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THE PREPARATION OF PER ACIDS AND THEIR SALTS

by

Robert Roy Coons

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

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INTRODUCTION

There are a number of acids to which the prefix "per" has been applied, for example, perchloric, periodic and permanganic. In these cases the prefix "per" denotes only that they contain relatively more oxygen than the chloric, the iodic and the manganic acids. Price[1] defines true per acids "as those which are either formed by the action of hydrogen peroxide on ordinary acids, or else give rise to hydrogen peroxide on treatment with dilute sulphuric acid; with concentrated sulphuric acid many of them evolve ozonized oxygen, thus behaving similarly to the metallic peroxides and to hydrogen peroxide itself. In some cases the free acids are not known, but the same definition will apply to the formation or decomposition of their salts".

In the following table[1] the elements forming per acids are underscored:

III		IV		V		VI	
$\underline{\text{B}}$		$\underline{\text{C}}$		$\underline{\text{N}}$		O	
	Al		Si		$\underline{\text{P}}$		$\underline{\text{S}}$
Sc		$\underline{\text{Ti}}$		$\underline{\text{V}}$		$\underline{\text{Cr}}$	
	Ga		Ge		As		$\underline{\text{Se}}$
Y		$\underline{\text{Zr}}$		$\underline{\text{Cb}}$		$\underline{\text{Mo}}$	
	In		$\underline{\text{Sn}}$		Sb		Te
$\underline{\text{La}}$(?)		Ce		-		-	
	-		-		-		-
Yb		-		$\underline{\text{Ta}}$		$\underline{\text{W}}$	
	Tl		Pb		Bi		-
-		Th		-		$\underline{\text{U}}$	

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[1] Price, Per-Acids and Their Salts, p. 1-8, (1912).

Leaving out of consideration the elements in the first two rows, short periods, of the periodic table, it will be observed that the formation of per acids is confined to groups IV, V and VI, and more particularly, with the exception of tin and selenium to family A of these groups. With hydrogen peroxide as one of the reacting substances, under proper conditions, per acids and per acid salts may be formed from the following elements: titanium[2], zirconium[3], vanadium[4], columbium[5], tantalum[6], chromium[7], molybdenum[8], tungsten[9], and uranium[10]. Per acids and their salts may be formed, not only by the use of hydrogen peroxide or its simple derivatives, such as sodium peroxide or barium peroxide, but also by electrolytic oxidation or anodic condensation[11].

Respecting the elements of family B, the chart shows only two which form per acids and per salts, namely tin and selenium. Tanatar[12] obtained a perstannic acid by the action of 30% hydrogen peroxide on stannic acid which had been precipitated from a solution of stannic chloride by sodium carbon-

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[2] Lévy, Compt. rend., 108, 294 (1889).
[3] Pissarjewsky, Zeitsch. anorg. Chem., 25, 378 (1900).
[4] Pissarjewsky, Zeitsch. physik. Chem., 43, 173 (1903).
[5] Balke and Smith, J.Am.Chem.Soc., 30, 1637 (1908).
[6] Melikoff and Pissarjewsky, Zeitsch.anorg.Chem., 20,340(1889).
[7] Wiede, Ber., 30, 2178 (1897); 31, 516 (1898).
[8] Pechard, Compt. rend., 114, 1481 (1892).
[9] Pechard, ibid., 112, 1060 (1891).
[10] Fairley, Jour. Chem. Soc., 31, 125 (1877).
[11] Caven and Lander, Systematic Inorganic Chemistry, p.305(1922).
[12] Tanatar, Ber., 38, 1184 (1905).

ate. The perstannic acid precipitated as a white amorphous powder. Spring[13] used barium peroxide in making perstannate. Dennis and Brown[14] reported an impure perselenate, analogous to potassium persulphate, prepared by electrolysis, in a divided cell, of a saturated solution of potassium selenate containing a little free selenic acid. A few years later Dennis and Koller[15] electrolyzed solutions of pure potassium selenate and pure selenic acid under conditions most favorable to the formation of potassium persulphate and persulphuric acid, but in no case was there any indication of the formation of either a perselenate or a perselenic acid. By employing solutions of different concentrations and varying the current density, Bauer[16] was unable to obtain a perselenate. Hanuš and Kallauner[17], who do not claim to have prepared a perbismuthate, obtained a product which gave less than 1% active oxygen.

