

ADSORPTION BY PRECIPITATES. I

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Adsorption of Anions by Precipitated Barium Sulphate¹

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, Mendelejeff² 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

¹ A portion of a thesis presented by J. L. Sherrick to the Faculty of the Rice Institute in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

² Pogg. Ann., 55, 214 (1842).

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 Smith¹ 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 Parker² and by Hulett and Duschak.³

The various text books of Quantitative Analysis have much to say as to the necessity for the absence of certain ions from the solution in which sulphates are to be determined as barium sulphate. Thus Fresenius⁴ states: "It (barium sulphate) has a great tendency, upon precipitation, to carry down

¹ Chem. News, 24, 61-64, 66-69 (1871).

² Zeit. anorg. Chem., 8, 413 (1895).

³ Ibid., 40, 196 (1904).

⁴ Fresenius: "Quantitative Chemical Analysis," 1, 169 (1908); Compare Treadwell-Hall: "Analytical Chemistry," 2, 464 (1907).

with its 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 completely precipitated out of it by means of sulphuric acid: the resulting precipitate too, contains phosphoric acid (Scheerer, Rube)."

As regards the mechanism of the contamination of barium sulphate by foreign substances, the views are many and divergent. Hulett and Duschak¹ consider as a possible explanation of chloride contamination the formation of such complex salts as BaCl.HSO_4 and $(\text{BaCl}_2)\text{SO}_4$. Silberberger² for the contamination by potassium nitrate claims the formation of a complex $\text{NO}_3.\text{BaSO}_4.\text{BaSO}_4.\text{K}$; and for potassium chloride $\text{Cl.BaSO}_4.\text{BaSO}_4.\text{BaSO}_4.\text{K}$. He states further that sodium salts are not retained by barium sulphate in the form of complexes. Johnson and Adams³ conclude that it is a phenomenon of adsorption. Richards⁴ compares the contamination with ferric sulphate⁵ to the occlusion of hydrogen by palladium which probably involves both solid solution and adsorption. Schneider⁶ looks upon it as a case of solid solution; but Küster and Thiel⁷ and also Korte⁸ conclude that the contamination is an adsorption phenomenon. Smith⁹ states that it is neither a case of solid solution nor adsorption; but is the result of the

¹ Loc. cit.

² Monatshefte Chemie, **25**, 220 (1904).

³ Jour. Am. Chem. Soc., **32**, 588 (1910).

⁴ Zeit. anorg. Chem., **23**, 383 (1900).

⁵ Glendenning and Edgar: Chem. News, **24**, 140 (1871); Sloane: *Ibid.*, **44**, 221 (1882); Gladding: Jour. Am. Chem. Soc., **16**, 398 (1894).

⁶ Zeit. phys. Chem., **10**, 425 (1893).

⁷ Zeit. anorg. Chem., **19**, 97 (1898); **22**, 424 (1899).

⁸ Jour. Chem. Soc., **81**, 1503 (1905).

⁹ Jour. Am. Chem. Soc., **39**, 1152 (1917).

formation of a complex of the composition $\text{Ba}(\text{Fe}(\text{SO}_4)_2)_2$. Weiser¹ 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, aluminium, 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 Hartl² find that when barium sulphate is added to a colloidal gold solution, the solution is decolorized and destroyed. Patten² finds that, when barium sulphate is boiled with solutions of the chlorides of iron, manganese, and chromium, some of the metal passes into the solid in each case. Hulett and Duschak³ 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 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 the presence 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 precipi-

¹ Jour. Phys. Chem., **21**, 315 (1917).

² Jour. Am. Chem. Soc., **25**, 186 (1903).

³ Loc. cit.

tation of a colloid that owes its stability to 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 Schulze,¹ 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 of 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 salt solution. In this way a series of determinations are made until that concentration of salt solution is found that will just cause a coagulation of the drop. A second method consists in adding the salt solution 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 the different ions may require different lengths of time for attaining equilibrium. Furthermore, although agitation usually has very little effect on the most 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.² 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 Schulze:³ "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

¹ Jour. prakt. Chem., (2) 25, 43 (1882); 27, 320 (1884).

