I. STUDIES OF THE DISTRIBUTION OF INORGANIC SUBSTANCES BETWEEN AQUEOUS AND NON-AQUEOUS PHASES

II. STUDIES IN COULOMETRIC ANALYSIS

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George Myron Arcand

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ABSTRACT

The distribution of arsenic (III) between aqueous HCl solutions and β-β' dichlorodiethyl ether has been studied. Arsenic chloride species have been proposed, equilibrium constants have been calculated relating these species in the aqueous solutions, and distribution constants have been calculated for each species. The data from the distribution experiments have been correlated with solubility and electromotive force data taken from the literature.

A partial study has been made of the distribution of ferric thiocyanate and of KSCN and NaSCN between aqueous solutions and tributyl phosphate. Sufficient data were taken to indicate that the distribution of the alkali thiocyanates is strongly dependent on the ionic strength of the aqueous solutions and that species of ferric thiocyanate other than $(Fe(SCN)_3)_x$ are extracted by tributyl phosphate.

A coulometric method for determining microgram quantities of bromate has been developed which made use of electrolytically generated cuprous copper as the intermediate. Optimum conditions for the titration were determined. Quantities of bromate ranging from 18 to 240 micrograms have been determined within 0.3 microgram.

A coulometric method for the determination of ammonia has been developed which made use of electrolytically generated bromine in alkaline solutions as the intermediate. The effects of pH and of certain metal ions on the titration were studied. Quantities of ammonia ranging from 14 to 230 micrograms have been determined within 0.2 microgram.

TABLE OF CONTENTS

PART I.

STUDIES OF THE DISTRIBUTION OF INORGANIC SUBSTANCES BETWEEN AQUEOUS AND NON-AQUEOUS PHASES

PART I. A. DISTRIBUTION OF TRIPOSITIVE ARSENIC BETWEEN HYDROCHLORIC ACID AND β-β' DICHLORODIETHYL ETHER

The study of the behavior of a substance in a two-phase solvent system should provide information necessary for the better understanding of the species present in both phases. Work on the systems, HCl (aq) - Fe(III) - isopropyl ether (1), (2), and HCl(aq) - Fe(III) - β-β' dichlorodiethyl ether (3) resulted in the proposition that $HFeCl_4$ is the predominant iron species in 6-8 VF HCl. Yost and White (4) demonstrated the possible existence of H_2OsO_5 and calculated its first acid dissociation constant from data found in a study of the system, NaOH(aq) - Os(VIII) - CCl_4.

The work described here was undertaken in an effort to establish some basis for predicting what compounds of tripositive arsenic exist in aqueous HCl solutions. Preliminary work in this laboratory (5) and that of Irvine and co-workers (6) have shown that tripositive arsenic can be extracted from HCl solutions by a number of organic solvents. Of these, β-β' dichlorodiethyl ether appeared to be most suited for the desired study, since it is easily purified, is easily handled, and dissolves only small amounts of HCl and water while dissolving relatively large quantities of arsenic. Isopropyl ether is almost as effective an extracting agent, but is miscible with HCl solutions 9 VF and above. Correlations of the results of this work with conductivity (7), solubility (8), (9), and electromotive force data (10) permit the prediction of the species of tripositive arsenic present, the calculation of constants for the equilibria between these species in the aqueous solutions, and the calculation of distribution constants for the phase equilibria between certain of these species.

Experimental

Reagents and equipment. Technical grade β-β' dichlorodiethyl ether was distilled twice at a pressure of 20 mm of Hq. Fractions which boiled between 79° and 80° C. were collected (11). Peroxides formed rapidly if distillation was attempted at atmospheric pressure. To each liter of ether was added 1×10^{-5} mole of catechol in order to prevent the formation of peroxides (1). Arsenic forms a compound with catechol (12), but the amount involved is insignificant. When a sample of treated ether was tested with acidified potassium iodide solution, no iodine color appeared, thus indicating that the ether was free from peroxide. There was no significant peroxide formation over a period of two months.

Arsenic stock solutions were prepared by heating 28.93 gram portions of Reagent grade arsenic trioxide in 12 VF HCl until all of the solid dissolved. When cool, the solution was transferred to a one liter volumetric flask and diluted to mark with 12 VF HCl. An oily liquid, assumed to be arsenic trichloride (13), usually separated from the solution as it was cooling, but dissolved when the mixture was diluted. The above procedure was used in order that all stock solutions would be 0.287 VF in arsenic trichloride. (Note: Extreme caution should be exercised when handling solutions of tripositive arsenic in 12 VF HCl. Arsenic trichloride is quite volatile and is extremely toxic.) It is possible to keep the stock solutions for several months without significant change in the tripositive arsenic concentration.

Standard silver nitrate and potassium iodate solutions were prepared from dried, weighed samples of the Reagent grade salts. Potassium thiocyanate (0.01 VF) was prepared by accurately diluting a 0.1 VF solution which had been standardized against silver nitrate. Sodium hydroxide solutions were prepared by diluting 10 ml portions of carbonate free 50 percent sodium hydroxide stock to one liter and standardizing this against analytical grade potassium acid phthalate.

Calibrated volumetric equipment was used for all analyses. When a concentrated or non-aqueous solution was measured, the pipet was calibrated for delivery of that specific solution. The densities of these solutions were determined with a calibrated 25 ml picnometer.

Distribution Measurements. Preliminary qualitative distribution experiments with neutral solutions containing tripositive arsenic and either sodium chloride or sodium perchlorate showed that no significant quantity of arsenic was extracted. Similar experiments with HCl solutions showed that no significant quantity of arsenic was extracted from HCl solutions until the acid concentration was about 4 VF or from $HClO_4$ solutions at any concentration.

A 100 ml. portion of the stock solution (0.287 VF in arsenic trichloride and 12.3 VF in HCl) was pipetted into a 250 ml. volumetric flask and diluted with HCl and water to give the final solution which had the desired concentration of HCl and which was 0.115 VF in arsenic. A 100 ml. portion of this solution and 100 ml. of ether were pipetted into a 250 ml. Squibb separatory funnel. The tip of the funnel was covered with a rubber policeman and all joints were sealed with paraffin. Mixing was obtained by rocking the funnel slowly back and forth 100 times, then the funnel was placed in a water bath thermostated at $25^{\circ} \pm 0.1$ C. Vigorous shaking caused the formation of emulsions with concentrated HCl solutions. The mixing process was repeated five times over a period of three hours after which the funnel was allowed to stand in the water bath for not less than 72 hours. The ether phase was drawn off through the stopcock; the first 5 ml. were discarded since this portion was most likely to entrap drops of the aqueous phase. About 85 ml. of the remaining ether phase were drawn into a dry glass stoppered weighing bottle. The bottle was immediately closed to prevent escape of HCl vapor. Twenty-five milliliter portions of the ether phase were pipetted from the bottle into three 60 ml. separatory funnels, each of which contained 10 ml. of water. The funnels were shaken vigorously, the phases separated, and the aqueous phases retained. The ether phases were washed five more times with 10 ml. portions of water. The six washings from one of the separatory funnels were combined and this solution was then analyzed for one of the desired components, i.e., tripositive arsenic, chloride, or hydrogen ion. The same was done with the washings from the other two separatory funnels. The tripositive arsenic was titrated with standard potassium iodate to the iodine monochloride endpoint (14); chloride was determined with standard silver nitrate by a modified Volhard method (15); and hydrogen ion was determined by titration with standard sodium hydroxide until a pH of 7 was indicated on a Beckman Model F pH meter. The acid was determined as a check on the chloride determination; the hydrolysis of any arsenious chloride compound yields equal quantities of chloride and hydrogen ion. The same general procedure was used to determine the distribution of HCl between ether and aqueous solutions of appropriate acid concentrations. In all cases, determinations were made of the various components in the aqueous solutions before equilibration with the ether.

The initial formal concentrations of HCl ranged from 5.9 to 12.3. Experiments with aqueous solutions of lower acid concentrations were not made because of the difficulties of accurately determining the small quantities of arsenic and chloride extracted. The coulometric determination of arsenic (16) would have been adequate for this purpose. A method for the determination of small quantities of chloride was tried (17), but was found to be unsatisfactory because the small amounts of ether in the washings interfered with the organic indicator and caused erratic results.

The major sources of error in these experiments are believed to be in the separation of phases after equilibration and in the washing procedure. Although the 72 hour settling period decreases the number of aqueous droplets in the ether phase, it is almost impossible to avoid entrapping some of the aqueous phase at the wall of the separatory funnel. It is not unreasonable to expect some of this aqueous phase to be carried out with the ether. In addition, some loss might be expected in the several transfers required by the washing procedure. Therefore, errors of 1 to 2 percent could be expected.

The anlytical methods employed can be expected to give results accurate to 2 to 3 parts per 1000.

In view of the sources of error, it is somewhat surprising to find that the maximum standard deviation of these measurements was less than one percent. This deviation was found in the value for the total chloride in the ether phase in equilibrium with an aqueous solution 12 VF in HCl. The danger of loss of HCl vapor from such a solution is great since the partial pressure of HCl is about 17 mm. of Hg. (18). Thus it is not surprising to find the minimum precision at this point.

Solubility Measurements. A knowledge of the molecular character of the solid phase in equilibrium with solutions saturated with arsenic trioxide is necessary if the solubilities in HCl (9) and in $HClO_4$ (8) are to be correlated. Both $HClO_4$ and HCl saturated with arsenic trioxide readily supersaturated on cooling; several hours often elapsed before the appearance of the first crystals and these grew slowly over a period of several days. Supersaturated 4 VF HCl and 4 VF $HClO_4$ solutions were allowed to stand for about 24 hours in order to obtain enough precipitate for analysis. Quite large, well formed octahedral crystals were formed. X-ray analyses by D. E. Petersen of this laboratory showed them to have the same crystal structure as arsenic trioxide. Other portions of the precipitate were washed with alcohol, dried by evaporation, weighed, and the arsenic determined. The percentage of arsenic present corresponded to that in pure arsenic trioxide. It is possible, of course, that washing with alcohol could carry away some other arsenic compound. However, it seems evident that the predominant species precipitated from solutions up to 4 VF in either HCl or $HClO_4$ is arsenic trioxide.

Data

Table I shows the data obtained from the distribution experiments described above and the calculated ratios of chloride to tripositive arsenic found in the ether phases. The concentrations of HCl in the ether phases in equilibrium with the corresponding concentrations of aqueous HCl are shown in Column VII and were calculated with the aid of Figure 1. The data used in plotting Figure 1 are shown in Table II.

Isopropyl ether was used to extract arsenic from 4.88 VF and 6.95 VF HCl solutions as a check on previous results obtained in this laboratory (19). These data are shown in Table III. The concentrations of HCl in ether (Column VII) are taken from the data of Nachtrieb and Conway (20). It will be noted that the Cl/As ratio of the 6.95 VF HCl system is lower than that for a similar system containing β-β' dichlorodiethyl ether. This is probably caused by a difference in distribution constants.

Calculation of Distribution and Equilibrium Constants. It will be noted that the Cl/As ratio in the ether phase has a value of about three when the aqueous HCl concentration is between 9.13 and 12.3 VF. When the acid concentration is less than 9 VF, the ratio decreases quite rapidly. This would suggest that the predominant

TABLE I

The Distribution of Arsenic (III) between Aqueous Hydrochloric Acid and β-β′ Dichlorodiethyl Ether and the Calculated Chloride - Arsenic Ratio in the Ether Phase

Column II shows initial aqueous HCl concentrations; Column III the calculated equilibrium aqueous HCl concentrations; Column IV the initial aqueous arsenic concentrations; Column V the ethereal chloride concentrations; Column VI the ethereal arsenic concentrations; Column VII shows the concentration of HCl in the ether phase in equilibrium with the corresponding concentration of aqueous HCl shown in Column III and as determined from Figure 1. Column VIII shows the difference between Columns V and VII and represents ether phase chloride bound to arsenic. Column IX shows the ratio of chloride to arsenic in the ethereal arsenic compounds.

I Number of Detns	II HCl_{aq} initial	III (VF) equil.	IV $As(III)_{aq}$ (VF)	V Cl_{et} (VF)	VI $As(III)_{et}$ (VF)	VII HCl_{et} (VF)	VIII Cl_{et} (VF)	IX $Cl_{et}/As(III)_{et}$
5	12.3	11.8	0.115_6	0.590 ±.004	0.1118 ±.0005	0.250	0.340	3.03
5	9.16	8.90	0.114_9	0.3313 ±.0007	0.1078 ±.0002	0.018	0.313	2.90
2	8.45	8.20	0.115_2	0.2952 ±.0003	0.1018 ±.0001	0.011	0.284	2.78

TABLE I (cont.)

I Number of Detns	II HCl_{aq} initial	III (VF) equil.	IV $As(III)_{aq}$ (VF)	V Cl_{et} (VF)	VI $As(III)_{et}$ (VF)	VII HCl_{et} (VF)	VIII Cl_{et} (VF)	IX $Cl_{et}/As(III)_{et}$
2	8.02	7.76	0.115_1	0.2695 ±.0003	0.0970 ±.0000	0.007	0.262	2.71
2	7.00	6.76	0.115_1	0.1798 ±.0002	0.0747 ±.0001	0.001	0.179	2.39
2	6.57	6.39	0.115_5	0.1396 ±.0001	0.0620 ±.0001	-----	0.140	2.25
5	5.88	5.72	0.115_2	0.0801 ±.0003	0.03944 ±.00009	-----	0.080	2.03

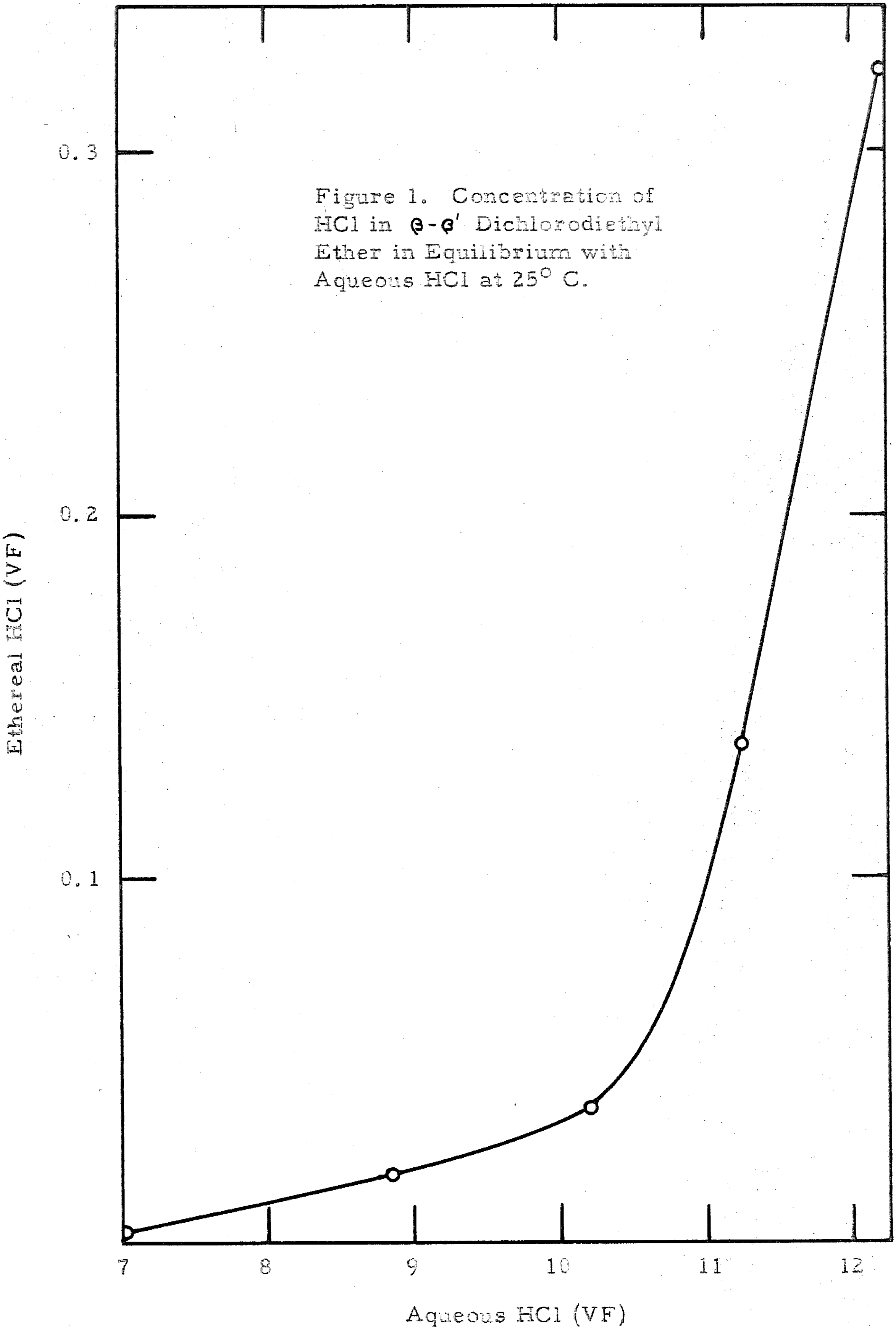

Figure 1. Concentration of HCl in β-β′ Dichlorodiethyl Ether in Equilibrium with Aqueous HCl at 25° C.