Pinerua Alvarez[18] claims to have prepared sodium perarsenate by dissolving disodium arsenate in water and alcohol, cooling to 0°, and then adding sodium peroxide. No analyses were made, however. Aschkenasi[19] reported perarsenates prepared by means of barium peroxide and hydrogen peroxide, the

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[13] Spring, Bull. Soc. Chim., (3), 1, 180 (1889).
[14] Dennis and Brown, J. Am. Chem. Soc., 23, 358 (1901).
[15] Dennis and Koller, ibid., 41, 949 (1919).
[16] Bauer, Unpublished Thesis, Library, Iowa State College, Ames, Iowa, (1927).
[17] Hanuš and Kallauner, Zeitsch. anorg. Chem., 70, 232 (1911).
[18] Alvarez, Chem. News, 94, 269,(1906).
[19] Aschkenasi, German Patent 296,796 (1914).

solid being obtained by evaporation of the solutions under reduced pressure and gentle heating.

THE PURPOSE OF THE INVESTIGATION

From a perspective view of the picture presented in the introduction, the contrast in the number of elements of families A and B that form per acids and per salts, came the suggestion for the present study. Tin is the only element of family B that distinctly forms the per salts. The purpose of this investigation is to use several methods with a typical member of family B in preparing per acids and per salts. Arsenic was selected, since, from its position in the periodic table, it would probably be the most likely to form per acids and the corresponding salts.

HYDROGEN PEROXIDE METHOD

Disodium Arsenate

Experimental

Materials

H_2O_2, 30%, Merck and Co.

$Na_2HAsO_4.7H_2O$, C.P., Baker and Adamson.

$Na_2S_2O_3.5H_2O$, C.P., Wilkins-Anderson.

Iodine, Resulbimed, Baker and Adamson.

H_2SO_4, C.P., Grasselli Chemical Co.

HCl, C.P., Grasselli Chemical Co.

NH_4OH, C.P., Grasselli Chemical Co.

KI, C.P., Baker and Adamson.

$NaHCO_3$, C.P., Baker and Adamson.

Starch, Soluble, General Chemical Co.

P_2O_5, Anhydrous, Merck and Co.

Procedure and Observations

About 10 g. of disodium arsenate were added to 50 cc. of a 5% solution of hydrogen peroxide at room temperature. No precipitate formed. The solution was evaporated over concentrated sulphuric acid under reduced pressure and a white residue was left.

A second preparation was made by treating a solution of disodium arsenate saturated at 0° with 50 cc. of 30% hydrogen peroxide. Before being mixed, the two solutions were cooled to 5° by means of salt and ice. No precipitate formed. The mixture was evaporated over concentrated sulphuric acid under reduced pressure and a white residue was left which was very hygroscopic. It was kept in a desiccator over phosphorus pentoxide.

Analysis of Products.

The Mohr method[20] was used in analyzing for the per cent of arsenic. To a weighed sample of the unknown, dissolved in 200 cc. of distilled water, were added 2-3 grams of solid potassium iodide and 20 cc. of dilute sulphuric acid (1:1). The resulting solution was evaporated to 75 cc. and the excess iodine removed with aqueous sodium thiosulphate. The solution was then diluted to 250 cc., made neutral to methyl orange indicator with ammonium hydroxide, a minimum amount of sulphuric acid added to make the solution slightly acid, and then an excess of sodium bicarbonate was added to make the solution neutral. The arsenic was titrated with standard iodine solution and starch used as an indicator. The first residue contained 23.72% arsenic.