² Hardy: Zeit. phys. Chem., 33, 385 (1900).

³ Loc. cit.

be obtained. The effect of these factors may be shown best by an example. Dilute sulphuric acid (9.8 grams per liter of H_2SO_4) immediately precipitates arsenic sulphide solution dropped into it. On the other hand a solution one-third as strong, that is, with 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 the 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."

Kato¹ 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'² nephelometer for determining the critical concentration failed and viscosity meas-

¹ Mem. Coll. Sci. Eng. Kyoto Imp. Univ., 2, 137 (1909-10).

² Richards and Wells: Am. Chem. Jour., 31, 235 (1904).

urements¹ proved valueless. The concentration of electrolyte necessary for coagulation that was finally adopted, was the concentration in which the colloid settled within 24 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 for comparison of the coagulative power of electrolytes."

The results of Kato's investigation 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 alike, 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, which 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 Hardy 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;² 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 electrolytes 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

¹ Kawamura: Jour. Coll. Sci. Tokyo Imp. Univ., 25, Art. 8 (1908).

² Hardy: Loc. cit.; Cf. Bancroft: Jour. Phys. Chem., 19, 363 (1915).

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 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 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 concentration. Leighton,¹ 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 by the above method 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.

¹ Jour. Phys. Chem., 20, 32, 188 (1916).

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.

Osaka¹ 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 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 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 taken: Some water was put in the bottom of a small glass vessel of desiccator form about 9 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 percent of its weight. As the solutions used in the experiments were about one-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."

These results were obtained under the assumption that charcoal takes up the same amount of water from the saturated

¹ Mem. Coll. Sci. Kyoto, 1, 267 (1915).

vapors as it does when placed in the liquid. It is a question whether this is true¹ 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 been said it is probable that the most accurate results may be obtained by choosing a suitable adsorbing material and analyzing for the adsorbed 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 barium salt. By this procedure three ions were kept constant throughout the series of experiments and the fourth was varied. The concentrations 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.

¹ See Von Schroeder: "Über Erstarrungs und Quellungserscheinungen von Gelatin," *Zeit. phys. Chem.*, **45**, 109 (1903); Cf. Bancroft: *Jour. Phys. Chem.*, **16**, 1395 (1912).

Special methods of analysis were required to determine the ions adsorbed by barium sulphate since such small quantities of material were involved. Hulett and Duschak¹ 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, bromide, iodide, chlorate, permanganate, nitrate, nitrite, cyanide, sulphocyanate, ferricyanide and ferrocyanide. In the interest of accuracy a number of determinations were made in every case and the

¹ Loc. cit.

average taken. The determinations of the various ions will be taken up separately.

The Adsorption of Chlorine Ion

As before mentioned Hulett and Duschak 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 dissolved 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 barium sulphate was hastened by heating in a hot water bath. Allen and Johnston¹ 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

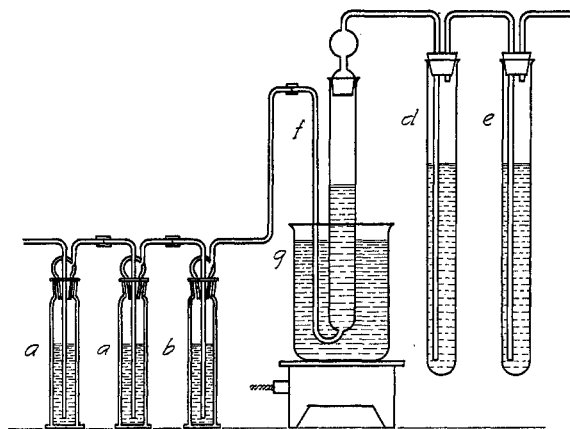


Fig. I

that recommended by Hulett and Duschak. The apparatus is shown in Figure I. The precipitate, together with the as-

¹ Jour. Am. Chem. Soc., 32, 594 (1918).

bestos 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 *c* was attached as quickly as possible and air was aspirated slowly through the apparatus. The wash bottle *a* contained 20 percent 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 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. Using these precautions a sharp end-point was possible and check results were readily obtained.

