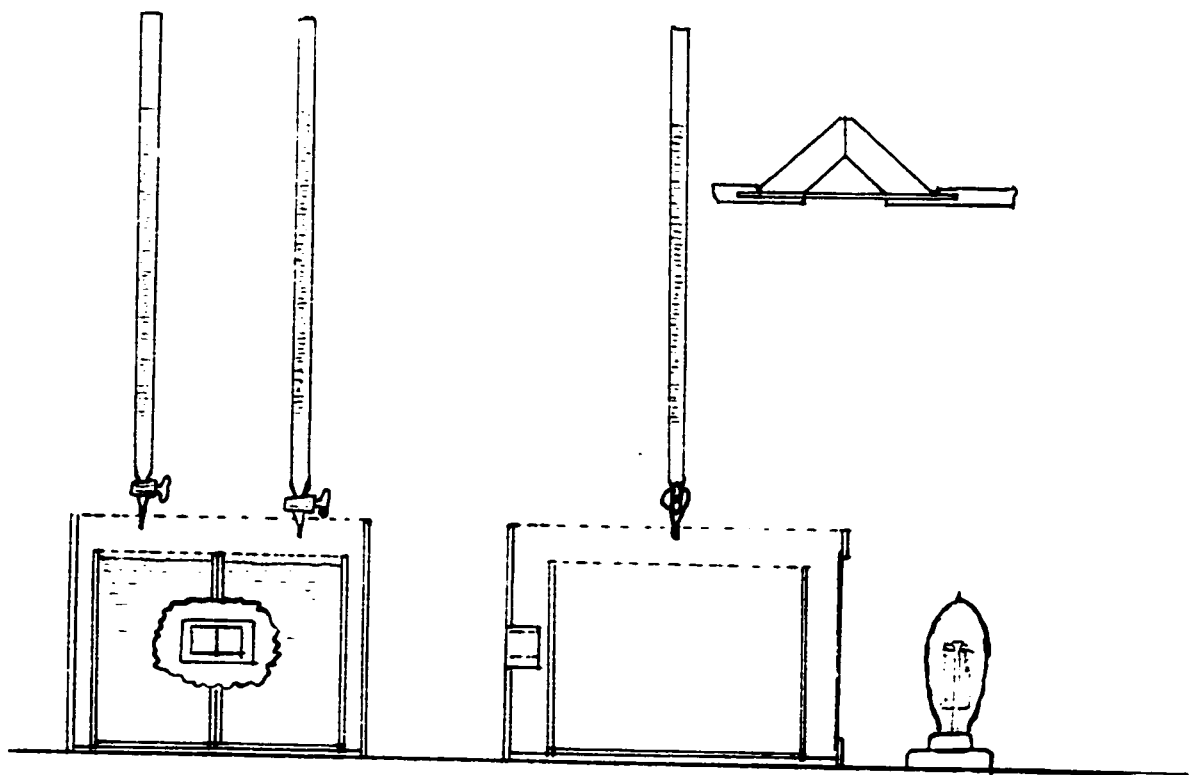
N/100 Na_2SO_3 cc.	Adsorption of permanganate ion			Average
	grams	grams per 100 mols	gram equivalents per 100 mols	
56.52	0.01339	334.91	2.816	2.847
56.90	0.01253	313.36	2.845	
57.48	0.01367	341.81	2.974	
57.35	0.01364	341.01	2.868	
56.66	0.01349	336.93	2.838	

Adsorption of Nitrate Ion.

The attempt was made to determine nitrate ion by the method found so convenient for the halogens. Fresenius⁴⁶ gives a method for the determination of nitrates which consists in distilling the nitric acid liberated from a nitrate by the action of dilute sulphuric acid. However, as it was necessary to use concentrated acid in order to dissolve the barium sulphate, the method of Fresenius could not be used directly. After repeated attempts to modify it to suit our needs, it was decided to use the Förster⁴⁷ modification of the Kjeldahl method for nitrogen. This fitted in with our scheme of things admirably, since the concentrated acid used at the beginning of this procedure served to dissolve the barium sulphate precipitate; the phenol, used with the concentrated acid, had no interfering action. The only modification

in the preliminary treatment, over that given in Olsen's Quantitative Chemical Analysis, was that, in order to dissolve all the barium sulphate precipitate, it was found expedient to increase the amount of phenol-sulphuric acid used. The ammonia evolved was received in N/100 sulphuric acid solution and the excess titrated back with N/100 sodium hydroxide solution, using cochineal as an indicator.

At the outset great difficulty was experienced in getting a satisfactory end point with the dilute solutions used; and determinations could not be checked to anything like the required accuracy. This difficulty was overcome by the use of a colorimeter constructed for the purpose. We had on hand a colorimeter which contained a set of glass prisms, by the use of which the color of the solution in two receptacles might be compared with but a very fine dividing line between the two fields. The prisms were fitted in one side of a small box painted black; and a ground glass in the side opposite. Two specially constructed rectangular glass cells of approximately 500 cc. capacity were used for holding the solutions whose color was to be compared. Figure II shows the arrangement of the parts of the apparatus.

