I. AN ION-EXCHANGE METHOD FOR A VOLUMETRIC DETERMINATION OF SULFATE.

II. A STUDY OF IRON(III) SULFATE COMPLEX IONS.

III. A SODIUM COULOMETER.

IV. A SODIUM-ION GLASS ELECTRODE.

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ABSTRACT

A procedure has been developed for a volumetric determination of sulfate in solutions containing iron(III), chloride, and br[illegible]. A solution is passed through the hydrogen form of a cation exchange resin, the effluent is titrated for hydrogen and for halide ion, and the sulfate is calculated from these titrations. The procedure was successfully used for a determination of sulfur in a pyrite ore.

The complexing of iron(III) with sulfate was studied both spectrophotometrically and by an equilibrium ion-exchange distribution method. Association constants and extinction coefficients for the $FeSO_4^+$ and $Fe(SO_4)_2^-$ complex ions were obtained from these studies.

Resistance measurements and a study of the effect of current flow were made on a redesigned sodium coulometer. A number of the liabilities inherent in a sodium coulometer were considered.

A literature survey was made on the behavior of clay, ion-exchange, and glass membranes in solutions of various ionic species. Glass-membrane electrodes were prepared from four types of glass. The sodium-ion response of these electrodes in various buffer solutions was determined by following the change in potential of a glass-membrane electrode--buffer solution--calomel

electrode system caused by varying the sodium-ion concentration of the solution. Resistance measurements were made on some of the glass membranes.

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PART I

AN ION-EXCHANGE METHOD FOR A VOLUMETRIC DETERMINATION OF SULFATE*

The methods for the determination of sulfate are the least satisfactory of the well-established procedures of quantitative analysis. Search for a rapid, accurate, and widely applicable method has produced a voluminous literature on this subject.

The gravimetric determination of sulfate as barium sulfate is not only time-consuming but also is not accurate unless corrections are introduced for errors due to coprecipitation and to solubility. Moreover, the optimum temperature for drying the precipitate to constant weight is quite uncertain since it is strongly dependent on the conditions obtaining at the time of precipitation. The usual volumetric methods in which sodium rhodizonate or the disodium salt of tetrahydroquinone are used as indicators are rapid but they are considered to be accurate only to within one percent.

The introduction of ion exchange resins into analytical procedures has permitted a rapid and accurate determination of sulfate in solutions where it is the only anion present. Samuelson

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* The material of this section has been published in shorter form in the article by Whiteker, R. A., and Swift, E. H., Anal. Chem., 26, 1602 (1954).

found as early as 1939 (1) that a sodium sulfate solution was quantitatively converted to sulfuric acid upon passage through a column containing the hydrogen form of a cation exchange resin and that the sulfate could be determined by titrating the resulting acid. Subsequently this method has been applied to a number of simple sulfate solutions. In 1949 a procedure was suggested by Futterknecht (2) for the rapid determination of sodium sulfate in the presence of sodium chloride in dye baths. In this method, which the author did not quantitatively investigate, the amount of sodium sulfate present was assumed to be equal to the difference between the total salt concentration of the solution as found by ion exchange and the amount of chloride present. Recently, a method has been reported for determining the percentage of residual sulfur in burnt pyrite ores by use of an anion exchange resin (3). This method involves a fusion of the sample with sodium peroxide and sodium and potassium carbonates, treatment of the melt with hydrochloric acid, followed by passage of an aliquot of the solution through the chloride form of an anion exchange resin. The increase in chloride in the effluent solution over that present in the influent solution is assumed to be equal to the sulfate present in the aliquot. This procedure is rapid but the data presented in the paper do not permit an evaluation of the accuracy.

The present investigation is essentially an examination of the method proposed by Futterknecht (2) which came to my attention only after this work was almost completed. The purpose of this study was to provide a method which could be used for determining both rapidly and accurately the sulfate present in solutions which contain as anions only sulfate and those halides precipitated by silver ion.

Certain wet methods for dissolving iron pyrites introduce nitrate ion into the solution. Since such solutions must be evaporated to dryness with hydrochloric acid in order to dehydrate silica, nitric acid is volatilized at the same time and the method can conveniently be applied to a determination of the sulfur in a pyrite ore.

EXPERIMENTAL

Apparatus and Reagents. The ion exchange columns used were similar to those shown by Swift (4). The resin column of Amberlite IR-120 (analytical grade), 18 to 40 mesh was 16 mm. in diameter and was 21 to 23 cm. long.

All solutions were prepared from reagent-grade chemicals used without further purification. At times, the laboratory distilled water was below standard; therefore redistilled water prepared from ordinary distilled water by distillation from an alkaline permanganate solution was used for the preparation of all solutions and for wash water except where specifically noted.

Preliminary Experiments. In order to determine the optimum conditions for an accurate and rapid method certain experimental factors such as initial total cation concentration, rate of flow through a resin column, and volume of wash solution were investigated.

The solutions used for these and subsequent experiments were as follows: (1) Sodium chloride, 0.1*N*. (2) Sodium sulfate, 0.2*N*. (3) A solution 0.1*N* in sodium sulfate and 0.1*N* in sodium chloride, hereafter referred to as the sulfate-chloride solution. (4) A composite solution 0.1*N* in sodium sulfate and approximately 0.08*N* in ferric chloride, 0.02*N* in potassium bromide and 0.015*N* in hydrochloric acid, hereafter referred to as the simulated pyrite solution. All normalities given refer to metathetical equivalents.

1. Effect of Initial Cation Concentration

A series of experiments in which sulfate-chloride solutions of varying concentrations were passed through the columns at 3 to 4 ml. per minute followed by 125 ml. of rinse water indicated that a small negative error of 2 parts per thousand might result if the total cation concentration of the influent solution is as high as 0.2*N*. Although this evidence was not conclusive, the maximum concentration of the influent solutions used thereafter was 0.1*N*.

2. Effect of Flow Rate

Complete exchange was obtained with 0.1*N* solutions at flow rates up to 10 ml. per minute. Higher rates were not investigated since a flow rate of 10 ml. per minute appeared to be as rapid as could conveniently be handled by one operator if two runs were made concurrently. Thus, if a total volume of 150 ml. is passed through each of two columns concurrently at 10 ml. per minute, only 15 minutes is required to prepare two solutions which are ready for acid and halide titrations.

3. Effect of Wash Volume

Experiments with 0. 1N solutions showed that a minimum volume of 50 ml. of wash water is required with a flow rate of 10 ml. per minute. To provide for an adequate safety factor the use of at least 75 ml. of wash water is recommended.

In summary, the cation concentration in the influent solution should not be greater than 0. 1N, the flow rate may be as high as 10 ml. per minute, and the volume of wash water should be at least 75 ml.

Regeneration. Quantitative exchange of sodium ion for hydrogen ion was found to occur until a resin column was approximately 50% converted to the sodium form. The columns used in these experiments each contained approximately 40 cc. of Amberlite IR-120, which have a total exchange capacity of 80 meq. (5). Thus 400 ml. of a 0. 1N solution could be passed through such columns before regeneration was necessary. However, in this work the columns were usually regenerated after only 20 to 25 meq. of cations had been exchanged.

The columns were regenerated by first back-washing with distilled water to clean and redistribute the resin and then down-washing with 6N hydrochloric acid. This process was then repeated, and for columns which contained iron, the second wash with hydrochloric acid was continued until 20 to 30 ml. of effluent solution gave only a faint pink color upon addition of 1 to 2 ml. of 1F (volume formal, formula weights per liter) potassium thiocyanate. Next the column was rinsed with ordinary distilled water until the effluent solution had a pH greater than 4 and finally with redistilled water until the pH of the effluent solution was greater than 5. 3.

An initial wash with 100 ml. of a 1F sodium citrate solution did not appear to diminish the volume of 6N hydrochloric acid required to remove iron from a column. Another laboratory has suggested the use of sulfurous acid to reduce the iron to iron (II), which is more readily eluted. However, after such a treatment great care would have to be taken to remove both sulfurous and sulfuric acids.

In general, such an elaborate regeneration process is unnecessary since under ordinary conditions it is unnecessary to remove exchanged cations as completely as was done in this work. The final rinse with redistilled water may be omitted if a blank correction is made as described below.

Procedure. An aliquot of the solution to be analyzed was pipetted into a beaker, diluted if necessary so that the total cation concentration was not greater than 0.1$\underline{N}$, and then passed through a cation exchange column at ca. 3 ml. per minute. The beaker and column were washed with several 5- to 10-ml. portions of redistilled water; one portion was allowed to drain almost to the top of the resin bed before the next portion was added to the column. The solution level in the column was never permitted to fall below the top of the resin bed in order to avoid air entrapment. Finally, the column was filled to the top with redistilled water and allowed to drain until a total of 100 ml. of wash water had passed through the column.

The effluent solution was titrated with standard 0.2$\underline{N}$ sodium hydroxide to a pH of 6.5 to 7.5; magnetic stirring was used and the end point determined with a glass electrode pH meter. Then 8 to 10 ml. of 2% dextrin and 8 to 10 drops of 0.1% dichlorofluorescein in alcohol were added, and the solution was again stirred and was titrated with standard 0.1$\underline{N}$ silver nitrate until a persistent pink color was obtained.

The equivalents of sulfate were calculated by subtracting the equivalents of halide from the equivalents of hydrogen ion.

$$(1)\ \text{Eq. } SO_4^{=} = \text{eq. } H^+ - \text{eq. } X^-$$

A pH meter is used for the acid titration in preference to an indicator for several reasons. The color of a suitable pH indicator might mask the pink color of the halide end point. A pH meter permits a more rapid titration since the end point can be anticipated by following the pH of a solution during a titration. Rapid addition of standard base is possible until the solution reaches a pH of 4; then drops or partial drops can be added until a pH of 6. 5 to 7. 5 is attained. Since the sulfate is determined by the difference between the equivalents of acid and halide, the acid titration should be carried out with the highest possible accuracy. In the experiments of this investigation the equivalents of sulfate and halide were approximately equal. Hence any error in the acid determination would result in an error of twice this magnitude in the equivalents of sulfate found. The use of a pH meter permits volume increments of 0. 01 ml. to be made near the end point since even very small additions of base produce a considerable change in the pH of the solution.

Originally, acid titrations were made to a pH of approximately 5. 5 since a redistilled-water wash of a regenerated column yields an effluent solution of approximately this value. However, it was found that the hydrogen-ion and chloride-ion concentrations of such a solution are approximately equal, and that more accurate results were obtained if the titrations were made to a pH between

6.5 and 7.5.

The halide titrations are made in somewhat larger volumes (ca. 200 ml.) than are normally used with dichlorofluorescein, and this tends to make the color change of the end point less distinct. Decreasing the volume of rinse water from 100 ml. to the suggested minimum of 75 ml. would help somewhat, though probably not significantly. It was found that very reproducible titrations of the halide ion could be made if a comparable aliquot of a standard sodium chloride solution is diluted to a volume comparable to that of the solution to be titrated, dextrin and dichlorofluorescein are added, and the solution is titrated with an equivalent volume of standard silver nitrate. This equivalence-point mixture then is used as a comparison solution for subsequent titrations. Such a mixture should be kept in the dark except for the few seconds when it is used for obtaining end points. If this precaution is taken, the comparison mixture is stable for 2 to 3 hours, and very reproducible titrations can be made.

An attempt was made to use Carbide and Carbon Chemicals Corporation's Polyethylene glycol 400 as a protective colloid in the halide titration as suggested by Dean _et_. _al_. (6). However, no concentration of the Polyethylene glycol 400 which prevented coagulation of the silver chloride precipitate was found. In general, coagulation began 0.3 to 0.4 ml. before the equivalence point and the white precipitate first produced gradually became pink with no indication of an end point.

CONFIRMATORY ANALYSES

The data obtained from confirmatory analyses of the sulfate-chloride solution are given in Table I. A 25-ml. aliquot of the solution was diluted with 25 ml. of redistilled water and passed through a column at 2.5 ml. per minute. Washing was done with 100 ml. of redistilled water.

Table II gives the data obtained from confirmatory analyses of the simulated pyrite solution. A 25-ml. aliquot was diluted with 25 ml. of redistilled water and passed through a column at rates varying from 3 to 10 ml. per minute; 100 ml. of redistilled water were used as the wash solution.

The results given in Tables I and II show the accuracy and precision of the proposed volumetric procedure. The precision obtained with the simulated pyrite solution is not as good as that with the sulfate-chloride solution; however, all of the determinations gave results for sulfate which are within ±0.2% of the quantity taken.

It should be emphasized that redistilled water was used in all experiments reported for this investigation. The ionic concentration of the tap distilled water at times was such that its use would have necessitated a very large blank correction. If only

Table I

Confirmatory Analyses of Sulfate-Chloride Solution

Flow Rate: 2.5 ml. per Minute

Na_2SO_4 taken: 2.530 Meq.

NaCl taken: 2.546 Meq.

Expt.	H^+ found, Meq.	Cl^- found, Meq.	$SO_4^=$ calc., Meq.	Sulfate Error, %
1	5.072	2.545	2.527	-0.12
2	5.077	2.545	2.532	+0.08
3	5.074	2.545	2.529	-0.04
4	5.076	2.544	2.532	+0.08
5	5.077	2.546	2.531	+0.04
6	5.076	2.545	2.531	+0.04
		Average	2.530	+0.01
		Standard Deviation		0.08

Table II

Confirmatory Analyses of Simulated Pyrite Solution at Various Flow Rates

Expt.	Flow Rate, ml/min.	$SO_4^=$ taken, Meq.	H^+ found, Meq.	X^- found, Meq.	$SO_4^=$ Calc., Meq.	Sulfate Error, %
A 1	3	2.515	5.397	2.886	2.511	-0.16
2	3	2.515	5.395	2.884	2.511	-0.16
3	3	2.515	5.399	2.885	2.514	-0.04
4	3	2.515	5.405	2.885	2.520	+0.20
5	3	2.515	5.403	2.886	2.517	+0.08
6	3	2.515	5.403	2.884	2.519	+0.16
7	3	2.515	5.397	2.883	2.514	-0.04
8	3	2.515	5.399	2.884	2.515	0.0
9	3	2.515	5.397	2.885	2.512	-0.12
10	3	2.515	5.405	2.885	2.520	+0.20
11	3	2.515	5.399	2.885	2.514	-0.04
12	3	2.515	5.401	2.885	2.516	+0.04
				Average	2.515	+0.01
B 1	3	2.517	5.400	2.886	2.514	-0.12
2	3	2.517	5.407	2.893	2.514	-0.12
3	3	2.517	5.406	2.888	2.518	+0.04
4	3	2.517	5.413	2.892	2.521	+0.16
5	3	2.517	5.404	2.886	2.518	+0.04
6	3	2.517	5.411	2.892	2.519	+0.08
				Average	2.517	+0.01

Table II (continued)

Expt.	Flow Rate, ml/min.	$SO_4^=$ taken, Meq.	H^+ found, Meq.	X^- found, Meq.	$SO_4^=$ Calc., Meq.	Sulfate Error, %
C 1	3	2.518	5.404	2.887	2.517	-0.04
2	3	2.518	5.398	2.885	2.513	-0.20
3	5	2.518	5.404	2.885	2.519	+0.04
4	5	2.518	5.406	2.884	2.522	+0.16
5	7	2.518	5.402	2.882	2.520	+0.08
6	7	2.518	5.406	2.884	2.522	+0.16
7	10	2.518	5.402	2.883	2.519	+0.04
8	10	2.518	5.402	2.884	2.518	0.0
				Average	2.519	+0.03

Average of 26 Determinations +0.02

Standard Deviation 0.12

chloride is present in the water used, no blank correction would be necessary since chloride would be converted into hydrochloric acid in passing through a column and the effluent solution is titrated for both acid and halide.

If the distilled water contains anions other than chloride, a blank correction should be made as described below.

A regenerated column is washed with the distilled water until the pH of the effluent is approximately constant; the lower this pH, the higher the concentration of salts in the water. A pH of approximately 5 indicates that the water is reasonably free of ions and will yield only a small blank correction (approximately 2 to 4×10^{-6} eq.). Then a volume of the distilled water equal to the total volume of solution to be used in an actual experiment--sample volume plus rinse volume--is passed through a column at the experimental flow rate. The hydrogen ion in this effluent solution is then determined by titrating with standard base to a pH of 7. The chloride in this solution is estimated in the following way. Varying volumes of a stock chloride solution (ca. $2 \times 10^{-3}\underline{M}$) are added to each of several beakers containing halide-free water of the same volume as the titrated solution. The range of chloride-ion concentrations to be covered by these solutions can be estimated from the amount of base used in the acid titration. All solutions are then acidified with 0.2 ml. of 6$\underline{N}$ sulfuric acid; 2.00 ml. of 0.1$\underline{N}$ silver nitrate are added, and the chloride in the titrated solution is estimated by comparing the precipitate produced in it with those produced in the known chloride solutions.

With the quantities of chloride which were found to be present in the distilled water, estimates accurate to within 1 to 2×10^{-6} eq. of chloride were possible by this procedure. The difference between the equivalents of hydrogen ion and chloride ion found in the blank is a measure of the other anions present in the distilled water and may be called the blank correction. If impure distilled water is used, Equation (1) must be modified by subtracting both the equivalents of halide and the blank correction from the equivalents of hydrogen to obtain the equivalents of sulfate.

$$(2)\ \text{Eq. } SO_4^{=} = \text{eq. } H^{+} - \text{eq. } X^{-} - \text{blank correction}$$

Blank corrections of 2×10^{-6} eq., 4×10^{-6} eq., and 49×10^{-6} eq. were found for redistilled water, a local commercially available distilled water, and a tap distilled water, respectively. Because the blank correction for redistilled water was less than the uncertainty in the volumetric measurements, Equation (1) was used to calculate all the results presented for this investigation.

CONTINUOUS FLOW PROCEDURE

An alternative procedure which involved a continuous flow of the solution to be analyzed through a column was investigated. This procedure was based on the assumption that upon continued passage of a solution through a column, a steady state should be reached in which the acid concentration of the effluent solution would be equal to the cation concentration of the influent solution. Such a procedure would permit acid and halide titrations to be made in a much smaller volume than does the method previously described, as no rinsing would be required. Preliminary experiments showed that 75 to 80 ml. of a solution with a total cation concentration of 0. 1N had to be passed through a column at 1 to 3 ml. per minute before a steady state was reached in which the subsequent effluent solution was of constant composition.

A solution which was approximately 0. 1N in total cations was passed through a regenerated column at a flow rate of 1 to 3 ml. per minute. The first 75 to 80 ml. of effluent solution were discarded. The next 160 to 165 ml. were collected in some experiments in a single beaker and in others in approximately 55-ml. portions in three separate 40 x 80 mm. weighing bottles. In order to prevent evaporation, the collecting vessels were covered with a piece of cardboard during the collecting operations. Three 50-ml. aliquots were then taken and titrated for acid and halide as has been described. The results obtained by the two methods of collection were the same within the limits of the volumetric measurements and indicated that a steady state had been attained.

Table III gives the data obtained from the continuous flow procedure for three series of experiments.

The results of these experiments indicate that for the conditions investigated this procedure is not as accurate as the procedure described earlier. It appears that the accuracy of the procedure is dependent on the rate of flow through a column even for the low rates used. Flow rates less than 1 ml. per minute were not investigated, as these would be impractical because of the time required.