This residue was analyzed by the Bunsen method[21] for the oxidizing equivalent. To a weighed sample in a carbon dioxide flask were added 20 cc. of concentrated hydrochloric

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[20] Scott, Standard Methods of Chemical Analysis, 1, p.36 (1927).
[21] Foulk, Notes on Quantitative Analysis, p. 181, (1930).

acid, the mixture heated, and the distillate passed into potassium iodide solution. The free iodine was titrated with standard thiosulphate solution. A 0.5 g. sample of the first residue was equivalent to 1.15 cc. of 0.10065 N. sodium thiosulphate solution.

A blank of disodium arsenate, which contained 27.25% arsenic, was analyzed by the Bunsen method. From these data 1 cc. of the 0.10065 N. thiosulphate solution was found to be equivalent to 0.17 g. of arsenic.

The residue of the second hydrogen peroxide preparation analyzed by the Mohr method showed 31.15% arsenic. One gram samples analyzed by the Bunsen method required 111.5 cc. of 0.0964 N. sodium thiosulphate solution.

Samples of disodium arsenate used as blanks for analysis by the Bunsen method gave 1 cc. of 0.0964 N. thiosulphate solution equivalent to 0.163 g. of arsenic.

Explanation and Interpretation of Results

Since 1 g. of the first hydrogen peroxide residue, containing 23.72% arsenic, requires 2.3 cc. of 0.10065 N. sodium thiosulphate solution, and 1 cc. of the thiosulphate is equivalent to 0.17 g. of arsenic, according to the blank, then 0.2372 g. of the element is equivalent to 1.4 cc. of the standard reagent. This value of 1.4 subtracted from 2.3 gives 0.9 cc. of thiosulphate solution, which is the equivalent of the active oxygen per gram -- i.e., 0.15%.

Since 1 cc. of 0.0964 N. sodium thiosulphate solution is equivalent to 0.163 g. of arsenic, as shown by analysis of disodium arsenate blank, then the 0.3115 g. of arsenic in a gram sample of the second hydrogen peroxide residue would be equivalent to 1.90 cc. of the thiosulphate solution. This value subtracted from 111.5, which represents the number of cubic centimeters of 0.0964 N. sodium thiosulphate required in analyzing 1 g. samples of the second hydrogen peroxide residue by the Bunsen method, gives 109.6 cc. of the standard reagent, which is the equivalent of the active oxygen -- i.e., 8.45%.

Similar experiments were performed by Petrenko[22]. By the interaction of hydrogen peroxide and sodium arsenate, probably the tertiary salt, he obtained a compound of the composition $Na_9As_3O_{17}.21H_2O$, which he regarded as a hydrate of sodium arsenate in which part of the water was replaced by hydrogen peroxide. He assigned the following formula: $3\ Na_3AsO_4.5H_2O_2.16H_2O$. Theoretically this product would give 7.4% active oxygen.

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[22] Petrenko, J. Russ. Phys. Chem. Soc., 34, 391-2, (1902). Original not seen. Abstracted in Jour. Chem. Soc., 82, Pt. 2, 499 (1902).

BARIUM PEROXIDE METHOD

Acid Solution

Experimental

Materials

$H_3AsO_4 \cdot 1/2\ H_2O$, C.P., Baker and Adamson.

As_2O_3, C.P., Merck and Co.

NaOH, Reagent, 95%, Baker and Adamson.

BaO_2, Technical, Anhydrous, Merck and Co.

For other reagents used see materials under hydrogen peroxide method.

Procedure and Observations

One hundred and forty grams of arsenic acid, dissolved in 200 cc. of distilled water, were treated with 40 g. of barium peroxide in the following manner: About 15 g. of the barium peroxide were placed in 50 cc. of distilled water in a flask. The arsenic acid solution and the barium peroxide were added alternately in small quantities to the flask, which did not rise above 10°. The mixture was shaken frequently for two hours and then placed in an automatic refrigerator over night. Addition of potassium iodide to a portion of the filtrate, which had been diluted with four or five volumes of water, showed the presence of active oxygen since appreciable quantities of free iodine were liberated immediately. The iodine was not titrated. The filtrate was evaporated over concentrated sulphuric acid under reduced pressure.