Figure 2.

A standard colored solution was prepared by taking suitable equivalent volumes of the standard titrating solutions, adding three drops of cochineal solution⁴⁸ and diluting to a volume approximately equal to that obtained in the titration of the unknown solutions. The solution was prepared new each day upon which titrations were made. Its preparation constituted a restandardization of the solutions each time. The solution which served as a standard was placed in one of the glass cells and the solution to be titrated in the other. The titration was made directly in the cell and the color compared as the titration proceeded. By means of this colorimeter, it was readily possible to duplicate results within less than 0.1 cc. of N/100 solution. The apparatus was used in all determinations of nitrogen by the Kjeldahl method.

Determination of "blank". As the reagents used contained small quantities of nitrates, it was necessary to run a series of blank determinations for the purpose of making the necessary corrections. The same amounts of solution were taken as used in the subsequent experiments and the directions in Olsen, previously referred to, were closely followed. The result of a series of determinations is given in Table XVIII. The correction that must be applied is expressed in cubic centimeters of N/100 solution.

Table XVIII.

Determination of "blank" for nitrate.

Determination	1	2	3	Average
Cc. of N/100 solution.	14.65	14.76	15.07	14.85

Determinations on known weights of nitrates. Weighed samples of nitrates were taken and treated by the Forster modification of the Kjeldahl process. The results are given in Table XIX.

Table XIX.

Determinations on nitrates.						
Salt	Weight		Percent found	Cc. N/100 solution	Taken	Difference.
	Taken	found		Theoretical		
KNO_3	0.0317	0.0321	101.2	31.55	31.64	0.51
$\text{Ba}(\text{NO}_3)_2$	0.0505	0.0512	101.3	33.63	33.82	0.59

Adsorption of nitrate ion. Barium sulphate was precipitated in the usual way with barium nitrate in excess. The adsorbed nitrate was determined by the Kjeldahl method. The results are shown in Table XX.

Table XX.

Adsorption of Nitrate Ion.						
Cc N/100 solution			Adsorption of nitrate ion			
Total	Blank	Adsorption value.	grams	grams per 100 mols	gram equivalents per 100 mols.	
49.55	14.83	34.72	0.02152	539.16	8.680	Aver.
48.09	14.83	33.26	0.02062	515.53	8.325	
48.25	14.83	33.42	0.02072	518.02	8.358	
48.75	14.83	33.92	0.02102	525.51	8.490	
48.25	14.83	33.42	0.02072	518.02	8.358	
49.89	14.83	35.06	0.02173	543.43	8.765	
48.45	14.83	33.62	0.02084	521.11	8.405	8.482

The results given in the above table show that nitrate ion is adsorbed strongly. This is in line with the warning usually given in text books of analytical chemistry that nitrates must be absent from solutions in which sulphate is to be determined as barium sulphate. It also confirms the conclusions reached by Mendeljeff a long time ago that barium sulphate carries down nitrates more readily than chlorides. By referring to our results on chlorides it will be seen that under similar conditions five times as many equivalents of nitrate ion are adsorbed as of chloride ion.

Adsorption of nitrite ion.

Since the Kjeldahl method for nitrogen proved so satisfactory for the determination of the amount of nitrate ion, it seemed likely that it would serve also for the determination of nitrite ion.

Determination of "blank". Since it was found in the previous experiments that the amount of nitrates present in the solutions used for the determinations was relatively large when compared with the amount of adsorption, it was necessary to make frequent "blank" determinations under conditions identical with those used in the regular experiments. The plan followed was to make up quantities of solutions sufficient to carry out the experiments on a given ion; and to make the determinations of the blank along side the others. Table XXI gives the blank determinations for the experiments on nitrites.

Table XXI.

Determination No.	1	2	3	4	Average
Cc. of N/100 solution.	16.57	16.31	16.70	16.31	16.47

Determinations on known weights of nitrites.

As has been observed in these investigations, the rate at which the salt was attacked determined the accuracy of the analysis. In the first experiment with a known weight of barium nitrite in the form of a powder, the action was so rapid that, when the salt was treated with the phenol-sulphuric acid, some nitrogen dioxide was unquestionably lost. The amount found under these conditions was less than 95% of the theoretical. In a second experiment a single crystal of barium nitrite was taken with the idea that the slower action on the single crystal would favor the retention of all the oxides of nitrogen by the phenol acid mixture. In this case the results showed an accuracy of approximately 98% of the theoretical. The method was therefore regarded as quite satisfactory for the determination of adsorbed nitrite ion, since the action would be very slow indeed on account of the slow solution of the barium sulphate. The results of the two experiments are given in Table XXII.