ANALYSIS OF PYRITE ORES

A sample of pyrites for confirmatory analyses was prepared by grinding technical grade iron pyrites and reserving material which was smaller than 200 mesh but not so small as to cause dusting. Some oxidation occurs if iron pyrites are ground finer than 100 mesh; however, since only a comparison of a conventional gravimetric procedure with the volumetric method of this investigation was desired, the smaller size was chosen in order to obtain greater homogeneity of the sample. The ground ore was mixed, dried at 110° to 115° C. for two hours, and stored under carbon dioxide in a desiccator.

The preparation of a solution of a pyrite ore for a barium sulfate precipitation involves so many sources of error that for this

Table III

Analyses of Simulated Pyrite Solution by Continuous Flow Procedure

Expt.	Flow Rate, Ml. /Min.	SO_4^{--} Taken, Meq.	H^+ Found, Meq.	X^- Found, Meq.	SO_4^{--} Calcd., Meq.	Sulfate Error, %
A 1	1	2.515	5.396	2.885	2.511	-0.16
2	1	2.515	5.400	2.886	2.514	-0.04
3	1	2.515	5.394	2.884	2.510	-0.20
4	1	2.515	5.396	2.885	2.511	-0.16
5	1	2.515	5.402	2.886	2.516	+0.04
				Average	2.512	-0.10
				Standard deviation		0.10
B 1	2	2.515	5.387	2.881	2.506	-0.36
2	2	2.515	5.387	2.883	2.504	-0.44
3	2	2.515	5.394	2.884	2.510	-0.20
4	2	2.515	5.387	2.884	2.503	-0.48
5	2	2.515	5.391	2.882	2.509	-0.24
6	2	2.515	5.387	2.881	2.506	-0.36
				Average	2.506	-0.35
				Standard deviation		0.11
C 1	2	2.516	5.389	2.883	2.506	-0.40
2	2	2.516	5.389	2.884	2.505	-0.44
3	2	2.516	5.391	2.881	2.510	-0.24
4	2	2.516	5.387	2.879	2.508	-0.32
5	2	2.516	5.387	2.881	2.506	-0.40
				Average	2.507	-0.36
				Standard deviation		0.08

work it was decided to prepare stock solutions and analyze aliquots by both procedures. The method used for the gravimetric determination of sulfur essentially followed that given by Swift (7), but with the modifications described below.

Procedure. A mixture of 30 ml. of 16N nitric acid and 9 ml. of 12N hydrochloric acid was prepared and swirled until brown fumes appeared. Fifteen drops of liquid bromine were then added, and the whole solution was transferred to a 150-ml. beaker containing an accurately weighed 1-gram sample of the pyrite ore. The mixture was allowed to stand 20 minutes, heated, and finally evaporated almost to dryness. Five milliliters of 12N hydrochloric acid were added, the residue disintegrated with a stirring rod, the mixture evaporated to dryness, and the residue heated for 20 minutes. Two milliliters of 12N hydrochloric acid were added and the residue was again disintegrated with a stirring rod. The quantity of hydrochloric acid should be kept at a minimum; otherwise unnecessarily large volumes of standard base and silver nitrate will be required for the titrations. Then 100 ml. of distilled water were added, the mixture was heated and filtered, and the silica was washed. The filtrate and washings were diluted to volume in a 250-ml. volumetric flask with distilled water.

Gravimetric Determination. A 50-ml. portion of the ore solution was pipetted into each of two beakers which contained 50 ml.

of distilled water, and the resulting solution was passed through a cation exchange column at the rate of 12 to 15 ml. per minute. The column was washed with 200 ml. of distilled water at the same rate. The effluent was heated almost to boiling, and then 8 ml. of 1N barium chloride were diluted to 50 ml. and added dropwise. After standing for 24 hours, the precipitate was filtered through a porous porcelain crucible, washed until free of chloride ion, and then heated to constant weight in an electric furnace at 500°C.

The results for two such gravimetric determinations for each of two samples of ore are shown in Table IV.

Table IV

Gravimetric and Volumetric Determinations of Sulfur in Pyrite Ore

Sample	Sample Weight, g.	Percent Sulfur Gravimetric	Percent Sulfur Volumetric
1	1.0636	46.82	46.70
		46.83	46.68
2	0.9619	46.84	46.79
		46.87	46.74
			46.71
			46.74
3	0.4091	46.78	
4	0.3168	46.82	
	Average	46.83	46.73
	Standard Deviation	0.03	0.04

A gravimetric determination of two other samples of ore was carried out exactly as described by Swift (7), a cation exchange column being used as the optional method for removal of ferric ion. The results for these two determinations are given for samples 3 and 4 in Table IV. The values obtained for the six gravimetric determinations indicate that this method of preparing a solution of a pyrite ore, though lengthy, is capable of yielding reproducible analyses.

Volumetric determination. A 25-ml. portion of the ore solution was diluted with 25 ml. of redistilled water and then passed through a regenerated cation exchange column at a flow rate of 3 to 4 ml. per minute. The column was then washed with a total of 100 ml. of redistilled water; only 5 to 10 ml. of water were used for each of the first three or four washings. Titrations of the effluent solution were made as described.

The data from six volumetric determinations of the two sulfate solutions are given in Table IV.

The results given in Table IV show that reproducible values are obtained by both methods; however, the average of the volumetric values is 2.1 parts per thousand less than the average of the gravimetric values. No attempt was made to make corrections in the gravimetric determination for errors due to coprecipitation of barium chloride, and Blasdale (8) found a +0.17% error under somewhat similar conditions. The accuracy obtained with the simulated pyrite solution indicates that the results of the volumetric method may be more accurate than those of the gravimetric method.

Student Confirmatory Analyses. On the basis of the results of this investigation a procedure for student use was written for a comparison of this volumetric method with the gravimetric method as given in Swift (7). Analyses of the pyrite ore were made by students in the sophomore course in analytical chemistry at the California Institute of Technology (1953-1954), and by a senior, L. W. Richards, who prepared the pyrite sample for analysis. The sophomore students had no previous experience with an analysis of this kind; Mr. Richards had made a similar gravimetric determination as a sophomore and had performed some preliminary experiments on the volumetric method.

A sample of the same crude pyrite ore as was used for the confirmatory analyses discussed above was ground so that the particles would pass a 100-mesh screen. The analyses were made as has been described except that the ion-exchange procedure for the elimination of ferric iron in the gravimetric determination was not used. Iron(III) was eliminated either by reduction to iron(II) with powdered aluminum or precipitated as hydrous ferric oxide with ammonium hydroxide.

Table V

Student Determinations of Sulfur in Pyrite Ore

Method	Analyst	No. of Expts.	Average Value %	Range %	Average Deviation %
Grav.	Soph.	24	46.43	46.02-46.98	0.22
Grav.	LWR	4	46.70	46.53-46.81	0.08
Vol.	Soph.	32	46.27	45.88-46.67	0.19
Vol.	LWR	4	46.59	46.58-46.61	0.01

The results of these student analyses are presented in Table V. Values obtained by the sophomore students which were obviously in error because of calculations or poor technique were discarded. The deviations of the discarded values from the mean of those retained were in all cases greater than 2.5 times the average deviation of those retained. There appears to be no satisfactory explanation for the large discrepancies between the values found by the sophomores and those found by Mr. Richards. It is to be noted that in both series of experiments the results obtained with the volumetric procedure are 2 to 4 parts per thousand less than those obtained by the gravimetric procedure.

Time has not permitted study of the other common cations which might be present in sulfate solutions; however, the experiments of Samuelson (9) indicate that quantitative exchange can be expected for all these cations except chromium(III). Unpublished experiments by Mr. G. Crabbs in this laboratory have confirmed the observations of Samuelson that solutions which contain the chromium(III)-sulfate complex are not quantitatively converted to sulfuric acid on passage through a cation exchange column.

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PART II

A STUDY OF IRON(III) SULFATE COMPLEX IONS

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Ion-Exchange and Spectrophotometric Investigation of Iron(III) Sulfate Complex Ions

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The distribution equilibria of iron(III) between an ion-exchange resin and solutions at $\mu = 1.0$, $(H^+) = 1.0$, containing $HClO_4$ and H_2SO_4, and $(Fe^{III}) \sim 3 \times 10^{-4}$ F have been measured at 28° and interpreted in terms of the equilibrium constants, $K_1 = (FeSO_4^+)/(Fe^{+++})(SO_4^-) = 95$, $(K_2/K_1) = (Fe(SO_4)_2^-)/(FeSO_4^+)(SO_4^=) = 9.4$. Spectrophotometric studies at 27 ± 2° of similar solutions show a marked contribution to the absorption spectrum by $FeSO_4^+$ in the 270–350 mμ range, and lead to a value of K_1 of 101–121. The recommended value is therefore 107(±20) liter/mole. The absorption spectra of Fe^{III} solutions at $(H^+) = 4 \times 10^{-3}$ F with $(SO_4^-) = 0.1$–0.9 M are consistent with the value of 9.4 for K_2/K_1. The extinction coefficients of $FeSO_4^+$ and $Fe(SO_4)_2^-$ have been determined. Data on the affinity of sulfate for various cations are tabulated and reviewed.

It is common knowledge that iron(III) is complexed in sodium sulfate and sulfuric acid solutions. A faint yellow color develops upon addition of sulfuric acid to a ferric perchlorate solution in dilute perchloric acid. Spectrophotometric studies show a marked increase in light absorption in the 270–350 mμ range for such solutions, but the published data are not amenable to analysis in terms of the mass action law.[1] Experiments on the Zimmermann–Reinhardt "preventative solution" show that the strong color of a ferric chloride solution is considerably reduced by addition of sulfuric acid; addition of phosphoric acid then causes only a small further diminution of the color.[2] The formal potential of the iron(II)–iron(III) couple at 25° is −0.732 volt in 1 F $HClO_4$[3] and −0.69 volt in 1 F H_2SO_4,[4] indicating complexing of iron(III) in the latter medium.

From a quantitative study of the inhibiting effect of sulfate on the rate of oxidation of iodide by ferric ion, Sykes has deduced a value of 1.04×10^3 liter/mole for the mass action equilibrium constant, $(FeSO_4^+)/(Fe^{+++})(SO_4^=)$, at 18° and an ionic strength of 0.066.[5]

In the present study, further knowledge about the stabilities, the formulas, and the absorption spectra of iron(III) sulfate complex species has been obtained by equilibrium ion-exchange distribution and spectrophotometric experiments.

Ion Exchange

Theory.—The method is based on the idea that the distribution coefficient of iron(III) between an aqueous phase and an ion-exchange resin depends on the concentration of ferric ion, Fe^{+++}, in the aqueous phase. At a given formal (total) Fe^{III} concentration, the concentration of Fe^{+++}, and therefore the distribution coefficient, can be affected by the addition of a complexing agent. A convenient method of determining the relative concentration of iron in the aqueous phase before and after equilibration with the resin is to use radioactive iron and counting methods.

The following assumptions are made in analyzing the data. (a) The only iron species adsorbed by the resin is Fe^{+++}. (b) The activity coefficients for the various ionic species in the aqueous phase are constant as the composition of a solution is varied, providing the ionic strength is constant. (c) The amount of Fe^{+++} adsorbed by the resin is sufficiently small so that the activity coefficients of Fe^{+++} and H^+ in the resin are constant. (d) Perchlorate ion is a non-complexing anion.

Using (a), a distribution constant, Q', for the exchange of ferric and hydrogen ion between an aqueous phase and a resin may be written[6]

$$Q' = \frac{(Fe^{+++})_R(H^+)^3\gamma_{Fe^{+++}R}\gamma^3_{H^+}}{(Fe^{+++})(H^+)^3_R\gamma_{Fe^{+++}}\gamma^3_{H^+R}} \qquad (1)$$

where the γ's are activity coefficients, parentheses indicate concentrations in moles per liter of solution or moles per kilogram of resin, and the subscript R indicates that the ion is in the resin.

Using (b) and (c), a mass-action equilibrium constant, Q_0, may be defined for a series of experiments at a fixed ionic strength.

$$Q_0 = \frac{(Fe^{+++})_R(H^+)^3}{(Fe^{+++})(H^+)^3_R} \qquad (2)$$

Let c_0 and c_f be the initial and final volume—formal (total) concentrations of Fe^{III} in solution before and after equilibration with the resin, V = volume of solution, g = weight of resin, C' = capacity of resin in equivalents of H^+ per kg. of resin. Using assumption (b) for cases where ferric iron forms complexes with an anion B, such as sulfate

$$(Fe^{+++}) = \frac{c_f}{1 + K_1(B) + K_2(B)^2 + \ldots + K_n(B)^n} \qquad (3)$$

where K_n is the mass-action equilibrium constant for the reaction

$$Fe^{+++} + nB = FeB_n \qquad (4)$$

Then

$$Q_0 = \frac{(c_0 - c_f)(V/g)(H^+)^3[1 + K_1(B) + K_2(B)^2 + \ldots]}{c_f[C' - 3(c_0 - c_f)(V/g)]^3} \qquad (5)$$

The apparent distribution coefficient, Q_A, is defined in terms of experimentally determinable quantities.

$$Q_A = \frac{(c_0 - c_f)(V/g)(H^+)^3}{c_f[C' - 3(c_0 - c_f)(V/g)]^3} \qquad (6)$$

Then

$$(Q_0/Q_A) = 1 + K_1(B) + K_2(B)^2 + \ldots \qquad (7)$$

Q_0 is measured in perchloric acid solutions with (B)

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[1] A. v. Kiss, J. Abraham and I. Hegedüs, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

[2] O. L. Barneby, THIS JOURNAL, **36**, 1429 (1914).

[3] E. H. Swift, "Introductory Quantitative Analysis," Prentice-Hall, Inc., New York, N. Y., 1950, p. 509.

[4] G. H. Walden, Jr., L. P. Hammett and S. M. Edmonds, THIS JOURNAL, **56**, 57 (1934).

[5] K. W. Sykes, *J. Chem. Soc.*, 124 (1952).

[6] R. E. Connick and S. W. Mayer, THIS JOURNAL, **73**, 1176 (1951).

= 0 and an effort is made to deduce the values of the K's from the variation of Q_A with (B).

Experimental

The cation-exchange resin, Dowex-50, 100–200 mesh, in the sodium form was washed with hydrochloric acid and then with distilled water until free of chloride. It was partially dried in air and then allowed to equilibrate with the vapor over a one formal sodium perchlorate solution for several weeks in an evacuated desiccator. The capacity of four different batches of resin varied from 2.99 to 3.02 eq./kg. of resin. This was determined by titration with sodium hydroxide and a *p*H meter, using vigorous stirring, to a *p*H of 7–8. Iron(III) solutions were prepared from reagent grade ferrous ammonium sulfate by oxidizing with liquid bromine, boiling, and dilution with perchloric acid. Sulfuric and perchloric acids were prepared from the concentrated reagent grade acids and standardized with sodium hydroxide.

The radioactive isotope used was the 46.3 day Fe^{59}. Because of its reasonably penetrating β and γ radiations, it is much easier to assay than the longer lived Fe^{55} isotope. It was supplied by the Oak Ridge National Laboratory as catalog item 26 PX with a specific activity of 1450 millicurie per gram, and no significant chemical or radioactive impurities.[7]

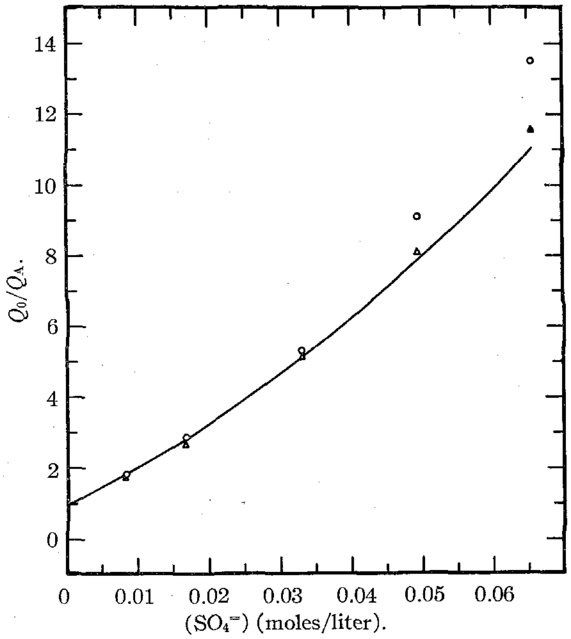

Fig. 1.—Q_0/Q_A *vs.* $(SO_4^{=})$ for two experiments (Δ and O). The solid line is the theoretical curve for $K_1 = 95$, $K_2 = 893$. For each experiment, $c_0 = 3 \times 10^{-4}$ *F*, and 100 ml. of sample was equilibrated with 2.00 g. of resin. For the Δ experiment, the detailed experimental conditions are listed in the table below. Q_0, in this case, was 8.05.

$(HClO_4)$ formula wt./l.	(H_2SO_4) formula wt./l.	$(SO_4^{=})$ moles/liter	(H^+) moles/liter	μ	Activity of aqueous phase, counts/min.[a]
1.003[b]	0.0	0.0	1.003	1.00	700
1.008	.0	.0	1.008	1.01	133
0.875	.112	.0084	1.004	1.01	205
.751	.224	.0167	1.008	1.03	270
.501	.449	.0331	1.016	1.05	383
.250	.723	.0495	1.023	1.07	459
.0	.964	.0655	1.030	1.10	512

[a] Four-ml. sample of aqueous phase counted in solution counter. [b] Sample not contacted with resin.

Radioassay was performed directly on the aqueous solutions using a Mark 1, Model 70 Radiation Counter Laboratories thin wall jacketed counter, with an annulus volume of *ca.* 4 ml. The observed counting efficiency was 150 disintegrations per count.

Solutions used for the distribution equilibrium experiments typically contained 3–6 × 10^{-4} *F* inactive iron(III), sufficient active iron to give counting rates of 500–1000 counts/min., and perchloric and sulfuric acid such that the ionic strength and hydrogen ion concentration were 1.0. The procedure for a run was to prepare seven 100-ml. solutions in 125-ml. glass-stoppered conical flasks, all containing the same amount of iron, but with varying amounts of sulfuric and perchloric acids. One of the two solutions that contained only perchloric acid was used to measure the initial amount of radioactivity. Two (2.00) grams of resin was added to each of the other six solutions, the stoppers were sealed with paraffin, and the flasks were rotated in a thermostated water-bath at 28.3° for 20–24 hours. The solutions were then radioassayed.

Check radioassays showed that the sample preparation and counting procedures were reproducible to 1–2%, although the resin distribution experiments were less satisfactory.

Results.—Figure 1 exhibits a plot of the values of Q_0/Q_A as a function of $(SO_4^{=})$ for several typical runs. Qualitatively, there is a marked decrease in the distribution coefficient when sulfuric acid is substituted for perchloric acid. Since all experiments were at an ionic strength of 1.0 and at $(H^+) = 1.0$, they cannot reveal whether sulfuric acid, bisulfate ion, or sulfate ion is the complexing species. The spectrophotometric studies reported below show that the first complex is $FeSO_4^+$; therefore, the ion-exchange data are analyzed in terms of the assumption that $(SO_4^{=})$ is the (B) of equations 3–7. We have used 0.075 mole/liter for the mass action dissociation constant of HSO_4^- at 28° in a solution of ionic strength 1.0.[8]

The data have been analyzed in terms of a simplified version of equation (7), $(Q_0/Q_A) = 1 + K_1(SO_4^{=}) + K_2(SO_4^{=})^2$. K_1 was deduced from the limiting slope of plots like Fig. 1 and K_2 from the limiting slope of a plot of $(Q_0/Q_A) - 1 - K_1 \cdot (SO_4^{=})$ *vs.* $(SO_4^{=})^2$. The resulting values of the association constants are shown in Table I.