TABLE II

Distribution of HCl between Aqueous Hydrochloric Acid and β-β′ Dichlorodiethyl Ether

Column II shows the initial aqueous HCl concentrations; Column III the calculated equilibrium aqueous HCl concentrations; and Column IV the concentration of HCl in the ether phase in equilibrium with that in the aqueous phase.

I Number of Detns	II HCl_{aq} (VF)	III HCl_{aq} (VF)	IV HCl_{et} (VF)
6	12.4	12.1	0.322 ±.003
4	11.4	11.2	0.1562 ±.0011
5	10.4	10.4	0.0363 ±.0002
5	9.12	9.10	0.0186 ±.0002
4	7.22	7.22	0.0029_3 $\pm.0001_4$

TABLE III

The Distribution of Arsenic (III) between Aqueous Hydrochloric Acid and Isopropyl Ether and the Calculated Chloride - Arsenic Ratio in the Ether Phase

Column III shows the initial calculated concentrations of HCl after corrections have been made for the formation of arsenic chloride compounds. Other column designations are the same as those for Table I.

I Number of Detns	II HCl_{aq} (VF)	III HCl_{aq} (VF)	IV $As(III)_{aq}$ (VF)	V Cl_{et} (VF)	VI $As(III)_{et}$ (VF)	VII HCl_{et} (VF)	VIII Cl_{et} (VF)	IX $Cl_{et}/As(III)_{et}$
2	6.95	6.81	0.115_3	0.1843 ±.0000	0.0847 ±.0001	0.013	0.171	2.02
3	4.84	4.77	0.117	0.0397 ±.0002	0.0234 ±.0002	0.005	0.0347	1.48

species in both aqueous and ether phases is $AsCl_3$ when the aqueous HCl concentration is high. The decrease in the Cl/As ratio at lower acid concentrations suggests that other species are being extracted and that these, too, exist in the aqueous phase. One cannot say that the Cl/As ratio directly represents the species present in the aqueous phase, for this would be true only if the distribution constants were the same for all species. That this is not so is indicated by the decrease in the amount of arsenic extracted as the concentration of aqueous HCl decreases. It is of interest to note that the amount of arsenic extracted begins to decrease rapidly at about the same acid concentration that the Cl/As ratio begins to decrease. This also seems to support the assumption that $AsCl_3$ is the predominant species in concentrated HCl solutions.

The experimental data may be analyzed in several different ways, depending on which of the following assumptions is employed.

Assumption (1). The species present in the aqueous phase under some or all of the conditions of the experiments are $AsCl_3$, $As(OH)Cl_2$, $As(OH)_2Cl$, $As(OH)_2^+$, and H_3AsO_3; those present in the ether phase are $AsCl_3$, $As(OH)Cl_2$, and $As(OH)_2Cl$.

Assumption (2). The species present in both phases are $AsCl_3$, $As(OH)Cl_2$, and $As(OH)_2Cl$.

Assumption (3). The species present in the aqueous phase are $AsCl_3$, $As(OH)_2Cl$, $As(OH)_2^+$, and H_3AsO_3; those present in the ether phase are $AsCl_3$ and $As(OH)_2Cl$.

Assumption (4). The species present in both phases are $AsCl_3$ and $As(OH)_2Cl$.

Calculations based on Assumption (1) yield the best results. The assumption of the existence of arsenic trichloride is reasonable, since it has been prepared by the reaction of arsenic trioxide with concentrated HCl (21) and appeared to be present during the preparation of the arsenic stock solutions used in these experiments. As mentioned above, the distribution experiments also support this assumption. The existence of the hydroxychlorides has been mentioned by some authors, (22), (23), (24), but the evidence has been questioned by others, (25), (26). Prased and co-workers (27) state that they prepared $AsOCl{:}H_2O$, but give no details of method or any references.

The results of the conductivity measurements of Washburn and Strachan (7) suggest that arsenious acid undergoes a basic dissociation

$$HAsO_2 = AsO^+ + OH^-$$

or (1)

$$H_3AsO_3 = As(OH)_2^+ + OH^-$$

The formula, $As(OH)_2^+$, is used because one might reasonably expect arsenic to retain a coordination number of three as in arsenious acid. Calculations would be the same for either representation. Randall (28) made a recalculation of their data and arrived at a value of 5×10^{-15} for the equilibrium constant for the above reaction.

The assumptions were used to make preliminary calculations that $AsCl_3$ is the only arsenic species present in significant quantity in 12 VF HCl, $AsCl_3$ and $As(OH)Cl_2$ are the predominant arsenic species present in 9 VF HCl, and all arsenic species (i. e., $AsCl_3$, $As(OH)Cl_2$, $As(OH)_2Cl$, $As(OH)_2^+$, and H_3AsO_3) exist in significant quantities in 5.9 VF HCl.

According to the above assumptions, when the HCl concentration is 12 VF, the distribution coefficient for $AsCl_3$ can be immediately calculated, that is

$$[AsCl_3]_{et}/[AsCl_3]_{aq} = D_3 \tag{2}$$

where $[AsCl_3]_{et}$ is the molal concentration in the ether phase and $[AsCl_3]_{aq}$ is that in the aqueous phase. No attempt was made to analyze the aqueous phases after equilibration with ether. Other work in this laboratory (5) and that of Irvine and co-workers (6) have shown that tripositive arsenic is not oxidized under the conditions of the experiments. The concentration of arsenic in the aqueous phase was calculated from the final concentration of arsenic in the ether phase by application of proper corrections for the changes in phase volumes (6).

It is possible to calculate a distribution constant for $As(OH)Cl_2$ and an equilibrium constant to relate $AsCl_3$ and $As(OH)Cl_2$ from data taken when the aqueous phase was 9 VF in HCl.

$$[As(OH)Cl_2]_{et}/[As(OH)Cl_2]_{aq} = D_2 \tag{3}$$

$$As(OH)Cl_2 + H^+Cl^- = AsCl_3 + H_2O \tag{4}$$

$$[AsCl_3]_{aq} \cdot a_{H_2O}/[As(OH)Cl_2]_{aq}(a_\pm)^2_{HCl} = K_4 \tag{5}$$

The activity of water (29) is represented by a_{H_2O} and the mean activity of H^+Cl^- as defined by Latimer (30) is represented by $(a_\pm)_{HCl}$. A series of equations may be set up relating the concentrations of both species in both phases.

$$[Cl^-]_{et} = 3[AsCl_3]_{et} + 2[As(OH)Cl_2]_{et} \tag{6}$$

$$[As(III)]_{et} = [AsCl_3]_{et} + [As(OH)Cl_2]_{et} \tag{7}$$

$$\text{Therefore}[AsCl_3]_{et} = [Cl^-]_{et} - 2[As(III)]_{et} \tag{8}$$

$$\text{and} \quad [As(OH)Cl_2]_{et} = 3[As(III)]_{et} - [Cl^-]_{et} \tag{9}$$

Combination of equations (5) to (8) with equation (2) permits the calculation of $[AsCl_3]_{aq}$. Then $[As(OH)Cl_2]_{aq}$ can be calculated by subtracting the $[AsCl_3]_{aq}$ from the total concentration of arsenic in the aqueous phase. K_4 and D_2 can then be calculated.

The following equations are necessary when the aqueous phase is 5.9 VF in HCl.

$$[As(OH)_2Cl]_{et}/[As(OH)_2Cl]_{aq} = D_1 \tag{10}$$

$$As(OH)_2Cl + H^+Cl^- = As(OH)Cl_2 + H_2O \tag{11}$$

$$[As(OH)Cl_2]_{aq} \cdot a_{H_2O}/[As(OH)_2Cl]_{aq}\,(a_\pm)^2_{HCl} = K_3 \tag{12}$$

$$[As(OH)_2Cl]_{aq} \cdot a_{H_2O}/[H_3AsO_3]_{aq}\,(a_\pm)^2_{HCl} = K_2 \tag{13}$$

$$[As(OH)_2{}^+]_{aq} \cdot a_{H_2O}/[H_3AsO_3]_{aq}\,(a_\pm)_{HCl} = K_1 \tag{14}$$

The equilibrium constant, K_1, is found by dividing Randall's equilibrium constant by the equilibrium constant for water.

The equilibrium constant, K_2, can be calculated from the solubility of arsenic trioxide in HCl (9) and in $HClO_4$ (8). The concentration of tripositive arsenic in 1 VF $HClO_4$ is assumed to be the sum of the concentrations of H_3AsO_3 and of $As(OH)_2{}^+$, while that in 1 VF HCl is assumed to be the sum of the concentrations of H_3AsO_3, $As(OH)_2{}^+$, and $As(OH)_2Cl$. By using K_1, $[H_3AsO_3]_{aq}$ in a $HClO_4$ solution can be calculated.

$$S_{HClO_4} = [H_3AsO_3]_{aq}(1 + K_1\,(a_\pm)_{HClO_4}/a_{H_2O}) \tag{15}$$

where S_{HClO_4} is twice the formal solubility of arsenic trioxide in $HClO_4$. The concentration of $As(OH)_2Cl$ in a HCl solution of the same activity should then be

$$[As(OH)_2Cl]_{aq} = S_{HCl} - S_{HClO_4} \tag{16}$$

where S_{HCl} is twice the formal solubility of arsenic trioxide in HCl. The constant, K_2, was calculated by using these solubilities in 1 VF $HClO_4$ and in 1 VF HCl because the activities of the two acids are very nearly the same and $As(OH)_2Cl$ should be the only arsenic chloride species present in the HCl solution in significant quantity.

The preliminary solubility measurements previously described indicate that the distribution constant for H_3AsO_3 is negligibly small. Therefore, if one assumes that the tripositive arsenic enters the ether phase only as unionized chloride species, the following expressions may be formulated:

$$[As(III)]_{et} = D_3[AsCl_3]_{aq} + D_2[As(OH)Cl_2]_{aq} + D_1[As(OH)_2Cl]_{aq} \tag{17}$$

$$[Cl^-]_{et} = 3D_3[AsCl_3]_{aq} + 2D_2[As(OH)Cl_2]_{aq} + D_1[As(OH)_2Cl]_{aq} \tag{18}$$

Subtracting equation (17) from equation (18) and combining the result with equation (5) yields

$$[Cl^-]_{et} - [As(III)]_{et} = (2D_3K_4(a_\pm)^2_{HCl}/a_{H_2O} + D_2)[As(OH)Cl_2]_{aq} \quad (19)$$

With these equations, it is possible to calculate the concentrations of $AsCl_3$ and $As(OH)Cl_2$ in both phases.

By means of equations (13) and (14), $[As(OH)_2^+]_{aq}$ and $[As(OH)_2Cl]_{aq}$ can be expressed in terms of $[H_3AsO_3]_{aq}$. Thus

$$\begin{aligned}&[As(III)]_{aq} - ([AsCl_3]_{aq} + [As(OH)Cl_2]_{aq}) = \\ &[As(OH)_2Cl]_{aq} + [As(OH)_2^+]_{aq} + [H_3AsO_3]_{aq} = \\ &\left(\frac{K_1(a_\pm)_{HCl}}{a_{H_2O}} + \frac{K_2(a_\pm)^2_{HCl}}{a_{H_2O}} + 1\right)[H_3AsO_3]_{aq}\end{aligned} \quad (20)$$

Therefore, both $[H_3AsO_3]_{aq}$ and $[As(OH)_2^+]_{aq}$ can be calculated. The remaining aqueous arsenic concentration must be made up by $[As(OH)_2Cl]_{aq}$. Similarly, since the concentrations of $AsCl_3$ and $As(OH)Cl_2$ in the ether phase have been calculated, the remaining arsenic in that phase must be in the form of $As(OH)_2Cl$. There is now sufficient information for the calculation of D_1 and K_3.

Equations (17) and (18) are general and can be used to refine the calculations once approximate values for the constants have been obtained. If these equations are solved to eliminate the $AsCl_3$ term, the following results.

$$[\mathrm{Cl}^-]_{et} - 3[\mathrm{As(III)}]_{et} = -D_2[\mathrm{As(OH)Cl_2}]_{aq} - 2D_1[\mathrm{As(OH)_2Cl}]_{aq} \quad (21)$$

In order for this equation to have a non-negative solution, $[\mathrm{Cl}^-]_{et}$ must be less than $3[\mathrm{As(III)}]_{et}$. However, the experimental results show that, when the aqueous HCl concentration is 12 VF, the $[\mathrm{Cl}^-]_{et}$ is approximately 1 percent greater than $3[\mathrm{As(III)}]_{et}$, which is within experimental error just three times the ethereal arsenic concentration. Thus, the left side of the equation becomes zero. Since both D_1 and D_2 are real, positive numbers, the arsenic hydroxychloride concentrations must be negligibly small. Therefore, the assumption that $AsCl_3$ is the only chloride species of arsenic present in significant quantity in 12 VF HCl must be retained.

It can be seen from Table I that about 96 percent of the tripositive arsenic is extracted from solutions 10 to 12 VF in HCl. The fact that both the distribution coefficient and the Cl/As ratio remain essentially constant in this range tends to eliminate the possibility of the existence of a higher chloride species such as $HAsCl_4$ in the system studied.

Significant concentrations of $As(OH)_2^+$ and H_3AsO_3 in the aqueous solutions which are 12 VF in HCl would change the value of D_3 by decreasing the concentration of $AsCl_3$ in the aqueous phase. However, calculations show that the concentrations of these species are negligible in solutions of that acid concentration. Thus, the assumption is valid that the only arsenic species present in significant quantity in 12 VF HCl is $AsCl_3$.

Equations (17) and (18) can be solved to eliminate the $As(OH)Cl_2$ term. Combination of this resultant equation with equations (5) and (12) yields the following:

$$[Cl^-]_{et} - 2[As(III)]_{et} = D_3[AsCl_3]_{aq} - D_1[As(OH)_2Cl]_{aq}$$

$$= (D_3K_3K_4(a_\pm)^4_{HCl}/a^2_{H_2O} - D_1)\,[As(OH)_2Cl]_{aq} \qquad (22)$$

This equation is used to calculate the concentrations of $As(OH)_2Cl$ and $AsCl_3$ in the system which is 9 VF in HCl. Application of equations (5), (12), (13), and (14) permits the calculation of the concentrations of $As(OH)_2^+$ and H_3AsO_3 in the aqueous phase and the concentrations of $As(OH)Cl_2$ in both phases. Now a new D_2 and K_4 can be calculated. While the concentrations of $As(OH)_2Cl$ and $As(OH)_2^+$ in the 9 VF HCl solutions are relatively small, they are significant. The concentration of H_3AsO_3 is very small.

D_1 and K_3 are recalculated in the manner previously described. Successive approximations are continued until the values of the various constants converge. The constants which follow are the results of such a series of calculations.

$D_1 = 0.175$

$D_2 = 2.94$

$D_3 = 55$

$K_1 = 0.5$

$K_2 = 0.085$

$K_3 = 3.4 \times 10^{-4}$

$K_4 = 6.25 \times 10^{-5}$

The constants, K_1 and K_2, were calculated previously and were not affected by the approximations above.

Formulae can be derived which express the concentrations of tripositive arsenic and chloride in the ether phase in terms of the initial concentrations of arsenic and chloride respectively in the aqueous phase. The concentration of arsenic in the ether phase is

$$[As(III)]_{et} = [As(III)]_i - ([AsCl_3]_{aq} + [As(OH)Cl_2]_{aq} + [As(OH)_2Cl]_{aq} + [As(OH)_2^+]_{aq} + [H_3AsO_3]_{aq}) \quad (23)$$

where $[As(III)]_i$ is the concentration of tripositive arsenic in the aqueous phase before equilibration with ether. It is assumed that the equilibrium volumes of the aqueous and ether phases are equal. While this is not true, the error caused by such an approximation is well within the desired limits of accuracy.