A second preparation was made from the arsenic acid. To an aqueous solution of 196 g. of arsenic pentoxide, cooled with ice and salt to 8°, 66 g. of barium peroxide were added. The cold mixture was stirred frequently for three hours, and most of the barium peroxide dissolved. Upon the addition of 96 g. of aqueous sodium hydroxide, added slowly to keep the temperature of the mixture low, a white precipitate of barium arsenate[23] was formed. After removal of the insoluble salt with suction the filtrate thus obtained was divided into two parts: The first was evaporated over concentrated sulphuric acid under reduced pressure; the second was evaporated on a steam plate.

Analysis of Products

The residues obtained from the arsenic acid preparations were analyzed by the Bunsen method for the oxidizing equivalents. No indications of active oxygen were shown. No further analyses were made.

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23. Aschkenasi, German Patent 299,300 (1914).

Sodium Arsenate

Experimental

Materials

For reagents used see materials under hydrogen peroxide method.

Procedure and Observations

To 100 cc. of disodium arsenate solution saturated at 0° was added an excess of barium peroxide. The mixture, kept at a temperature of 5-10° by means of salt and ice, was shaken every few minutes for two hours and then placed in an automatic refrigerator over night. The filtrate was evaporated over concentrated sulphuric acid under reduced pressure, and a white residue was left.

Analysis of Residue

The residue, which was analyzed by the Mohr method, showed 18.13% arsenic. One gram of the preparation analyzed by the Bunsen method required 4.17 cc. of 0.0964 N. sodium thiosulphate solution.

Explanation and Interpretation of the Results

Since 1 g. of the barium peroxide residue, which contains 18.13% arsenic, requires 4.17 cc. of 0.0964 N. sodium thiosulphate solution, and 1 cc. of the thiosulphate is equivalent to 0.163 g. of arsenic, as shown by analysis of the blank, then 0.1813 g. of arsenic is equivalent to 1.12 cc. of the standard thiosulphate reagent. This value subtracted from 4.17 gives 3.05 cc. of standard thiosulphate which is equivalent to 0.47% active oxygen in the residue.

ELECTROLYTIC METHOD

Disodium Arsenate

Experimental

Materials

As_2O_3, C.P., Baker and Adamson.

HNO_3, C.P., Grasselli Chemical Co.

For other reagents used see materials under hydrogen peroxide method.

Procedure and Observations

A solution of disodium arsenate saturated at 0° was made the anolyte inside a porous cup. Arsenic pentoxide, prepared by oxidation of arsenic trioxide with nitric acid and repeated evaporation on the sand bath, was dissolved in ten volumes of distilled water and made the catholyte around the porous cup. The apparatus[24] consisted of a porous cup placed inside a liter beaker. The cathode was a platinum wire surrounding the porous cup; the anode, formed of a platinum wire sealed in a glass tube with mercury connections with a surface area of 0.3 sq. cm., was placed inside the porous cup. An anodic current density of one ampere per sq. cm. was used for sixteen hours. The temperature was kept between 0° and 5°. A black deposit collected on the cathode, but no precipitate was

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[24] Elbs, Electrolytic Preparations, p. 35, (1903).

obtained at the anode.

A second solution of disodium arsenate saturated at 0° was electrolyzed for eight hours with an anodic current density of 0.7 amperes per sq. cm. During the electrolysis the temperature of the solution varied from 0° to 10°. The apparatus[25] consisted of an anode, the one used in the preceding experiment, surrounded by a glass tube to serve as a diaphragm. The cathode consisted of a ring of platinum wire placed outside the diaphragm. No precipitate was formed.