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 aspirated Hours	Conc. H ₂ SO 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

Determinations of Chlorine in BaCl₂.2H₂O.—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 content 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 BaCl₂.2H₂O

Weight of BaCl ₂ .2H ₂ O		Percent chlorine		Difference expressed in cc N/100 solution
Taken	Found	Theoretical	Found	
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 subdivision 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.¹ 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 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 then serve 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 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 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° 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 adsorbed chloride ion was deter-

¹ Weiser: Jour. Phys. Chem., 21, 315 (1917).

mined. The results of a series of determinations are given in Table III. In the first column is given the number of cubic centimeters of $N/100$ AgNO_3 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 BaSO_4			Average
	Gram	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 the same excess of barium chloride was employed as there was excess 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 BaSO_4			Average
	Gram	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	57.43	1.547	
6.89	0.00245	61.20	1.722	
6.79	0.00241	60.26	1.697	
6.84	0.00244	60.96	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 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 a $M/10$ 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 stop-cock; 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 procedure should tend to increase the total amount of adsorption. The results of a series of determinations are given in Table V.

TABLE V
Adsorption of Chloride Ion
(BaSO₄ from Na₂SO₄ with excess BaCl₂)

N/100 AgNO ₃ cc	Chloride ion adsorbed by BaSO ₄			Average
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
7.00	0.00249	62.13	1.750	1.760
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	
7.10	0.00252	63.01	1.775	

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 univalent¹ cations, it follows that greater peptization of barium sulphate should

¹ Freundlich: "Kapillarchemie," 354 (1909).

result when the precipitation was effected from sulfuric acid solution than from sodium sulphate solution.¹ 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 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
(BaSO_4 from H_2SO_4 with excess BaCl_2)

$N/100$ AgNO_3 cc	Chloride ion adsorbed by BaSO_4			Average
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
9.0	0.00319	79.88	2.250	2.294
9.0	0.00319	79.88	2.250	
9.4	0.00333	83.43	2.350	
9.3	0.00330	83.54	2.325	

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

¹ Weiser: Loc. cit.

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.—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; adsorbed in a solution of potassium iodide; and finally titrated with an *N/10* 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.

TABLE VII
Determination of Bromine in Bromides
(Fine powder)

Salt	Weight		Percent Found	Cc of <i>N/100</i> solution		
	Taken	Found		Required	Taken	Difference
BaBr ₂ ·2H ₂ O	0.0509	0.0468	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	0.0842	0.0775	92.0	50.54	46.52	4.02
BaBr ₂ ·2H ₂ O	0.0386	0.0349	90.4	23.17	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	85.1	11.26	9.56	1.70

The results were disappointing, to say the least, as in no case did we obtain more than 92.3 percent 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 and, 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 percent 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 and hence 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 the 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 case than in the latter. A second factor is the following: In so far as the hydrobromic acid formed 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 it would act on the iodine liberated by the bromine reducing it to hydriodic 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 the 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 $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$		Percent Found	Cc of $N/100$ solution		
Taken	Found		Theoretical	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	18.85	18.41	0.44

In the above series of experiments the lowest result obtained was 96.4 percent of the theoretical, while the highest was 98 percent. 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 quantitative 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 $M/10$ solution of sodium sulphate to 50 cc of $M/10$ barium bromide diluted with 160 cc of water. The precipitate was treated as previously described and the amount of

bromide ion adsorbed was determined. The results of a series of determinations are given in Table IX.