Table XXII.

Determinations on Barium Nitrite.						
Sample	Weight		Percent	Cc. N/100 Sol.		
Ba(NO ₂) ₂	Taken	Found	found	Theo- reti- cal.	Taken	Diff.
Powdered	0.0417	0.0394	94.5	33.71	31.93	1.81
Single crystal	0.0424	0.0414	97.7	34.28	33.48	0.80

Adsorption of nitrite ion. A series of six determinations were made of nitrite ion adsorbed in barium sulphate precipitated in the regular manner in the presence of excess barium nitrite. The results are given in Table XXIII.

Table XXIII.

Adsorption of Nitrite Ion.					
Cc. N/100 Solution				Adsorption of nitrite ion.	
Total	Blank	Adsorp- tion value	grams	grams per 100 mols	Gram equiva- lents per 100 mols.
45.85	16.47	29.38	0.01251	537.37	7.345
45.98	16.47	29.51	0.01357	539.56	7.578
46.37	16.47	30.40	0.01398	349.60	7.300
46.74	16.47	30.27	0.01392	343.13	7.563
46.61	16.47	30.14	0.01386	346.61	7.535
46.97	16.47	29.50	0.01357	339.25	7.375
					Aver.
					7.467

By comparing the results tabulated above with those obtained for nitrates, it will be seen that there is very little difference between the equivalent amount of adsorption in the two cases; as will be pointed out in the later discussion of results, this is what one might expect on account of the close similarity between the two ions.

In considering methods for the accurate determination of cyanide, sulphocyanate, ferrocyanide, and ferricyanide ions, conflicting statements were found regarding the action of the different cyanides with concentrated sulphuric acid. Dyer⁴⁹ and Olsen⁵⁰ claim that certain

cyanides with concentrated sulphuric acid do not give a quantitative yield of ammonia; but that some oxides of nitrogen are formed. Olsen states that the Forster modification of the Kjeldahl method is necessary in evaluating certain cyanides. Williams⁵¹, however, claims that in every case the cyanides give a quantitative yield of ammonium sulphate when treated with concentrated sulphuric acid. Nevertheless, it was decided to use the Forster modification of the Kjeldahl method, as we desired to keep the methods as uniform as possible and wished to guard against the loss of any oxides of nitrogen which might be formed.

Adsorption of Cyanide Ion.

Determination of "blank." The blanks run in connection with these experiments are given in Table XXIV.

Table XXIV.

Determination	1	2	3	4	Average
Cc. N/100 solution	16.70	16.11	16.25	16.54	16.40

Determinations on known weights of mercuric cyanide. The Kjeldahl method gives very reliable results for cyanides as shown by the experiments given in Table XXV.

Table XXV.
Determinations on $\text{Hg}(\text{CN})_2$

Weight		Percent found	Cc. N/100 solution.		
Taken	found		Theoreti-cal.	Taken	Difference
0.0502	0.0504	100.4	39.75	39.90	0.15
0.0498	0.0495	99.5	39.43	39.15	0.28

Adsorption of cyanide ion. Four millimols of barium sulphate were precipitated in the regular way with barium cyanide in excess and the adsorbed cyanide ion determined by the Kjeldahl method. The results are given in Table XXVI.

Table XXVI.

Adsorption of Cyanide Ion.

Cc. N/100 solution			Adsorption of cyanide ion.		
Total	Blank	Adsorption value	grams	grams per 100 mols	gram equivalents per 100 mols.
17.60	16.40	1.20	0.00037	8.32	0.320
17.52	16.40	1.12	0.00029	7.16	0.280
17.52	16.40	1.12	0.00029	7.16	0.280
18.01	16.40	1.61	0.00042	10.46	0.40
17.40	16.40	1.00	0.00028	7.07	0.275

Adsorption of Sulphocyanate Ion.

Determination of "blank." The determination of blanks made in connection with this set of experiments are given in Table XXVII.

Table XXVII.

Determination	1	2	3	Average.
Cc. N/100 solution.	14.35	14.79	15.04	14.39

Determination on a known weight of $\text{Ba}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$. That the Kjeldahl method is quite as accurate for the determination of small amounts of sulphocyanates as for cyanides is shown by the analysis in Table XXVIII.

Table XXVIII
Determination of $\text{Ba}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$.

Weight		Percent found	Cc. of N/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0324	0.0327	100.9	22.55	22.57	0.22

Adsorption of sulphocyanate ion. The usual weight of barium sulphate was precipitated with barium sulphocyanate in excess and the adsorbed sulphocyanate ion determined. The results of a series of determinations are given in Table XXIX.

Table XXIX.