On substitution of the equilibrium constants, equation (23) becomes

$$[As(III)]_{et} = [As(III)]_i - (A + B + C + E + 1)\,[H_3AsO_3]_{aq} \quad (24)$$

where

$$A = K_2K_3K_4(a_\pm)^6_{HCl}/a^3_{H_2O}$$

$$B = K_2K_3(a_\pm)^4_{HCl}/a^2_{H_2O}$$

$$C = K_2(a_\pm)^2_{HCl}/a_{H_2O}$$

$$E = K_1(a_\pm)_{HCl}/a_{H_2O}$$

Similarly, substitution of the equilibrium constants into equation (17) gives the following:

$$[As(III)]_{et} = (D_3A + D_2B + D_1C)\,[H_3AsO_3]_{aq} \tag{25}$$

Equations (24) and (25) can be solved simultaneously to give

$$[As(III)]_{et} = \frac{(D_3A + D_2B + D_1C)\,[As(III)]_i}{(D_3 + 1)A + (D_2 + 1)B + (D_1 + 1)C + E + 1} \tag{26}$$

Similarly, the concentration of chloride bonded to arsenic in the ether phase can be calculated. The equilibrium constants are substituted in equation (18):

$$[Cl^-]_{et} = (3D_3A + 2D_2B + D_1C)\,[H_3AsO_3]_{aq} \tag{27}$$

Combining equations (25) and (27),

$$[\mathrm{As(III)}]_{et} = \frac{(D_3A + D_2B + D_1C)\,[\mathrm{Cl}^-]_{et}}{3D_3A + 2D_2B + D_1C} \tag{28}$$

But equation (26) gives $[\mathrm{As(III)}]_{et}$ in terms of $[\mathrm{As(III)}]_i$. Thus

$$[\mathrm{Cl}^-]_{et} = \frac{(3D_3A + 2D_2B + D_1C)\,[\mathrm{As(III)}]_i}{(D_3 + 1)A + (D_2 + 1)B + (D_1 + 1)C + E + 1} \tag{29}$$

By means of equations (26) and (29), $[\mathrm{As(III)}]_{et}$ and $[\mathrm{Cl}^-]_{et}$ can be calculated for any aqueous HCl concentration between 5.9 VF and 12.3 VF. Such calculations were made for the experimental points. The calculated experimental results are compared in Table IV. The term, $[\mathrm{Cl}^-]_{et}$, refers to the chloride present in the ether phase as compounds of arsenic.

Calculations based on Assumption (2) lead to a different set of formulae. Since the solubility of arsenic trioxide decreases with decreasing acid concentration in all acids except HCl (8), the assumption that the basic dissociation of H_3AsO_3 is very small might be reasonable. Washburn and Strachan (7) worked with HCl solutions, so their results might be interpreted as due to a decrease in HCl concentration through the formation of $As(OH)_2Cl$.

$$H_3AsO_3 + H^+Cl^- = As(OH)_2Cl + H_2O \tag{30}$$

Thus, it is possible to assume that the only species which exist in significant quantities in the systems in question are $AsCl_3$, $As(OH)Cl_2$,

TABLE IV

Comparison of Experimental and Calculated Values of Ethereal Arsenic and Chloride Concentrations

Calculations are based on Assumption (1) in the text. Column II shows the calculated equilibrium concentrations of HCl in the aqueous phase; Column III the aqueous tripositive arsenic concentrations; Columns IV and V, respectively, the observed and calculated equilibrium ethereal tripositive arsenic concentrations and Columns VII and VIII, respectively, the observed and calculated equilibrium ethereal chloride concentrations after corrections have been made for the distribution of HCl between the two phases.

I HCl_{aq} (VF)	II HCl_{aq} (VF)	III $As(III)_i$ (VF)	IV $As(III)_{et\ obs}$ (VF)	V $As(III)_{et\ calc}$ (VF)	VI % Diff.	VII $Cl_{et\ obs}$ (VF)	VIII $Cl_{et\ calc}$ (VF)	IX % Diff.
12.3	11.8	0.115_6	0.111_8	0.113_2	1.3	0.340	0.339	-0.3
9.16	8.90	0.114_9	0.107_8	0.109_0	1.1	0.313	0.325	3.8
8.45	8.20	0.115_2	0.101_8	0.105_0	3.1	0.284	0.300	5.6
8.02	7.76	0.115_1	0.097_0	0.099_7	2.8	0.262	0.274	4.6
7.00	6.76	0.115_1	0.074_7	0.075_0	0.4	0.179	0.182	1.7

TABLE IV (cont.)

I HCl_{aq} (VF)	II HCl_{aq} (VF)	III $As(III)_i$ (VF)	IV $As(III)_{et\ obs}$ (VF)	V $As(III)_{et\ calc}$ (VF)	VI % Diff.	VII $Cl_{et\ obs}$ (VF)	VIII $Cl_{et\ calc}$ (VF)	IX % Diff.
6.57	6.39	0.115_5	0.062_0	0.062_3	0.5	0.140	0.142	1.4
5.88	5.72	0.115_2	0.0394_4	0.0394_4	0.0	0.080	0.076	-5.0

and $As(OH)_2Cl$. There is the possibility that some H_3AsO_3 might be present. However, there is no information available which will allow the calculation of the concentration of H_3AsO_3 when Assumption (2) is used.

Equations may be derived in the manner previously described. The equations used to make successive approximations are shown:

In 9 VF HCl,

$$[Cl^-]_{et} - 2[As(III)]_{et} = (D_3K_3K_4(a_\pm)^4_{HCl}/a^2_{H_2O} - D_1)[As(OH)_2Cl]_{aq} \quad (31)$$

In 5.9 VF HCl,

$$[Cl^-]_{et} - [As(III)]_{et} = (2D_3K_4(a_\pm)^2_{HCl}/a_{H_2O} + D_2)[As(OH)Cl_2]_{aq} \quad (32)$$

The constants calculated in this way are

$D_1 = 0.145$ $\qquad K_3 = 2.5 \times 10^{-4}$

$D_2 = 2.6$ $\qquad K_4 = 6.8 \times 10^{-5}$

$D_3 = 55$

Similarly, the concentrations of tripositive arsenic and of chloride bonded to arsenic which are in the ether phase can be calculated.

If $\quad F = \dfrac{K_3K_4(a_\pm)^4_{HCl}}{a^2_{H_2O}}$, and $G = \dfrac{K_3(a_\pm)^2_{HCl}}{a_{H_2O}}$

then

$$[\mathrm{As(III)}]_{et} = \frac{(D_3F + D_2G + D_1)\,[\mathrm{As(III)}]_i}{(D_3 + 1)F + (D_2 + 1)G + (D_1 + 1)} \qquad (33)$$

$$[\mathrm{Cl}^-]_{et} = \frac{(3D_3F + 2D_2G + D_1)\,[\mathrm{As(III)}]_i}{(D_3 + 1)F + (D_2 + 1)G + (D_1 + 1)} \qquad (34)$$

Calculations were made for the experimental points and the results are shown in Table V.

Since there is no independent evidence for the existence of $As(OH)Cl_2$, the postulate that $AsCl_3$ and $As(OH)_2Cl$ are the only chloride forms of arsenic in the HCl solutions is not unreasonable (third assumption). A mathematical treatment similar to that already described was carried out, the results of which are shown in Table VI. $As(OH)_2^+$ and H_3AsO_3 were assumed to be present. The final equations are shown:

$$D_1 = [\mathrm{As(OH)_2Cl}]_{et}/[\mathrm{As(OH)_2Cl}]_{aq} \qquad (10)$$

$$D_3 = [\mathrm{AsCl_3}]_{et}/[\mathrm{AsCl_3}]_{aq} \qquad (2)$$

$$K_3' = [\mathrm{AsCl_3}]_{aq} \cdot a^2_{H_2O}/[\mathrm{As(OH)_2Cl}]_{aq}\,(a_\pm)^4_{HCl} \qquad (35)$$

Successive approximations were not necessary in this case, because there were enough equations to permit an exact solution. The calculated constants are

TABLE V

Comparison of Experimental and Calculated Values of Ethereal Arsenic and Chloride Concentrations

Calculations are based on Assumption (2) in the text. Column designations are the same as those in Table IV.

I HCl_{aq} (VF)	II HCl_{aq} (VF)	III $As(III)_i$ (VF)	IV $As(III)_{et}$ obs (VF)	V $As(III)_{et}$ calc (VF)	VI % Diff.	VII Cl_{et} obs (VF)	VIII Cl_{et} calc (VF)	IX % Diff.
12.3	11.8	0.115_6	0.111_8	0.113_2	1.3	0.340	0.338	-0.5
9.16	8.90	0.114_9	0.107_8	0.108_8	0.9	0.313	0.320	2.0
8.45	8.20	0.115_2	0.101_8	0.104_8	3.0	0.284	0.300	5.6
8.02	7.76	0.115_1	0.097_0	0.098_9	2.0	0.263	0.278	5.7
7.00	6.76	0.115_1	0.074_7	0.073_2	-2.0	0.179	0.186	4.0
6.57	6.39	0.115_5	0.062_0	0.060_6	-2.3	0.140	0.144	3.3
5.88	5.72	0.115_2	0.0394_4	0.0395_0	0.2	0.080	0.080	0.0

TABLE VI

Comparison of Experimental and Calculated Values of Ethereal Arsenic Concentrations

The calculations are based on Assumption (3) in the text.

I HCl_{aq} (VF)	II $As(III)_i$ (VF)	III $As(III)_{et\ obs}$ (VF)	IV $As(III)_{et\ calc}$ (VF)	V % Diff.
12.3	0.115_6	0.111_8	0.114_0	2.0
9.16	0.114_9	0.107_8	0.112_6	4.5
8.45	0.115_2	0.101_8	0.111_3	9.3
8.02	0.115_1	0.097_0	0.108_3	11.6
7.00	0.115_1	0.074_7	0.084_7	13.4
6.57	0.115_5	0.062_0	0.067_9	9.5
5.88	0.115_2	0.0394	0.0398	0.9

$D_1 = 0.398$ $\quad K_1 = 0.5$

$D_3 = 55$ $\quad K_2 = 0.085$

$K'_3 = 4.3 \times 10^{-8}$

The formula for the concentration of tripositive arsenic in the ether phase is

$$[\mathrm{As(III)}]_{et} = \frac{(D_3H + D_1I)\,[\mathrm{As(III)}]_i}{(D_3 + 1)H + (D_1 + 1)I + J + 1} \tag{36}$$

where $H = K_2K'_3(a_\pm)^6_{HCl}/\, a^3_{H_2O}$

$I = K_2(a_\pm)^2_{HCl}/\, a_{H_2O}$

$J = K_1(a_\pm)_{HCl}/\, a_{H_2O}$

It can be seen from Table VI that the results of calculations based on the third assumption are not as satisfactory as those based on the first and second assumptions. Calculations based on the fourth assumption gave results not greatly different from those listed in Table VI.

Correlation with other data

Since calculations based on the first two assumptions given above fit the experimental data equally well (Tables IV and V), it is desirable to find some way to decide which of the two interpretations is the more reasonable.

Conductivity and Solubility Measurements. - One should infer from the second assumption that there is little basic dissociation of H_3AsO_3. Thus, the total concentration of arsenic in a $HClO_4$ solution saturated with arsenic trioxide should equal the concentration of H_3AsO_3 in that solution. Since the activity of water is essentially the same in HCl (29) and $HClO_4$ (31) solutions of the same hydrogen ion activity up to 4 VF acid, the H_3AsO_3 concentration should be the same in HCl and $HClO_4$ solutions of the same activity which are saturated with arsenic trioxide. Under this assumption, the effects noted by Washburn and Strachan (7) must be caused by the formation of an unionized arsenic hydroxychloride. The decrease in conductivity could then be caused by a decrease in HCl concentration.

$$\mathrm{HCl} = 1000\, L_{.1\,\mathrm{F\,HCl}} / \Lambda_{.1\,\mathrm{F\,HCl}} \qquad (37)$$

where L is the measured specific conductance and Λ is the equivalent conductance of a 0.1 F HCl solution. According to equation (30), the decrease in HCl concentration must equal the concentration of $As(OH)_2Cl$.

$$\begin{aligned}[\mathrm{As(OH)_2Cl}] &= [\mathrm{HCl}]_i - [\mathrm{HCl}]_f \\ &= 1000(L_i - L_f)/\Lambda_{.1\,\mathrm{F\,HCl}} \qquad (38)\end{aligned}$$

The subscripts, i and f, designate the quantities without arsenic and with arsenic, respectively.

$$\Lambda_{.1\text{ F HCl}} = 391.3 \qquad (32)$$

From the data of Washburn and Strachan

$L_i = 0.03952$

$L_f = 0.03886$

$H_3AsO_3 = 0.0494$ VF

Therefore $[As(OH)_2Cl] = 0.0016$ M

$[H_3AsO_3] = 0.0477$ M

The equilibrium constant, K_2, calculated on this basis, was found to have a value of 5.6 as compared with the value, 0.085, previously calculated.

Knowledge of K_2 should permit the calculation of the solubility of arsenic trioxide in HCl. A plot of the solubility of arsenic trioxide against $HClO_4$ concentration (8) is shown in Figure 2. If the concentrations of $As(OH)_2Cl$ are calculated at several acid activities and added to the corresponding H_3AsO_3 concentrations taken from Figure 2, the solubilities of arsenic trioxide in HCl at these activities should be found. A plot of such a solubility versus HCl concentration is shown in Figure 3 (line 1). It is evident that the calculated value for K_2 is unsatisfactory.

An attempt was made to calculate K_2 by using only the

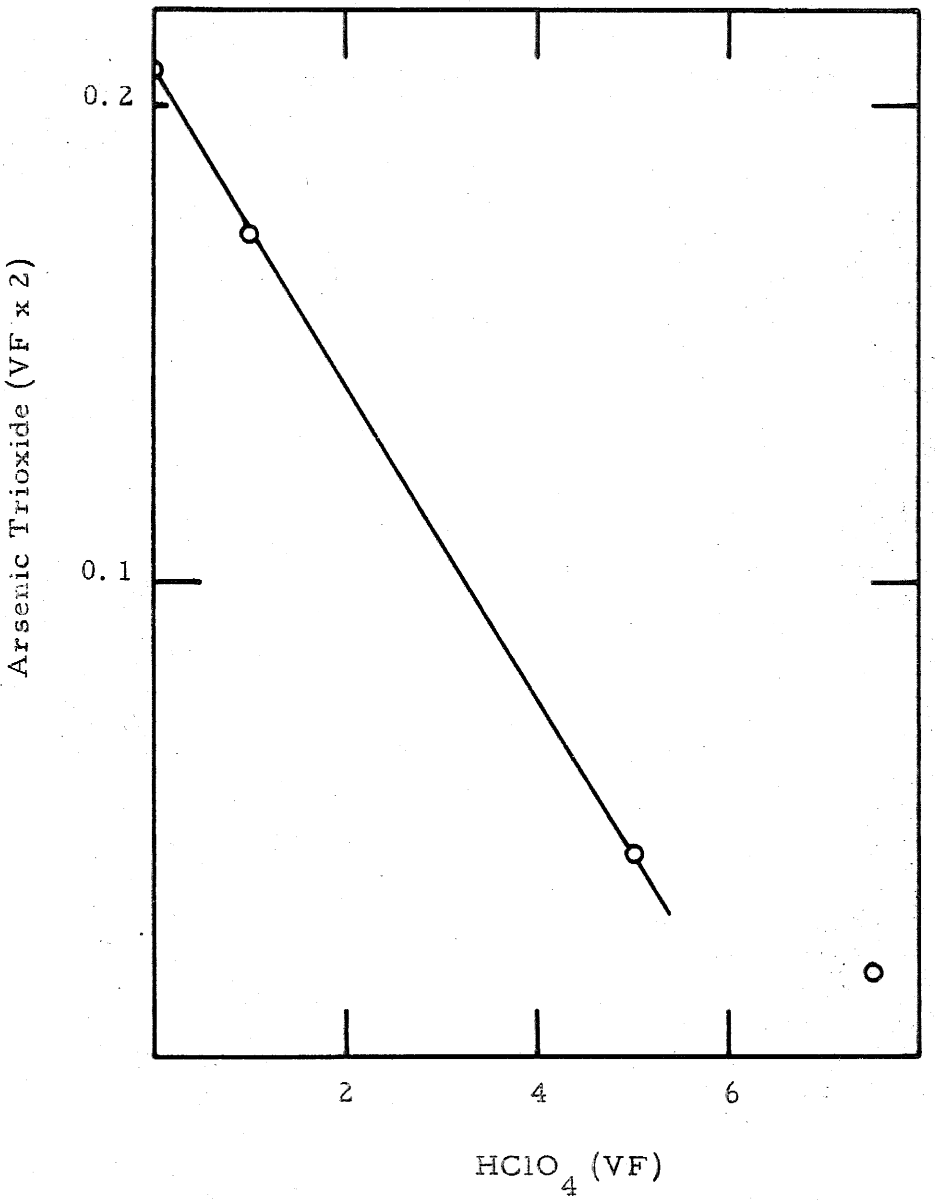

Figure 2. Solubility of As_2O_3 in $HClO_4$. The plotted solubility is twice the formal solubility of As_2O_3.