Table I

Association Constants for Iron(III) Sulfate Complexes at 28°, μ = 1.0

c_0, formula wt./l.	Q_0	K_1, l./mole	K_2, l./mole
3 × 10^{-4}	7.88	95.5	562
3 × 10^{-4}	8.80	98.0	927
3 × 10^{-4}	7.85	87.8	905
3 × 10^{-4}	8.05	92.4	964
6 × 10^{-4}	8.80	99.6	1232
3 × 10^{-4}	8.45	97.0	800
Av.	8.31	95.1	898
Av. dev.	0.41	3.6	159

We can offer no satisfactory explanation for the variation of Q_0 from experiment to experiment displayed in Table I. Furthermore, in experiments in which no inactive iron was added to the Fe^{59} solution, *i.e.*, with $c_0 \sim 2\text{–}6 \times 10^{-7}$ *F*, values of Q_0 that ranged from 2–4 were obtained. It was suspected, but never completely proved, that these low values of the distribution coefficient were due to reduction of the Fe^{III} to Fe^{II} by the resin.

It is evident from Fig. 1 that the Q_A values for high values of $(SO_4^{=})$ were not reproducible, and that some of the experiments indicate that the formation of higher complexes, such as $Fe(SO_4)_3^{\equiv}$ should be considered. However, it is unlikely that the assumptions that the mass action law is valid at constant ionic strength and the resin behaves ideally and absorbs only Fe^{+++} and not $FeSO_4^+$ are sufficiently good to justify a more elaborate analysis of the data, even

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[7] "Catalog and Price List No. 4," Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennesse, March, 1951, p. 13.

[8] G. J. Doyle and N. Davidson, This Journal, **71**, 3491 (1949). This value is based on the value of 0.0101 for the thermodynamic ionization constant of HSO_4^-. (H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 430.)

if the experiments were more reproducible. The amount of Fe^{+++} adsorbed by the resin was always less than 0.07 equivalent per kg. so that assumption (c) is probably valid.[6]

It is difficult to estimate the absolute accuracy of the constants presented in Table I. The qualitative fact of complexing by sulfate is unmistakably demonstrated by these experiments; confirmation to 10% of the value of K_1 is obtained by the spectrophotometric studies. Confirming evidence for the formation of a negative complex like $Fe(SO_4)_2^-$ is the observation that the anion-exchange resin, Amberlite IRA-400, absorbs significant quantities of ferric iron from sulfate solutions.[9]

Spectrophotometry

Experimental.—Hydrated ferric perchlorate was prepared by heating ferric chloride with excess perchloric acid, evaporating to fumes and then until incipient precipitation. The pale violet crystals which separated on cooling were recrystallized twice from a minimum amount of water and then dissolved to give a solution that was 1 *F* in $HClO_4$. The solution was standardized iodometrically.[10]

Measurements were made at room temperature, 27 ± 2°, with a Beckman Model DU ultraviolet spectrophotometer using a hydrogen lamp and quartz cells with a path length of 1.00 cm. Solutions used were at an ionic strength of 1.06 ± 0.07 unless otherwise specified.

Results.—As shown in Fig. 2, there is a marked increase in the light absorption, due to Fe^{III}, in the 270–350 mμ wave length range, when sulfuric acid or sodium sulfate is added. The light absorption is much greater in 0.9 *F* Na_2SO_4 than in 1.0 *F* H_2SO_4, suggesting that the species which complexes the iron is $SO_4^=$, not HSO_4^-. The following experiment shows conclusively that this is the case. A series of solutions were prepared from $Fe(ClO_4)_3$, $NaClO_4$, $HClO_4$ and H_2SO_4 with $(Fe^{III}) = 5.12 \times 10^{-4}$ *F*, $\mu = 1.0$, but with variable amounts of total sulfate and acid so that the free sulfate ion was fixed at 0.0193 ± 0.0002 *M* (calculated assuming $K_{HSO_4^-} = 0.075$) although the hydrogen and bisulfate ion concentrations varied from 0.08 to 1.0 and 0.021 to 0.26 *M*, respectively. The absorption spectra of the several solutions were almost identical. Figure 2, curves 4 and 5, illustrates this for the extreme values of (H^+) used. The small difference in the two spectra is attributed to different concentrations of $FeOH^{++}$. The spectra in Fig. 2 are in qualitative agreement with those presented by Kiss, *et al.*[1]

A quantitative study of the equilibria involved was made for two series of solutions at $\mu = 1.0$, $(H^+) = 1.0$, $(Fe^{III}) = 5.12 \times 10^{-4}$ *F*, with the formal concentration of sulfuric acid varying from 0.021 to 1.0 *F*. The data have been analyzed by plotting *D* *vs.* $(D - D_0)/(SO_4^=)$, where D = observed optical density; $D_0 = \epsilon_0(Fe^{+++})_0$ = optical density of a solution *sans* sulfate, but having the same formal concentration of ferric ion, $(Fe^{+++})_0$, and hydrogen ion as all the other solutions; ϵ_0 is the formal extinction coefficient of Fe^{III} at this acidity, in the absence of sulfate.

If $FeSO_4^+$ is the only important complex species

$$D = \epsilon_1(Fe^{+++})_0 - (D - D_0)/(K_1(SO_4^=)), \quad (8)$$

where ϵ_1 is the extinction coefficient of $FeSO_4^+$.[11]

Examples of the analysis of the data for the two experiments are exhibited in Fig. 3 for the wave length 295 mμ. The plots give reasonably good straight lines, showing that the principal complex species formed in the concentration range used for these experiments is $FeSO_4^+$. For the experiment in which the sulfate ion concentration was varied from 0.066 to 0.0028, the points for $(SO_4^=) > 0.011$ fall above the best straight line through the points of lower concentration. This is due to the formation of significant amounts of $Fe(SO_4)_2^-$; the points at lower sulfate concentration are therefore used to compute ϵ_1 and K_1 of equation (8). The plots for all wave lengths at 5 mμ intervals between 290 and 340 mμ showed the same features as those for 295 mμ. The values of K_1 and their average deviation for the two series of experiments were 101 (±2.3) and 121 (±2.3). There is a systematic error between the two experiments which is larger than the random errors of either one. The extinction coefficients, ϵ_1 (λ), obtained from the two experiments agreed to ±7%; the average values are plotted in Fig. 4.

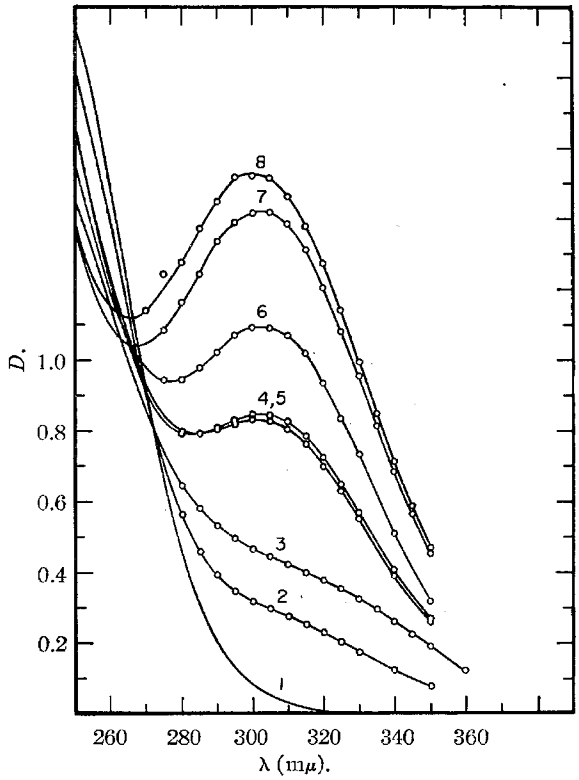

Fig. 2.—Absorption spectra of iron(III) in solutions containing sulfuric acid and sulfate ion, $D = \log_{10}(I_0/I)$, 1-cm. cells. (1) Calculated curve for solutions which are 5.12×10^{-4} *F* in Fe^{III} and 1 *F* in $HClO_4$. The values of *D* have been calculated from the best values of ε obtained from solutions varying from 1.28×10^{-2} *F* to 3.20×10^{-4} *F* in Fe^{III}, all 1 *F* in $HClO_4$. (2) 5.12×10^{-4} *F* Fe^{III}, 1.003 *M* H^+, 0.00275 *M* $SO_4^=$. (3) 5.12×10^{-4} *F* Fe^{III}, 4×10^{-3} *F* $HClO_4$, 0.94 *F* $NaClO_4$. (4) 5.12×10^{-4} *F* Fe^{III}, 1.0 *M* H^+, 0.0194 *M* $SO_4^=$. (5) 5.12×10^{-4} *F* Fe^{III}, 0.08 *M* H^+, 0.0194 *M* $SO_4^=$. (6) 5.12×10^{-4} *F* Fe^{III}, 1.068 *M* H^+, 0.0655 *M* $SO_4^=$. (7) 5.12×10^{-4} *F* Fe^{III}, 4×10^{-3} *F* $HClO_4$, 0.333 *F* Na_2SO_4. (8) 5.12×10^{-4} *F* Fe^{III}, 4×10^{-3} *F* $HClO_4$, 0.920 *F* Na_2SO_4. The order of increasing optical density at the extreme left-hand edge of the plot (λ = 250 mμ) is 7, 8, 3, 6, 4 and 5, 2, 1.

The use of equation (8) for the analysis of spectrophotometric data for complex ions is rather uncommon in the literature; it is therefore worthy of mention that we have treated our data by the more familiar equation[12]

$$(Fe^{+++})_0/(D - D_0) = [1/(\epsilon_1 - \epsilon_0)][1 + 1/(K_1(SO_4^=))] \quad (9)$$

and obtained essentially the same results. Equation (8) appears to be more attractive than (9) in that K_1 is directly determined from the slope of the plot, whereas in (9), the ratio of intercept to slope must be calculated.

In order to obtain larger relative concentrations of $Fe(SO_4)_2^-$, solutions with higher concentrations of free sulfate ion were prepared. These contained: $(Fe^{III}) = 5.12 \times 10^{-4}$ *F*, $(H^+) = 4 \times 10^{-3}$ *F*, and (a) 0.92 *F* Na_2SO_4, (b) 0.333 *F* Na_2SO_4, and (c) 0.100 *F* Na_2SO_4, 0.70 *F* $NaClO_4$. The absorption spectra of (a) and (b) are given in Fig. 2. The spectra showed a saturation effect as the sulfate ion concentration increased. Accordingly, an effort was made to analyze them according to the mass-action law, even though (a) had an ionic strength of 2.76, using $K_1 = 107$, and $(K_2/K_1) = 9.4$, and ϵ_1 from Fig. 4. The calculated ex-

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[9] Unpublished experiments by M. Czerczewski in this Laboratory.

[10] E. H. Swift, THIS JOURNAL, **51**, 2682 (1929).

[11] This method of analysis is due to W. B. Lewis, Thesis, University of California at Los Angeles, 1942; we learned of it from T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).

[12] H. McConnell and N. Davidson, *ibid.*, **72**, 3164 (1950).

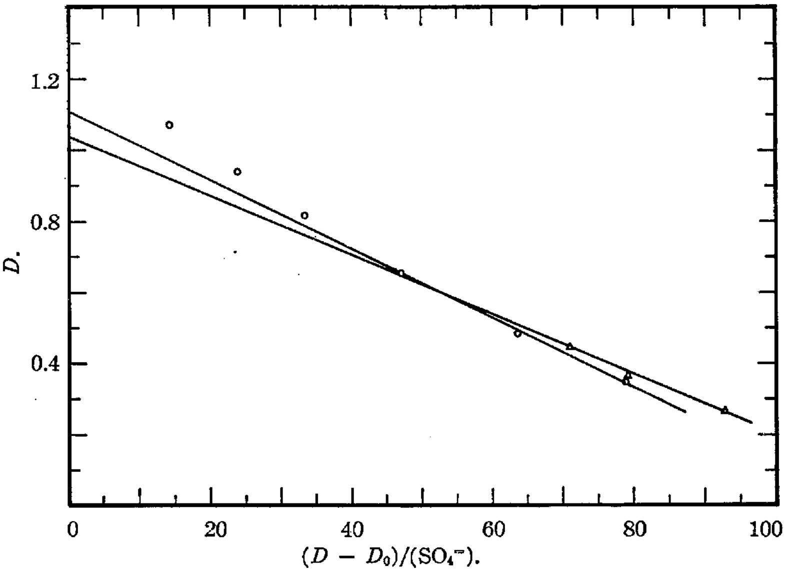

Fig. 3.—Plots of D vs. $(D - D_0)/(SO_4^=)$ for λ = 295 mμ for solutions at $\mu = 1.0$, $(H^+) = 1.0$. O and Δ are for two different experiments. For the O experiment, the experimental conditions for the six points, reading from left to right, are

H_2SO_4 (*f*)	0.998	0.501	0.301	0.161	0.0798	0.0396
$HClO_4$ (*f*)	.004	.501	.703	.841	.924	.961
$(SO_4^=)$ (calcd.)	.0655	.0338	.0205	.0111	.00552	.00275

tinction coefficients of $Fe(SO_4)_2^-$, ϵ_2, from the three solutions agreed to ±5%; the average values of ϵ_2 are shown in Fig. 4. The deviations of the calculated ϵ's from the average were systematic and indicate a small contribution to the optical density by a more strongly colored $Fe(SO_4)_3^=$ species.

Incidental to the main purposes of this investigation, the absorption spectra of Fe^{III} at $\mu = 1$ and $(H^+) = 1.0$ *M* and 4×10^{-3} *M* have been obtained. The absorption spectra of Fe^{+++} and $FeOH^{++}$ have been calculated, using 2.0×10^{-3} for the first hydrolysis constant of Fe^{+++} at $\mu = 1$ and 27°.[13] The results for ϵ of $FeOH^{++}$ fall between the two sets of values given by Rabinowitch and Stockmayer[14] and Olson and Simonson.[15] It should be recalled that the former authors rather arbitrarily selected 1×10^{-3} for the hydrolysis constant of Fe^{+++}; their spectrophotometric data gave values of $K_{H}\epsilon_{FeOH^{++}}$ only.

Discussion

In conclusion, the value of the association constant $K_1 = (FeSO_4^+)/(Fe^{+++})(SO_4^=)$ at $\mu = 1$ and 28° has been measured as 95 ± 4 (average deviation) (liter/mole) by the equilibrium ion-exchange method, and as 101(±2) and 121(±2) in two spectrophotometric experiments. The agreement between the two methods of measuring K_1 is satisfactory, in view of experimental error and the limited validity of the assumptions used to interpret the data. We accordingly recommend the value 107 ± 20 for K_1.[16] The ion-exchange method gives a value of 9.4 for $(K_2/K_1) = (Fe(SO_4)_2^-)/(Fe(SO_4)^+)(SO_4^=)$, and this value is consistent with spectrophotometric data for Fe^{III} solutions at high sulfate concentrations.

The value of $K_1 = 107$ is not directly comparable to the value of 1.04×10^3 at $\mu = 0.06$ and 18° determined by Sykes,[5] because of the differences in ionic strength and temperature. According to the equation

$$-\log_{10}\gamma = 0.5z^2\left[\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.2\mu\right] \qquad (10)$$

used by him to estimate a thermodynamic constant, the present investigation gives 6.8×10^3 for the thermodynamic formation constant of $FeSO_4^+$ at 27° as compared to 1.5×10^4 calculated by Sykes.

Table II displays some of the measured values of the association constants of sulfate with several cations. The results shown are for ionic strengths in the range 0.5–3.5, where the constants should not be strongly dependent on ionic strength. The data are too sparse and their reliability too uncertain to justify an extensive discussion. We note however the increase in association constants with increasing charge on the cation. For most of the cases studied, the ratio (K_1^2/K_2) is about 10. For those cases where the question has been examined, the complexing anion is always

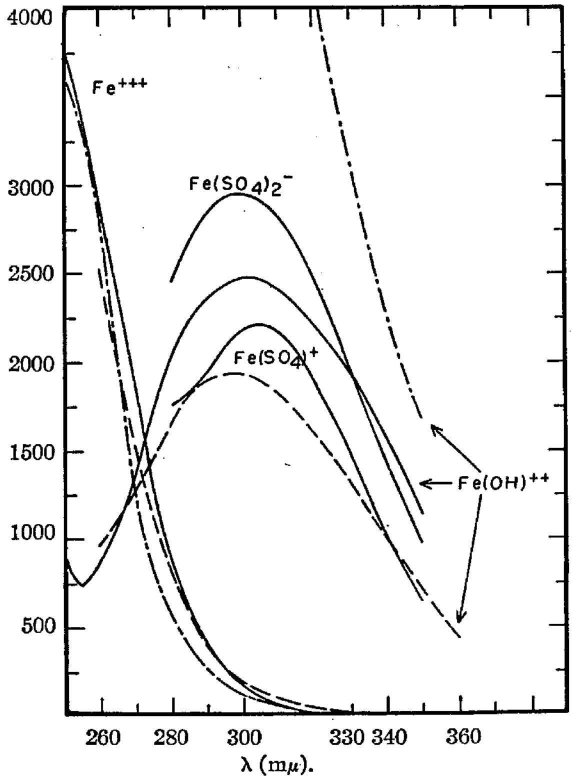

Fig. 4.—Extinction coefficients of some complex iron species. $\epsilon = (1/cl)\log_{10}(I_0/I)$. ——, this research; — — —, Olson and Simonson; – – – – – –, Rabinowitch and Stockmayer.

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(13) W. C. Bray and A. V. Hershey, THIS JOURNAL, **56**, 1889 (1934).

(14) E. Rabinowitch and W. Stockmayer, *ibid.*, **64**, 335 (1942).

(15) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

(16) Any fractional error in the assumed value of 0.075 for $K_{HSO_4^-}$ used in the calculations results in an approximately equal fractional error in the calculated values of K_1 and K_2/K_1.

TABLE II

ASSOCIATION CONSTANTS OF SOME COMPLEX SULFATES[a]

Ion	K_1, $(MSO_4)/(M)(SO_4)$	K_2/K_1, $M(SO_4)_2/(MSO_4)(SO_4)$	Remarks
U^{+4} [17]	1740	150	25°, $\mu = 3.5$, $(H^+) = 2.0$
Th^{+4} [18,b]	2100	240	25°, $\mu = 2.0$, (H^+) varied
Zr^{+4} [19,c]	6140	708	25°, $\mu = 2.0$, $(H^+) = 2.0$
Fe^{+3}	107	9	28°, $\mu = 1.0$, (H^+) varied
Ce^{+3} [6]	60		25°, $\mu = 0.5$–0.9, $(H^+) \sim 10^{-3}$
Ce^{+3} [20]	34		25°, $\mu = 0.5$, $(H^+) \sim 10^{-2}$
	17.5		$\mu = 1.0$, $(H^+) \sim 10^{-2}$
Cu^{++} [21]	4		25°, $\mu = 1.0$
Cu^{++} [22,d]	9		20°, $\mu = 1.0$
Cd^{++} [23]	7		$\mu = 3.0$
VO_2^{++} [24]	67		25°, $\mu = 3.5$, $(H^+) = 2.0$
Ag^{+} [23]	1.7	1	$\mu = 3.0$

[a] For the sake of intercomparison of results, equilibrium constants for the reaction $M + HSO_4^- \rightarrow MSO_4 + H^+$ have been converted to the form presented here using $K_{HSO_4^-} = 0.075$. [b] The authors use 0.084 for $K_{HSO_4^-}$; for comparative purposes, the results have been recalculated for $K_{HSO_4^-} = 0.075$. There is evidence for the formation of $Th(SO_4)\cdot(HSO_4)^+$ at high acidity. [c] A value for $[Zr(SO_4)_3^{=}]/[Zr(SO_4)_2](SO_4^{=})$ of 1 was also measured. [d] The formation of $Cu(SO_4)_3^{-4}$ was also inferred.

sulfate, not bisulfate (see however *footnote (b)* of Table II).