Cc. N/100 solution			Adsorption of sulphocyanate		
Total	Blank	Adsorption value	grams	grams per 100 mols	gram equivalents per 100 mols
15.96	14.39	0.97	0.00058	1.41	0.243
15.53	14.39	0.64	0.00037	0.93	0.160
16.02	14.39	1.13	0.00065	1.64	0.293
15.00	14.39	1.01	0.00053	1.46	0.253
15.53	14.39	0.64	0.00037	0.93	0.160
15.53	14.39	0.64	0.00037	0.93	0.160
16.02	14.39	1.13	0.00065	1.64	0.293
Average - -					0.230

On account of the very small quantity of cyanide and sulphocyanate ions adsorbed by barium sulphate, the results show considerable variation among themselves although the actual difference in terms of cc. of N/100 solution is very slight. However, the average of a series of determinations, such as those made, gives a fairly satisfactory index of the amount adsorbed.

Adsorption of Ferrocyanide Ion.

Preparation of barium ferrocyanide. This salt was prepared in the following way:⁵¹ A strong barium chloride solution was added to a moderately strong solution of sodium ferrocyanide. Barium ferrocyanide, $\text{Ba}_2\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, separated out as a light yellow crystalline powder. This precipitate was washed with water, filtered and recrystallized several times from water. One hundred cubic centimeters of water dissolves 0.34 grams of the salt, at 15.5°C. and 1.01 grams at 100°C.

Determination of "blank." Sufficient quantity of solutions were prepared for making the determinations on both ferrocyanides and ferricyanides. Consequently, the same blank correction applied to both. The determinations are given in Table XXX.

Table XXX.

Determination	1	2	3	4	Average
Cc. N/100 solution	16.44	16.50	16.50	16.64	16.47

Determinations on known weights of ferrocyanide of potassium. In order to test the Kjeldahl method for the determination of complex cyanides, a sample of $K_4Fe(CN)_6 \cdot 3H_2O$ was treated in the usual way. The results are given in Table XXXI.

Table XXXI
Determinations on $K_4Fe(CN)_6 \cdot 3H_2O$

Weight		Percent found	Cc. of N/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0091	0.0088	97.8	12.98	12.76	0.56
0.0120	0.0119	99.2	17.19	16.90	0.29

Since the results were quite satisfactory, a series of determinations were carried out for the determination of both ferrocyanide and ferricyanide ion adsorbed in barium sulphate.

Adsorption of ferrocyanide ion. The usual amount of barium sulphate was precipitated in the regular way in the presence of excess barium ferrocyanide. The results of the determination of adsorbed ferrocyanide ion in the precipitates so obtained, are given in Table XXXII.

Table XXXII.
Adsorption of ferrocyanide ion.

Cc. N/100 solution			Adsorption of ferrocyanide ion		
Total	Blank	Adsorption value	grams	grams per 100 mols	gram equivalents per 100 mols
95.95	16.47	79.46	0.02309	702.14	13.242
94.77	16.47	78.30	0.02767	691.79	13.050
97.97	16.47	81.50	0.02831	720.17	13.533
96.50	16.47	79.93	0.02822	705.41	13.305
93.42	16.47	76.95	0.02720	680.00	12.925
			Average---		
			13.201		

Adsorption of ferricyanide ion.

Preparation of barium ferricyanide. This salt was prepared by agitating barium ferrocyanide with an excess of manganous ferricyanide suspended in water. The solution was filtered and evaporated under reduced pressure. The salt, $\text{Ba}_2(\text{Fe}(\text{CN})_6)_2 \cdot 20\text{H}_2\text{O}$, appeared as fine red crystals which were quite stable and very soluble in water.⁵¹

Adsorption of ferricyanide ion. The usual quantity of barium sulphate was precipitated in the regular way, with barium ferricyanide in excess, and the adsorbed ferricyanide ion determined. Five determinations were made with the results as given in Table XXXIII.

Table XXXIII.

Adsorption of Ferricyanide Ion.

<u>Cc. N/100 solution</u>			<u>Adsorption of ferricyanide ion</u>		
<u>Total</u>	<u>Blank</u>	<u>Adsorp- tion value</u>	<u>Grams</u>	<u>grams per 100 mols</u>	<u>gram equiva- lents per 100 mols</u>
39.19	16.47	22.72	0.00905	200.77	2.640
38.05	16.47	21.58	0.00763	190.69	2.698
37.54	16.47	21.07	0.00744	186.19	2.635
37.41	16.47	20.94	0.00740	185.04	2.612
37.95	16.47	21.48	0.00759	189.63	2.683
					<u>Average</u> 2.695

The results of the series of determinations on anions adsorbed by barium sulphate are summarized in Table XXXIV. The ions are arranged in the order of adsorption beginning with the least adsorbed.

Table XXXIV

Adsorption of Anions by Barium Sulphate

- (a) Ion.
- (b) Number of gram equivalents ions adsorbed per 100 mols of barium sulphate.
- (c) Number of gram ions adsorbed per 100 mols of barium sulphate.
- (d) Grams contamination per 100 grams of barium sulphate, in terms of the barium salt of the ion.
- (e) Percentage contamination by weight of ion.
- (f) Percentage contamination by weight of barium salt.