TABLE IX
Adsorption of Bromide Ion

$N/100 \text{ Na}_2\text{S}_2\text{O}_8$ cc	Bromide ion absorbed by BaSO_4			Average
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
3.68	0.00294	73.51	0.920	
3.07	0.00245	61.32	0.768	
3.27	0.00261	65.32	0.818	
3.17	0.00243	60.82	0.793	
3.27	0.00261	65.32	0.818	
3.48	0.00278	69.52	0.870	

Adsorption of Iodide Ion

Determination of Iodine in Potassium Iodide.—It was thought that the same method used 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 percent of the theoretical amount of iodine was obtained, although all color of the element had disappeared. It was thought that the low results might be due to 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, after which 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 this apparatus were as unsatisfactory as those preceding. It was noted, however, that a considerable quantity of iodine vapor was swept into the potassium iodide solution but relatively little of it remained as such, indicating that reduction had taken place. In view of our experiments with the bromides these results might be expected. Since hydriodic acid is a much stronger reducing agent than is 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 iodide than with potassium iodide for the action would be slower under these conditions and the oxidation by the chromic acid would be 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 10 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 24 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 solution added.¹ It was then distilled, and the distillate caught in a solution of potassium iodide. All the iodine was obtained in this way and it was subsequently titrated with $N/100$ sodium thiosulphate in the usual way. The results are given in Table X.

¹ Scott: "Standard Methods of Chemical Analysis," 205 (1917).

TABLE X

Weight of KI		Percent Found	Cc of N/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0147	0.0143	97.3	8.85	8.62	0.23
0.0130	0.0126	97.0	7.83	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 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.

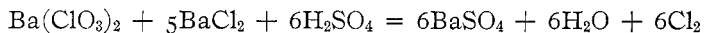
TABLE XI
Adsorption of Iodide Ion

$N/100$ $Na_2S_2O_8$ cc	Iodide ion adsorbed by $BaSO_4$			Average
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
0.3	0.00038	9.52	0.075	0.056
0.2	0.00025	6.35	0.050	
0.1	0.00013	3.17	0.025	
0.3	0.00038	9.52	0.075	

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 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 0.2 gram 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 3 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 thio-sulphate. The following reaction was expected to take place between the chloric and hydrochloric acids:



The results are given in Table XII.

TABLE XII
Determinations on Ba(ClO₃)₂.H₂O
(In light)

Weight of Ba(ClO ₃) ₂ .H ₂ O		Percent found	Cc of <i>N</i> /100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0105	0.0079	75.2	39.08	29.36	9.72
0.0110	0.0086	77.9	40.94	31.92	9.02
0.0114	0.0099	87.0	42.43	36.93	5.50
0.0135	0.0111	82.5	50.25	41.43	8.82
0.0139	0.0104	75.1	51.74	38.83	12.91

The results obtained show only from 75 percent to 87 percent 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 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 much 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 or potassium iodide as such, for the following reaction would then take place¹: $5\text{KI} + \text{ClO}_2 + 4\text{HCl} = 5\text{I} + 5\text{KCl} + 2\text{H}_2\text{O}$.

On the other hand if some of this ClO_2 were decomposed by the light before reaching the potassium iodide solutions, low results would be expected. 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 dark)

Weight of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$		Percent found	Cc of $N/100$ solution		
Taken	Found		Theoretical	Taken	Difference
0.0114	0.0092	80.2	42.43	34.07	8.36
0.0130	0.0079	60.9	48.39	29.46	18.93
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 experi-

¹ Luther and McDougall: Zeit. phys. Chem., 62, 199, 242 (1908).

ments with chlorates very much greater but the gases were 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 with 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. 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		Theoretical	Taken	Difference
0.0130	0.01283	98.7	48.39	47.78	0.61
0.0133	0.01336	100.4	49.54	49.72	0.18
0.0130	0.0132	101.5	48.39	49.31	0.92

The above results are very satisfactory compared with the previous determinations. Accordingly in all subsequent experiments where a rapid reaction was likely 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.

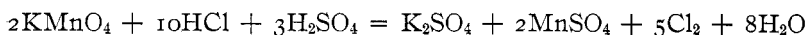
TABLE XV
Adsorption of Chlorate Ion

$N/100 \text{ Na}_2\text{S}_2\text{O}_8$ cc	Chloride ion adsorbed by BaSO_4			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	Average
138.41	0.01925	481.32	5.767	5.837
135.45	0.01884	471.02	5.644	
146.39	0.02036	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 $KMnO_4$.—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 was added 3 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 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 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 barium sulphate precipitated in the regular way in the presence of excess barium permanganate. The results are given in Table XVII.