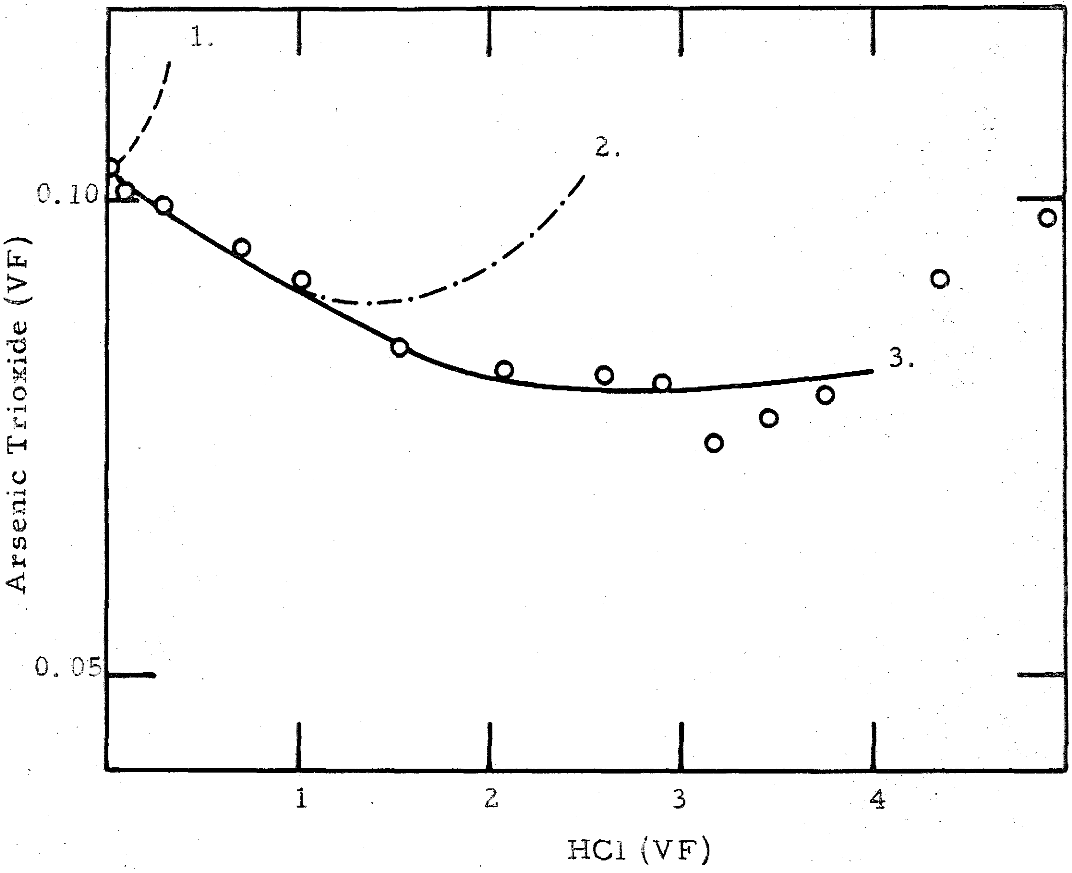

Figure 3. Formal Solubility of As_2O_3 in aqueous HCl.

0 - Literature solubility.

1 - Calculated solubility assuming presence of arsenic hydroxychlorides, but no significant amount of $As(OH)_2^+$.
K_2 = 5.6 is calculated from conductivity data (3).

2 - Solubility calculated using same assumptions as for Line 1 except that K_2 = 0.07 is calculated from solubility data in 0.5 VF HCl & $HClO_4$ solutions.

3 - Calculated solubility assuming presence of arsenic hydroxychlorides & $As(OH)_2^+$.
K_2 = 0.085 is calculated from solubility & conductivity data.

available solubility data. It was assumed that when the acid concentration is 0.5 VF, the only arsenic chloride species present in significant quantity is $As(OH)_2Cl$. By subtracting the saturation concentration of arsenic in $HClO_4$ from that in HCl, the concentration of $As(OH)_2Cl$ was calculated. The concentration of H_3AsO_3 was assumed to be the saturation concentration in $HClO_4$, as before. The new K_2, equal to 0.07, was used to calculate the solubility of arsenic trioxide in higher concentrations of HCl. The results are shown in Figure 3 (Line 2) and are seen to be unsatisfactory. It will be noted that this value for K_2 is not greatly different from the one used in the analysis of the distribution data under the first assumption.

If one accepts equation (1) and the constant calculated by Randall (28) as correct, one must assume that the concentration of arsenic in a $HClO_4$ solution saturated with arsenic trioxide is the sum of the concentrations of H_3AsO_3 and $As(OH)_2^+$. For a particular acid activity, the concentration of H_3AsO_3 is

$$[H_3AsO_3] = S_{HClO_4}/(1 + K_1 (a_\pm)_{HClO_4}/ a_{H_2O}) \qquad (39)$$

The calculated concentrations of H_3AsO_3 for various $HClO_4$ activities from 0.35 to 14.4 are plotted against the hydrogen ion activities in Figure 4.

The difference between the solubilities of arsenic trioxide

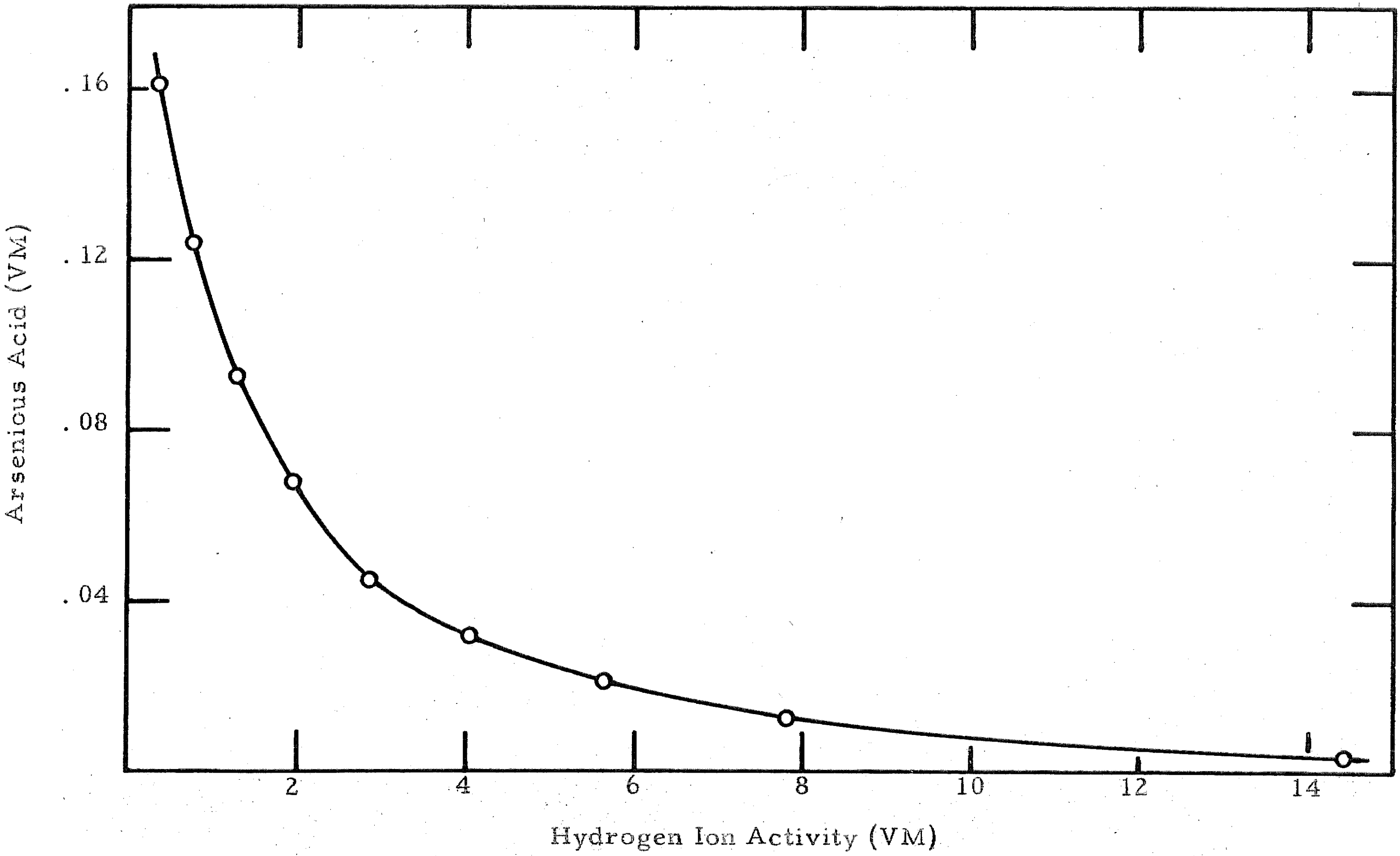

Figure 4. Concentration of Arsenious Acid in Perchloric Acid
Calculations made according to Assumption 1.

in 1 VF $HClO_4$ and HCl was assumed to equal twice the concentration of $As(OH)_2Cl$ in the HCl solution. The calculation of K_2 under this assumption has already been described. The concentrations of $As(OH)_2Cl$ were calculated at other acid activities and the values added to the concentrations of arsenic in $HClO_4$ solutions of the same activity. It was necessary to correct the acid concentrations for the formation of $As(OH)_2^+$ and $As(OH)_2Cl$ so that, in each case, the first value for the concentration of $As(OH)_2Cl$ was only approximate. The second calculation gave the desired result. The calculated solubilities of arsenic trioxide in HCl are shown in Figure 3 (Line 3) where they are plotted against the HCl concentration. These calculated values agree much more closely with the experimental values of Garrett and co-workers (9). However, the calculated solubility of arsenic trioxide drops considerably below the experimental solubility when the HCl concentration exceeds 3.5 VF.

It will be noted (Figure 2) that the solubility of arsenic trioxide seems to be a linear function of the formal concentration of $HClO_4$ from 0 to 5 VF $HClO_4$. The solubility at 7.5 VF $HClO_4$ does not lie on the line. Since it is known that arsenic trioxide dissolves very slowly in acid solutions, there is some possibility that the solubility measurements in $HClO_4$ are not correct. Also, there is the possibility that the solid phase in equilibrium with the

HCl solution is not composed solely of arsenic trioxide. Caven and Lander (23) mention the existence of $As(OH)_2Cl$ crystals which precipitate when an excess of water is added to $AsCl_3$; Garrett and co-workers (9) stated that there was some uncertainty concerning the composition of the solid phases in their experiments. Thus it is possible that not all of the $As(OH)_2Cl$ formed remains in solution. If this is the case, the activity coefficients of $As(OH)_2Cl$ must be very large and may be quite different from those of H_3AsO_3.

The activity of $As(OH)_2^+$ was not considered in any of the calculations made here. There is no reason to expect that the activity coefficient for this charged ion would remain constant and equal to unity throughout the range of acid activities considered. However, no data are available concerning the activity of this species.

It is not unreasonable to assume that the activity coefficients of the various uncharged chloride compounds of arsenic are about the same. Since the activities of these species appear in both numerator and denominator of all equations, the activity coefficients would tend to cancel. Thus, the use of concentrations instead of activities in these cases seems justifiable.

The calculation of solubilities presents another problem. The formation of H_3AsO_3 may be represented by the following equation:

$$As_2O_3 + 3\ H_2O = 3\ H_3AsO_3 \qquad (40)$$

Although H_3AsO_3 is an uncharged molecule, its activity coefficient cannot be assumed to equal unity at all acid concentrations. Thus, activity effects could profoundly influence the concentration of H_3AsO_3 in a solution saturated with arsenic trioxide. Here, too, the activity coefficients of $As(OH)_2^+$ could be important. These effects would be of particular importance at the higher acid concentrations and could explain the difference between the calculated and experimental results shown in Figure 3.

Electromotive Force Measurements. - Foerster and Pressprich (10) found that the measured potentials for the As(III) - As(V) half-cell in HCl were quite different from the calculated values. They used the following equation for the half-cell reaction

$$H_3AsO_3 + H_2O = H_3AsO_4 + 2\ H^+ + 2\ e^- \qquad (41)$$

According to the Nernst equation

$$E = E^o - (RT/nF)(\ln[H_3AsO_4]/[H_3AsO_3]) - \ln(a_{H^+}/a_{H_2O})) \qquad (42)$$

Foerster and Pressprich assumed that the only effect to be considered in the calculation of the potentials was the variation in hydrogen ion activity, since the ratio, $[H_3AsO_4]/[H_3AsO_3]$, was kept equal to unity. However, the present work has shown that the concentrations of H_3AsO_3 and the potentials at various HCl concentrations can be calculated only by applying the equilibrium constants found above. The results of such a series of calculations are shown in Table VII and are compared with the experimental values found by Foerster and Pressprich. The half-cell standard potential value of -0.559 v. given by Latimer (33) was used. It is seen that the calculated and observed values agree reasonably well except in 1 VF and 8 VF acid solutions. The reasons for these differences are not known. However, the system in 8 VF HCl is very complicated. As Foerster and Pressprich point out, there is the possibility of a chloride complex with pentapositive arsenic. Also, these workers used the $I^- - I_3^-$ half-cell to decrease the equilibration time of their systems. Thus, there is a good possibility that air will oxidize iodide at the acid activity of an 8 VF HCl solution. Since most of the iodide is already oxidized by the pentapositive arsenic, a relatively small aditional oxidation by air could cause a serious change in potential. Admittedly, the potential should be controlled by the As(III) - As(V) half-cell, but slow equilibration between the arsenic and iodine couples could allow the air oxidation to become effective. Similarly, the slowness of the reaction between pentapositive arsenic and iodide in 1 VF HCl could account for the apparently high measured values in this range.

TABLE VII

Comparison of Observed and Calculated Potentials

The observed potentials are those measured by Foerster and Pressprich (10). The calculated potentials are based on the first assumption in the text.

HCl (VF)	$-E_{obs}$	$-E_{calc}$
1	0.580	0.559
2	0.601	0.597
4	0.641	0.643
6	0.703	0.696
8	0.808	0.756

It is therefore apparent that the agreement between experimental data and calculated results for solubility and electromotive force measurements best supports the first assumption used for the calculation of the constants.

Summary

The distribution of tripositive arsenic between aqueous HCl solutions and both β-β' dichlorodiethyl and isopropyl ether has been investigated. The hydrolysis products from the ether phases have been analyzed and the ratios of chloride to arsenic established at various HCl concentrations. These ratios vary with the HCl concentration which indicates that more than one chloride species of arsenic is present in both phases.

With the aid of the constant,

$$K_1 = [As(OH)_2^+]\, a_{H_2O}/[H_3AsO_3]\ (a_\pm)_{HCl} = 0.5$$

which was calculated from the data of Randall (28), the following constants were calculated by analysis of the distribution data and of solubility data taken from the literature:

$$K_2 = [As(OH)_2Cl]\ a_{H_2O}/[H_3AsO_3]\ (a\pm)^2_{HCl} = 0.09$$

$$K_3 = [As(OH)Cl_2]\ a_{H_2O}/[As(OH)_2Cl]\ (a_\pm)^2_{HCl} = 3 \times 10^{-4}$$

$$K_4 = [AsCl_3]\, a_{H_2O}/[As(OH)Cl_2]\ (a_\pm)^2_{HCl} = 6 \times 10^{-5}$$

$$D_1 = [As(OH)_2Cl]_{et}/[As(OH)_2Cl]_{aq} = 0.18$$

$$D_2 = [As(OH)Cl_2]_{et}/[As(OH)Cl_2]_{aq} = 2.9$$

$$D_3 = [AsCl_3]_{et}/[AsCl_3]_{aq} = 55$$

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PART I. B. THE DISTRIBUTION OF FERRIC, POTASSIUM, AND SODIUM THIOCYANATES BETWEEN AQUEOUS SOLUTIONS AND TRIBUTYL PHOSPHATE

The data obtained by Melnick, Freiser, and Beeghly (1) in their study of the extraction of ferric thiocyanate from aqueous solutions by tributyl phosphate suggest that the extracted species is $(Fe(SCN)_3)_x$. However, they analyzed only the aqueous phases for Fe(III) after equilibration, thus leaving some doubt concerning the substances in the tributyl phosphate phases. The present work was begun in an attempt to identify these substances and thereby determine the species being extracted. The necessity for determining the amount of thiocyanate being extracted in the absence of iron led to a study of the distribution of potassium and sodium thiocyanates between the two phases. Lack of time prevented further study of the problem.

Experimental

Materials. - Technical grade tributyl phosphate was washed with aqueous ferrous sulfate, next with 1 VF NaOH, then with 1 VF HCl, and finally with distilled water until the washings showed a pH of 5 or greater. The phosphate was distilled at a pressure of 7 mm. of Hg. The portion collected boiled between 149° and 150° C.

Reagent grade salts were used to prepare all solutions.

Standard $AgNO_3$ was prepared from dried and weighed $AgNO_3$. Thiocyanate solutions were standardized against standard $AgNO_3$. $Hg(NO_3)_2$ solutions were standardized against standard thiocyanate by the Volhard method (2). $Na_2S_2O_3$ solutions were standardized against known weights of reagent grade KIO_3 (3). Ferric nitrate solutions were standardized iodometrically (4).