(a)	(b)	(c)	(d)	(e)	(f)
Iodide	0.056	0.353	0.0469	0.0304	0.3462
Sulphocyanate	0.220	0.220	0.1195	0.0547	0.1195
Cyanide	0.310	0.310	0.1258	0.0346	0.1256
Bromide	0.351	0.351	0.5291	0.2846	0.5265
Chloride	1.760	1.760	0.7352	0.2301	0.7791
Ferricyanide	2.695	0.392	1.6033	0.7391	1.5957
Permanganate	2.947	2.947	2.2902	1.4512	2.2390
Chlorate	5.337	5.337	3.6401	2.0264	3.6921
Nitrite	7.467	7.467	3.7194	1.4725	3.5969
Nitrate	3.492	3.432	4.7500	2.2540	4.5346
Ferrocyanide	13.201	3.300	6.3350	2.9936	6.4393

It is needless to say that the absolute amounts of the various ions adsorbed by barium sulphate, as given in the above table, would be obtained only under the specific experimental procedure that was followed in the precipitation and subsequent treatment of the salt. By varying the conditions one would expect to find a variation in the absolute amounts adsorbed but the order of ions should remain approximately the same.

The so-called "law of Schulze", that the precipitating power of an ion for a given colloidal solution is a function of its valence or the electrical charge which it carries, has been accepted rather blindly in the past. Bancroft⁵², however, calls attention to the fact that it is only an approximation and, at best, serves only for a rough guide. As a matter of fact, it is hard to see why, when all the work which has been done on the precipitating power of electrolytes furnishes so much evidence

to the so-called law, chemists should place so much undue confidence in it. On the other hand, since there really seems to be some basis for the generalization, it would be eminently desirable to so modify it so as to bring it altogether in line with known facts.

Hardy⁵³ goes even further than Schulze and states: "The precipitating power of a salt is dependent upon the valence of its ions. The effective ion has always the opposite electric sign from that of the particles".

For many years this was regarded as the whole truth in regard to the matter and it was believed that only that ion of the electrolyte, which had an opposite electric charge to that carried by the particles of the colloidal solution, was important in causing precipitation. In late years, however, due to the growing realization of the specific nature of adsorption, this view has been changed and it is now realized that both the anion and cation of an electrolyte have a bearing on the precipitation for any given colloidal solution. Likewise, from this same specific nature of adsorption, the disperse phase itself has an important bearing.

Picton and Linder⁵⁴ were among the first to call attention to the fact that some of the ions of the electrolyte were adsorbed and carried down in the coagulated material.

The modern theory of colloid chemistry is to the effect that the colloidal particles are kept in suspension by surface films which prevent the coalescence of the particles. Bancroft⁵⁵ states: "Coalescence may be prevented by a non-electrical film, by an electrical film, or by any combination of these two. An electrical suspension is due to the preferential adsorption of some ion. So long as the particles are all charged positively or all charged negatively, they will repel each other and not coalesce. Neutralization of this charge causes precipitation through agglomeration."

Neutralization of the charge may be brought about by the addition of electrolytes. In this case the ions of the electrolyte are adsorbed until the particles are electrically neutral and, hence, the electrical film being removed, they precipitate.

Now let us assume that we have a colloidal solution which has been stabilized by the preferential adsorption of a certain cation; if it is only necessary that the charge be neutralized and if we assume that only the anion of the added electrolyte is effective, then, although on account of the preferential adsorption of ions it will require different concentrations of the different anions

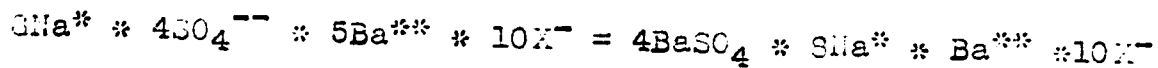
to bring about precipitation, the amounts of the adsorbed anions in the coagulated material should be equivalent when precipitation has once taken place. This is manifestly not the case as there would then be no reason for the different precipitating powers for different salts of a given anion.

Leaving out of consideration the many interfering factors coming into the determination of adsorption values by the precipitating power of electrolytes and passing over the many assumptions necessary to explain the results obtained, we believe that the precipitating power of an ion does not truly measure the amount of adsorption of that ion. It seems that the precipitating power of an electrolyte gives only the concentrations at which the ions of that electrolyte will be adsorbed sufficiently to neutralize the charge existing on the colloidal particles. If we take a colloidal solution, the particles of which are positively charged, and precipitate it by a series of sodium salts of various anions, although the concentration of solution necessary in each case might be different in order to bring about a sufficient adsorption to cause precipitation, nevertheless, when this sufficient concentration has been reached, if precipitation depends only on the neutralization of the positive charge, the amount of anion adsorbed in each case should be equivalent, assuming that the sodium ion does not play a role. However, as we have changed the concentration of sodium ion, we are not entirely justified in assuming its influence to be negligible and it seems in this case that according to the concentration necessary to cause precipitation, the adsorption of the anions, over and above that necessary for the neutralization of the original charge, would follow the adsorption isotherm for sodium in the disperse phase under consideration.