TABLE XVII
Adsorption of Permanganate Ion

$N/100 \text{ Na}_2\text{S}_2\text{O}_8$ cc	Adsorption of permanganate ion by BaSO_4			
	Gram	Grams per 100 mols	Grams Equivalents per 100 mols	Average
56.32	0.01339	334.91	2.816	2.847
56.90	0.01253	313.36	2.845	
57.48	0.01367	341.81	2.874	
57.35	0.01364	341.01	2.868	
56.66	0.01348	336.93	2.833	

Adsorption of Nitrate Ion

The attempt was made to determine nitrate ion by the same method found so convenient for the halogens. Fresenius¹ 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 is necessary to use concentrated acid in order to dissolve the barium sulphate, the method of Fresenius could not be used directly. After repeated unsuccessful attempts to modify it to suit our needs, it was decided to use the Foerster² modification of the Kjeldahl method for nitrogen. This fitted in with the scheme of things admirably since the concentrated sulphuric acid used at the beginning of this procedure served to dissolve the barium sulphate precipitate; the phenol, used with the concentrated acid having 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 necessary to increase the amount of phenol-sulphuric acid used. The ammonia evolved was received in $N/100$ sulphuric acid and the excess titrated back with $N/100$ sodium hydroxide solution using cochineal as an indicator.

¹ Rose: Zeit. anal. Chem., 1, 309 (1862); Gladstone: Jour. prakt. Chem., 64, 442 (1855).

² Chem. Zeit., 12, 1555 (1889); 13, 229 (1889).

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 solutions 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 300 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.

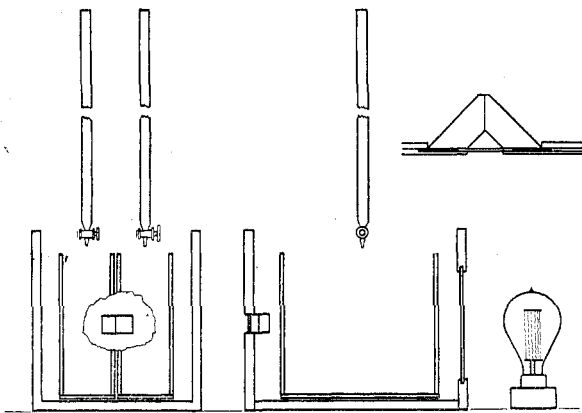


Fig. II

A standard colored solution was prepared by taking suitable equivalent volumes of the standard titrating solutions, adding three drops of cochineal solution¹ and diluting to a volume approximately equal to that obtained in the titrations 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.

¹ Made by digesting 1 part of crushed cochineal with 10 parts of 25 percent alcohol.

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 colors were compared as the titration proceeded. By means of this colorimeter it was readily possible to duplicate results to 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 solutions were taken as used in the subsequent experiments and the directions in Olsen, previously referred to, were followed closely. 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"

Determination	1	2	3	Average
Cc of $N/100$ solution	14.65	14.76	15.07	14.83

Determination on Known Weights of Nitrates.—Weighed samples of nitrates were taken and treated by the Foerster modification of the Kjeldahl process. The results are given in Table XIX.

TABLE XIX
Determinations on Nitrates

Salt	Weight		Percent found	Cc of $N/100$ solution		
	Taken	Found		Theoretical	Taken	Difference
KNO_3	0.0317	0.0321	101.2	31.33	31.64	0.31
$Ba(NO_3)_2$	0.0505	0.512	101.3	38.63	39.22	0.59

Adsorption of Nitrate Ion.—Barium sulphate was precipitated in the usual way with barium nitrate solution in excess.