A third solution of disodium arsenate saturated at 0° was electrolyzed for twelve hours, the temperature ranging from 0° to 8°. The apparatus used was the same as that described in the first paragraph of page 19. An anodic current density of 1.5 amperes per sq. cm. was used. No precipitate collected at the anode.

Analysis of Products.

All three solutions, after electrolysis, were analyzed by the Bunsen and Mohr methods, the first two showing no evidence of active oxygen. Five cubic centimeters of the third solution gave by the Bunsen method an oxidizing equivalent of 1.75 cc. of 0.10065 N. sodium thiosulphate solution; and by the Mohr method an equivalent of 59.05 cc. of 0.0678 N. iodine solution.

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[25] Partington, A Textbook of Inorganic Chemistry, p.518,(1927).

Explanation of Results

A blank of disodium arsenate analyzed by the Bunsen method shows that 1 cc. of 0.10065 N. thiosulphate solution is equivalent to 0.17 gram of arsenic. The 59.05 cc. of iodine solution give 0.15 g. of arsenic which is equivalent to 0.9 cc. of the standard thiosulphate reagent. This value subtracted from the oxidizing equivalent of the sample obtained by the Bunsen method represents the amount of active oxygen, or 1.75 - 0.9 = 0.85 cc. of 0.10065 N. thiosulphate, which shows approximately 2% of the arsenic capable of setting free active oxygen.

Disodium Arsenate Plus Sodium Fluoride

Experimental

Materials

NaF, C.P., Baker and Adamson.

$Na_2HAsO_4.7H_2O$, Baker and Adamson.

For other reagents used see materials under hydrogen peroxide method.

Procedure and Observations

To 125 cc. of disodium arsenate, saturated at 0° was added 1 g. of sodium fluoride. This solution was electrolyzed for ten hours, at 0-12° by the use of an anodic current density of 0.7 to 1.8 amperes per sq. cm. There was formed a small amount of precipitate, which was readily soluble. (See reference 25 for the apparatus used.)

To 125 cc. of a second solution of disodium arsenate saturated at 0° were added 2.5 g. of sodium fluoride. During the electrolysis the temperature varied from 0° to 10°. The solution was kept cold by means of salt and ice. An anodic current density of two to three amperes per sq. cm. was used for sixteen hours. A white precipitate collected in the bottom of the tube. (See reference 25 for the apparatus used.)

Analysis of Products

The precipitate and the solutions, obtained from the electrolysis of disodium arsenate and sodium fluoride as described in the two preceding paragraphs, were analyzed by the Mohr method for the per cent of arsenic, and by the Bunsen method for the oxidizing equivalent. No active oxygen was indicated.

SODIUM PEROXIDE METHOD

Disodium Arsenate

Experimental

Materials

Na_2O_2, Reagent, C.P., Wilkins-Anderson.

C_2H_5OH, 95%, U. S. Industrial Alcohol Co.

P_2O_5, Anhydrous, Merck and Co.

$Na_2HAsO_4.7H_2O$, C.P., Baker and Adamson.

NaOH, 95%, Baker and Adamson.

$H_3AsO_4.1/2H_2O$, C.P., Baker and Adamson.

$KMnO_4$, Reagent, Merck and Co.

For other reagents used see materials under hydrogen peroxide method.

Procedure and Observations

To 25 g. of disodium arsenate, dissolved in 1500 g. of distilled water in a 4 liter round bottom flask, 1700 cc. of 95% ethyl alcohol were added. (See reference 18). Fifty grams of sodium peroxide were added to this mixture in small quantities and at intervals of five to ten minutes to prevent an appreciable increase in the temperature. The mixture was stirred with a motor for five hours in order to obtain a uniform product. By means of salt and snow the contents of the flask were kept at -10° throughout the procedure. About 500 cc. of absolute ethyl alcohol were added and the copious white precipitate was filtered out by means of suction. Since previous experiments had proved the instability of the moist preparation at ordinary temperatures, the room was cooled to 4° to retard the rate of decomposition as much as possible. The white precipitate, washed three or four times with absolute alcohol, was dried over phosphorus pentoxide under reduced pressure. This required from one to two weeks depending upon the frequency of renewing the anhydrous phosphorus pentoxide and of evacuating the desiccator. The pressure was reduced ordinarily to 2 cm. of mercury.