It has been demonstrated in a number of cases that it is possible to prepare either a positive or negative colloidal solution of the same material and this by having one or the other of the reacting substances in excess. Thus Lottermoser⁵⁶, by the addition of an excess of alkali halide to silver nitrate, prepared a colloidal solution of silver halide that owed its stability to adsorbed halogen ion, since it moved to the anode under electrical stress. On the other hand, when a slight excess of silver nitrate was added to the alkali halide, a colloidal solution of silver halide resulted which owed its stability to adsorbed silver ion, since it moved to the cathode. A positively charged colloidal solution of barium sulphate has been prepared by Kato⁵⁷ and by Recoura⁵⁸; and Weiser describes a negative colloidal solution of the same substance prepared by one of his students.

If we consider the quite general contamination of precipitates it might not be too great a step to assume that all precipitates in the process of formation pass through the colloidal condition, even though they may exist in this condition for but an infinitesimal period of time. The change from this colloidal state, with the ensuing precipitation, must then come about through the neutralization of the charge of the adsorbed ion.

Let us assume that we first have barium sulphate formed by the interaction of sodium sulphate with an excess of a soluble barium salt, or in terms of ions:



We have the barium sulphate formed as a solid; it is peptized by the adsorption of Ba and Na ions to the momentary formation of a positive colloidal solution; now, there ensues a further adsorption of negative X ions until the previously adsorbed positive ions are neutralized and the solid barium sulphate is precipitated. Evidently, since the concentration of sodium and barium ions are approximately the same for the experiments with the different anions, we would expect under these conditions that the final adsorption values of all the anions would be equivalent. This is clearly not the case if we consider our results previously tabulated.

On the other hand, let us assume that the solid barium sulphate is peptized by the anion (x); then this adsorbed anion is neutralized by a secondary adsorption of sodium and barium ions until precipitation ensues. Manifestly, in this case, since in each set of experiments (x) is represented by a different anion, we would expect to get a different adsorption value for (X). Of course the mere fact that the adsorption of positive and negative ions is taking place simultaneously need not interfere with our course of reasoning. This set of assumptions seem to fit the case for our adsorption values better than the former set but it seems contrary to the fact that a negative colloidal solution of barium sulphate is formed in the presence of excess sulphate ion. Since we know that it is possible to pass from a colloidal solution, the particles of which are negatively charged to one whose particles are positively charged, this need not necessarily set aside our previous explanation.

The thought came that possibly the one set of assumptions might apply to the precipitation in the presence of one of the reacting substances and the other set to precipitation in the presence of an

excess of the other reacting substance. If this were so barium sulphate precipitated in the presence of an excess of sodium sulphate should show equivalent adsorption values for all anions. We do know, at any rate, that the amount of adsorption is very different in the two cases. In order to see if there was any basis for this thought, we then conducted some experiments with the chlorates and permanganates. The results are given in Tables XXV and XXVI.

Table XXV.

Adsorption of Chlorate Ion.

(Na ₂ SO ₄ in excess)				
N/100 Na ₂ SO ₃ cc.	Chlorate ion adsorbed by BaSO ₄			Average
	grams	grams per 100 mols	gram equivalents per 100 mols	
53.4	0.00742	135.37	2.225	2.266
55.2	0.00733	192.05	2.300	
54.6	0.00760	139.96	2.275	

Table XXVI.

Adsorption of Permanganate Ion.

(Na ₂ SO ₄ in excess)				
N/100 Na ₂ SO ₃ cc.	Permanganate adsorbed by BaSO ₄			Average
	grams	grams per 100 mols	gram equivalents per 100 mols	
27.5	0.00655	163.63	1.375	1.366
26.5	0.00631	157.63	1.325	
23.0	0.00667	166.60	1.400	

We see that the adsorption values are nowhere near the same and although their absolute values are much less they still preserve the same order as in the former series determined in the presence of an excess of the barium salt.

Discussion of Results

From the results of this investigation the order of adsorption of the ions by precipitated barium sulphate is: ferrocyanide > nitrate > nitrite > chlorate > permanganate > ferricyanide > chloride > bromide > sulphocyanate > iodide, the ferrocyanide ion being adsorbed the most and iodide the least. From a consideration of this order and of the absolute amount of adsorption in each case we find very little reason to place much credence in Schulze's law. Although we find a quadrivalent ion the most strongly adsorbed, we find four univalent ions more strongly adsorbed than the trivalent ferricyanide. Furthermore, contrary to what is implied in Schulze's law, we find a very wide variation in the amount of univalent ions adsorbed. This amount varies from 3.432 gram anions per 100 mols for nitrate to 0.056 gram anions per 100 mols for iodide ion. If the adsorption values are expressed in gram anions instead of gram equivalent anions the order becomes: nitrates > nitrites > chlorate > ferrocyanide > permanganate > chloride > ferricyanide > bromide > sulphocyanate > iodide, the nitrate ion being adsorbed the most and the iodide the least. Here there is nothing even to suggest Schulze's law.