The adsorbed nitrate ion 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 by BaSO ₄			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	Average
49.55	14.83	34.72	0.02152	538.16	8.680	
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	8.480	
48.25	14.83	33.42	0.02072	518.01	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	

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 Mendelejeff 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 5 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 determination of the amount of adsorbed 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 condi-

tions 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 N/100 solution	16.57	16.31	16.70	16.31	16.47

Determinations on Known Weights of Nitrites.—As has been observed frequently 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 very rapid and 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 percent of the theoretical. In a second experiment a single crystal of barium nitrite was taken with the idea that the slower action on a 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 percent 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 solubility of barium sulphate. The results of the two experiments above described are given in Table XXII.

TABLE XXII
Determinations on Barium Nitrite

Sample	Weight		Percent found	Cc N/100 solution		
	Taken	Found		Theoretical	Taken	Difference
Powdered	0.0417	0.0394	94.5	33.71	31.90	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

N/100 solution			Adsorption of nitrite ion by BaSO ₄			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	Average
45.85	16.47	29.38	0.01251	337.87	7.345	
45.98	16.47	29.51	0.01357	339.36	7.378	
46.87	16.47	30.40	0.01398	349.60	7.600	
46.74	16.47	30.27	0.01392	322.99	7.568	
46.61	16.47	30.14	0.01386	346.61	7.535	
45.97	16.47	29.50	0.01357	339.25	7.375	7.467

By comparing the results tabulated above with those obtained for nitrates it will be seen that there was little difference between the amount of adsorption in the two cases; as will be pointed out in the later discussions this result 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. Dyer¹ and Olsen² 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 Foerster modification of the Kjeldahl method for nitrogen is necessary in evaluating certain cyanides. Williams,³ 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 Foer-

¹ Chem. Centr., (3) 17, 433 (1886).

² "Quantitative Chemical Analysis," 189 (1910).

³ "The Chemistry of Cyanogen Compounds," 90 (1915).

ster 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 Weight of Mercuric Cyanide.—The Kjeldahl method gives very reliable results for cyanide 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		Theoretical	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 manner with barium cyanide in excess and the adsorbed ion determined by the Kjeldahl method. The results are given in Table XXVI.

TABLE XXVI
Adsorption of Cyanide Ion

N/100 solution			Adsorption of cyanide ion by BaSO_4			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	Average
17.68	16.40	1.28	0.00033	8.32	0.320	
17.52	16.40	1.12	0.00029	7.18	0.280	
17.52	16.40	1.12	0.00029	7.18	0.280	
18.01	16.40	1.61	0.00042	10.46	0.403	
17.49	16.40	1.09	0.00028	7.08	0.273	0.310

Adsorption of Sulphocyanate Ion

Determination of "Blank."—The determinations of blanks made in connection with this set of experiments are given in Table XXVII.

TABLE XXVII

Determination No.	1	2	3	Average
Cc N/100 solution	14.85	14.79	15.04	14.89

Determination on a Known Weight of $Ba(SCN)_2 \cdot 2H_2O$.—That the Kjeldahl method is quite as accurate for the determination of small amounts of thiocyanates as for cyanide is shown by the analysis tabulated in Table XXVII.

TABLE XXVII
Determination of $Ba(SCN)_2 \cdot 2H_2O$

Weight		Percent found	Cc N/100 solution		
Taken	Found		Theoretical	Taken	Difference
0.0324	0.0327	100.9	22.35	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 determined. The results of a series of determinations are given in Table XXIX.

TABLE XXIX
Adsorption of Sulphocyanate Ion

Cc N/100 solution			Adsorption of sulphocyanate ion by $BaSO_4$			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	Average
15.86	14.89	0.97	0.00056	1.41	0.243	
15.53	14.89	0.64	0.00037	0.93	0.160	
16.02	14.89	1.13	0.00065	1.64	0.283	
15.90	14.89	1.01	0.00058	1.46	0.253	
15.53	14.89	0.64	0.00037	0.93	0.160	
15.53	14.89	0.64	0.00037	0.93	0.160	
16.02	14.89	1.13	0.00065	1.64	0.283	

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 differences in terms of cc of $N/100$ solution are 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:¹ A strong barium chloride solution was added to a moderately strong solution of sodium ferrocyanide. Barium ferrocyanide, $Ba_2Fe(CN)_6 \cdot 6H_2O$, separated out as a light yellow crystalline powder. The precipitate was washed with water, filtered and recrystallized several times from water. 100 cc of water dissolved 0.34 gm of the salt at 15.5° and 1.01 g at 100° .