The ionic radii of Ce^{+3} and Fe^{+3} are quite different, 1.02 and 0.60 Å., respectively.[25,26] Nevertheless, these two tripositive cations have about the same affinity for $SO_4^{=}$. They also have about the same affinities for Cl^- and NO_3^-: $K_{CeCl^{++}} = 0.8$–1.1 ($\mu = 0.4$–1.5)[6]; $K_{FeCl^{++}} = 4$, ($\mu = 1.0$)[14]; $K_{CeNO_3^{++}} \sim 1$, ($\mu = 0.89$)[6]; $K_{FeNO_3^{++}} = 6.8$–0.6, ($\mu = 0.066$–0.6, 18°),[5] 0.3, ($\mu = 1$, 25°).[27] On the other hand, the relative affinities of Fe^{+3} and Ce^{+3} for OH^- are quite different, their hydrolysis constants being 2.0×10^{-3} and 5×10^{-8}, respectively, at $\mu = 1$.[28]

It may be noted that, at present, there is no decisive evidence on the question of whether, in some of these complexes, the complexing anion is in the first coördination sphere of the cation, displacing water molecules, or whether the anion and cation are separated by a layer of water molecules, in which case these are pure "ion-pair" complexes.

Acknowledgments.—We are indebted to Professor E. H. Swift for stimulating advice and suggestions. This research has been supported by the Atomic Energy Commission under contract AT-(11-1)-188.

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APPENDIX

This appendix is included to clarify and supplement some of the material presented in the preceding article.

It includes derivations for Equations (9) and (8) which were used for the analysis of the spectrophotometric data and which were not given in the paper for the sake of brevity.

Plots of Equations (8) and (9) were used to obtain values for the association constant, K_1, for two series of experiments with solutions of varying sulfate concentrations. The values obtained for K_1 at various wave lengths through the application of these two equations are compared in Table I of this appendix.

The values for the extinction coefficients of Fe^{+++}, $FeOH^{++}$, $FeSO_4^{+}$, and $Fe(SO_4)_2^{-}$ which were obtained in this investigation and are plotted in Figure 4 of the preceding article are given in Table II.

Recently, Sykes has reported some preliminary results on a new ferric sulfate complex study (1), and a discussion of his findings is included.

Some new spectrophotometric studies of iron(III) perchlorate solutions have recently been reported, and a short summary of the results which are relevant to this investigation is given.

1. Derivation of Equation (9).

Assuming that only the first complex of iron(III) and sulfate, $FeSO_4^+$, is important for the concentrations of sulfate considered, then the formal concentration of iron(III), $(Fe^{+++})_o$, may be expressed as

$$(a)\quad (Fe^{+++})_o = (Fe^{+++}) + (FeSO_4^+) + (FeOH^{++}).$$

Since 1-cm. cells were used, the optical density of a solution containing iron(III) and sulfate may be written

$$(b)\quad D = \epsilon_{Fe}\,(Fe^{+++}) + \epsilon_1\,(FeSO_4^+) + \epsilon_{OH}\,(FeOH^{++})$$

where ϵ_{Fe}, ϵ_1, ϵ_{OH} are the extinction coefficients for Fe^{+++}, $FeSO_4^+$, and $FeOH^{++}$ respectively.

The association constant for $FeSO_4^+$, K_1, is defined as

$$(c)\qquad K_1 = \frac{(FeSO_4^+)}{(Fe^{+++})(SO_4^=)} .$$

The hydrolysis of Fe^{+++} to form $FeOH^{++}$ is represented by the constant K_H.

$$(d)\qquad K_H = \frac{(FeOH^{++})\,(H^+)}{(Fe^{+++})}$$

At constant acidity a new constant, K_H', may be defined in terms of K_H and the hydrogen-ion concentration.

$$\text{(e)} \qquad K_H' = \frac{K_H}{(H^+)} = \frac{(FeOH^{++})}{(Fe^{+++})}$$

Using (d) and (e), Equations (a) and (b) may be rewritten as (f) and (g) respectively.

$$\text{(f)} \quad (Fe^{+++})_o = (Fe^{+++})\left[1 + K_1(SO_4^{=}) + K_H'\right]$$

$$\text{(g)} \quad D = (Fe^{+++})\left[\epsilon_{Fe} + \epsilon_1 K_1 (SO_4^{=}) + \epsilon_{OH} K_H'\right]$$

In a solution which contains the same formal concentration of iron(III) and the same acidity as the other solutions but without sulfate ion, the observed optical density, D_o, may be expressed as

$$\text{(h)} \qquad D_o = \epsilon_o (Fe^{+++})_o .$$

It then follows that

$$\text{(i)} \quad D_o = \epsilon_o (Fe^{+++}) + \epsilon_o (FeOH^{++}) = \epsilon_o (Fe^{+++})(1 + K_H')$$

and

$$\text{(j)} \quad D_o = \epsilon_{Fe} (Fe^{+++}) + \epsilon_{OH} (FeOH^{++}) = (Fe^{+++})(\epsilon_{Fe} + \epsilon_{OH} K_H')$$

where ϵ_o is the formal extinction coefficient of Fe(III) at this acidity in the absence of sulfate.

An expression for ϵ_o may be obtained from (i) and (j).

$$\text{(k)} \qquad \epsilon_o = \frac{\epsilon_{Fe} + \epsilon_{OH} K_H'}{1 + K_H'}$$

Equation (1) is obtained by combining (f), (g), and (h).

$$\text{(1)} \quad \frac{(D - D_o)}{(Fe^{+++})_o} = \frac{\epsilon_{Fe} + \epsilon_1 K_1 (SO_4^{=}) + \epsilon_{OH} K_H'}{1 + K_1 (SO_4^{=}) + K_H'} - \epsilon_o$$

On introducing the value of ϵ_o from (k) and simplifying, Equation (1) becomes

$$\text{(m)} \quad \frac{(D - D_o)}{(Fe^{+++})_o} = \frac{K_1 (SO_4^{=}) (\epsilon_1 - \epsilon_o)}{1 + K_1 (SO_4^{=}) + K_H'} .$$

Inverting (m) and grouping the terms appropriately

$$\text{(n)} \quad \frac{(Fe^{+++})_o}{(D - D_o)} = \frac{1}{(\epsilon_1 - \epsilon_o)} \left[1 + \frac{1 + K_H'}{K_1 (SO_4^{=})} \right].$$

If the acidity is kept high enough so that $K_H' \ll 1$, then Equation (n) becomes Equation (9) of the text.

$$\text{(9)} \quad \frac{(Fe^{+++})_o}{(D - D_o)} = \frac{1}{(\epsilon_1 - \epsilon_o)} \left[1 + \frac{1}{K_1 (SO_4^{=})} \right]$$

2. Derivation of Equation (8).

In this derivation the initial assumptions will be made that $FeSO_4^+$ is the only important sulfate complex of iron(III) and that the acidity is constant and sufficiently high so that $FeOH^{++}$ is unimportant. Then

(a) $(Fe^{+++})_o = (Fe^{+++}) + (FeSO_4^+)$

(b) $D_o = \epsilon_o (Fe^{+++})_o$

(c) $D = \epsilon_o (Fe^{+++}) + \epsilon_1 (FeSO_4^+)$

(d) $K_1 = \dfrac{(FeSO_4^+)}{(Fe^{+++})(SO_4^=)}$.

Equation (e) is the result of subtracting (b) from (c).

(e) $(D - D_o) = \epsilon_o \left[(Fe^{+++}) - (Fe^{+++})_o \right] + \epsilon_1 (FeSO_4^+)$

On introducing (a) into (e) and rearranging, Equation (f) is obtained.

(f) $\epsilon_o (FeSO_4^+) = \epsilon_1 (FeSO_4^+) - (D - D_o)$

Using Equation (d), the quantity $\epsilon_o (Fe^{+++})$ may be expressed as

$$(g) \qquad \epsilon_o\,(Fe^{+++}) = \frac{\epsilon_o\,(FeSO_4^{\,+})}{K_1\,(SO_4^{\,=})} .$$

Equation (h) results from the introduction of Equation (f) into (g).

$$(h) \qquad \epsilon_o\,(Fe^{+++}) = \frac{\epsilon_1\,(FeSO_4^{\,+})}{K_1\,(SO_4^{\,=})} - \frac{(D - D_o)}{K_1\,(SO_4^{\,=})}$$

Combining Equations (h) and (c)

$$(i) \quad D = \epsilon_1\,(FeSO_4^{\,+}) \left[1 + \frac{1}{K_1\,(SO_4^{\,=})}\right] - \frac{(D - D_o)}{K_1\,(SO_4^{\,=})} .$$

It follows from Equation (a) that the quantity $\epsilon_1\,(Fe^{+++})_o$ may be expressed as

$$(j) \quad \epsilon_1\,(Fe^{+++})_o = \epsilon_1\,(Fe^{+++}) + \epsilon_1\,(FeSO_4^{\,+}).$$

On introducing the value of (Fe^{+++}) from Equation (d), (j) becomes

$$(k) \quad \epsilon_1\,(Fe^{+++})_o = \epsilon_1\,(FeSO_4^{\,+}) \left[1 + \frac{1}{K_1\,(SO_4^{\,=})}\right] .$$

Equation (8) of the text now results by combining Equations (k) and (i).

$$(8) \quad D = \epsilon_1\,(Fe^{+++})_o - \frac{(D - D_o)}{K_1\,(SO_4^{\,=})}$$

3. Comparison of Values of K_1 Obtained from Plots of Equations (8) and (9).

Table I

Variation of K_1 with Wave Length

λ, mμ	K_1, l. mole^{-1} From Equation (8) Series A[a]	From Equation (8) Series B[b]	From Equation (9) Series A[a]	From Equation (9) Series B[b]
280	150[c]	108[c]	171[c]	109[c]
290	123	106	130	104
295	120	103	124	105
300	118	101	125	105
305	137[c]	102	147[c]	105
310	121	99	124	100
315	118	98	126	103
320	119	100	124	106
325	125	100	130	107
330	119	100	124	107
340	122	104	125	107
350	78[c]	109[c]	145[c]	121[c]
Average	121	101	126	105
Ave. Dev.	2	2	2	2

[a] The ($SO_4^=$) was varied from 0.0045 M to 0.0015 M.

[b] The ($SO_4^=$) was varied from 0.066 M to 0.0028 M.

[c] Value omitted in obtaining average.

4. Values of Extinction Coefficients Used to Plot Figure 4.

Table II

Variation of Extinction Coefficients for Various Iron(III) Species with Wave Length

λ, $m\mu$	$\epsilon_{Fe^{+++}}$	$\epsilon_{FeOH^{++}}$	$\epsilon_{FeSO_4^+}$	$\epsilon_{Fe(SO_4)_2^-}$
250	3800	904		
255	3456	741		
260	2899	922		
265	2353	1084		
270	1800	1385		
275	1286	1763		
280	901	2012	1760	2455
285	604	2240		
290	398	2372	1941	2845
295	254	2443	2098	2957
300	157	2487	2193	2962
305	93	2482	2209*	2927
310	60	2416	2158	2863
315	34	2331	2068	2699
320	21	2228	1882	2485
325	11.5	2102	1668	2247
330	7.9	1940	1479	1970
340	2.7	1565	1026	1451
350	0	1138	641	969

*Obtained by averaging values from Series B (See Table I), plot (8) and Series A and B, plot (9).

5. A New Ferric Sulfate Complex Study.

Sykes has recently reported some preliminary results of a spectrophotometric investigation of the $FeSO_4^+$ complex ion (1). He finds a value of 228 l. mole^{-1} for the association constant of the complex at 19° and an ionic strength of 0.15. By extrapolating to an ionic strength of unity using the activity coefficient function of Davies (2) a value of 112 l. mole^{-1} is obtained. This compares quite favorably with the value of 101-121 obtained by the spectrophotometric investigation reported in this section. Sykes says that a comparison of these constants is valid even though the temperature differed by 8° in the two investigations since ΔH for the association reaction has been found to be small.

There is also good agreement with the extinction coefficient for the $FeSO_4^+$ complex ion. Sykes finds a maximum of 2160 at 305 mμ, whereas this investigation has led to a value of 2209 also at 305 mμ.

Sykes reports that evidence has been obtained for the presence of a hydrogen sulfate complex, $FeHSO_4^{++}$, which has an association constant of about 60 l. mole^{-1} at 19° and an ionic strength of 0.15. This complex has its own electron-transfer spectrum but its extinction coefficients are smaller than those of the $FeSO_4^+$ complex, e.g., about 850 at 305 mμ. Hydrogen-sulfate complexing of this magnitude could not have occurred in solutions of this investigation without upsetting the agreement between these results and those of Sykes. This consideration leads Sykes to conclude that $FeHSO_4^{++}$ may be formed to a significant extent only in solutions of low ionic strength.

6. Recent Spectrophotometric Studies of Iron(III) Perchlorate Solutions.

A number of articles have been published recently on the dimerization of iron(III) in dilute perchloric acid solutions to form the polynuclear complex $Fe_2(OH)_2^{+4}$ (3, 4, 5). Milburn and Vosburgh (4) have reported a value of $K_d = 710$ at 25° and $\mu = 1$ as the equilibrium constant for the dimerization of $FeOH^{++}$ as expressed by Equation (a).

$$\text{(a)} \qquad 2\,FeOH^{++} = Fe_2(OH)_2^{+4}$$

They also report a vlue of $K_H = 1.62 \times 10^{-3}$ at 25° and $\mu = 1.07$ for the hydrolysis of Fe^{+++} to form $FeOH^{++}$. Appropriate combination of K_d and K_H leads to a value of $K_D = 1.86 \times 10^{-3}$ at 25° and $\mu = 1$ as the equilibrium constant for the dimerization of Fe^{+++} as expressed in Equation (b).

$$\text{(b)} \quad 2\,Fe^{+++} + 2\,H_2O = Fe_2(OH)_2^{+4} + 2\,H^+$$

The dimer would not have been present to any significant extent in most of the solutions used in this investigation as the concentration of iron(III) was kept low and the hydrogen-ion concentration was kept high. However, in the one solution in which $(Fe^{III}) = 5.12 \times 10^{-4}$ F and $(H^+) = 4 \times 10^{-3}$ M and from which values of the extinction coefficient of $FeOH^{++}$ were obtained, the concentration of dimer would have been approximately 2×10^{-5} M. Milburn and Vosburgh report a value of 925 for the extinction coefficient of $FeOH^{++}$ at 340 mμ. This is much smaller than the value of 1565 found in this investigation. The maximum absorption of the dimer was found to lie at 335 mμ by Mulay and Selwood (5), and it is very probable that the high value is in error because of the presence of a significant amount of the $Fe_2(OH)_2^{+4}$ complex.

The point shown in Figure 4 of the reprint where the extinction-coefficient curves for Fe^{+++} and $FeOH^{++}$ cross is called the isosbestic point and may be compared with those found by other investigators for the same two species. This investigation finds 1640 at 272 mμ ; Olson and Simonson (6) find approximately 1400 at 272 mμ ; Milburn and Vosburgh (4) find 1480 at 273 mμ ; and Siddall and Vosburgh (7) find 1450 at 272 mμ .

Milburn and Vosburgh (4) have determined the extinction coefficients of Fe^{+++} at wave lengths from 325 to 360 mμ. They report $\epsilon = 20.2$ at 325 mμ, $\epsilon = 7.3$ at 330 mμ, $\epsilon = 4.3$ at 335 mμ, $\epsilon = 2.8$ at 340 mμ, $\epsilon = 1.9$ at 345 mμ, $\epsilon = 1.2$ at 350 mμ, $\epsilon = 1.0$ at 355 mμ, and $\epsilon = 0.9$ at 360 mμ. These values compare favorably with those of this investigation which are presented in Table II of this appendix.

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PART III

A SODIUM COULOMETER

A coulometer may be defined as an instrument which measures the quantity of electricity (the number of coulombs) involved in some electrolytic process. A sodium coulometer performs this function by a gain or loss of metallic sodium, the change in weight being directly proportional to the number of coulombs. The sodium coulometer discussed in this section acts by a displacement of sodium ions through a glass under the influence of an electric field.

Glass is generally considered to be an insulator, but it was shown by Buff (1) as early as 1854 that at elevated temperatures it may act as a conductor. In 1890 Warburg (2) reported a method of introducing sodium electrolytically into a gas discharge tube. This method required the use of 1000 to 1200 volts and was possible only in gas-filled tubes.

In 1925 Burt (3) found that sodium could easily be introduced into an ordinary incandescent light bulb. In his experiments the light bulb was partially immersed in a bath of molten sodium nitrate which was maintained at approximately 312^{o} and which also contained a copper electrode. The filament of the bulb could be lighted either by direct current (early experiments) or by alternating current and was negative with respect to the copper electrode.

Burt explains the electrolytic action of the light-bulb apparatus in the following way. Upon passage of sufficient current the filament begins to glow and to emit thermionic electrons. The electrons move to the inner surface of the bulb under the influence of the electric field. Here they combine with sodium ions in the surface of the glass and form sodium metal. The depletion of sodium ions at the inner surface results in a migration of sodium ions from the interior of the glass. And sodium ions from the bath enter the glass to replace those which have migrated inward. By this process of displacement, sodium ions move from the bath through the glass and become neutral atoms by combination with electrons at the inner surface.

There is some doubt as to the oxidation product at the copper electrode. Burt (3) says that NO_3 has been observed coming off at the electrode. However, this gas is so unstable (4) that even if it were the initial product of the oxidation, decomposition products such as NO_2 and O_2 would be more likely to be observed.

The first sodium coulometer was prepared by Burt (3, 5). Use was made of a light bulb in which the filament was lighted with alternating current and the electrolytic field was applied between the mid-point of the filament and the molten bath.

This instrument was shown to be accurate to 1 part in 1000 (6).

In later experiments Burt (7, 8) used a redesigned coulometer which consisted of a glass bulb containing metallic sodium and a lead wire which was sealed through the glass and made contact with the sodium. This type of coulometer could be used either as an anode or as a cathode; i. e., sodium could be made to pass in either direction through the glass. A series of experiments were made by Burt in which one coulometer served as the cathode and another as the anode. The two coulometers agreed with each other to 1 part in 1000 and with a silver coulometer to 1 part in 500.

Stewart (9) continued the study of the sodium coulometer. His coulometers were prepared from Corning Glass Works' No. 015 soft lime glass tubing. Each bulb contained 15 g. of cadmium, and the anode bulb also contained 0. 5 g. of sodium. Electrical contact was made with the cadmium by means of a nickel wire brazed to a piece of platinum wire which was sealed through the glass. Molten sodium nitrate maintained at 340° was used as the bath. Three series of experiments were made: (1) the coulometers were in separate baths and both functioned as cathodes; (2) the coulometers were in separate baths and one was a cathode, the other an anode; (3) the coulometers were in the same bath with one an anode and the other a cathode. The anodic coulometers agreed with a silver coulometer to 1 part in 5000 while the cathodic coulometers were low and were accurate only to 1 part in 1000. The glass of the cathodic coulometers became slightly etched and Stewart suggested that the low cathode results might be due to an electrolytic loss of silicate ions.