Although chemically dissimilar ions of the same valence may show a wide variation in the degree of adsorption, indicating that adsorption is a specific property of ions, it was observed that nitrate and nitrite ions which are more nearly related chemically were adsorbed to about the same extent. Notwithstanding that there are many exceptions to Schulze's law, there is a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence. This makes it seem probable that there are two factors which determine the adsorption of ions by a given dispersing phase: the specific nature of adsorption and the valence of the ion. In the case of dissimilar ions of the same valence, like nitrate and iodide ions, there may be a wide variation in the degree of adsorption just as was found; on the other hand, with ions more nearly related and of the same valence, like nitrate ion and nitrite ion, one might expect to find a similar amount adsorbed, just as the experiments showed. Now it was thought that if a series of ions of much the same general character were selected, thus eliminating the specific factor as far as possible, one might be able to get a clearer insight into the effect of valence. Among the ions considered in this investigation, the cyanides seemed the most promising for such a comparison. This is particularly true of ferrocyanide and ferricyanide ions which are identical in chemical

composition but differ in valence. The results of this comparison are summarized in Table XIV. The adsorption values are expressed in gram equivalent anions per 100 mols of barium sulphate.

Table XIV.

Anion	Valence	Adsorption
Ferrocyanide	4	13.201
Ferricyanide	3	2.695
Cyanide	1	0.510
Sulphocyanate	1	0.220

In view of the quite generally known large adsorption of iron by barium sulphate, the objection may be raised that the increase in the adsorption value of the ferrocyanide ion over that of the cyanide and sulphocyanate ions is due to the presence of iron in the ion. Even if this were admitted, it can clearly not account for the great increase in the adsorption value of ferrocyanide ion over that of ferricyanide, these two values being respectively 13.201 and 2.695. In the first place, the iron was not present as the ferrous ions but exists as complex ions; in the second place, the values are based on the determination of the amount of nitrogen present in the precipitates; in the third place, if the iron had any great effect, it is rather hard to reconcile the conflicting facts that the trivalent iron is present in the ion of lower valency, which is adsorbed less. These results then seem to point to the conclusion that there is both a specific and a valence factor influencing the adsorption of ions. If the specific factor could be maintained absolutely constant, the amount of adsorption of an ion would be directly proportional to the valence.

It is of interest to compare the order of ions obtained by direct analysis of barium sulphate with the order deduced from coagulation experiments. From Hofmeister's⁵⁹ experiments on the coagulation of albumin in neutral or slightly alkaline solution, the order is sulphocyanate > iodide > chlorate > nitrate > chloride > acetate > citrate > phosphate > sulphate > tartrate, the sulphocyanate being adsorbed the most and the tartrate the least. In slightly acid solution Pauli⁶⁰ found the order of ions to be: sulphocyanate > iodide > bromide > nitrate > chloride > acetate. Combining these two orders

we get: sulphocyanate > iodide > bromide > chlorate > nitrate > chloride > acetate > citrate > phosphate > sulphate > tartrate. The result of combining the two series is to place bromide ion in relation to the others as the order agrees for all the other ions. By comparing this order of ions with that obtained with barium sulphate, we see that the two are almost exactly opposite. Selecting the ions common to the two series, Hofmeister's and our own, we find that the former is: sulphocyanate > iodide > bromide > chlorate > nitrate > chloride; while the latter is iodide < sulphocyanate < bromide < chloride < chlorate < nitrate. The orders are almost exactly reversed, the position of the chlorides being irregular. Csaka⁶¹ found the order of adsorption of anions by charcoal to be: iodide < nitrate < bromide < chloride < sulphate, the iodide being adsorbed the least. This order agrees with our own except in the case of the nitrate ion. From experiments on hydrous ferric oxide⁶² the order of adsorption of precipitating anions is: iodide < bromide < nitrate < chloride < hydroxyl < sulphate < dichromate, the iodide being adsorbed the least. This order is likewise more in accord with the results we obtained and is again the reverse of Hofmeister's series.

On account of the specific nature of adsorption, one might expect to get a variation in the order with each adsorbing medium, just as the results with barium sulphate, charcoal and ferric oxide seem to indicate. However, the similarity in the order with these three substances is rather striking considering that the actual conditions and methods of determination were different in each case. We are at a loss to account for the almost complete reversal of the order of ions with albumin from what it is with barium sulphate and the other substances cited. It is usually considered that albumin constitutes a special case and that it is fundamentally different from the other colloidal solutions.⁶³ This is certainly open to question; but there is no doubt but that further experimental work must be done before it will be possible to state, with any degree of assurance, the cause of this apparent discrepancy. To this end it is planned to carry out further determinations on the absolute amount of adsorption by different substances.