Determination of Blank.—Sufficient quantity of solutions were prepared for making the determinations on both ferrocyanides and ferricyanides. Consequently the same "blank" correction was 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	16.30	16.64	16.47

Determination on a Known Weight of Potassium Ferrocyanide.—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 $K_4Fe(CN)_6$

Weight		Percent found	Cc of $N/100$ solution		
Taken	Found		Theoretical	Taken	Difference
0.0091	0.0089	97.8	12.92	12.36	0.56
0.0120	0.0119	99.2	17.19	16.90	0.29

¹ Williams: Loc cit., p. 95.

Since the results are quite satisfactory for the purpose, a series of experiments were carried out for the determination of both ferrocyanide ion 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 in BaSO ₄			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	
						Average
95.93	16.47	79.46	0.02809	702.14	13.242	
94.77	16.47	78.30	0.02767	691.78	13.050	
97.97	16.47	81.50	0.02881	720.17	13.583	
96.30	16.47	79.83	0.02822	705.41	13.305	
93.42	16.47	76.95	0.02720	680.00	12.825	13.201

Adsorption of Ferricyanide Ion

*Preparation of Barium Ferricyanide.*¹—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, Ba₃[Fe(CN)₆]₂·20H₂O, appeared as fine red crystals which are quite stable and very soluble in water.

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

¹ Williams: Loc. cit., p. 138.

TABLE XXXIII
Adsorption of Ferricyanide Ion

N/100 solution			Adsorption of ferricyanide ion by BaSO ₄			
Total	Blank	Adsorption value	Gram	Grams per 100 mols	Gram equivalents per 100 mols	Average
39.19	16.47	22.72	0.00803	200.77	2.840	
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	2.618	
37.93	16.47	21.46	0.00759	189.63	2.683	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 equivalent ions adsorbed by 100 mols of BaSO₄.
 (c) Number of gram ions adsorbed per 100 mols of BaSO₄.
 (d) Grams contamination per 100 grams of BaSO₄ 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	0.056	0.0469	0.0304	0.0468
Sulphocyanate	0.220	0.220	0.1195	0.0547	0.1193
Cyanide	0.310	0.310	0.1258	0.0346	0.1256
Bromide	0.831	0.831	0.5291	0.2846	0.5263
Chloride	1.760	1.760	0.7852	0.2801	0.7791
Ferricyanide	2.695	0.898	1.6088	0.7391	1.5833
Permanganate	2.847	2.847	2.2902	1.4512	2.2390
Chlorate	5.837	5.837	3.8401	2.0864	3.6981
Nitrite	7.467	7.467	3.7194	1.4725	3.5869
Nitrate	8.482	8.482	4.7500	2.2540	4.5346
Ferrocyanide	13.201	3.300	6.8830	2.9986	6.4398

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. In order to test this out, experiments were carried out on the adsorption of chlorate ion and permanganate ion in the presence of excess sodium sulphate. The conditions of precipitation and subsequent treatment of the salt are identical with those previously described under the determinations of the respective ions with the exception that 50 cc of $M/10$ sodium sulphate was added to 40 cc of $M/10$ barium salt. The results are given in Tables XXXV and XXXVI.