In 1941 Steigman (10) showed the validity of Burt's mechanism for the movement of sodium ions through glass. Molten sodium nitrate containing Na^{24} was used for the bath and the metallic sodium collected during an hour's electrolysis exhibited only very little activity.

The purpose of the present investigation was to design a sodium coulometer which would be suitable for coulometric titrations. Such an instrument appeared to be more convenient to use and capable of greater accuracy than a conventional silver or gas coulometer. It could be used to great advantage in cases where constant current is impractical because of the instrumentation involved or where a variable current is desired, as, for example, in the approach to a potentiometric end point or in coulometric analysis with controlled cathode potential.

EXPERIMENTAL

Apparatus. The coulometers were prepared from a soft soda-lime glass, No. R-6 Standard Flint, made by the Kimble

Glass Division of the Owens-Illinois Glass Company. They were designed as shown in Figure 1, and each contained about 2 ml. of metallic sodium in an argon atmosphere. A platinum wire sealed through the glass made electrical contact with the sodium. The flat sides of the coulometer bulbs were blown as thin as possible so that the resistance of the coulometer system would be as small as possible.

The bath consisted of a No. 4 evaporating dish containing a 50% by weight mixture of sodium nitrate and sodium nitrite which melts at 221° (11). This bath was used in preference to molten sodium nitrate because of its lower melting temperature. The bath was heated by a 500-ml. Glas Col heating mantle. A coulometer could be supported in the bath by means of a glass tube which was rigidly attached to the coulometer with springs. A copper lead wire made contact with the platinum wire of a coulometer within the supporting glass tubing by means of a small clip. A tin can shielded the bath and coulometers from air currents. The whole coulometric apparatus is shown in Figure 2.

Filling a Coulometer. Sodium was added to a coulometer in the following way.

A sand bath was first prepared from two 7"-tall tin cans. The outer can was 6" in diameter and held the sand which surrounded the inner can, 4" in diameter. Two or three medicine

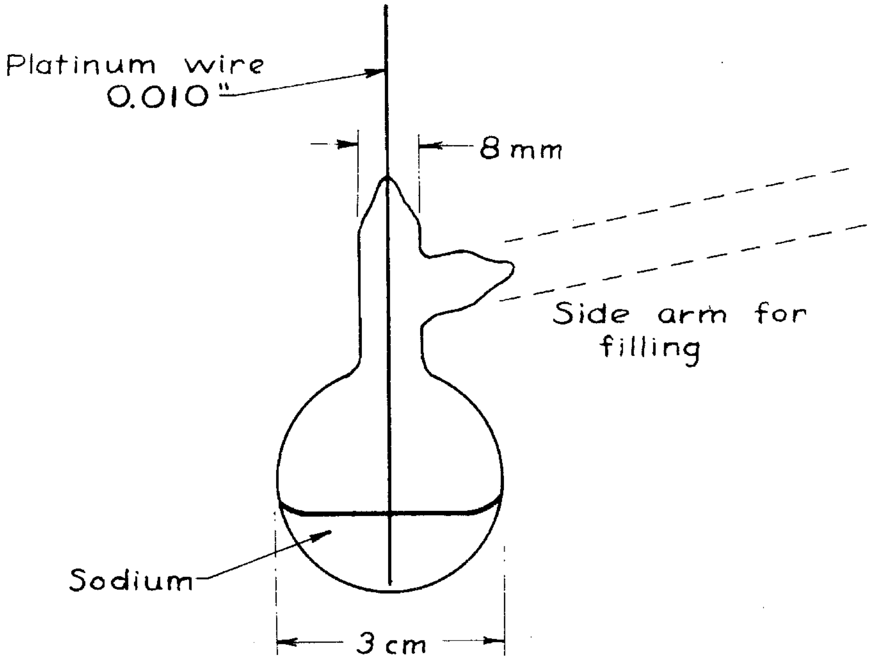

Figure 1

A Sodium Coulometer

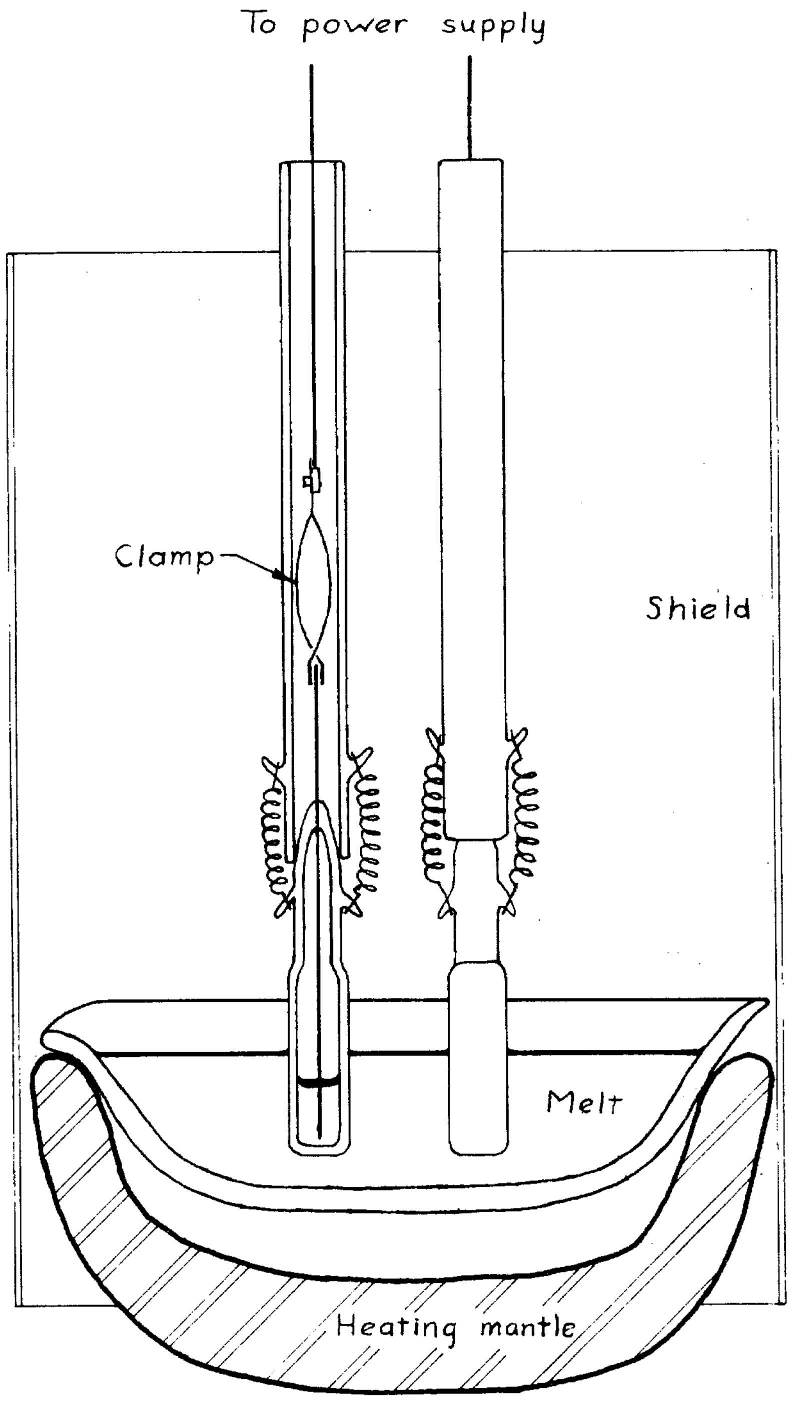

Figure 2

The Coulometer Apparatus

droppers with long, narrow tips were placed in the inner can and supported by stout copper wire so that the rubber bulbs remained outside the volume enclosed by the can. A coulometer bulb was placed at the bottom of the inner can and supported so that its side arm was almost vertical. The inner chamber was covered as much as possible with a watch glass and the whole assemblage was heated on a hot plate. After the temperature of the inner chamber had reached approximately 160^{o}, argon, dried by passage through calcium chloride and "Drierite", was continuously passed in. A cube of fresh sodium about 1.5 cm. on an edge was cut, placed in a crucible, and quickly lowered with tongs to the bottom of the inner can. While the sodium was melting, the coulometer was flushed out with the argon. The droppers were flushed out by alternately squeezing and releasing the dropper bulbs several times. About 2 ml. of the molten sodium was transferred to the coulometers by means of the droppers. Each dropper was used to deliver only one portion of sodium since the sodium has a tendency to stick to glass and to solidify in the tip of a dropper as it cools during the transferring operation. Since liquid sodium does not flow easily along a glass surface, it is necessary to deliver the sodium into the body of the coulometer or to shake it out of the side stem while still molten. After the filling operation, the side stem was stoppered tightly with a cork, and the coulometer was removed from the bath and allowed to cool in an atmosphere of argon. When the coulometer became cool enough to handle, the side stem was pulled off leaving the sodium sealed under an argon atmosphere.

Attempts to fill a coulometer under nitrogen or carbon dioxide were unsuccessful. A nitrogen stream did not keep the inner chamber sufficiently free from oxygen so that the sodium burned to form sodium peroxide. Carbon dioxide prevented the burning of sodium but some slow reaction caused the formation of sodium carbonate at the surface of the sodium in a coulometer.

<u>Resistance of Coulometers in Series.</u> In order to determine the optimum operating temperature of the sodium nitrate-sodium nitrite bath, it was first necessary to measure the resistance of the system--coulometer (cathode), molten bath, coulometer (anode). It was decided that a total resistance of about 1000 ohms would be suitable for initial experiments. With this resistance, electrolysis for thirty minutes at 118 volts would produce a change in weight of about 50 mg. in each coulometer.

The bath was heated until the salts melted. Meanwhile, two coulometers were lowered to the surface of the bath in several discrete steps, allowing thermal equilibrium to be attained at each step. Finally, the coulometers were lowered into the bath until the flat sections were almost completely immersed in the liquid. The coulometers were arranged in the bath with the flat sides next to one another, as shown in Figure 2, and about 1.5 cm. apart.

The temperature of the bath was slowly increased, and the resistance of the coulometer system was determined at a number of temperatures. The data obtained from the temperature-resistance measurements are plotted in Figure 3. The bath was not heated above 310° as this was the approximate temperature corresponding to the maximum voltage which could be used with the 500-ml. heating mantle.

While the coulometers were being heated, a reddish-brown permanent coloration appeared at the sodium-glass interface. It was suspected that this effect might be due to reduction of toluene by the sodium since the sodium had been stored under toluene. However, a permanent yellowish-brown coloration also appeared on heating coulometers which contained sodium taken directly from a sealed can. Thus reduction of toluene can at best be only a partial explanation for the phenomenon.

Effect of Passing Current through the Coulometers.

Two coulometers were slowly lowered into a molten bath and placed side by side as in the preceding section. The power supply for these experiments consisted of a 118-volt bank of storage batteries and was connected to the coulometers through an ammeter and a knife switch.

When the switch was closed the current through the

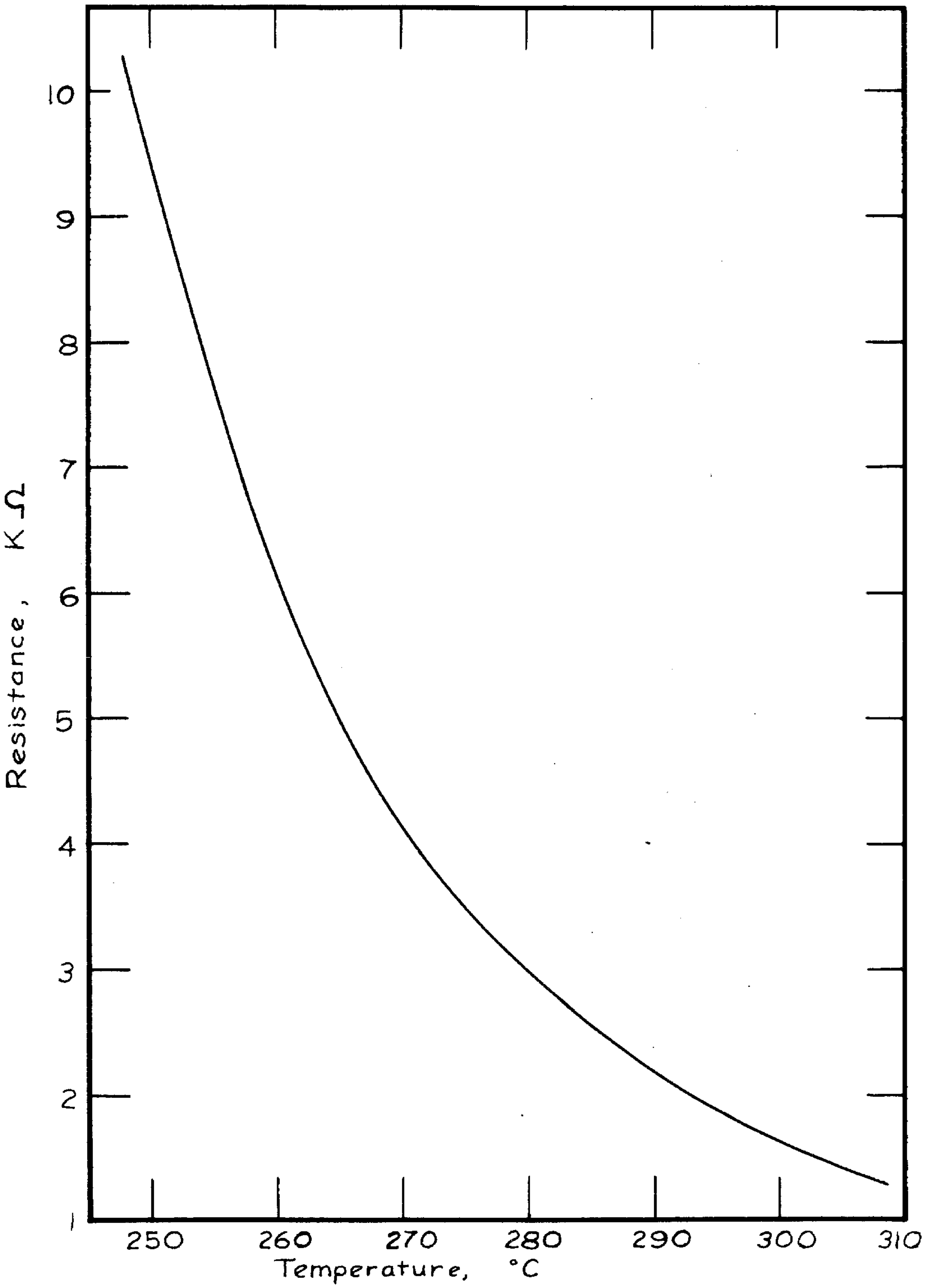

Figure 3

Variation of Resistance with Bath Temperature circuit began to increase slowly and the temperature of the bath began to rise. The resistance of the system, measured just after the switch was opened, was found to have dropped considerably. There is quite probably a heating of the coulometers due to the current passing through them which causes the resistance of the system to decrease and the temperature of the bath to increase.

The data obtained from a more quantitative study of the effect of passing current through the system are given in Table I.

Table I

Effect of Current on the Coulometer System

Switch	Time Since Switch Closed, min.	Time Since Switch Opened, min.	Temp., °C	Res., ohms	Current, ma.
Open			299	1730	
Closed	0		299		68
"	1		300		89
"	2		300.5		93
"	3		301		96
"	4		301.8		99
Open		0	302.2	1460	
"		1	301.3	1560	
"		2	301.2	1580	
"		3	301.5	1610	
"		4	301	1630	
"		5	300.4	1650	

Effect of Heating Kimble Glass in the Molten Bath.

Experiments on the solubility of Kimble Glass in molten sodium nitrate-sodium nitrite agreed with those of Burt (3, 12), who tested the solubility of a light bulb in molten sodium nitrate. Heating a coulometer bulb in the molten bath for twenty-four hours did not cause as much as a 0.1 mg. change in weight.

CONCLUSIONS

The preliminary experiments which were discussed in the preceding section did not prove or disprove the applicability of a sodium coulometer to a coulometric titration. However, they have demonstrated that a sodium coulometer has a number of liabilities which would greatly limit its usefulness.

Some of the disadvantages of such a coulometer are discussed below.

1. The coulometer bulbs are difficult to prepare. They must be made from a glass in which a large percentage of the sodium ions are mobile. This requires the use of a soft glass which makes the glassblowing a very delicate operation. It is hard to prepare uniform coulometer bulbs. To aid the glassblower, the machine shop prepared a mold in which to blow the bulbs. Unfortunately, when the mold was used, the flat sides could not be made thin enough. The resistance of two of these bulbs in a molten bath at 310° was 2750 ohms as compared to about 1250 ohms for the bulbs used in the experiments described above.

2. The filling operation is tedious and not always successful. Perhaps the surest way of filling a coulometer with sodium is to distill it into the bulb in an evacuated system.

3. A sodium coulometer with a metal cathode is limited to currents of about 100 ma. due to local heating and fracturing of

the glass (13).

4. In order to obtain the desired generation current, the coulometer system must be maintained at a rather high temperature, and a high direct-current voltage must be supplied.

5. The coulometers are fragile so that extreme care must be exercised in handling them. This is especially true when placing them into the molten bath or removing them from it.

6. The time for a coulometric determination is greatly increased because of the manipulations which are necessary with the use of a sodium coulometer.

7. There is some danger inherent in the use of a molten bath and in the use of sodium at high temperatures.

8. The lower limit for the number of equivalents which could be measured using a sodium coulometer is set by the small atomic weight of sodium. For two coulometers in series a weight change of 10 mg. of sodium for each coulometer would be necessary for a reproducibility of 1 part per 1000 if a semi-micro analytical balance were used. This change in weight corresponds to 42 coulombs. For comparison, a gas coulometer can be made to be accurate to about 10 coulombs (14).

In view of these considerations and the interest in a glass electrode which could be used for sodium-ion measurements, this investigation was discontinued in favor of a study of a "sodium electrode."

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PART IV

A SODIUM-ION GLASS ELECTRODE

INTRODUCTION

During the last two decades there have been a considerable number of investigations on the behavior of many different kinds of membranes in solutions of various ions at various concentrations. The ultimate goal of these studies is the development of specific electrodes which could be used for determining the activity of a given ion in a solution. Such electrodes would be comparable to the "glass electrode" which is now almost universally used for the measurement of hydrogen-ion activities.

A difference in potential results when solutions of different concentrations are separated by a membrane which exhibits some degree of selectivity towards the various ions present. Electromotive-force measurements have been made on cells containing membranes prepared from material of a widely different nature. This material includes animal tissues, vegetable tissues, geological formations, clay, glass, cellulose-based synthetic sheets, and resinous ion-exchange membranes (1).

Since clay, ion-exchange resins, and glass appear to be the most promising materials for specific membranes, a brief discussion of the most important studies of their behavior will be given.

Marshall and his collaborators have investigated membranes prepared from crystals of hydrated zeolitic minerals and by the evaporation of colloidal clay suspensions. Electrodes prepared from certain of these mineral membranes have been used to measure the activities of potassium (2, 3), ammonium (4), sodium (5), calcium (6, 7), magnesium (8, 7), and barium (7) ions in aqueous solutions and in colloidal clay systems. The electrodes at best were accurate to about 5%. The membranes were attacked in acid solutions and could be used only in solutions with a pH of 4 or above. The concentration range in which activity measurements were reliable depended on the cation and the particular membranes used. The useful concentration range was always greater with unipositive ions than with dipositive ions and varied from 0. 1 M with potassium to as low as 0. 004 M with magnesium. In all cases the lower concentration limit was about 10^{-4} M.