Analysis of the Precipitate

Analysis of the precipitate by the Bunsen method for the oxidizing equivalent, in terms of sodium peroxide, showed 23.24%. (See Table I.)

Analysis of the precipitate by the Mohr method for the per cent of arsenic gave 6.24%. (See Table I.)

The percentage of sodium peroxide, determined by titrating the sample in acid solution with standard potassium permanganate showed 22.84%. (See Table I.)

In analyzing for the per cent of sodium the following procedure was used: The arsenic was removed as the sulfide by adding hydrogen sulfide to the solution made strongly acid with hydrochloric acid. The resulting mixture, saturated with hydrogen sulfide, was heated in the pressure bottles in order to assure the precipitation of all the arsenic and to coagulate the sulfide. The filtrate was then evaporated to dryness three or four times on a steam plate, concentrated hydrochloric acid having been added each time. Sulphate ions were removed by adding aqueous barium chloride to the warm hydrochloric acid solution. After the sample was digested on the hot plate an hour or two, the solution was made alkaline with ammonium hydroxide and the excess barium removed with ammonium carbonate. The filtrate was evaporated to dryness in platinum dishes, the residue heated to 500° in the electric furnace, and the sodium chloride weighed. The sodium found equalled 21.30%. (See Table I.)

Samples of the precipitate, titrated with standard hydrochloric acid solution, phenolphthalein as indicator, showed 17.38% sodium. (See Table I.)

A summary of the analyses is given in the following table:

TABLE I

Analysis of Na_2O_2 Precipitate

Weight of Sample (Gram)	Bunsen Method Per Cent Na_2O_2	$KMnO_4$ Method Per Cent Na_2O_2	Mohr Method Per Cent Arsenic	Total Sodium Per Cent	Titration with HCl Per Cent Sodium
0.4922 0.5399 0.7160 0.4353	23.26 23.36 23.24 23.10 23.23				
0.6759 0.6251 0.7679		22.74 22.87 22.84 22.90			
0.8056 0.6055 0.7363			6.26 6.23 6.24 6.22		
0.4834 0.6945				21.25 21.30 21.34	
0.6199 0.7148 0.7541					17.48 17.16 17.38 17.53

Titration of Arsenic Acid with Sodium Hydroxide

In order to interpret the data of Table I on page 27, it is necessary to know the number of replaceable hydrogen atoms indicated by the phenolphthalein change in the titration with hydrochloric acid. This was determined by electrometric titration of 1.0848 g. of arsenic acid with standard sodium hydroxide solution. The ordinary electrometric apparatus with hydrogen electrode and calomel half cell was used. The phenolphthalein changed at the second break of the curve which is shown in Figure 1. This gave 54.39% arsenic.

Samples of the same arsenic acid analyzed by Levol[26] method showed 54.38% arsenic.

Explanation and Interpretation of Results

In titrating a basic solution of an arsenate with standard acid, phenolphthalein as indicator, the change of color occurs when one equivalent of the metal in the salt has been replaced by one equivalent of the hydrogen. This is shown in the curve, Figure 1. The 17.38% of sodium from titration of the unknown with standard hydrochloric acid solution gives the sodium as sodium peroxide, sodium hydroxide, and one equivalent of the metal in combination with the arsenic. The total sodium should equal that obtained by titration of the preparation with standard hydrochloric acid solution, phenolphthalein