TABLE XXXV
Adsorption of Chlorate Ion
(Na_2SO_4 in Excess)

$N/100 \text{ Na}_2\text{S}_2\text{O}_8$ cc	Chlorate ion adsorbed by BaSO_4			
	Gram	Grams per 100 mols	Gram equivalents per 100 mols	Average
53.4	0.00742	185.37	2.225	2.266
55.2	0.00768	192.05	2.300	
54.6	0.00760	189.96	2.275	

TABLE XXXVI
Adsorption of Permanganate Ion
(Na_2SO_4 in excess)

$N/100 \text{ Na}_2\text{S}_2\text{O}_8$ cc	Permanganate ion adsorbed by BaSO_4			
	Gram	Grams per 100 mols	Gram equivalent per 100 mols	Average
27.5	0.00655	163.63	1.375	1.366
26.5	0.00631	157.68	1.325	
28.0	0.00667	166.60	1.400	

From the above experiments it is evident that the absolute amount of the adsorption is less when the precipitation

is carried out in the presence of excess sodium sulphate. However, the chlorate ion is adsorbed more than permanganate ion which is in accord with the previous results. The experiments on chloride ion adsorbed in the presence of excess sodium sulphate as described at the beginning of this paper show that chloride ion is adsorbed much less than either permanganate or chlorate ion. This is in the right direction but the results are not strictly comparable since the precipitation and subsequent treatment of the barium sulphate were different in the case of the chloride ion.

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 > cyanide > sulphocyanate > iodide, the ferrocyanide being adsorbed the most and the iodide the least. From a consideration of this order and of the absolute amount of the 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 8.482 gram anions per 100 mols for nitrate ion to 0.056 gram ions per 100 mols for iodide ion. If the absorption values are expressed in gram anions instead of gram equivalent anions the order becomes: nitrate > nitrite > chlorate > ferrocyanide > permanganate > chloride > ferricyanide > bromide > cyanide > 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 that determine the adsorption of ions by a given disperse phase: the specific nature of adsorption and the valence of the ion. In the case of dissimilar ions of the same valence like nitrate ion and iodide ion there may well 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 indicate. 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 it was 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 XXXVII. The adsorption values are expressed in gram equivalent anions per 100 mols of barium sulphate.

TABLE XXXVII

Anion	Valence	Adsorption
Ferrocyanide	4	13.201
Ferricyanide	3	2.695
Sulphocyanate	1	0.220
Cyanide	1	0.310

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 over that of cyanide and sulphocyanate 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

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 ferric and ferrous ion but exists in complex ions; in the second place, the values are based on the determinations 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 ferric 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's¹ 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 a slightly acid solution Pauli² 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 fix 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 al-

¹ Pflüger's Archiv., 24, 247 (1887); Cf. Bancroft: Jour. Phys. Chem., 19, 350 (1915).

² Hofmeister's Beiträge zur. chem. Physiol., 5, 27 (1904).

most exactly reversed; the position of chlorides being irregular. Osaka¹ found the order of adsorption of anions by charcoal to be: iodide < nitrate < bromide < chloride < sulphate, the iodide ion being adsorbed the least. This order agrees with our own except in the case of nitrate ion. From experiments on hydrous ferric oxide² 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 nearly 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 media 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 method 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 other colloidal solutions.³ 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 for analytical purposes, the data indicate what barium salts should be used in making colloidal barium sulphate by double decomposition. Since barium sulphate is a positive colloid it is most stable in the presence of slightly adsorbed anions like

¹ Mem. Col., Sci. Kyoto Imp. Univ., 1, 267 (1915).

² Freundlich: "Kapillarchemie," 352-358 (1909).

³ *Ibid.*, 434 (1909).

sulphocyanate or iodide. This explains why von Weimarn¹ 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. Kato² 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 anion adsorbed was determined by direct analysis of the precipitate by a suitable method. 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 ion 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 Schulze'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

¹ *Zeit. Kolloidchemie*, 3, 282 (1908).

² *Loc. cit.*

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 coagulation concentration of the colloid by electrolytes. It is more probable that the relatively small effect of the ion with the same charge as the colloid 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 ions of the same general character the specificity of adsorption should not be so pronounced and the valency 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 Schulze's law.

8. With ions which are not similar and yet have the same valence, the specificity 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 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 barium sulphate, precipitated from barium sulphocyanate solution.

11. Since barium ion is adsorbed more strongly by barium sulphate than is sulphate ion, one should expect, other conditions remaining 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 like manner, since hydrogen ion is more readily adsorbed than any other univalent cation one should expect, under otherwise constant conditions, 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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