In their study of mineral membranes, Marshall and his collaborators have prepared membranes which were sensitive to tripositive, dipositive, and unipositive ions, to both dipositive and unipositive ions, to just unipositive ions, and some which did not respond to any ions. In some cases even the membranes sensitive to unipositive ions appeared to be more or less specific for certain ions. They did not find any membrane which was sensitive only to multipositive ions and which was not also sensitive to unipositive ions.

Recently, resinous ion-exchange membranes have been used for the determination of ionic activities. Wyllie and Patnode (9) have made potential measurements on membranes prepared from the sodium form of Amberlite IR-100 (a sulfonated phenolic cation-exchange resin) moulded with a methyl methacrylate bonding resin. The potentials of several cells each of which contained 1.0 M and 0.1 M sodium chloride solutions separated by one of these membranes ranged from 52.4 to 53.3 mv. at 22°. These potentials are in very good agreement with a theoretical value of 53.8 mv. calculated from the mean ion activity coefficients for sodium chloride given by Robinson and Harned (10). When 3 M sodium chloride solutions were used, the measured potentials were always 10 to 20 mv. lower than the calculated potentials. The membranes were also sensitive to hydrogen ion and gave potentials within 1 mv. of those measured with a glass electrode in solutions as concentrated as 1 F in hydrochloric acid.

Sinha has greatly extended the available information on the use of resin membranes for ion-activity measurements. The membranes which he investigated were prepared from a number of different cation-exchange resins by moulding a mixture of the resin and polystyrene. Certain of these membranes were useful for activity measurements in solutions as concentrated as 0.3 M in sodium, potassium, or hydrogen ions (11). Activities of the dipositive ions, calcium and magnesium, have also been measured with resin membrane electrodes (12). The upper concentration limit for which the activity measurements were reliable is not as high as with the unipositive ions, but it appears to be approximately 0.1 M which is about 10 times higher than was found for the best of the clay membranes. Some of the carboxylic-acid membranes were found to be quite insensitive to calcium ions in low concentrations. Such membranes were useful for the measurement of the sodium-ion activity in solutions containing both calcium and sodium as long as the concentration of calcium was less than 0.002 M.

Anion-exchange membranes similar to the cation-exchange membranes discussed above have also been prepared by Sinha (13). These membranes were found to be useful for a measurement of the chloride-ion activity in solutions less concentrated than 0.01 M in chloride. The potentials obtained in these solutions were dependent on the cation present, and the results for solutions containing dipositive ions were reliable to higher concentrations than for solutions containing unipositive ions. The membranes were also applicable to the measurement of the sulfate-ion activity of solutions less concentrated than 0.005 M in sulfate.

Sinha has just recently reported the results of the first potentiometric titrations carried out with the use of resin membranes (14). These included a titration of hydrochloric acid with sodium hydroxide, sodium chloride with silver nitrate, the chloride in a sodium chloride-sodium sulfate mixture with silver nitrate, and potassium sulfate with barium chloride or barium acetate. The titration curves showed well-marked inflections, but the data did not indicate the accuracy of such titrations.

The response of glass membranes to various cations has been the subject of numerous investigations dating at least from 1909 (15). Horovitz (16) in 1923 and Schiller (17) in 1924 investigated the cation response of several different kinds of glass and showed that in addition to having a hydrogen-ion function, glass electrodes may act as a sodium, potassium, zinc, or silver electrode depending on the composition of the glass. Those glasses which contained sodium behaved partially as sodium electrodes, those with potassium, as potassium electrodes, etc.

The development of a glass electrode suitable for the measurement of hydrogen-ion activity is too extensive a topic to be considered here. For an excellent treatment of this subject, the reader is referred to the monograph by Dole, The Glass Electrode (18), and the recent book by Bates, Electrometric pH Determinations (19).

In 1930 MacInnes and Dole (20) concluded that a glass having the eutectic composition of the ternary system SiO_2-Na_2O-CaO was the most satisfactory for a hydrogen-ion electrode. This glass has subsequently been made commercially available by the Corning Glass Works as their No. 015 glass. Reasoning from the work of Horovitz (16) and Schiller (17), the 015 glass should act as a sodium electrode since it contains 21.4 mole percent sodium oxide (21). At room temperature, however, electrodes made from Corning 015 glass show significant deviations from a true hydrogen electrode only in solutions of pH 9 and above, if the sodium-ion concentration is greater than about 0.1 M. Gardiner and Sanders (22) found that at 50° an electrode made from 015 glass gave a potential which was independent of pH and a linear function of pNa ($-\log [Na^+]$) in solutions whose pH was greater than 11 and which had a sodium-ion concentration greater than 0.5 M.

In 1932, Ssokolof and Passynsky (23) reported the results of a study of the deviations of glass electrodes of different compositions from perfect hydrogen electrodes. They found large deviations in solutions of high pH when the solution contained the same cation as did the glass, or a cation of the same periodic group but of a smaller atomic number. They also found that a lithia lime glass was suitable for electrodes that acted as nearly perfect hydrogen electrodes up to a pH of 13 in solutions which did not contain lithium ion. Steric factors appear to play a very important role in the selectivity of a glass membrane.

Recently, pH electrodes have become commercially available which do not respond to sodium ion unless the pH of the solution is greater than 12.5 for solutions in which the sodium-ion concentration is about 0.1 M. These electrodes presumably contain a large amount of lithium oxide, and it has been shown that the errors in alkaline solutions containing lithium ion are two to three times as large as those found for solutions containing an equal concentration of sodium ion (24). Potassium and other ions appear to give only very small errors even at very high pH. This is in accord with the steric considerations mentioned above.

In 1934 Lengyel and Blum (25) presented the results of an extensive study of the electrical properties of a glass electrode as the composition of the glass was systematically varied. They found that in general glasses could be classified into two groups. One group, designated as type D_1, included those which acted as hydrogen electrodes over a wide range of pH; the other group, designated as type D, included those which gave an imperfect hydrogen response but functioned well as sodium electrodes even in solutions of fairly low pH. Glasses of type D gave potentials almost independent of pH in solutions of pH 4 and above and exhibited almost the theoretical dependence of potential on sodium-ion concentration. Glasses of type D contained acidic oxides such as Al_2O_3 and B_2O_3 in addition to the SiO_2 and basic oxides contained in glass of type D_1. Zachariasen (26) says that glass has a definite but irregular crystalline structure which is determined by the network of silicate ions. Changes in the type of basic oxide present do not alter the structure, but if acidic oxides are added, the silicate network is altered and the electrical properties of the glass become vastly different. Lengyel and Blum (25) found that the selectivity of a glass membrane was not much affected by increasing the percentage of acidic oxides above 10 mole percent. It appears that the introduction of these acidic oxides causes the hydrogen-ion function to decrease in importance and the influence of other ions to increase.

In 1942 Tendeloo and Zwart Voorspuij (27) reported the first of a series of investigations on the response of glass membranes to certain ions. The glasses studied all contained Al_2O_3, CaO, Li_2O, and SiO_2 in varying proportions. The response of these glasses towards various cations was unpredictable and even electrodes prepared from glass of the same melt often acted quite differently. Later, Van Schuylenborgh and Vervelde (28) prepared glass electrodes which were somewhat specific for either sodium or potassium ions. These electrodes were used to measure the activity of sodium or potassium ions in systems of known pH which contained either sodium or potassium ions but not both. Similar electrodes were used to measure the activities of sodium, potassium, and hydrogen ions in determining titration curves for various dialyzed clay minerals (29).

In 1931 Urban and Steiner (30) used a glass made by the Kimble Glass Company to determine the activity of sodium ions in a mixture of sodium chloride and potassium chloride. In alkaline solutions above a pH of 13 the potential was found to be linearly related to log (Na^+) if the potassium-ion concentration was held constant. A change in the potassium-ion concentration caused a parallel displacement in a plot of the potential versus log (Na^+). An average error of 3.6% was found for a sodium-ion determination of five solutions in which the initial sodium hydroxide concentration was 0.25<u>F</u> and the potassium chloride concentration varied from 0.125 <u>F</u> to 2.00 <u>F</u>.

A preliminary report of a potentiometric titration of sodium ions by means of a glass electrode was given at the 1953 International Congress of Pure and Applied Chemistry in Stockholm by O. Tomiček (31). Sodium ions in milligram quantities were titrated with glass electrodes prepared from "the usual laboratory glass" by precipitation with zinc uranyl acetate in a 90% ethanol solution. The titration curve was said to give a well-marked inflection, and the method was applicable in the presence of potassium ions if the potassium-ion concentration was of the same order of magnitude as the sodium or less.

The present investigation was undertaken to determine the sodium-ion response of various commerically-available glasses. The ultimate goal of such a study would of course be the development of a glass electrode which is specific for sodium ions. However, even a sodium-ion glass electrode which is applicable only under rather limited conditions would be valuable in volumetric analysis. Such an electrode could be used to determine the sodium-ion concentration of a solution by a suitable titration in which the change in sodium-ion concentration is followed. If an electrode could be prepared which is independent of pH, then with suitable standardization, it could be used directly to measure the pNa of a solution.

EXPERIMENTAL

Apparatus. The kinds of glass used to prepare electrodes for the sodium-response experiments discussed in this section were the following: (1) No. R-6 Standard Flint manufactured by the Kimble Glass Division of the Owens-Illinois Glass Company; (2) No. 015 manufactured by the Corning Glass Works; (3) Corning No. X857BY; (4) Corning No. 7280. The approximate compositions of these four glasses as given by the manufacturers are shown in Table I. A complete analysis for the X857BY and the 7280 glasses could not be obtained.

Table I

Composition of Glasses Used as Electrodes

	Type of Glass			
Constituent	R-6 wt. %	015 mol %	X857BY wt. %	7280 wt. %
SiO_2	67.7	72.0	a	a
B_2O_3	1.5			
Al_2O_3	2.8		a	
ZrO_2				a
Na_2O	15.1	21.5	35	12
K_2O	1.2			
BaO	2.0			
CaO	5.6	6.5		
MgO	4.0			

[a] Present as a major constituent of the glass, but approximate percentage could not be obtained.

Preparation of Electrode Shells. Electrode shells consisting of a thin glass membrane fused to 8-mm. glass tubing were prepared by somewhat different methods for the four types of glass studied.

1. R-6 glass. A thin bubble was blown on a piece of R-6 glass tubing. The bubble was carefully broken away from the tubing,

and a piece about 15 mm. in diameter was chosen from a section which was very thin but yet which was thick enough so that it had not buckled during cooling. This thin glass membrane was placed on the end of a piece of 8-mm. tubing which had been clamped in a vertical position, and it was held in place with a small disk cut from a 1.0-cm. carbon rod. The membrane was fused to the tubing by means of a small flame directed on the upper surface of the carbon disk. During this operation the carbon disk was pressed firmly against the end of the tubing. A light flaming of the broken edges of the membrane which extended beyond the edges of the tubing completed the preparation of the electrode shell.

2. 015 glass. The 015 glass was supplied by the Beckman Division of Beckman Instruments, Inc. in the form of an 11-mm. glass bulb sealed to a piece of 8-mm. glass tubing. This electrode shell was probably prepared by dipping a piece of heated tubing into molten 015 glass, removing the desired amount of molten glass, and then blowing the bulb.

3. X857BY glass. The end of a piece of 8-mm. X857BY tubing to be used as a stem was heated in a flame in such a way as to thicken the walls of the tubing but yet keep the same bore diameter. This was essential with this soft glass in order to prevent the tubing from being pushed out of shape during the operation of fusing the membrane to the stem. A thin glass bubble was blown from another

piece of tubing. Then the bubble and the heated, thickened end of the stem were momentarily joined in the tip of a small flame, and as they were being removed from the flame, the two pieces of tubing were gently pulled in opposite directions. The entire unit was heated over a low Bunsen-burner flame, and tweezers were used to break the bubble from around the seal. The broken edges of the bubble were fire-polished by heating with a small flame directed on the stem a short distance from the membrane.

4. 7280 glass. The method used to prepare an electrode shell from the 7280 glass was similar to that already described for the X857BY glass. However, the 7280 glass acts much like Pyrex in its glass-working properties, and so the stem-thickening operation was not necessary.

The method used with the X857BY glass appeared to be more satisfactory than that used with the R-6 glass, but any method seems to require a great deal of practice unless one is an expert glassblower.

An electrode shell was tested for leaks by placing the open end in a beaker of water and allowing it to remain in the water for at least 24 hours.

<u>Preparation of a Sodium-Ion Glass Electrode</u>. No one description is applicable to all of the electrodes used in this investigation since the design was changed frequently. The most satisfactory

design, however, appeared to be that used with the X857BY and the 7280 glasses. An electrode of this type is shown in Figure 1 and is described in the following paragraph. Any features of the electrodes prepared from the R-6 and the 015 glass which are different from this model will be mentioned when the results obtained with these particular electrodes are presented.

A shielded cable was cut off from a broken commercial glass electrode and the insulation partially removed to give a shielded lead as shown in Figure 1. A piece of 0.010" platinum wire was tightly wrapped around the inner lead and a few drops of solder were added to provide better electrical contact. A piece of 5-mm. R-6 tubing was drawn out to form a nozzle and then cut off 4 inches from the nozzle tip. The shielded lead was inserted in this piece of tubing so that the platinum wire extended through the nozzle tip. Finally the nozzle tip was closed by heating with a small Bunsen-burner flame.

The protruding piece of platinum was bent in the form of a small loop and a silver-silver chloride electrode was prepared on it essentially by the method of Brown (32). The $KAg(CN)_2$ plating solution was prepared from reagent-grade chemicals with silver nitrate present in a slight excess. Three similarly-prepared electrodes were simultaneously silver-plated by electrolyzing the plating solution for 130 min. at 4 ma. The silver deposits were

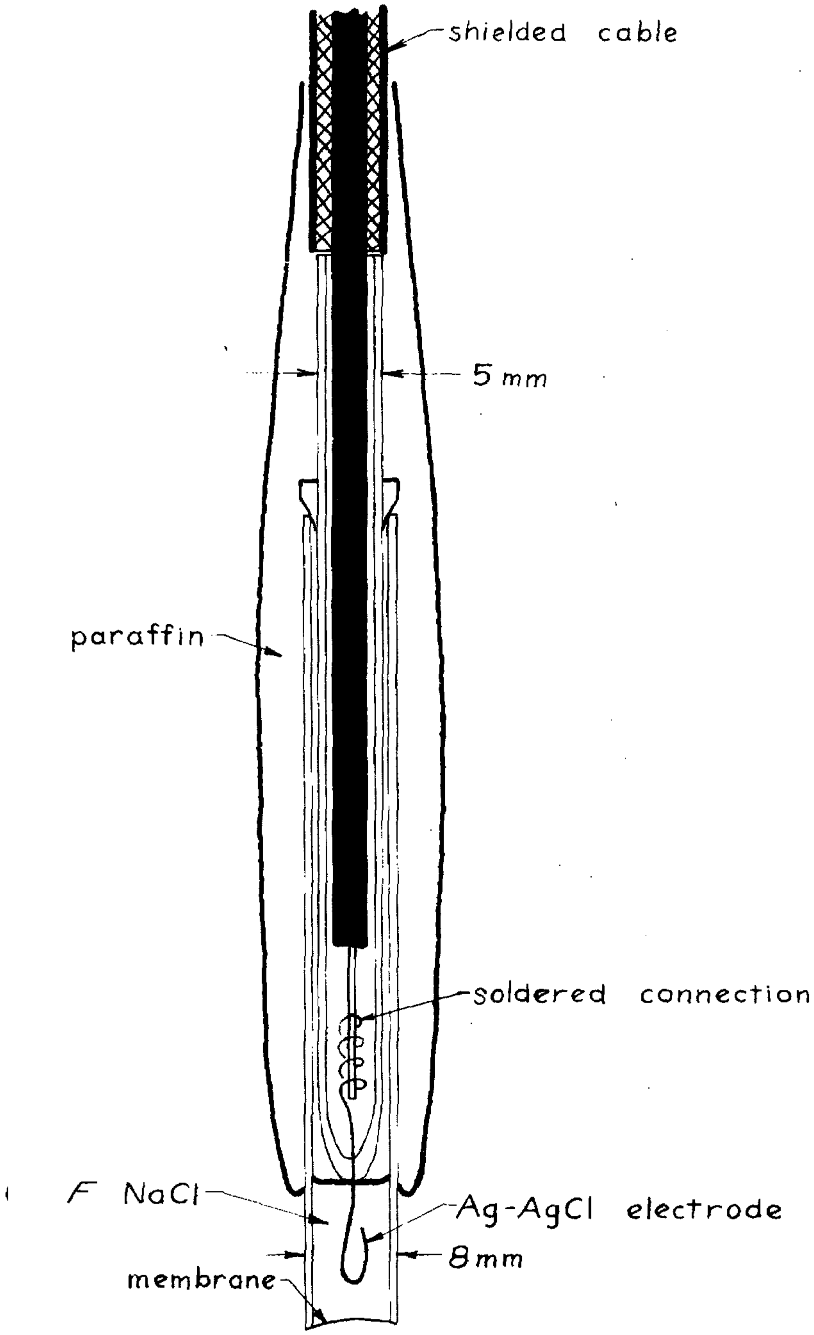

Figure 1

A odium-Ion Glass Electrode

carefully rinsed and then partially oxidized anodically to silver chloride by electrolyzing a 0.1 F hydrochloric acid solution for 25 min. at 3 to 5 ma. The completed silver-silver chloride electrodes were carefully rinsed and shorted together in distilled water until used.

In order to prepare a sodium-ion glass electrode for study, one of these silver-silver chloride electrodes was inserted into an electrode shell made from the glass to be investigated. These shells were cut about 3-1/4" long and contained sufficient 0.1 F sodium chloride to just completely cover the wire loop. The inner glass tube was held in place by means of a small piece of rubber tubing with a tapered end. A piece of electrical tape was wrapped around the junction of the inner tube and the shielded cable. Finally the whole apparatus was coated with a layer of paraffin from just above the inner glass tube to just below the surface of the sodium chloride solution. Electrodes prepared in this way did not show any appreciable electrostatic leakage.

Buffer Solutions. The buffer solutions used in this investigation consisted of the following:

Buffer Solution 5--a mixture of 51.5 ml. of 0.2 F K_2HPO_4 and 48.5 ml. of 0.1 F citric acid.

Buffer Solution 7--a mixture of 82.4 ml. of 0.2 F K_2HPO_4 and 17.6 ml. of 0.1 F citric acid.

Buffer Solution 9--a 0.05 F $K_2B_4O_7$ solution.

Buffer Solution 11--a solution 0.03 F in K_2HPO_4 and 0.006 F in K_3PO_4.

RESULTS

The Sodium-Ion Response of Various Glasses. The sodium-ion response of the four types of glass was determined by following the change in potential developed at the surface of a glass membrane as the sodium-ion concentration of a buffer solution was varied. This change in potential was determined by measuring the electromotive force of a sodium-ion glass electrode--buffer solution--saturated calomel electrode system with either a Beckman Model H pH Meter or a Model G pH Meter. In all cases the initial solution volume was 100 ml. and the sodium-ion concentration was changed by the addition of either 1.017 F NaCl or 0.1017 F NaCl.