Distribution Measurements. - Twenty-five ml. portions of aqueous solution and of tributyl phosphate were pipetted into 60 ml. separatory funnels. The mixtures were shaken and placed in a water bath thermostated at 25° C. ± 0.1 for one hour, after which they were again shaken and allowed to stand in the bath for an additional three hours. Ten ml. portions of each phase were taken for analysis. Only the organic phase was analyzed for iron; both phases were analyzed when the aqueous phase contained only NaSCN. The change in phase volumes was measured by mixing 10 ml. portions of aqueous solution and of tributyl phosphate in a 50 ml. buret and noting the change in reading of the interface between phases. In all cases, the equilibrium ratio of volumes was $V_o/V_a = 1.16$, where V_o was the volume of the organic phase and V_a the volume of the aqueous phase. This was not done when iron was present in the system, but the phase volume change in the latter case appeared to be approximately the same.

Analyses. - The portion of the organic phase to be analyzed for iron was pipetted into a separatory funnel and 10 ml. of 16 VF nitric acid were added. The mixture was shaken carefully and allowed to stand until its color was a yellowish brown indicating that the thiocyanate had been oxidized. The aqueous phase was drawn off and the organic phase washed with five 10 ml. portions of water, the washings being retained and combined with the acid portion. The combined washings were evaporated to dryness and the iron determined iodometrically as described by Swift (4). The disappearance of starch-iodine color or tri-iodide color indicated the end-point. It was necessary to add 5 ml. of CCl_4 near the endpoint of the titration in order to dissolve the small amounts of tributyl phosphate containing iodine and adhering to the sides of the beaker.

The portion of the organic phase to be analyzed for thiocyanate was pipetted into a separatory funnel, 10 ml. of water and 5 ml. of 1 VF $HClO_4$ were added and the mixture was titrated with standard $Hg(NO_3)_2$ until the organic phase was colorless. Determinations of thiocyanate in aqueous solutions were made by the Volhard method (2).

That portion of the organic phase to be analyzed for sodium was pipetted into a separatory funnel and was washed with six 10 ml. portions of water. The washings were retained, combined, and evaporated to dryness on a water bath. The residue was dissolved in 15 ml. of ethyl alcohol and 15 ml. of ethyl ether and the sodium was determined volumetrically as described by Swift (5).

Data

Iron Thiocyanate Distributions. - The data obtained from the iron thiocyanate distributions are shown in Table I. Column VII shows the calculated concentration of thiocyanate which was extracted in the absence of the iron. Only one such blank measurement was made at a pH of 1.9; the concentration of thiocyanate in the organic phase was 0.0116 VF in equilibrium with an aqueous thiocyanate concentration of 0.1269 VF. The blank concentration could not be applied directly, because the amount of thiocyanate remaining in the aqueous phase when Fe(III) was extracted was much less than that remaining when only KSCN was extracted. Also, as was shown previously, the equilibrium pH of the aqueous solution containing Fe(III) was much lower than that when no Fe(III) was present in the system. The values for Column VI were calculated by assuming that the distribution of thiocyanate between the aqueous and tributyl phosphate phases would vary with the equilibrium concentration of thiocyanate in the aqueous phase in the same way at pH of 1.8 as at pH of 6.6. The thiocyanate concentration in the aqueous solution was calculated from the initial aqueous concentration and the final concentration in tributyl phosphate. Distribution coefficients were

TABLE I

Distribution of Ferric Thiocyanate between Aqueous Solutions and Tributyl Phosphate and the Calculated Thiocyanate-Iron Ratio

Column II shows the initial aqueous KSCN concentration; Column III the initial aqueous $Fe(NO_3)_3$ concentration; Column IV the equilibrium organic phase thiocyanate concentration; Column V the equilibrium organic phase iron concentration; Column VI the calculated organic phase KSCN concentration; and Column VII the corrected organic phase concentration of thiocyanate which is bonded to iron. The aqueous phase contained sufficient 1VF $HClO_4$ to make the initial pH = 1.8.

I Number of Expts	II SCN_i (VF)	III $Fe(III)_i$ (VF)	IV SCN_o (VF)	V $Fe(III)_o$ (VF)	VI Corr. (VF)	VII SCN_o (corr) (VF)	VIII SCN_o (corr)/$Fe(III)_o$
4	0.1519	0.1120	0.1366 ±.0008	0.0497 ±.0010	0	0.1366	2.75
2	0.1507	0.0559	0.1382 ±.0008	0.0472 ±.0001	0	0.1382	2.93
4	0.2995	0.0556	0.1702 ±.0011	0.0518 ±.0003	.0081	0.1621	3.13

calculated for the KSCN system when the pH was 6.6 and the variation with the equilibrium concentration of KSCN noted. This variation was then applied to the system at a pH of 1.8 in order to calculate the amount of thiocyanate that should be extracted by tributyl phosphate in the absence of iron. One can readily see that only roughly approximate values can be calculated by this method. The actual values should be somewhat larger. No correction was made for ionic strength, although activity effects appear to be significant.

The values shown in Column VII of Table I are found by subtracting those in Column VI from those in Column V and represent the thiocyanate carried into the tributyl phosphate phase as a result of the presence of iron.

Potassium and Sodium Thiocyanate Distributions. - The data obtained from the equilibration of neutral (pH = 6.6) potassium thiocyanate solutions with tributyl phosphate are shown in Table II. The aqueous thiocyanate concentrations shown in Column III are calculated from the initial aqueous concentrations, the final concentrations in the organic phases, and the measured equilibrium ratio of the phase volumes.

Distributions using systems containing NaSCN were performed to allow variation of the aqueous thiocyanate concentrations while maintaining an essentially constant ionic strength. Table II shows the results of those experiments which were completed. The

TABLE II

Distribution of Potassium and Sodium Thiocyanates between Aqueous Solutions and Tributyl Phosphate

Column II shows the initial aqueous alkali thiocyanate concentration; Column III the equilibrium aqueous thiocyanate concentration; Column IV the final organic phase thiocyanate concentration; and Column V the equilibrium organic phase sodium concentration. Potassium thiocyanate is used except where sodium is indicated. No acid was added to these solutions.

I No. of Expts.	II SCN_i (VF)	III SCN_a (VF)	IV $SCN_o \times 10^3$ (VF)	V $Na(I)_o \times 10^3$ (VF)	VI $SCN_o/SCN_a \times 10^2$
4	0.100_0	0.106	1.69 ±.03		1.59
4	0.148_8	0.158	3.03 ±.03		1.92
4	0.199_0	0.211	4.64 ±.02		2.20
4	0.298_0	0.309	8.84 ±.06		2.86
4	0.997	0.993	71.1 ±.7		7.16
4	0.595	0.592_2	43.2 ±.1	42.0 ±2.2	7.3
4	0.952	0.900	109.2 ±.8	111.2 ±2.8	12.2

sodium concentration in the organic phase was also determined and found to be essentially the same as the thiocyanate. In this case, the aqueous thiocyanate concentration at equilibrium was determined experimentally and agreed within 1% with the calculated value.

Discussion

pH Measurements. - Experiments indicated that the amount of thiocyanate extracted depended on the pH of the aqueous solution, thus suggesting that HSCN was entering the tributyl phosphate phase. It was therefore necessary to determine the pH of the aqueous solutions before and after equilibration with the tributyl phosphate. This was done by means of a glass electrode pH meter for three representative systems.

Twenty-five ml. of 1.01 VF KSCN, initially at a pH of 6.9, were equilibrated with 25 ml. of tributyl phosphate. The pH of the aqueous phase at equilibrium was 6.7. This change is so slight as to be unimportant.

A solution of 24 ml. of 0.992 VF NaSCN and 1 ml. of 1 VF $HClO_4$ having a pH of 1.9 was equilibrated with 25 ml. of tributyl phosphate. The pH of the aqueous solution at equilibrium was 4.0. This change indicates that a considerable amount of hydrogen ion is taken into the organic phase. No attempt was made to equilibrate a $HClO_4$ solution with tributyl phosphate, so it is not known if any $HClO_4$ was extracted as such.

A solution which was 0.0560 VF in $Fe(NO_3)_3$, 0.152 VF in KSCN and 0.01 VF in $HClO_4$ had a pH of 2.2. Twenty-five ml. of this solution were equilibrated with 25 ml. of tributyl phosphate. The pH of the aqueous solution at equilibrium was 2.3. In this case, the amount of thiocyanate extracted independently of the iron was probably small, thereby accounting for the slight change in pH. The measured change could easily be due to a change in ionic strength.

The Distribution of Ferric Thiocyanate. - The second set of experiments shown in Table I was made with an initial thiocyanate to iron ratio in the aqueous phase of 2.7 to 1. The adjusted ratio (Column VIII) in the organic phase at equilibrium was found to be 2.93 to 1. The difference between this and 3 to 1 is just a little greater than might be expected from experimental error. Similarly, the third set of experiments, performed with an initial thiocyanate to iron ratio in the aqueous phase of 5.4 to 1 gave an adjusted equilibrium ratio in the organic phase of 3.13 to 1. Since the calculated distribution of KSCN between the two phases was only approximate, one might expect that a refinement of the correction could cause the ratio in the organic phase to approach 3 to 1. Thus one might say that the predominant species extracted under these conditions is $[Fe(SCN)_3]_x$. The first set of experiments, performed with an initial thiocyanate to iron ratio in the aqueous phase of 1.35 to 1, gave an equilibrium ratio in the organic phase of 2.75. Here, the deviation from 3 to 1 is greater than can be accounted for by experimental error. Since the correction for the thiocyanate concentration in the organic phase was zero, any adjustment of this value would lower the ratio. No iron is extracted in the absence of thiocyanate. Thus, there appears to be a definite decrease in the ratio of thiocyanate to iron in the organic phase as the initial ratio in the aqueous phase decreases below 3 to 1.

The data of Melnick and co-workers (1) suggest the possibility that x in the formula, $(Fe(SCN)_3)_x$ might be greater than 1. They equilibrated 40 ml. portions of aqueous solutions which had SCN/Fe(III) ratios of 1, 3, 5, and 10 with 25 ml. portions of tributyl phosphate. In one set, the initial aqueous Fe(III) concentration was 0.0255 VF and in the second, 0.255 VF. When the ratios of thiocyanate to Fe(III) were 3 and above, the percentage of the iron which was extracted was essentially independent of the initial Fe(III) concentration. However, when the ratio was 1, about 28% of the iron was extracted from the solution having the smaller Fe(III) concentration while about 34% was extracted from that having the larger Fe(III) concentration. The difference is only 6% of the total iron. However, if equilibrium Fe(III) concentrations are calculated for the aqueous and tributyl phosphate phases, it can be seen that the distribution coefficient for the system having the lower iron concentration is 0.56 while that for the system having the higher iron concentration is 0.73. This is a change of 30% and is quite significant. One would not expect to observe a significant difference at the higher SCN/Fe(III) systems because most of the iron is extracted and a change in the distribution coefficient would not cause a large change in the total amount of iron extracted. A value of 2 for x might be expected because Fe(III) usually has a coordination number of 6, which might lead to the formation of the complex, $Fe(SCN)_6^{-3}$. This could then combine with Fe^{+++} to form $Fe\ Fe(SCN)_6$. It must be remembered, however, that ionic strength changes may have a profound effect on the extraction and might easily account for the observed differences.

The Distribution of Potassium and Sodium Thiocyanate. - Table II shows that the distribution coefficients of potassium and sodium thiocyanate vary with the aqueous alkali thiocyanate concentrations. That this could be an ionic strength effect is shown in Figures 1 and 2. Figure 1 is a plot of the equation

$$\log D' = \log D - C\mu^{1/2}/(1 + \mu^{1/2}) \qquad (1)$$

where $D' = C_o/C_a^2$, $D = C_o/C_a^2\ \gamma^2$, and $C = 2AZ^2$. C_o is the concentration of thiocyanate in the organic phase and C_a is that in the aqueous phase at equilibrium. Figure 2 is a plot of the equation

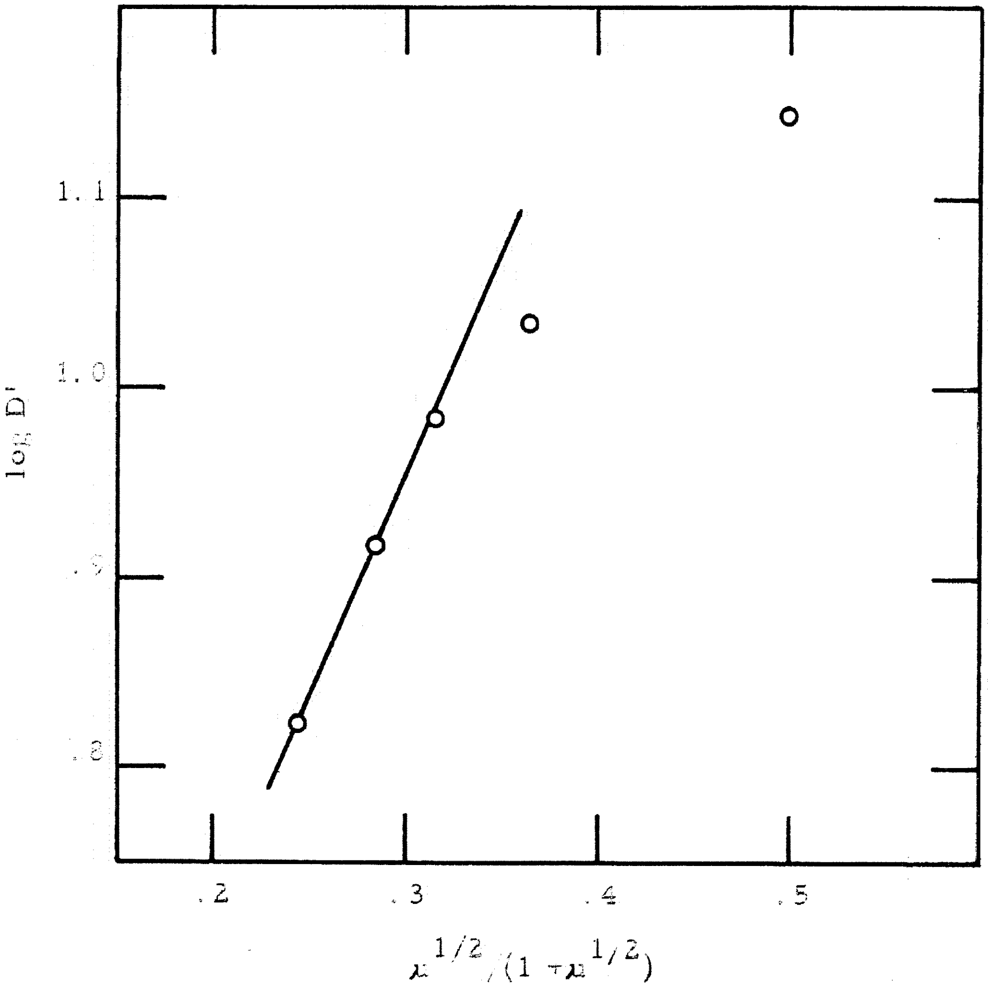

Figure 1. Calculated Effect of Ionic Strength on Measured Distribution Coefficient.