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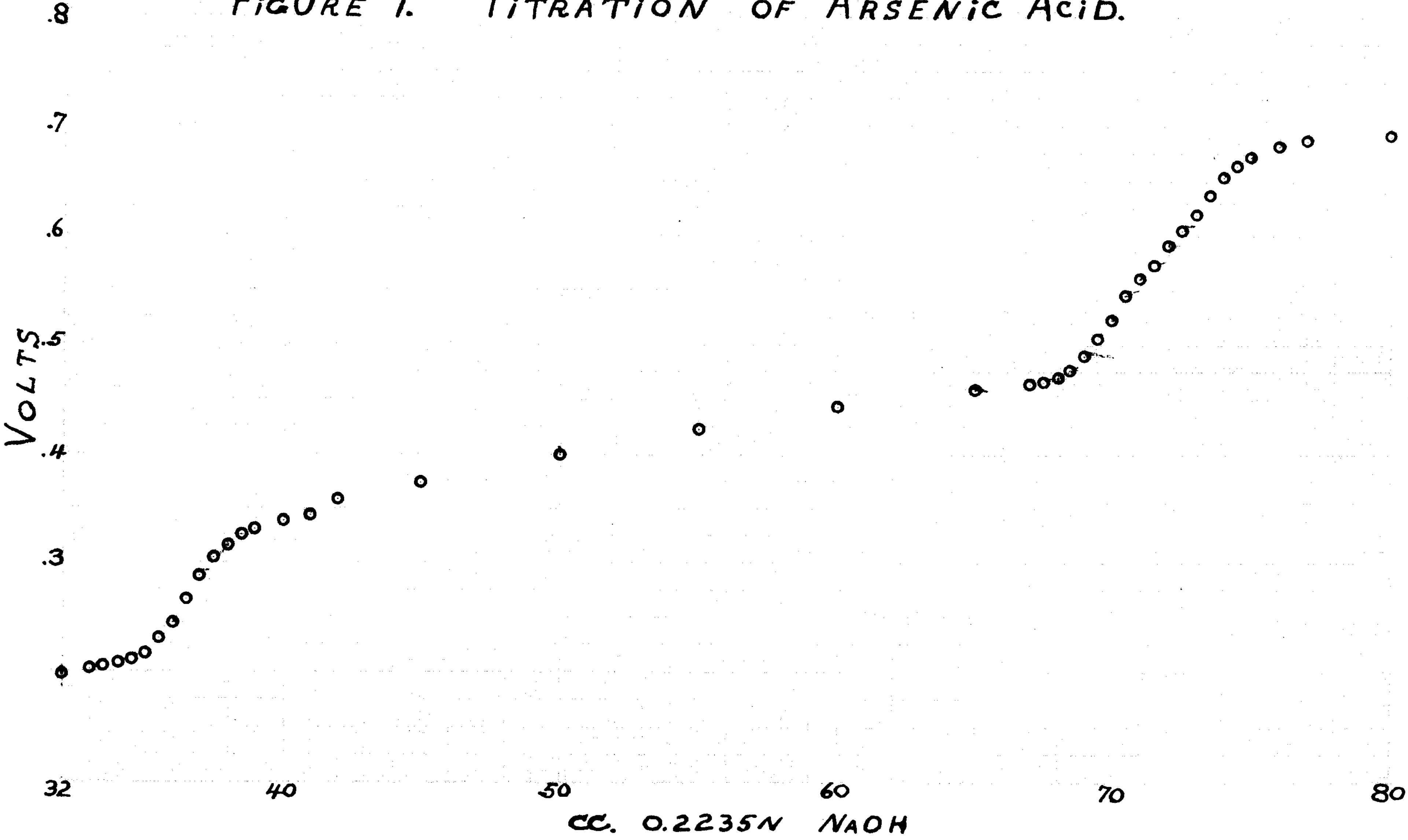
[26] Treadwell and Hall, Analytical Chemistry, 2, p.201,(1924).