The results obtained from sodium-ion response measurements with various electrodes are discussed below. The most significant results are presented by a plot of the potential of a sodium-ion glass electrode with respect to a saturated calomel electrode (abbreviated as S. C. E.) versus the negative logarithm of the sodium-ion concentration. Concentrations were used rather than activities since the data did not seem to justify a more rigorous evaluation.

1. R-6 glass.

Electrode K_1. Electrode K_1 was essentially the same as the electrode shown in Figure 1 except that the internal silver-silver chloride electrode was only partially immersed in the 0.1 F NaCl solution and a mercury pool made contact between the platinum wire and the inner lead of the shielded cable.

The sodium-ion response of Electrode K_1 was determined in Buffer Solutions 5, 7, and 11. The curves obtained from these data are plotted as solid lines in Figure 2. The potential readings of the buffer solutions before the addition of any sodium chloride are given at $-\log(Na^+) = 5.5$, and the appropriate curves are extrapolated to these values. The region of extrapolation is indicated by the dashed portions of the curves, and this convention is continued with the remaining figures of this section.

It can be seen from Figure 2 that there is essentially no potential change in any of the buffer solutions until the sodium-ion concentration becomes greater than 10^{-2} M. Even in this concentration range sodium ions have only a small effect on the potential readings. It should also be noted that the electrode does not function well as a hydrogen electrode since there is only about 12 mv. difference in potential between a solution of pH 5 and one of pH 11.

The effect of sodium and hydrogen ions on the measured potential appears to be anomalous. With the R-6 glass an increase

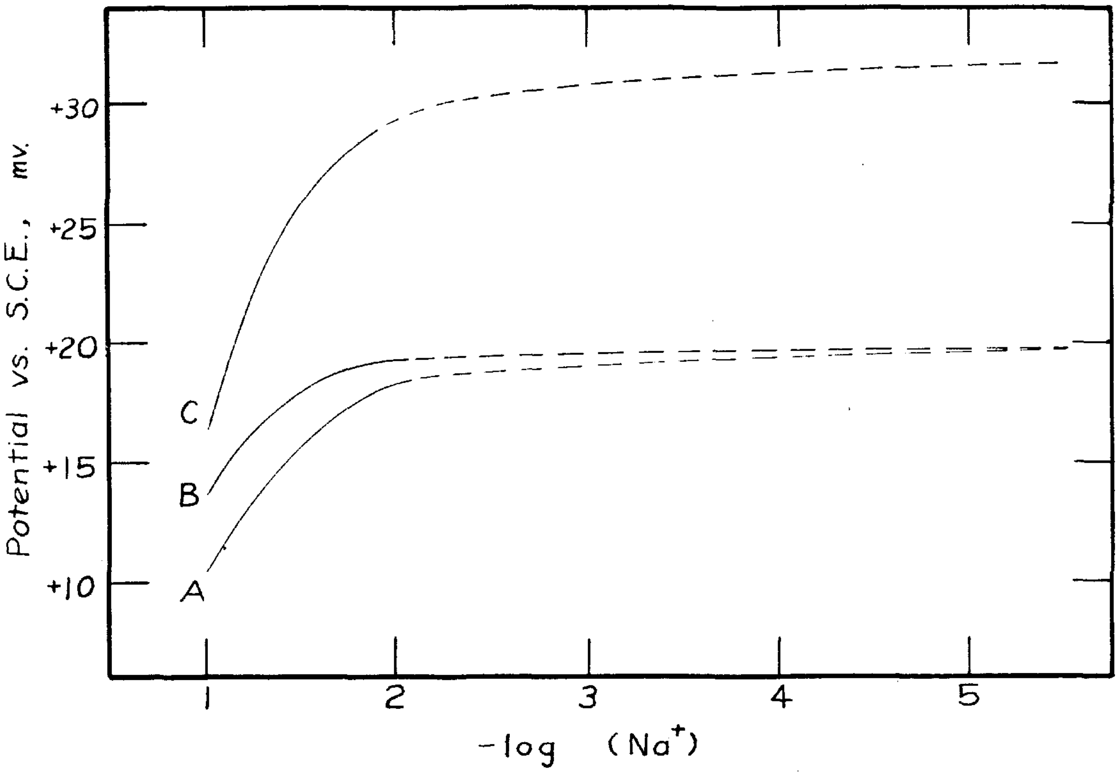

Figure 2

Sodium-Ion Response of Electrode K_1

(A) Buffer Solution pH 5

(B) Buffer Solution pH 7

(C) Buffer Solution pH 11

in the sodium- or hydrogen-ion concentration causes a decrease in potential, whereas with all other glasses tested, an increase in either species causes an increase in potential. No explanation can be offered for this behavior.

Electrode K_2. The internal cell of Electrode K_2 consisted of a piece of platinum foil immersed in Buffer Solution 5 saturated with quinhydrone. A mercury pool made contact between the platinum and the shielded lead.

The sodium-ion response of Electrode K_2 was determined in Buffer Solutions 5, 7, and 11. The results obtained were similar to those given for Electrode K_1, but because of the difference in internal cells, the potentials obtained with Electrode K_2 were more positive.

2. 015 glass.

Electrode C_1. The internal cell of Electrode C_1 consisted of a platinum wire immersed in a saturated quinhydrone solution with a pH of approximately 3.

A series of experiments were made to compare the behavior of Electrode C_1 and the Beckman Type E Glass Electrode, designed for use in high pH solutions, in solutions of high pH with various amounts of ethanol. Figure 3 gives a comparison of the sodium-ion response of these two electrodes in the following solutions: (A) 100 ml. of Buffer Solution 11; (B) 50 ml. of 95% ethanol and

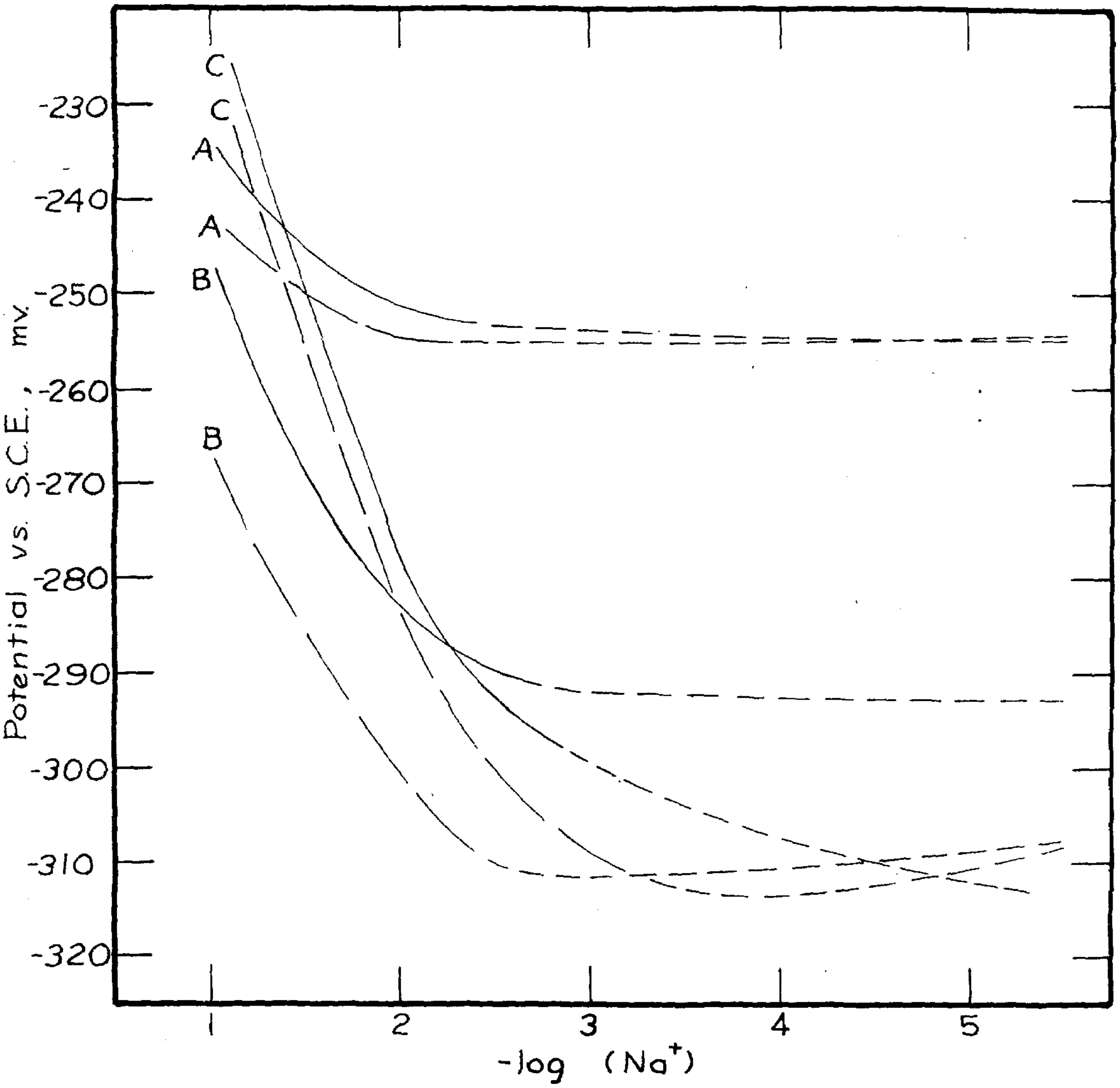

Figure 3

Sodium-Ion Response of Electrode C_1 and Beckman Type E Electrode

Electrode C_1 ———— Type E —— ——

(A) Buffer Solution II

(B) 50 % ethanol, 50 % Buffer Solution II

(C) 75 % ethanol, 8 % Buffer Solution II

50 ml. of Buffer Solution 11; (C) 90 ml. of 95% ethanol, 10 ml. of Buffer Solution 11, and 20 ml. of water. The excess water had to be added in Solution C in order to keep salts from precipitating.

From the curves of Figure 3 it may be seen that the sodium-ion response of Electrode C_1 is not too much greater than that of the Type E Electrode. However, the Type E Electrode is not affected by as low a concentration of sodium ions as is Electrode C_1. The presence of ethanol increases the degree of sodium-ion response of both electrodes and also lowers the threshold concentration to which both electrodes respond. In addition, the more ethanol present, the greater the potential change for a given change in the sodium-ion concentration.

The results of these measurements in ethanolic solutions indicated that the accuracy of Tomiček's potentiometric titrations (31) may be partially due to the fact that the titrations were made in a 90% ethanol solution. In addition to decreasing the solubility of sodium zinc uranyl acetate the ethanol may also have increased the degree of sodium-ion response of the glass electrode used.

Electrode C_2. Electrode C_2 was similar to Electrode C_1 except that the acidified quinhydrone solution was also approximately 0.2 F in sodium chloride. It was thought that perhaps a moderate concentration of sodium ions in the internal solution was necessary for the sodium-ion response of the membrane.

Electrode C_2 was never successfully investigated since the internal standardization of the electrode as indicated by standardization with a given buffer solution was constantly changing. This was presumably caused by decomposition of the quinhydrone solution.

3. X857BY glass.

Electrodes X_1 and X_2. Sodium-ion response measurements were made with Electrode X_1 in Buffer Solution 11 by using a Model H pH Meter, and with Electrode X_2 in Buffer Solutions 7, 9, and 11 by using a Model G pH Meter. The results obtained from these measurements are plotted in Figure 4.

The data obtained in the various buffer solutions with Electrode X_2 show that the electrode is only slightly affected by hydrogen ions and that the degree of sodium-ion response is greater the lower the hydrogen-ion concentration of a solution. Even in the most alkaline solutions investigated, however, the degree of sodium-ion response is still quite small.

A comparison of the curves obtained for the two electrodes in Buffer Solution 11 shows the difference in character of the response obtained with electrodes prepared from the same glass. The difference in the degree of response may be due in part to a difference in the sensitivity of the membrane surfaces. However, the difference in potential range is only an apparent one since pH

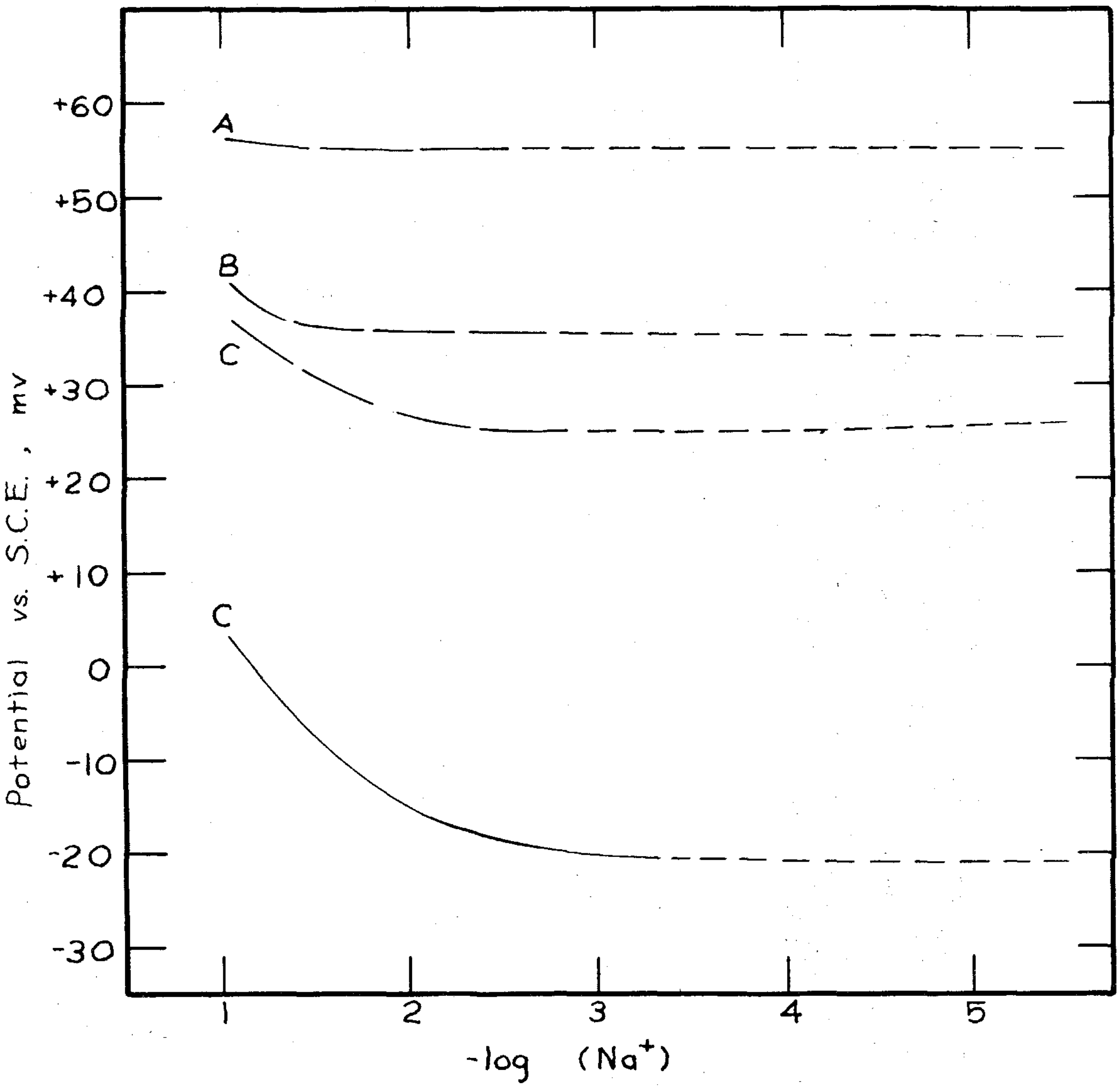

Figure 4

Sodium-Ion Response of Electrodes X_1 and X_2

Electrode X_1 ———— Electrode X_2 —— ——

(A) Buffer Solution 7

(B) Buffer Solution 9

(C) Buffer Solution 11

readings obtained with the two electrodes were in the same range. The discrepancy was undoubtedly introduced by the fact that the zero of potential for the Model G pH Meter is at a pH of 7.8 while for the Model H it is at a pH of 7.0. Since a Beckman General Purpose Glass Electrode designed for use with a Model G pH Meter was used for the standardization of both meters, the potentials obtained with the Model H are all approximately 48 mv. low. The Model H pH Meter was also used with Electrodes X_1, X_2, C_1, and C_2, and since only the relative shapes of the potential curves were considered, the observed potential readings were also used in presenting the data obtained with these electrodes.

It is worth noting that potential measurements were made with a General Purpose Glass Electrode at the same time as with Electrodes X_1 and X_2. In general, the sodium-ion response of the Beckman Electrode was of the same order of magnitude as that obtained with electrodes made from the X857BY glass.

4. 7280 glass.

Electrode Z_1. The data obtained from sodium-ion response measurements with Electrode Z_1 are given in Figure 5. Here again there is a definite sodium-ion effect which is more pronounced the more alkaline the solution, but the degree of response is greater than for any of the other glasses studied. The response curves are essentially straight lines to lower sodium-ion

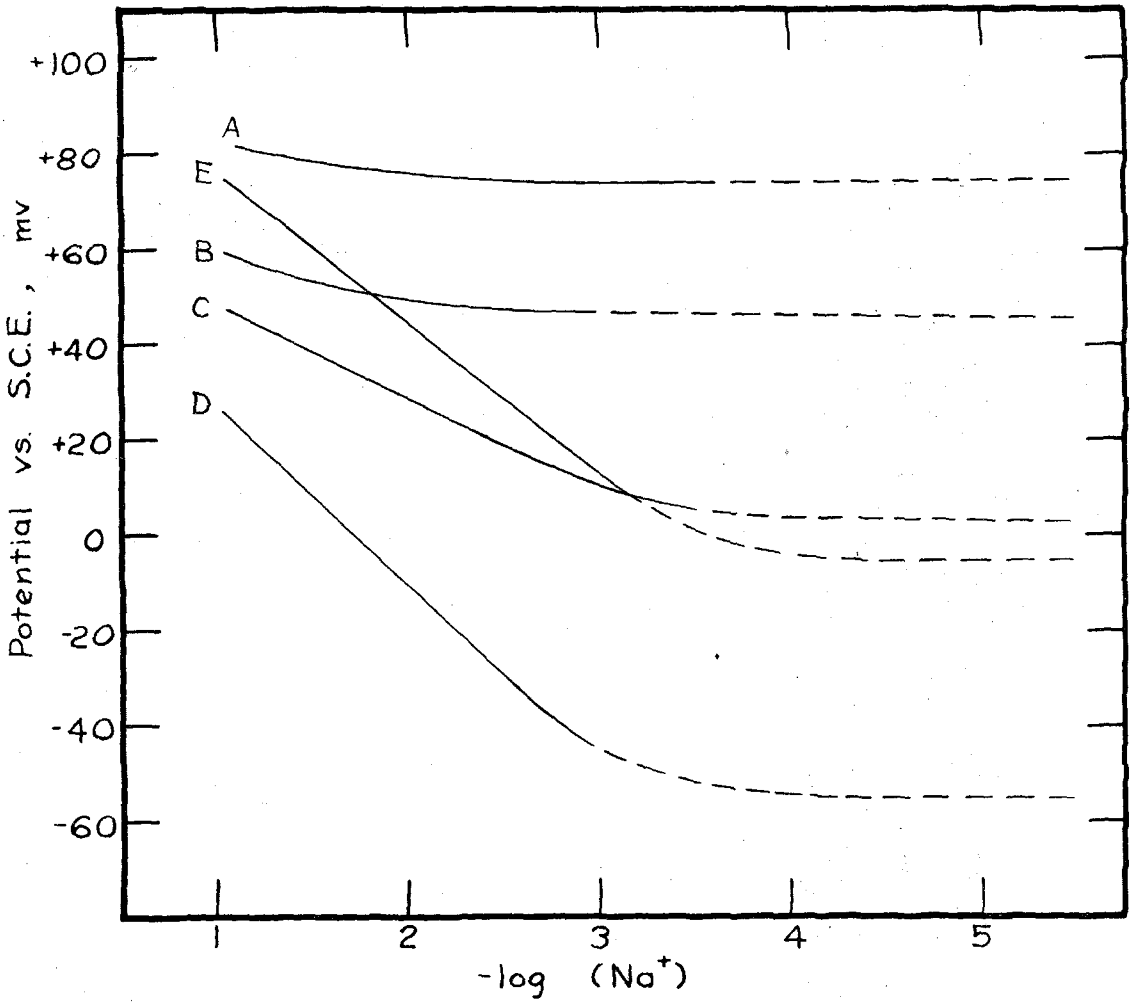

Figure 5

Sodium-Ion Response of Electrode Z_1

(A) Buffer Solution 5

(B) Buffer Solution 7

(C) Buffer Solution 11

(D) Buffer Solution 11

(E) 48% ethanol, 52% Buffer Solution 11

concentrations than those obtained with the other glasses.