Calculations are based on equation (4).
$D' = C_o/C_a^2$

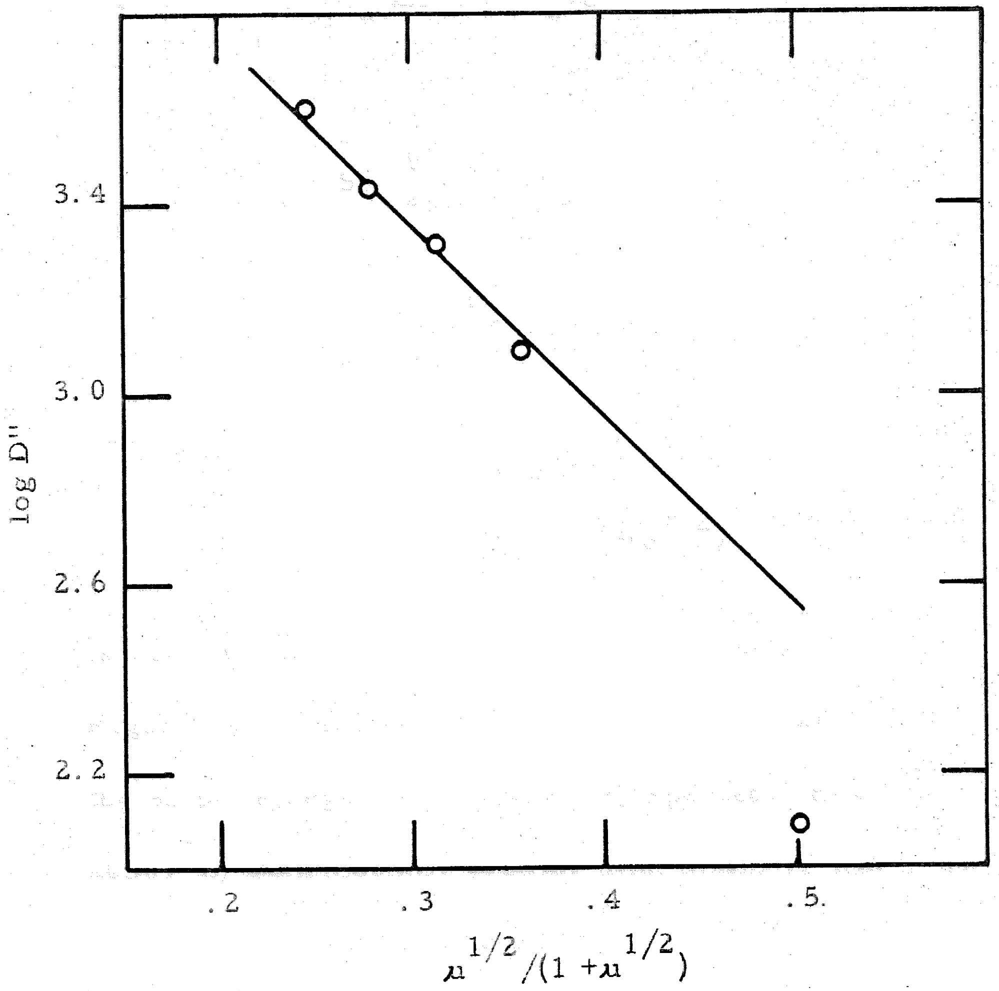

Figure 2. Calculated Effect of Ionic Strength on Measured Distribution Coefficient of KSCN

Calculations are based on equation (2). $D'' = C_o^2/C_a^2$

$$\log D'' = \log D - C u^{1/2}/(1 + u^{1/2}) \qquad (2)$$

where $D'' = C_o^2/C_a^2$ and $D = C_o^2/C_a^2 \quad {}^2$. These equations correspond to the reactions

$$K_a^+ + SCN_a^- = KSCN_o \qquad (3)$$

and $$K_a^+ + SCN_a^- = K_o^+ + SCN_o^- \qquad (4)$$

respectively. The modified Debye-Huckel expression,

$$-\log \quad = AZ^2 u^{1/2}/(1 + u^{1/2}) \qquad (5)$$

is applied only to the species in the aqueous phase. The plot in Figure 2 seems to fit the data better than that in Figure 1. Also, the slope is negative as would be expected. However, the slope is about -2, considerably greater than would be true if the simple explanation held. The data are insufficient to show which of the above possibilities is more nearly correct. It seems improbable that the KSCN would be completely ionized in the organic phase, or that the activity coefficients of whatever species are present in the organic phase would equal one. Some intermediate explanation seems more probable.

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PART II

STUDIES IN COULOMETRIC ANALYSIS

PART II. A. COULOMETRIC TITRATION OF BROMATE

Use of Copper (II) as Intermediate

During the investigation of a coulometric determination of ammonia, the necessity arose to determine accurately microgram quantities of bromate. If equation (1) can be made to proceed quantitatively to the right, the problem reduces to one of determining bromine.

$$6\ H^+ + BrO_3^- + 8\ Br^- = 3\ Br_3^- + 3\ H_2O \qquad (1)$$

Buck and Swift (1) determined aniline by generating an excess of bromine and back titrating the excess with electrolytically generated cuprous copper. Such a method has the advantage that no extra standard solution must be added to the system, thus minimizing the danger of loss. This procedure should be applicable to the determination of bromate.

Experimental

Reagents. - All chemicals were reagent grade. Solutions other than that of bromate were made by dissolving in distilled water amounts of the salts weighed with such accuracy as was required. Acid solutions were made by diluting commercially available concentrated acids. No attempt was made to purify the distilled water.

Potassium bromate (Baker and Adams C. P.) was heated for seven hours at 140° C. A 1.5 gram portion was accurately weighed, dissolved in water in a 500 ml. volumetric flask and the flask filled to the mark. The concentration of the stock solution was checked by titration according to the method described by Kolthoff and Sandell (2). The concentration determined by titration agreed within 0.1 percent with that calculated from the weight of salt taken; therefore, all further stock solutions were made by weight. A 10 ml. portion of the stock solution was pipetted into a 1000 ml. volumetric flask and diluted with distilled water to give a solution of the desired concentration. This procedure was used to make each of the samples used in the confirmatory titrations described later.

Apparatus. - All volumetric flasks were calibrated at 20° C. Pipettes were calibrated for delivery at 20° C.

The titration apparatus was similar to that described by Meier, Myers, and Swift (3) as modified by Ramsey, Farrington, and Swift (4). New equipment was constructed which had the following changes: The current regulating vacuum tubes, type 1C5, were replaced by type 6AU6 because the latter have more stable operating characteristics and give more dependable service. The 1-1/2 volt dry cell which supplied the filament voltage for the vacuum tubes was replaced by a 6 volt storage battery, Willard Signal Corps Battery BB-207/U and the 1-1/2 volt dry cell which supplied the indicator potential was replaced by a 2 volt storage cell, Willard

Signal Corps Battery BB-54-A. The batteries have the advantage of greater current capacity and, hence, greater stability. They have transparent plastic cases and are equipped with hydrometer pellets which indicate the state of charge at any time. When the apparatus was operated continuously for about nine hours each day, the 6 volt battery was put on a "trickle" charge at 0.6 amp. over night, thus maintaining it at full charge at all times.

The rubber stopper which served as a cap for the titration cell during operation was equipped with a short piece of glass tubing flared at the top to allow addition of solutions to the cell without exposing the electrodes to the air.

The indicator electrodes were made of 2 cm. by 2.5 cm. pieces of sheet platinum.

A Leeds and Northrop box type reflecting galvanometer, shunted with a rheostat to provide variable sensitivity, was used for current readings near the endpoint.

The generating current was determined by measuring the voltage drop across a Leeds and Northrop standard mercury resistor (99.99_8 absolute ohms) through which the current was passed. This current corresponded to $4.078_2 \times 10^{-8}$ equivalent per second at the medium rate and to $1.004_5 \times 10^{-7}$ equivalent per second at the high rate.

The voltage applied across the two indicator electrodes was measured with a Gray Instrument Company "Queen" potentiometer. In the future, this voltage will be designated the "indicator potential".

The acid solution in the isolated electrode compartment was kept identical with that in the cell.

Selection of "Indicator Potential". - Farrington, Meier, and Swift (5) found that the optimum applied "indicator potential" for the determination of the minimum indicator current in their copper-bromine system was 60 mv. Fluctuations of "indicator potential" should then have a minimal effect on the indicator current. On the other hand, Buck and Swift (1) used an "indicator potential" of 200 mv. for a similar system. However, the bromide concentrations used in the experiments reported here are considerably higher than those used by Buck and Swift and caused higher minimum currents. In order to avoid high minimum currents, a low "indicator potential" is desirable. Experiments showed that the indicator current was no longer a linear function of concentration after four or five seconds of generation when the "indicator potential" was as low as 90 mv. Further experiments indicated that linearity was maintained over the desired range when the "indicator potential" was greater than 120 mv. Most experiments were performed with an "indicator potential" of 150 mv.

Effect of Bromide and Cupric Copper Concentrations. -

Early in the work, there was evidence that the rate of the reaction

$$2\ CuBr_2^- + Br_3^- \longrightarrow 2\ Cu^{++} + 7\ Br^- \qquad (2)$$

is dependent on the concentrations of bromide and of cupric copper. A series of experiments was performed in which the concentrations of bromide and cupric copper were varied. The systems were 0.6 VF in H_2SO_4 and the "indicator potential" was 200 mv. Bromine was generated at 10 ma. for 60 seconds causing an indicator current of such magnitude that the microammeter was off scale. Cuprous copper was then generated at the same rate for a time equivalent to the bromine which had been formed. The results are compiled in Table I.

It is not possible to tell from these experiments whether the observed rate effect is dependent on the ratio of the concentrations of bromide and cupric copper or on the bromide concentration alone. However, essentially minimum concentrations of both were determined which was the primary practical problem in this case. It was noted that, while the reaction rate in solutions containing 0.01 VF $CuSO_4$ and 0.6 VF NaBr was sufficiently high, the efficiency with which cuprous copper was generated was apparently low, since the current minimum was not reached until 75 seconds of generation.

Loss of Bromine and Cuprous Copper. - Some loss of bromine and oxidation of cuprous copper might reasonably be expected,

TABLE I

Effect of Concentrations of Sodium Bromide and Cupric Copper on Reaction Rate

Bromine was generated at 10 ma. for 60 seconds causing an indicator current of such magnitude that the microammeter reading was off-scale. Cuprous copper was then generated at the same rate for a time equivalent to the amount of bromine which had been formed, i.e., 60 seconds. The time which elapsed after the generation of cuprous copper was begun until the meter reading was on-scale gave an indication of the rate of reaction between bromine and cuprous copper. Column III shows the approximate time from the beginning of Cu(I) generation until the meter reading was on-scale.

I NaBr (VF)	II $CuSO_4$ (VF)	III Action of Microammeter
0.2	0.2	On-scale reading at 65 sec.
0.2	0.04	On-scale reading at 5 min.
0.04	0.2	No on-scale reading at 10 min.
0.4	0.02	On-scale reading at 55 sec.
1.0	0.02	On-scale reading at 45 sec.
0.6	0.01	On-scale reading before all of the Br_2 was reduced, but current efficiency low.

since the concentration of bromine is relatively high initially and since no effort was made to exclude air which might oxidize the cuprous copper. Such losses would affect the accuracy of the determination of bromate.

The solutions used were 1 VF in NaBr, 0.02 VF in $CuSO_4$, and 1.2 VF in $HClO_4$. A small quantity of bromine was generated so that an indicator current was obtained which was on the linear portion of the current-time curve. The exact current was recorded. Bromine was then generated until an additional 10^{-5} equivalent was present in the solution, whereupon cuprous copper was generated until the initial indicator current was re-established. It was found that, under these conditions, the apparent loss of bromine amounted to 0.3 to 0.4 percent of the total. The true loss may have been somewhat larger because of oxidation of cuprous copper by oxygen during the titration.

When the above procedure was reversed by first generating cuprous copper and then titrating with bromine, the apparent loss of cuprous copper was about 1 percent of the total. Further experiments showed that this loss could be decreased by repeating the procedure several times on the same solution; this suggests that oxidizing materials were being slowly removed by the cuprous copper. Such a method of purification would hardly be feasible in practice, because the procedure is time-consuming.

The apparent bromine loss was quite constant for a given quantity of bromine initially in the solution. The loss, of course, was somewhat dependent on the length of time that bromine was present in the solution, but the variation for different titration times was not significant. This fact led to the development of the titration correction method described in the procedure.

Procedure.

1. Pre-treatment. The indicator electrodes were "pre-treated" before use whenever they had been out of operation for one hour or more. The 40 mm. by 80 mm. weighing bottle which served as a titration cell contained 10 ml. of 5 VF NaBr, 1 ml. of 1 VF $CuSO_4$, 5 ml. of 3 VF $HClO_4$, and 35 ml. of water. The cell was mounted and bromine generated at the high rate for about 100 seconds. The polarity of the generator electrodes was reversed and cuprous copper was generated until the indicator current decreased to about 25 μa. The cell was removed, the electrodes rinsed with distilled water, the cell mounted again, and the whole procedure repeated until the indicator electrodes had a constant sensitivity, i. e., the slopes of two consecutive current-time curves were the same. Two or three repetitions were generally sufficient.

2. Titration Correction. The current-time curve passes through a broad minimum in the region of the equivalence point of a titration of bromine with cuprous copper. Thus, it is not possible

to use the equivalence point for a titration endpoint. Titration to an arbitrarily selected indicator current on the linear portion of the curve is inaccurate because bromine is lost during the titration and because the sensitivity of the electrodes is not always the same in two different titrations. To correct for these errors, a small amount of bromine is generated to establish a reference current and a titration correction is made by generating a known additional amount of bromine and then generating an equivalent amount of cuprous copper so that an endpoint current is obtained. In practice, the reference current must be established before addition of the bromate sample, thus necessitating an additional correction for dilution.

If errors are to be kept as low as 0.2 to 0.3 µg., titration correction runs must be made before and after each titration. The electrode sensitivity usually decreases slowly with the number of runs made, but becomes fairly constant after 15 or 20 runs. The average of the correction constants determined before and after a titration was found to be quite accurate. If errors up to 1 µg. can be tolerated, a series of titration correction runs may be made to establish a correction constant which may then be used for all subsequent titrations. The titration correction is run as follows:

The titration cell contained 10.0 ml. of 5 VF NaBr, 1.0 ml. of 1 VF $CuSO_4$, 5.0 ml. of 3 VF $HClO_4$, and 25.0 ml. of water.

The cell was mounted and the "indicator potential" set at 150 mv. Bromine was generated for about 30 seconds, the polarity of the generator electrodes was reversed and cuprous copper was generated until the indicator current decreased to about 40 μa. This process eliminated any reductants in the solution. When the indicator current remained stable for a period of 60 seconds, the exact value was recorded. A stable current is defined as one which does not vary more than 0.2 to 0.3 μa. during the specified period.

Since the reaction between bromine and cuprous copper is only moderately rapid, the generation of cuprous copper should be stopped before the current reading has decreased to 40 μa. The current decreases fairly rapidly for a few seconds after generation has stopped, then more slowly. More cuprous copper or bromine may be generated in order to obtain the desired indicator current.

The cell was left in position and 10.5 ml. of water were added. An amount of bromine was generated which was equivalent to the amount of bromate to be titrated within 10 percent; the exact time of generation was recorded. Cuprous copper was generated until the indicator current decreased to about 40 μa. When the current was stable for 30 seconds, the exact value was recorded along with the time of generation of cuprous copper. Generation was continued in 1.0 second intervals until an amount of cuprous copper had been generated which was slightly in excess of the bromine previously generated. The current and time were recorded at each interval after the current was stable for 30 seconds. The cell was then removed, the electrodes rinsed and the acid in the isolated compartment changed.

3. Titration. The first part of the titration is described in the third paragraph of Section 2 above.

The cell was left in position and 10 ml. of bromate solution were pipetted into the cell. The inlet tube was washed with 0.5 ml. of water. Cuprous copper was generated until the indicator current was about 40 μa. Generation was continued in 1.0 second intervals until the indicator current was less than that calculated for the endpoint. The current and time were recorded as previously described.

4. Endpoint Calculation. The endpoint current for a titration was calculated as illustrated by the following example.

Figure 1 shows plots of indicator current against generation time in the vicinity of the endpoint. Figure 1a applies to a titration correction run and Figure 1b to a titration. In Figure 1a, i_o is the value of the indicator current recorded before dilution (Section 2, par. 3), Line I is the best straight line drawn through the plotted points in the vicinity of the endpoint, and t_{eq} is the known time required to generate an amount of cuprous copper equivalent to the bromine previously generated. The corresponding indicator current is designated i_{eq}. The current, i_{eq}, which corresponds to

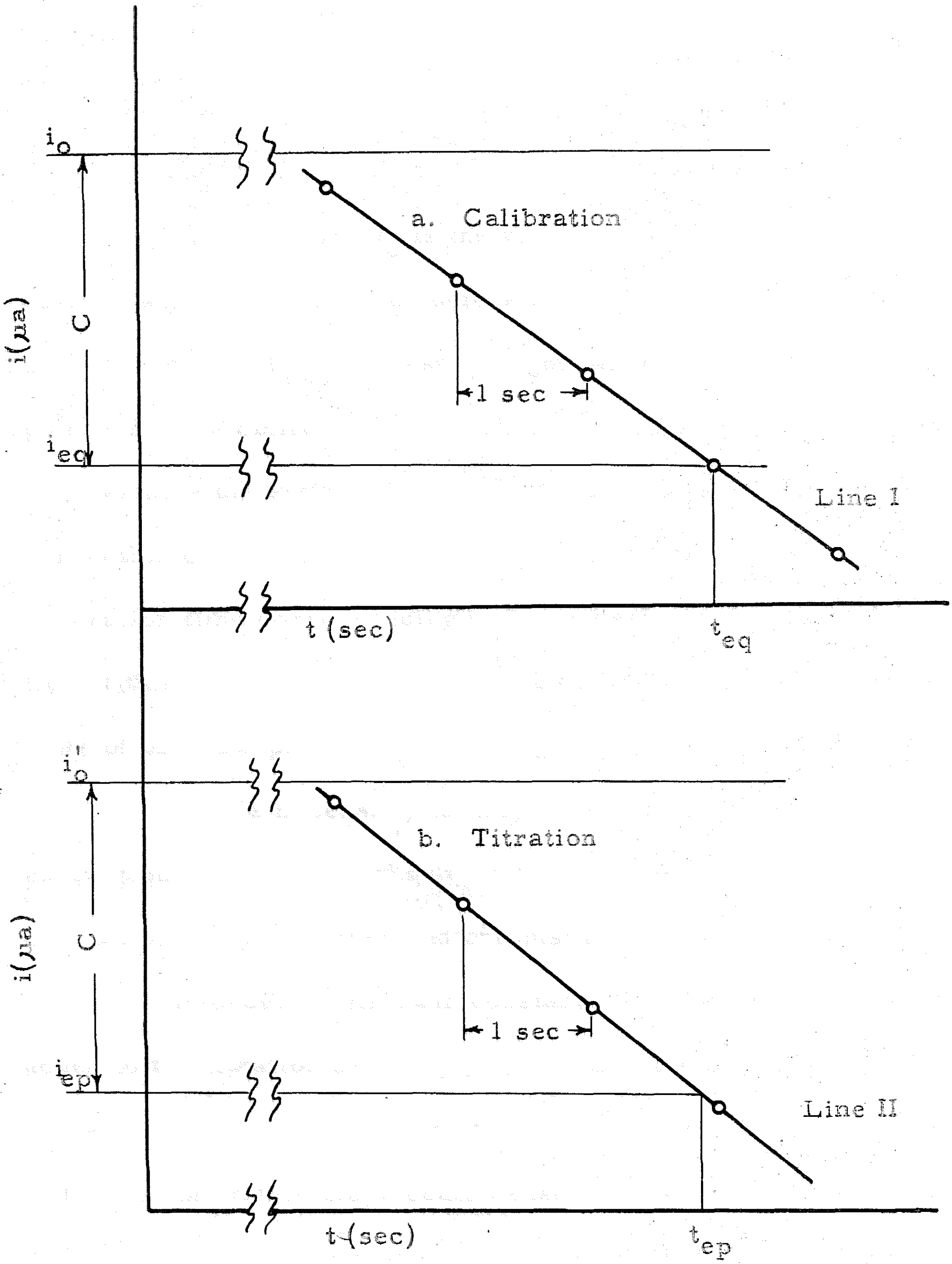

Figure 1. Diagram for Calculation of Titration Endpoint

the time, t_{eq}, is subtracted from the reference current, i_o, to give the correction constant, C, which will be used to calculate the endpoint current for the titration.