In addition to the anions that should be avoided in the solution from which barium sulphate is precipitated during analytical procedures, the data indicates what barium salts should be used in making colloidal barium sulphate by double decomposition. When barium sulphate is a positive colloid it is more stable in the presence of slightly adsorbed anions such as sulphocyanate or iodide. This explains why von Weimarn³⁴ obtained such a stable colloidal solution of barium sulphate by mixing alcoholic solutions of barium sulphocyanate and cobalt sulphate. In view of the stability of von Weimarn's colloid, we should expect to find cobalt ion strongly adsorbed by barium sulphate, since this would likewise have a stabilizing effect. Lato³⁴ used barium acetate in the preparation of his colloidal barium sulphate. Although we have not as yet determined the adsorption of acetate ion by barium sulphate, it is probably slight.

SUMMARY

The results of this investigation may be summarized as follows:

1. The adsorption of the following anions by precipitated barium sulphate has been determined: chloride, bromide, iodide, chlorate, permanganate, nitrate, nitrite, cyanide, sulphocyanate, ferrocyanide and ferricyanide. Barium sulphate was precipitated by mixing a solution of sodium sulphate with a solution of barium salts and the absolute amount of the anion adsorbed was determined by direct analysis of the precipitate. The conditions of precipitation and the subsequent treatment of the salt were maintained as nearly constant as possible, throughout.
2. The order of adsorption of anions is: ferrocyanide > nitrate > nitrite > chlorate > permanganate > ferricyanide > chloride > bromide > cyanide > sulphocyanate > iodide, the ferrocyanide being adsorbed the most and the iodide ion the least. Changing the conditions affects the absolute amount of adsorption but not the order of the ions.
3. The order of adsorption is not in accord with Schluzer's law: Although the tetravalent ferrocyanide ion is adsorbed the most, there are four univalent ions more strongly adsorbed than the trivalent ferricyanide ion. Furthermore, there is a wide variation in the amount of univalent ions adsorbed.
4. Determination of the order of ions by direct analysis of the adsorbing phase, when this is possible, is preferable to deducing the order from coagulation

data, on account of the greater accuracy of the former. It is probably inaccurate in any case to assume that the ion, with the same charge as the colloidal particles, has no effect in determining the critical concentration for coagulation of the colloid by electrolytes. It is more probable that the relatively small effect of the ion of the same charge as the colloidal particle may be lost sight of altogether because of the errors inherent in the experimental method.

5. The order of adsorption of anions by barium sulphate is the reverse of that deduced from Hofmeister's data on the coagulation of albumin by electrolytes. The order of adsorption by charcoal and by hydrous ferric oxide is apparently more nearly what it is with barium sulphate. Further experimental work is necessary in order to find out the cause of the apparent discrepancy in the case of albumin.

6. Two factors determine the adsorption of ions by a given adsorbing agent: the nature of the ion and the valence of the ion.

7. With the ions of the same general character, the specific nature of adsorption should not be so pronounced and the valence factor should predominate. Thus, we find nitrate and nitrite ion adsorbed by barium sulphate to about the same extent; and the order of adsorption of the cyanides by barium sulphate is ferrocyanide > ferricyanide > cyanide > sulphocyanate, which is in accord with the law of Schulze.

8. With the ions which are not similar and yet have the same valence, the specific nature of adsorption may be very pronounced. Thus, we find that barium sulphate adsorbs nitrate ion much more than iodide ion.

9. Mendelejeff's observation that nitrates are carried down by barium sulphate more readily than chlorides has been confirmed, as has been the statement, frequently met with in text books of analytical chemistry, to the effect that chlorates and nitrates should be absent from solutions in which sulphate is to be determined as barium sulphate.

10. Colloidal solutions of barium sulphate are usually positive due to the strong preferential adsorption of barium ion. The stability of the colloid should be greatest in the presence of a weakly adsorbed anion. This partly accounts for the stability of von Weimarn's colloidal solution of barium sulphate precipitated from barium sulphocyanate solution.

11. Since barium ion is adsorbed more strongly by barium sulphate than is sulphate ion, one would expect, other conditions being the same, to have greater peptization and greater anion adsorption in the presence of excess barium salt than in the presence of excess sulphate. In a like manner, since hydrogen ion is more readily adsorbed than any other univalent cation, one would expect to find greater anion adsorption when barium sulphate is precipitated from sulphuric acid solution than from sodium sulphate solution. These conclusions have been confirmed.

12. Methods have been applied and evolved for the estimation of minute amounts of material adsorbed by barium sulphate.

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