The greatest response is shown in Curves D and E which represent measurements made in Buffer Solution 11, and in an ethanol-Buffer Solution 11 mixture respectively. These two curves indicate that ethanol has little effect, if any, on the degree of sodium-ion response of the 7280 glass; it merely shifts the potential to higher values.

Curves C and D show the results obtained at different times in similar buffer solutions. The measurements for Curve D were made 11 days before those for Curve C, and there may have been a decrease in the sensitivity of the membrane surface during that time. A study of the effect of various cleaning agents on the sensitivity of Electrode Z_1 was made and the results of this study are presented in the next section. The difference in the potential range exhibited by Curves C and D may also have been the result of some surface effect.

In the case of the solutions represented by Curves D and E, the effect of large quantities of potassium chloride and sodium chloride on the membrane potential in solutions already 0.1 $\underline{M}$ in sodium ion was investigated. Addition of 0.5 g. of KCl to Solution D caused the potential measured by Z_1 to increase by 2 mv. and that measured by the General Purpose Glass Electrode to increase by 5 mv. Then addition of 0.5 g. of NaCl caused the Z_1 potential to increase by 9 mv. and the General Purpose Glass Electrode potential to increase by 12 mv. In the case of Solution E, addition of 1.0 g. of KCl increased the potential of Z_1 by 1 mv. and the potential of the General Purpose Glass Electrode by 10 mv. Addition of 1.0 g. of NaCl now resulted in an increase of 12 mv. in the potential of Z_1 and 18 mv. in the potential of the General Purpose Glass Electrode. These results show that potassium ions have very little effect on the 7280-glass electrodes and a much larger effect on the General Purpose Glass Electrodes. In the region of high sodium-ion concentration, the sodium-ion response of the General Purpose Glass Electrode appears to be somewhat greater than that of Electrode Z_1.

Electrode Z_2. The curves obtained from potential measurements with Electrode Z_2 are given in Figure 6. A comparison of these curves with the curves of Figure 5 for corresponding solutions shows the reproducibility of measurements made with different electrodes of the same glass. In general, the curves are quite similar, although Electrode Z_2 never gave as large a sodium-ion response as that obtained with Electrode Z_1 in the experiments represented by Curves D and E, Figure 5.

Curve D, Figure 6, shows the results obtained from potential measurements in Buffer Solution 11 in the low sodium-ion concentration region. The shape of this curve in dilute sodium

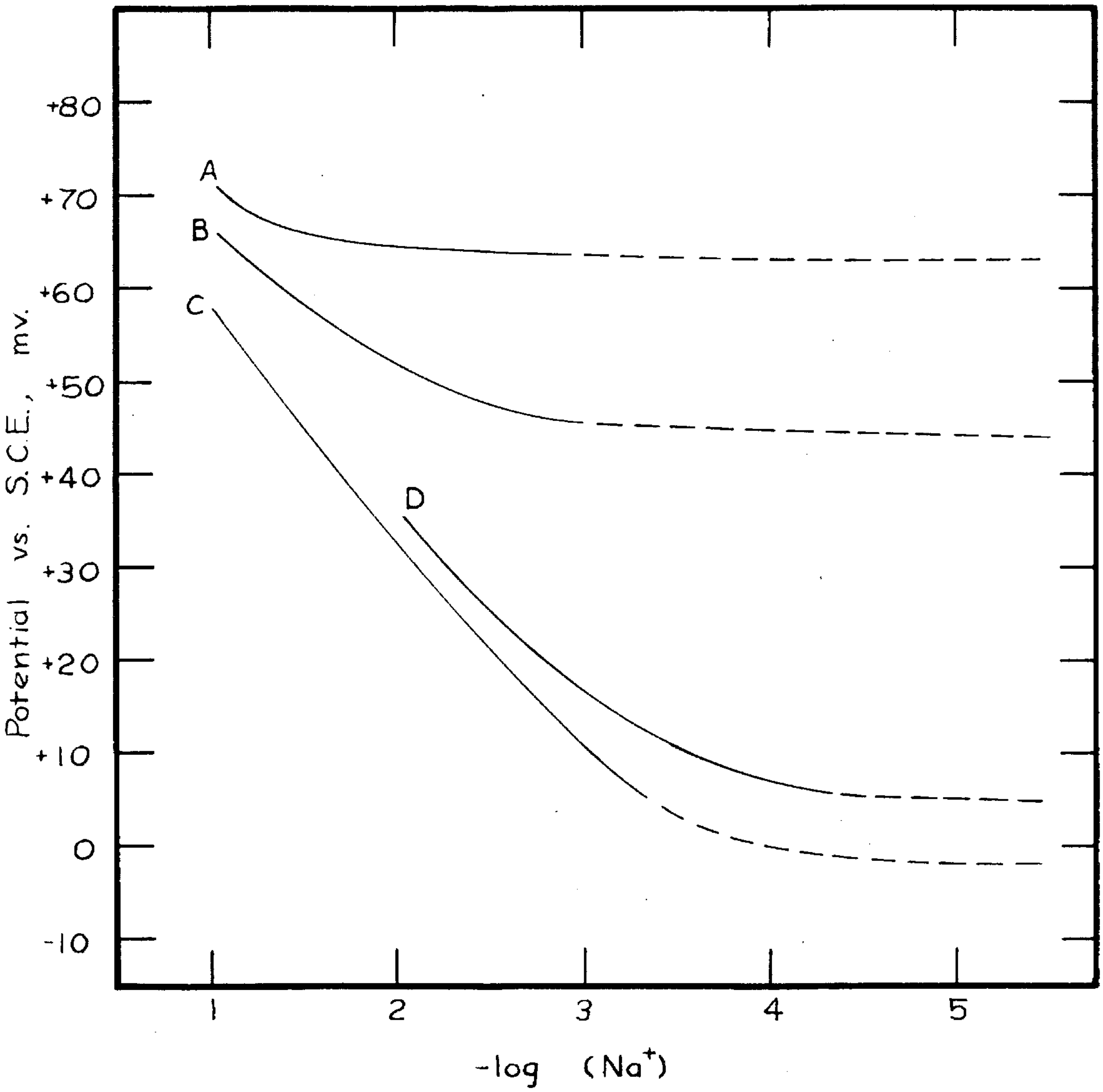

Figure 6

Sodium-Ion Response of Electrode Z_2

(A) Buffer Solution 5

(B) Buffer Solution 7

(C) Buffer Solution 11

(D) Buffer Solution 11

chloride solutions indicates that the method of extrapolation used in presenting the data obtained from these sodium-ion response measurements is probably valid.

Surface Effects. As has been mentioned before, it was suspected that the difference in the degree of sodium-ion response of Electrode Z_1 in similar buffer systems might be due to surface contamination. Consequently, a study was made of the effect of various cleaning agents on the sensitivity of Electrode Z_1. The membrane was soaked in a particular cleaning agent for a time and then tested for its sodium-ion response in Buffer Solution 11. The results of this study are given in Table II.

Table II

Effect of Cleaning Agents on Sensitivity of Electrode Z_1

Agent	Soaking Time, min.	Potential, mv. 0.01 M Na^+	Potential, mv. 0.1 M Na^+	Sensitivity mv./decade
None		22	40	18
12 N HCl	30	36	49	13
16 N HNO_3	30	36	52	16
Aqua Regia	90	28	45	17
20% $(NH_4)HF_2$	5	40	51	11

The sensitivity of the electrode is reported as the potential change in mv. obtained by increasing the sodium-ion concentration from 0.01 M to 0.1 M and may be compared to a sensitivity of 40 obtained for the experiment represented by Curve D, Figure 5.

Although the various cleaning agents used failed to increase the sensitivity of the electrode, surface contamination was not conclusively eliminated as a factor in decreasing the sensitivity. It may also be that some ageing process is occurring in the glass which alters the structure of the membrane surface and results in a decrease in sensitivity.

Resistance Measurements. A measure of the resistance of the various electrodes was necessary in order to eliminate the possibility that the low response was caused by an extremely high resistance and was not a property of the glass itself. The resistance measurements were made with a Type 544-B Megohm Bridge manufactured by the General Radio Co. This instrument operates as a d.-c. Wheatstone bridge and derives its sensitivity from a vacuum-tube voltmeter which indicates the bridge balance. Its accuracy is 3% to 100 megohms and 4% from 100 to 10,000 megohms. Resistance measurements were made with various electrode systems in Beckman Buffer Solution pH 7 with approximately 90 v. impressed across the electrode terminals. The results obtained from measurements of Electrodes X_1, X_2, Z_1, Z_2, and a Beckman General Purpose Glass Electrode are given in Table III.

Table III

Resistance Measurements of Various Electrode Systems

Electrode System	Resistance, Megohms
General Purpose and S. C. E.	142
X_1 and S. C. E.	0.70
X_2 and S. C. E.	0.42
X_1 and X_2	1.27
Z_1 and S. C. E.	785
Z_2 and S. C. E.	1140
Z_1 and Z_2	1900

In the systems measured, almost all the resistance is in the glass membrane; hence the values shown in Table III represent an approximation to the resistance of the various membranes.

Electrodes X_1 and X_2 had extremely low resistances so it may be concluded that the small sodium-ion response of these electrodes is a property of the X857BY glass.

Electrodes prepared from the 7280 glass not only showed the largest sodium-ion response of any of the glasses tested but also had the highest resistances. Even though Electrodes Z_1 and Z_2 had resistances approximately 10 times greater than that found for a Beckman General Purpose Glass Electrode, a consideration of the Model G pH Meter makes it seem reasonable that sodium-ion response measurements made with these electrodes are reliable. A Model G pH Meter is essentially a potentiometer employing a vacuum-tube amplifier as a null-point detector. It may be used to make accurate potential measurements of cells with internal resistances exceeding 1000 megohms providing the current flowing is sufficiently small so that the IR drop through the cell is not large enough to introduce a significant error into the pH measurements (32). The sensitivity of the galvanometer decreases if the cell resistance becomes exceedingly large and this in turn may result in the flow of excessive grid currents. Since, however, the galvanometer sensitivity was no greater with the General Purpose Glass Electrode than with the 7280-glass electrodes, the potential measurements made with these electrodes probably give a true picture of the effect of sodium ions on the membrane.

Resistance measurements were not made on the electrodes prepared from the R-6 and the 015 glasses since these had already been disassembled.

The resistance of a glass electrode as determined with a Megohm Bridge is probably only an approximate value, and if a more accurate measurement is desired, the method of Eckfeldt and Perley (33) is suggested.

CONCLUSIONS

Although this investigation did not lead to the preparation of a sodium-specific glass electrode, a considerable amount of information was obtained about the sodium-ion response of various kinds of glass.

The fact that all the glasses studied with the exception of the R-6 glass have a sodium-ion response which is greater the more alkaline the solution indicates that glass may act like a weak acid. The stronger the glass acid, the lower the pH at which the glass would act as a perfect sodium-ion electrode. The glasses of type D studied by Lengyel and Blum (25) must have been moderately strong acids to give a perfect sodium-ion response in solutions with a pH as low as 5. If the acid hypothesis is correct, then the zirconium glass, Corning No. 7280, acted as the strongest acid of those glasses studied. Since, however, the 7280 electrodes gave only 1/3 to 2/3 of the theoretical sodium-ion response even in solutions with a pH as high as 11, this glass would still be considered to be a very weak acid.

Although electrodes prepared from the 7280 glass would not be applicable to a potentiometric titration of sodium, it is very probable that they could be used for a determination of the sodium-ion concentration of a solution by the method of Urban and Steiner (30). Moreover, these electrodes should be applicable to solutions of lower pH than the Kimble-glass electrodes used by Urban and Steiner.

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PROPOSITIONS

1. Sinha has recently reported the use of resinous ion-exchange membranes in some simple potentiometric titrations (1).

a. It is proposed that a more quantitative investigation of these titrations be made.

b. Some further interesting titrations are proposed.

c. Sinha says that the titration of an acid with a base containing a cation of the same mobility in the resin as hydrogen ion would exhibit the sharpest inflection. It is suggested instead, that the sharpest inflection would occur in the titration with a base containing a cation which has the smallest mobility with respect to hydrogen ion. The potentiometric titration of an acid with various bases as determined with a resin-membrane electrode would test this suggestion.

(1) Sinha, S. K., J. Ind. Chem. Soc., 32, 35 (1955).

2. In a study of a procedure for the quantitative oxidation of hypophosphite by cerium (IV), Bernhart (2) has made a few orienting rate measurements. These data do not fit the rate law of Mitchell (3), and Griffith et. al. (4) which is applicable to the oxidation of hypophosphite by I_2, Br_2, $HgCl_2$, $CuCl_2$, IO_3^-, and Ag^+. A kinetic study of the oxidation is proposed. It is suspected that the data are unreliable and that the same rate law will be found.

(2) Bernhart, D. N., Anal. Chem., 26, 1798 (1954).

(3) Mitchell, A. D., J. Chem. Soc., 117, 1322 (1920).

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3. It has been reported that a cobalt (III)-sulfate solution prepared by electrolytic oxidation of cobalt (II)-sulfate is stable under proper conditions (5). It is suggested that the cobalt (II)-cobalt (III) system be investigated as an intermediate half-cell for secondary coulometric analysis.

(5) Bricker, C. E., and Loeffler, L. J., Paper presented at the Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, 1955. Reported in Anal. Chem., 27, 315 (1955).

4. The determination of equilibrium constants for complex-ion species from ion-exchange measurements has been made by Whiteker and Davidson (6) by taking limiting slopes from two plots. It is proposed that the two equilibrium constants may be obtained more simply and with greater reliability from a plot of

$$\frac{Q_o/Q_A - 1}{(SO_4^{=})} \quad \underline{\text{vs.}} \quad (SO_4^{=}).$$

(6) Whiteker, R. A., and Davidson, N. R., J. Am. Chem. Soc., 75, 308 (1953).

5. The triphenylmethylarsonium cation has been shown to form compounds with a number of metal anions which are soluble in various

organic reagents. The stable, crystalline compounds, triphenylmethylarsonium permanganate, $(Ph_3MeAs)(MnO_4) \cdot 1/2H_2O$ (7), and triphenylmethylarsonium dichromate, $(Ph_3MeAs)_2Cr_2O_7$ (8) have been prepared. It is proposed that a structure determination be made of these crystals. A knowledge of the arrangement of the atoms in these compounds would be useful in predicting which anions might form similar complexes, and might help to explain the non-ionic character of the bonding.

(7) Gibson, N. A., and White, R. A., Anal. Chim. Acta, 12, 115 (1955).

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6. Urban and Steiner used a glass-membrane electrode for a determination of the sodium-ion concentration of mixtures of sodium hydroxide and potassium chloride by measuring the change in potential caused by known increments of sodium hydroxide (9). Although the solutions were so alkaline that the membrane was probably insensitive to the hydrogen-ion concentration, similar experiments should have been made with known increments of sodium chloride. Since glass electrodes prepared from Corning No. 7280 glass give a reasonable sodium-ion response in solutions of pH 11 (10), it is suggested that the applicability of these electrodes to a sodium-ion determination by the method of Urban and Steiner be investigated. The effect of both hydrochloric acid and sodium chloride as the

internal solution should be studied.

(9) Urban, F., and Steiner, A., J. Phys. Chem., 35, 3058 (1931).

(10) This thesis, p. 86.

7. In a consideration of the probable reaction sequence for the oxidation of semicarbazide to biurea with sodium hypobromite, Wiley (11) postulates $NH_2CONHN = NNHCONH_2$ as an intermediate. Since the loss of nitrogen from this compound appears improbable, a mechanism is proposed which does not involve this intermediate. A radioactive tracer experiment would be helpful in determining the mechanism of the oxidation.

(11) Wiley, P. F., J. Am. Chem. Soc., 76, 5176 (1954).

8. In a recent report of a procedure for the determination of thallium (I) by oxidation with selenious acid. Desmukh (12) states that the hydrochloric acid plays a significant role in the redox process since thallium (I) could not be oxidized in the presence of even large concentrations of sulfuric, acetic, or perchloric acid. A consideration of the standard potential of the thallium (I)-thallium (III) system shows that oxidation cannot occur except in the presence of some species which strongly complexes thallium (III). It is suggested that the effect of complexing agents such as ethylenediamine tetraacetic acid, gluconic acid, and 8-quinolinol on the reducing potential of the thallium system be investigated in order to determine

if a less powerful oxidizing agent than selenious acid might be more suitable for the oxidation.

(12) Desmukh, G. S., Anal. Chim. Acta, 12, 319 (1955).

9. a. Sykes (13) has obtained evidence for a $FeHSO_4^{++}$ complex which was not found by Whiteker and Davidson (14) and suggests that it may be formed to a significant extent only in solutions of low ionic strength. It is proposed that experiments similar to those of Whiteker and Davidson be made at constant sulfate-ion concentration and at several low ionic strengths to test this suggestion.

b. A recent study by King and Neptune (15) obtained evidence for both $CrCrO_4^{+}$ and $CrHCrO_4^{++}$ complexes. It would be interesting to study the chromium (III)-sulfate system to see if both complex species are present here.

c. Since $HCrO_4^{-}$ is a much weaker acid than HSO_4^{-}, it is suggested that $MHSO_4^{++}$ complex ions might be observed only in solutions of very high acid concentrations.

(13) Sykes, K. W., The Chemical Society's Special Publication No. 1, 64 (1954).

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(15) King, E. L., and Neptune, J. A., J. Am. Chem. Soc., 77, 3186 (1955).

10. a. A revision of the scientific German Course (L 35) required of senior chemists is proposed.

b. It is proposed that junior applied chemists be given the option of taking either elementary German (L 32) or engineering mathematics (AM 15).

11. It is proposed that the iron bars be removed from the main door of the Gates Laboratory. Two 681-g. machinist's ball pein hammers should then be provided, one beside this door and the other beside the southeast door of the building. Whenever the building is locked, a conspicuous sign should be posed on the inside of each door with the inscription, "In Case of Fire, Break Glass."