In Figure 1b, i'_o is the value of the reference indicator current which was recorded before the addition of the bromate sample and Line II is the best straight line drawn through the plotted points in the vicinity of the endpoint. The current, i_{ep}, to be used to determine the endpoint time is calculated by subtracting the correction constant, C, from the reference current, i'_o. The generation time corresponding to i_{ep} is designated t_{ep}. Multiplication of this time by the generation rate yields the number of equivalents of bromate present in the sample.

If it is necessary to keep errors to 0.3 μg. or less, the correction constant, C, should be the average of that from a titration correction run just before and one just after the titration.

In order to maintain constant volume, all solutions were added to the titration cell by pipet, because the slope of the indicator current-time curve depends on the concentration of bromine present and variation in this slope could cause errors in the determination.

It was found that some of the solution from the cell diffused into the isolated electrode compartment if the acid in the compartment was not changed after one or two runs. When the concentration of bromide in the compartment became sufficiently great, bromine was formed during the time cuprous copper was being generated in the cell. Near the endpoint, diffusion of bromine from the isolated compartment caused the indicator current to drift and led to erratic titration results. This problem might be eliminated if a silver-silver chloride electrode were used in the isolated compartment. Any bromide which diffused into the compartment would then be precipitated as silver bromide.

Discussion and Results

Titration Correction. - The titration correction described above deserves some explanation. Most coulometric procedures which use the amperometric endpoint employ a blank in which the titrant is generated in the absence of the substance to be determined. A plot of current versus generation time is made and a straight line drawn through the points. The intercept of this line with the abscissa determines the correction in seconds to be applied to the actual titration time. Such a procedure would be unsatisfactory for the determination of bromate for several reasons. First, there is the effective loss of bromine previously discussed. Secondly, the high, broad minimum in the plot of current versus time would tend to decrease the accuracy of an extrapolation to the point of minimum current.

The loss of bromine during the titration seems to be quite reproducible for a given amount of bromine, so a correction should be possible. Buck and Swift (1) circumvented the second problem by titrating to an arbitrarily chosen current on the straight portion of the current-time curve. However, the bromide concentrations in their solutions were lower than those used here so that smaller minimum currents were obtained and their indicator electrodes received less drastic treatment, since the concentrations of bromine were kept small. When similar blanks were made under the conditions of the experiments described here, the times required to attain the arbitrarily selected current varied 0.3 to 0.4 seconds. Attempts made to adjust the current to its exact minimum before making the blank run were unsuccessful because this minimum is so broad as to make its lowest point very difficult to determine.

For the above reasons, the blank method was unsatisfactory. If some small amount of bromine were added to the solution before addition of the unknown, a small indicator current would flow. If the unknown were then added and the titration continued until the indicator current once again equaled the initial current, the effects of any impurities should be nullified, since only the excess bromine would be titrated while the impurities should affect only the bromine initially in the solution. However, when bromate is added to the solution in the cell, it immediately reacts with the bromide present as shown by equation (1). Therefore, it is necessary to measure the initial current before the addition of bromate. Addition of the bromate also dilutes the solution causing the current to decrease, since it is dependent on both the bromine and acid concentrations.

It is apparent that an additive correction constant should be dependent on the concentrations involved. That this dependence does not seriously affect the correction constant if sufficient care is exercised may be demonstrated.

Assume that the current flowing at any time is an additive function of the concentrations of bromine and acid. Thus

$$i = k_1[Br_2] + f[H^+] \qquad (2)$$

where i is the indicator current, k_1 is a proportionality factor for the diffusion controlled current, $[Br_2]$ represents the total bromine in the solution, and $f[H^+]$ is some function of the acid concentration. The difference in current, Δi, caused by dilution would be

$$\Delta i = k_1([Br_2]_2 - [Br_2]_1) + f[H^+]_2 - f[H^+]_1 \qquad (3)$$

The total current difference, ΔI, as determined by the titration correction, includes that due to effective bromine loss, δi.

$$\Delta I = k_1([Br_2]_2 - [Br_2]_1) + f[H^+]_2 - f[H^+]_1 - \delta i \quad (4)$$

The particular system under discussion is that previously described in the procedure. The initial current reading is taken when the volume of solution is 40 ml. The solution is diluted to 50 ml. before the titration begins. Therefore

$$[Br_2]_2 = 4/5\,[Br_2]_1$$

$$[H^+]_2 = 4/5\,[H^+]_1$$

and $$\Delta I = -k_1/5\,[Br_2]_1 - 1/5\,f\,[H^+]_1 - \delta i \qquad (5)$$

Suppose the amount of bromine initially generated varied ten percent, such that

$$[Br_2]'_1 = 1.1\,[Br_2]_1$$

Then $$(\Delta I)' = -1.1/5\,k_1[Br_2]_1 - 1/5\,f\,[H^+]_1 - \delta i \qquad (6)$$

and $$\Delta(\Delta I) = \Delta I - (\Delta I)' = 1/50\,k_1\,[Br_2]_1 \qquad (7)$$

or $$\Delta(\Delta I)/\Delta I = -1/10\,k_1\,[Br_2]_1/(k_1[Br_2]_1 + f[H^+]_1 + 5\,\delta i \qquad (8)$$

Thus, the relative error in the correction factor would be less than ten percent. In this particular system, the dilution effect alone decreases the indicator current about 10 µa., so that the error would amount to less than 1 µa. or probably less than 0.2 seconds of generation time, since the electrode sensitivity is 4 µa. per second. It is preferable to duplicate the initial bromine concentrations as nearly as possible in both calibrations and titrations. This is not difficult in practice.

It is possible to calculate a correction factor from the data from the titration correction runs. The endpoint current, i_{ep}, can be calculated by multiplying the reference current by this factor. Endpoint currents calculated with the correction factor and with the additive constant were identical. However, the additive correction constant is easier to use and is recommended.

Effect of Acid Concentration. - A practical upper limit to the acid concentration of the titration solution is set by its effect on the indicator current. Although the acid does not appear to affect the slope of the current-time curve, i.e., the indicator electrode sensitivity, it does affect the magnitude of the current minimum thus displacing the indicator current up or down with the acid concentration. Experiments were performed with solutions 1 VF in sodium bromide, 0.02 VF in copper sulfate and varying acid concentrations. The indicator potential was set at 200 mv. The results are shown in Table II. The reason for this phenomenon is not known. It is necessary to keep the acid concentration sufficiently low that the range of the microammeter will permit current readings that are on the linear portion of the current-time curve.

Perchloric acid was used instead of sulfuric acid,

TABLE II

Effect of Acid on Indicator Current Minimum

Acid	Concentration (VF)	i_m(ua)
H_2SO_4	0.6	17
	1.8	22
HCl	1.2	27
$HClO_4$	1.2	24
	2.4	43

because titrations made in the former gave better results. It may be that the higher activity of perchloric acid causes a more complete reaction between bromide and bromate.

As has been pointed out, it is desirable to keep the acid concentration as low as possible consistent with obtaining completeness of the reaction between bromide and bromate. Titrations were made according to the described procedure except that acid concentrations were varied. The results are shown in Table III. The data show that the titration results are independent of acid concentration in the range shown. When the acid concentration was less than 0.15 VF, the reaction between bromate and bromide was so slow that cuprous copper was in excess of the bromine present long before an equivalent amount had been generated. An acid concentration of 0.3 VF was chosen for the procedure.

Amount of Bromine Generated for Calibration. - Since the purpose of the calibration procedure is to correct for the apparent loss of bromine during the titration, the amount of bromine formed during the calibration should be close to that formed by the bromide-bromate reaction. It is therefore desirable to know how nearly equal these quantities must be in order that the calibration be valid. Experiments were performed using the standard procedure except that the amounts of bromine generated for calibration were varied. The samples contained 238.8 micrograms of bromate which is

TABLE III

Effect of Acid Concentration on the Determination of Bromate

Number of Detns	$HClO_4$ (VF)	Bromate Taken	(μg) Found	Error (μg)	(%)
3	1.2	238.7	238.4 ±0.2	-0.3	-0.1
5	0.6	238.7	238.6 ±0.6	-0.1	0.0
2	0.6	238.9	238.4 ±0.0	-0.5	-0.2
4	0.3	238.9	239.0 ±0.3	0.1	0.1
4	0.15	238.8	238.8 ±0.3	0.0	0.0
2		238.7	238.6 ±0.3	-0.1	0.0

equivalent to slightly more than 110 seconds of generation at the high rate. The amounts of bromine generated are indicated by the generation times. The results are shown in Table IV. Errors of less than 0.3 μg. were observed when the bromine was generated for 90 to 120 seconds during calibration. In order to be safe, the time of generation of bromine for calibration should agree with the time of titration within ten percent.

Indicator Electrode Stability. - The "pre-treatment" of the indicator electrodes described in the procedure proved to be a satisfactory method for rapidly stabilizing the electrodes after they had been allowed to stand one hour or more. Other workers have stabilized electrodes by "flushing", i.e., the indicator electrodes were connected to the generator anode, thereby making all three electrodes generator anodes and then bromine was formed for a few seconds. The theory was that sensitivity was destroyed by contamination of the electrode surfaces and that generation of a very active oxidizing agent on the surfaces would clean them. However, "flushing" seemed to destroy the sensitivity of the electrodes in the system described here, for the sensitivity steadily decreased under such treatment and rapidly reached a value which seriously decreased the accuracy of the titrations. No such drift occurred when the electrodes were not "flushed" between runs. When the electrodes were not used over a period of an hour or more, the sensitivity increased somewhat,

TABLE IV

Effect of Amount of Bromine Generated for Calibration

Titration time was 110 seconds

Number of Detns	Blank Time (sec)	Bromate (µg) Taken	Bromate (µg) Found	Error (µg)	Error (%)
5	70	238.8	238.0 ±0.6	-0.8	-0.4
4	90	238.8	238.8 ±0.1	0.0	0.0
3	120	238.9	239.2 ±0.0	+0.3	+0.1
4	130	238.8	239.5 ±0.7	+0.7	+0.3

and the electrodes became unstable. Two or three runs were necessary before they were once again sufficiently stable for use. The "pre-treatment" described in the procedure actually simulates a number of runs thus allowing a relatively rapid stabilization before actual calibrations and titrations are begun.

Confirmatory Titrations. - The results of a number of determinations performed as described in the procedure are shown in Table V. The generation rate was $1.004_5 \times 10^{-7}$ equivalents per second except during the last set of titrations when it was decreased to $4.078_2 \times 10^{-8}$ equivalents per second in order to obtain reasonable accuracy. The accuracy of the indicator current-time plot near the endpoint was assured by increasing the sensitivity of the Leeds and Northrop galvanometer to 2-1/2 divisions per microampere.

The accuracy of the method compares favorably with the amperometric method described by Kolthoff and Lingane (6). They report errors of about 0.3 percent for solutions 10^{-4} N. The average error with the coulometric method for comparable concentrations is 0.1 percent with a standard deviation of 0.2 percent for five samples. The relative error for the small concentration of bromate is high, the average being 0.9 percent. However, the absolute error is about 0.2 microgram, a value comparable with the absolute errors found in all of the titrations.

TABLE V

Confirmatory Titrations

Number of Detns	Bromate (μg) Taken	Bromate (μg) Found	Error (μg)	Error (%)
2	238.8	238.8 ±0.1	0.0	0.0
4	238.9	238.8 ±0.2	-0.1	0.0
4	186.8	186.7 ±0.3	-0.1	0.0
6	152.8	152.9 ±0.3	+0.1	+0.1
5*	18.7_0	18.5_3 $\pm0.1_2$	-0.1_7	-0.9

*Medium rate of generation used for this group only.

High generation rate used for all other determinations.

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PART II. B. COULOMETRIC TITRATION OF AMMONIA WITH HYPOBROMITE

Willard and Cake (1) and Kolthoff and Stenger (2) have developed methods for the determination of ammonia by oxidation with hypobromite according to the following equation:

$$2\ NH_3 + 3\ OBr^- = 3\ Br^- + N_2 + 3\ H_2O \qquad (1)$$

More recently, amperometric end-points have been described for titrations which are based on the same reaction (3), (4).

Bromine is known to disproportionate in basic solutions (5) according to the equation:

$$Br_2 + 2\ OH^- = BrO^- + Br^- + H_2O \qquad (2)$$

Thus it seemed that a coulometric determination of ammonia might be developed which utilized the electrolytic generation of bromine and was based on the reactions represented by equations (1) and (2).

Experimental

Reagents. - All solutions were prepared from reagent grade chemicals. Water was distilled from alkaline $KMnO_4$ in order to remove most of the reducing materials normally found in the tap distilled water. The special water was prepared in lots of about 2 liters each. Buffer solutions were prepared by dissolving 4.8 g. of

$Na_2B_4O_7$ 10 H_2O in 500 ml. of water to give solutions which were 0.025 VF in $Na_2B_4O_7$. The pH was adjusted to the desired value by adding NaOH pellets or concentrated $HClO_4$ as required.

Standard solutions of NH_4Cl, from 0.033 VF to 0.074 VF, were prepared by dissolving accurately weighed quantities of dried salt (Baker Analyzed Reagent) in specially distilled water in a volumetric flask. Aliquots of these standard solutions were accurately diluted to give concentrations ranging from 8.34×10^{-5} VF to 1.34×10^{-3} VF.

Bromine solutions were prepared by adding 5 g. of NaBr and 3 ml. of saturated bromine water to 1 liter of distilled water. These solutions were standardized coulometrically as described in the preceding section.

Apparatus. - The coulometric equipment used was described in the previous section. The generation rate was $1.004_5 \times 10^{-7}$ equivalents per second; the "indicator potential" was 150 mv. This value was selected in order that the titration might be carried out by generating an excess of bromine which would then be back titrated with cuprous copper; the procedure would be similar to that described in the preceding section. The back titration method was not used; therefore 150 mv. may not be the optimum value for the "indicator potential". The isolated electrode compartment contained 0.3 VF $HClO_4$.

A Leeds and Northrop box type reflecting galvanometer, shunted with a rheostat to provide variable sensitivity, was used for current readings near the endpoint.

All pH measurements were made with a Beckman Model F pH meter, standardized against Beckman pH 7 standard buffer solution.

Generator Current Efficiency. - In order to evaluate the feasibility of the proposed method, it was necessary to demonstrate that bromine could be generated with 100% current efficiency in alkaline solutions.

The blank solutions contained 25.0 ml. of water, 15.0 ml. of buffer (pH = 9.3), 10.0 ml. of 5 VF NaBr, 2.0 ml. of 9 VF $HClO_4$, and 1.0 ml. of 1 VF $CuSO_4$. The acid concentration was 0.3 VF. Blanks were run by generating bromine in 1.0 second intervals and recording the stable indicator current after each generation. The indicator current was considered to be stable when it did not vary more than 0.2 to 0.3 μa. in 30 seconds. A straight line was passed through the plotted points and some arbitrary current value was selected as the endpoint current. The time corresponding to this current was designated as the blank correction time.

A solution was prepared which contained 25.0 ml. of water, 15.0 ml. of buffer (pH = 9.3) and 10.0 ml. of 5 VF NaBr and which had a final pH of 8.8. In all cases, the pH of the titration solution before acidification was 0.3 to 0.5 units less than that of the buffer. This is not unreasonable, because the ionic strength of the buffer was about 0.05 VM while that of the titration solution was about 1 VM. Bromine was generated for 30.0 seconds, whereupon 2.0 ml. of 9 VF $HClO_4$ and 1.0 ml. of $CuSO_4$ were added, bringing the acid concentration to 0.3 VF. The polarity of the generator electrodes was reversed and cuprous copper was generated until the indicator current decreased to about 40 μa. The indicator current was recorded when it became stable. Generation of cuprous copper was continued in 1.0 second intervals until the indicator current had decreased below the arbitrary value selected for the endpoint. A straight line was drawn through the plotted points and the time corresponding to the endpoint current was taken as the titration time. The blank time subtracted from the titration time yielded the correct time from which the equivalents of cuprous copper generated could be calculated. In general, the number of equivalents was not calculated, but comparison was made by considering the anodic and cathodic generation times. In every case, it was found that less cuprous copper was generated than bromine. The apparent loss of bromine was equivalent to about 7 to 8 seconds of generation, and was reproducible to within 0.2 seconds.

Two sets of experiments were performed to attempt to determine if the error was due to low generation efficiency or if bromine was being lost in some manner.

Blank determinations were made as previously described. The titration solutions were prepared as follows: 15.0 ml. of water, 15.0 ml. of buffer solution, 10.0 ml. of 5 VF NaBr, and 10.0 ml. of standard bromine solution. The pH of the solution was 8.8. The solution was allowed to stand for about 30 seconds, then 2.0 ml. of 9 VF $HClO_4$ and 1.0 ml. of 1 VF $CuSO_4$ were added and the bromine was titrated as described previously. Again, losses were equivalent to about 7 seconds of generation. Similar experiments were performed in which bromine was added to the cell when the platinum electrodes were present to see if the electrodes had a catalytic effect; also various amounts of bromine were added to see if the effect was dependent on bromine concentration. In all cases, the loss was the same, suggesting that impurities in the solutions were being oxidized by hypobromite and that bromine could be generated in alkaline solution with 100% current efficiency. Since the losses were reproducible, a blank correction procedure seemed more feasible than purification of all materials used.

Procedure.

1. Blank Correction. The blank solution contained 25.0 ml. of water, 15.0 ml. of buffer solution (pH = 8.9), and

10.0 ml. of 5 VF NaBr. The pH of the solution was 8.5. Bromine was generated for 8 to 10 seconds and the indicator current allowed to stabilize. It was found that if the current was less than 10 µa., all of the reducing impurities were not removed. When the current stabilized at about 10 µa., 2.0 ml. of 9 VF $HClO_4$ were added, causing a rise in the indicator current to about 25 µa. The current was recorded and bromine was generated in 1.0 second intervals, the stable current being recorded at each interval. A straight line was drawn through the plotted points and the time corresponding to 30 µa. was taken as the blank correction time. Blank determinations were repeated until three consecutive determinations agreed within 0.2 second.

2. Titration. The titration solution contained 15.0 ml. of water, 15.0 ml. of buffer solution (pH = 8.9), 10.0 ml. of 5 VF NaBr, and 10.0 ml. of NH_4Cl solution. The NH_4Cl solution was added just before the cell was mounted so that losses through volatilization might be reduced. As bromine was generated, the indicator current usually rose to about 20 µa. and leveled off at about that value for most of the titration. Near the end of the titration, the current began to rise and the titration was stopped when the rate of rise was about 1 µa. in 5 seconds--usually 5 to 15 seconds before the endpoint. As the concentration of ammonia decreased during the titration, the rate of reaction decreased

allowing the observed rise in current near the endpoint. When generation was stopped, the reaction proceeded and the current decreased. The current was allowed to decrease until stable and, if lower than 10 μa., generation was continued in short intervals until the stable current was about 10 μa., 2.0 ml. of 9 VF $HClO_4$ were added and the generation of bromine was continued as described for the blank correction. The blank correction time was subtracted from the titration time to calculate the correct time, which was then used to calculate the number of equivalents of NH_4Cl which were present in the solution.

Discussion and Results

Effect of pH. - One might reasonably expect that some ammonia would be lost from an alkaline solution. On the other hand, the disproportionation of bromine and hypobromite would decrease with decreasing pH (5). Therefore, it was desirable to find the optimum pH for the titration.

The blank and titration procedures used were as described above, with the exception that the pH of the system was varied. The results of a series of experiments in which the pH varied from 8.2 to 10.0 are shown in Table I. It can be seen that 8.5 and 8.2 are the best pH values of those tried. However, a system at a pH of 8.2 is not convenient, because the current stabilization in the alkaline solution was excessively slow. Kolthoff and co-workers (3)

TABLE I

Effect of pH on the Determination of Ammonia

Number of Detns	pH	Ammonia (µg)		Error	
		Taken	Found	(µg)	(%)
3	10.0	56.81	57.22 ±0.14	-1.1	-1.9
7	8.8	227.4	226.2 ±0.3	-1.2	-0.6
5		56.81	56.62 ±0.12	-0.19	-0.4
5	8.5	227.5	227.3 ±0.2	-0.2	-0.1
6		56.81	56.98 ±0.12	+0.17	+0.3
1	8.2	227.4	227.7	+0.3	+0.1
3		56.81	57.17 ±0.20	+0.36	+0.6

found that a pH of 8.5 was most satisfactory for their procedure.

It is interesting to note that the observed errors shift from negative to positive as the pH of the system decreases. While the reason for this is not known, it would seem that two competing errors tend to cancel giving the best results at pH = 8.5. As was pointed out, one might reasonably expect some loss of ammonia from an alkaline solution. Clusius and Rechnitz (6) and Riley and co-workers (7) have shown that the oxidation of ammonia by hypobromite may form nitrous oxide as represented by the following equation:

$$2\,NH_3^+ + 4\,OBr^- = N_2O + 4\,Br^- + 3\,H_2O \qquad (3)$$

Thus, at the lower pH values, the losses of ammonia through volatilization may be less than the positive errors caused by the formation of nitrous oxide, the compensation resulting in small errors for the determination.

Other buffer systems were considered for the control of the pH during the titration. The carbonate - bicarbonate system is impractical, because the formation of CO_2 on acidification of the solution would tend to sweep bromine from the solution. Phosphate buffers were not used because the reagents available apparently contained reducing impurities which would have caused the blank corrections to be unreasonably large.

Effect of Excess Hypobromite. - The fact that fairly large negative errors were found when 227 μg. of ammonia were titrated at pH = 8.8 suggested the possibility of adding the sample after some quantity of bromine had been generated, thus allowing less time for the ammonia to escape the solution. A series of experiments was performed in which bromine was generated for certain fixed times after which the sample was added and the titration continued. The results are shown in Table II. It can be seen that the positive error increased as the initial excess of bromine (or hypobromite) was increased. This may be due to an increased formation of nitrous oxide when the hypobromite is in excess. Preliminary experiments indicated that bromate does not oxidize ammonia to any significant extent.

Endpoint Method. - Two possible methods for determining the endpoint were considered. An endpoint in the alkaline solution would have eliminated the necessity for adding acid to the solution with the resulting high indicator current. However, it was found that the indicator current in alkaline solution was not dependable and did not give a reliable indication of the amount of bromine which had been generated.

Another reason for determining the endpoint in acid solution is that it allows the possibility of back titration with cuprous copper if the endpoint is badly overrun. However, if the back

TABLE II

Effect of Excess Hypobromite on Determination of Ammonia

The ammonia sample was added to the solution after a quantity of bromine had been generated. The equivalents of bromine initially generated are shown in the second column; the total generated for the titration are shown in the third column. The pH of each solution was 8.8.

No. of Detns	Bromine Generated (equiv. x 10^7) Initial	Total	Ammonia (µg.) Taken	Found	Error (µg.)
1	230	401	227.4	228.8	+1.4
4	200	"	"	228.0 ±0.2	+0.6
3	100	"	"	227.5 ±0.2	+0.1
7	0	"	"	226.2 ±0.3	-1.2

titration method is used, care must be exercised to use exactly the same technique for the blank as for the titration. A few runs were made in which the blank correction was determined as described above and the titration was accomplished by a back titration method. In those cases, the errors were as large as +0.6 μg. as compared with errors of 0.2 μg. when the endpoint was determined as described in the procedure. The slope of the indicator current-time curve was greater when the bromine concentration was decreased by generating cuprous copper than was the slope when the bromine concentration was increased by generating bromine. The reason for this difference is not known.. However, it was sufficient to cause observed differences in the accuracy of the titration.

The concentration of NaBr was the same as that used in the determination of bromate and was selected because of the possible desirability of back titrating excess bromine with cuprous copper. No experiments were made in which this concentration was varied. However, Buck and Swift (8) used a bromide concentration of 0.1 VF for the determination of aniline, so a comparable concentration may be practical for the determination of ammonia.

For similar reasons, the acid concentration was made approximately 0.3 VF. It has been shown previously that this is the optimum acid concentration for the complete reduction of bromate by bromide. Since there may possibly be some bromate formed in the alkaline solution during the titration, it was desirable to make the acid concentration sufficiently high to insure the reduction of any bromate present.

The procedure such as that used by Laitinen (4) in which a single indicator electrode is employed has the advantage that the endpoint can be determined in alkaline solution. However, if small quantities of bromate are formed, positive errors would result, since the bromate does not oxidize ammonia under the conditions of the titration. The single indicator electrode could be used in acid solutions except that hydrogen might be formed at the applied potentials required.

Effect of Other Metal Ions. - If the above procedure could be utilized to eliminate the distillation process in the micro- Kjeldahl determination of nitrogen, it could greatly increase the ease with which that procedure is carried out. It is therefore necessary to know if the materials commonly employed as catalysts in the Kjeldahl digestion would interfere with the coulometric determination of ammonia.

The procedure used was that described above except that amounts of $CuSO_4$, $Hg(NO_3)_2$, and selenium were added which were typical of the amounts which would be found in a micro-Kjeldahl determination (9), (10). Selenium metal was dissolved in hot concentrated H_2SO_4 and then slowly diluted with water and the solution neutralized to a pH of 4. On dilution, some selenium re-precipitated. A portion of the mixture was filtered and experiments were performed using small quantities of the mixture and of the filtrate.

The results with $CuSO_4$ and $Hg(NO_3)_2$ are shown in Table III. It can be seen that neither $CuSO_4$ nor $Hg(NO_3)_2$ affect the accuracy of the ammonia determination.

The presence of selenium would affect the titration. No actual titration was made when selenium compounds were present, because it was found that the selenium species reduced hypobromite as rapidly as it was formed during the blank runs. Although the species of selenium involved is not known, experiments made with selenious acid showed the selenite reduced hypobromite as rapidly as does the selenium species from the sulfuric acid solution. It is evident that if selenium is to be used as a catalyst, some way must be found to remove it from the system before the ammonia determination is begun. Some experiments were performed in which metallic lead was added to the solution containing selenium in hopes that the selenium would be replaced. Apparently, most of the selenium was removed from the solution in this way, but four days were required to complete the replacement.

Confirmatory Titrations. - Table IV shows the results of a series of confirmatory titrations made by the procedure described

TABLE III

Effect of Metals on the Determination of Ammonia

The concentration of $CuSO_4$ was 6×10^{-4} VF; that of $Hg(NO_3)_2$ was 2×10^{-4} VF.

Added Metal	Ammonia Taken		(μg) Found	Error (μg)
Cu(II)	227.5		227.8	+0.3
			227.2	-0.3
		Ave	227.5	0.0
	56.81		57.13	+0.3
			57.06	+0.2
			56.82	0.0
		Ave	57.00	+0.2
Hg(II)	227.5		227.1	-0.4
	56.81		56.64	-0.2
			56.93	+0.1
			56.66	-0.2
		Ave	56.74	-0.1

TABLE IV

Confirmatory Titrations

Number of Detns	Ammonia (μg) Taken	Ammonia (μg) Found	Error (μg)	Error (%)
5	227.5	227.3 ±0.2	-0.2	-0.1
6	125.8	125.9 ±0.2	+0.1	+0.1
6	56.81	56.98 ±0.12	+0.17	+0.3
3	14.20	14.20 ±0.22	0.00	0.0

above. In all cases, the average error was less than 0.2 μg., while the standard deviation was about the same. Thus, one might expect a maximum error of 0.4 μg. in a determination involving quantities of ammonia between 14 μg. and 230 μg. Both the relative and absolute accuracies are somewhat better than those reported by Laitinen (4).

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PROPOSITIONS

1. Moore studied the rate of reduction of uranium (VI) by Sn (II) in HCl-salt solutions maintained at an ionic strength of seven, but was unable to interpret the effect of acid concentration on the rate. It is suggested that the constancy of the ionic strength does not assure constancy of the acid activity coefficient when the variations in acid concentration are large, and that the determination of the acid activity in acid-salt solutions of comparable ionic strength would permit proper interpretation of the observed effects. (R. L. Moore, J. Am. Chem. Soc. 77, 1504 (1955).).

2. The solubility of various inorganic salts in glacial acetic acid has been studied. (R. K. Birdwhistle and E. Griswold, J. Am. Chem. Soc. 77, 873 (1955).). Although the authors assume that the salts are completely unionized, the data indicate common ion and salt effects similar to those found in aqueous solutions. It is proposed that these effects may be interpreted as ionic activity phenomena.

3. It is proposed that the formation constant for $FeSO_4^+$ be determined at various temperatures to permit the calculation of ΔH for the complex formation. Careful control of temperature may also serve to eliminate the large fluctuations in the formation

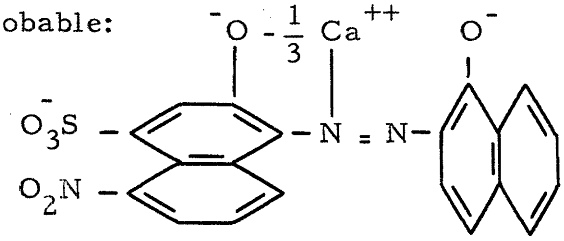
constant which were observed by Whiteker and Davidson. (R. A. Whiteker and N. Davidson, J. Am. Chem. Soc. 75, 3081 (1953).).

4. The solubility of arsenic trioxide is known to decrease with increasing acid concentration in most acid solutions. (A. Seidell, "Solubility of Inorganic and Metal Compounds", Vol. I, 3d. ed., p. 108, New York, D. van Nostrand Company, Inc., 1940). It is proposed that the lowered solubility is partly caused by the reversal of the equation:

$$\mathrm{As_2O_3 + 3\ H_2O = 2\ H_3AsO_3}$$

as the ionic strength of water is decreased and partly caused by a "salting out" of $\mathrm{H_3AsO_3}$. It is further proposed that the latter effect predominates.

5. Data recently published suggest that calcium (II) forms a bidentate chelate with Eriochrome Black T. (A. Young and T. R. Sweet, Anal. Chem. 27, 418 (1955).). Of the several possible structures, the following is proposed as being the most probable:



6. The spectrophotometric method by which the second ionization constants of certain disubstituted derivatives of barbituric acid were obtained is questioned. (T. C. Butler, J. M. Ruth, and G. F. Tucker, Jr., J. Am. Chem. Soc. 77, 1486 (1955).). It is suggested that the procedure and method of analysis described by Rosenblatt would be more applicable. (D. H. Rosenblatt, J. Phys. Chem. 58, 40 (1954).).

7. The amperometric endpoint system employed in coulometry is dependent on the current flow between dual platinum electrodes when two oxidation states of the coulometric intermediate are present in the solution. Some substances, e.g., Ce(III), which might be useful intermediates cause little or no current under these conditions. It is proposed that small quantities of appropriate materials, e.g., Tl(I), be added to titration systems of this sort to act as indicators. The material should satisfy the requirement for the formation of an indicator current and the half-cell potential for the conversion from one state to the other should be such that no significant transformation occurs until the titration endpoint has been reached.

8. On the basis of measurements of the distribution of perrhenate salts between aqueous solutions and nitromethane, Friedman and Haugen have suggested that perrhenate salts are completely

ionized in the organic phase. (H. L. Friedman and G. R. Haugen, J. Am. Chem. Soc. 76, 2060 (1954).). I suggest that the data given are insufficient to permit such a statement. I further suggest that the data can be interpreted as indicating no ionization in the organic phase.

9. It is proposed that microgram quantities of certain metal ions, e.g., Cu(II), Hg(II), Sb(III), may be determined by adding a known amount of organic complexing or chelating agent, e.g., Thionalide, in excess of the metal ion and titrating the excess with electrolytically generated silver ion. The amperometric endpoint may be used. (R. L. Kowalkowski, J. H. Kennedy, and P. S. Farrington, Anal. Chem. 26, 626 (1954).).

10. Gutowsky and co-workers were able to distinguish between various phosphorous compounds containing oxygen, chlorine, and fluorine by nuclear magnetic resonance studies. It is proposed that CCl_4 solutions containing As(III) extracted from HCl solutions be studied using nuclear magnetic resonance methods in an attempt to identify the arsenic (III) chloride species present. (H. S. Gutowsky, D. W. McCall, and C. P. Schlicter, J. Chem. Phys. 21, 279 (1953).).

11. It is my belief that students should not enter Caltech directly from high school.