FIGURE 1. TITRATION OF ARSENIC ACID.



as indicator, plus two hydrogen equivalents. The percentage of the metal, one equivalent, combined with 6.24% arsenic, is 1.915% sodium. Then 17.38% plus 3.83%, which is two sodium equivalents, gives 21.21% for the total sodium according to this conception. These results check reasonably well with those obtained in analyzing for the metal, 21.30%, as shown in Table I.

The difference between the amount of sodium peroxide by the Bunsen method and that found by the titration with standard potassium permanganate is due to the oxidizing equivalent given by the analysis of a blank containing the same quantity of arsenic. The checks should be better, however, since there is 0.25% variation.

If a perarsenate were present would this be shown in the potassium permanganate titration? Persulphates do not decolorize potassium permanganate[27] unless salts, such as manganese sulphate[28], or catalysts[29], such as platinum, are present. Percarbonates are determined by adding a known weight of the solid salt to a dilute solution of sulphuric acid, and titrating the hydrogen peroxide liberated with potassium permanganate[30]. In strongly acid solution the red perchromates

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[27] Friend, Jour. Chem. Soc., 85, 597 (1904); 87,738 (1905).

[28] Baeyer and Villiger, Ber., 33, 2488 (1900).
Price, Jour. Chem. Soc., 83, 543 (1903).

[29] Price, Ber., 35, 291 (1902).
Price and Friend, Jour. Chem. Soc., 85, 1526 (1904).

[30] Brown, J. Am. Chem. Soc., 27, 1222 (1905).

do not reduce permanganate; in alkaline solution the amount of permanganate entering into reaction increases with the alkalinity of the solution to a maximum of 5.5 equivalents[31]. Since some per salts react with permanganate and others do not, the reaction of permanganate on perarsenate, if present, would have to be determined by experiment. The analyses were made on the assumption that potassium permanganate does not react on the perarsenate. Since the data of Table I check on the basis that the preparation was a mixture of sodium peroxide, sodium hydroxide, trisodium arsenate, and some water of crystallization, it is reasonable to conclude that no perarsenate was present. From the data of Table I calculations show that the product was $2\ Na_3AsO_4.7Na_2O_2.2NaOH.75H_2O$.

The conclusion is similar to, but not identical with that of Rudenko[32] who maintains that the compound prepared by Alvarez and described by him as a perarsenate, $NaAsO_4$, was merely a mixture of the salt with hydrated sodium peroxide. His conclusion was confirmed by examining the compound by the method which Riesenfeld and Reinhold[33] employed to distinguish between percarbonates and carbonates with peroxides of crystallization. He assigns the formula Na_2HAsO_4. aq. and Na_2O_2.aq.

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[31] Riesenfeld, Ber., 41, 3941 (1908).

[32] Rudenko, J. Russ. Phys. Chem. Soc., 44, 1209 (1912). Original not seen. Abstracted in Chemical Abstracts 7, 738 (1913).

[33] Riesenfeld and Reinhold, Ber., 42, 4377 (1909).

What is the explanation for this lack of uniformity in the product obtained? The writer suggests that the variation in the composition of the compound as prepared by the method of Alvarez may be due to a number of causes, such as temperature differences, amount of alcohol used, the hydration of the arsenate originally employed, rate of adding the sodium peroxide, etc. The same individual trying to carry out the same procedure on two different occasions would probably not get identical products. Furthermore, the precipitate is unstable. The preparation, as shown by analyses from day to day, even when kept at 0° and over reasonably dry phosphorus pentoxide in a desiccator, decomposed gradually, the instability increasing with increase in moisture and temperature. With the decomposition of the product, the percentage of sodium peroxide decreases, and that of the sodium and arsenic increases.

THE FLUORINE METHOD

The Preparation of Fluorine

Experimental

Materials

KHF_2, Scherring-Kahlbaum.

K_2CO_3, Anhydrous, C.P., Mallinckrodt.

H_2F_2, 48%, J. T. Baker Chemical Co.

Procedure and Observations

The apparatus used in generating gaseous fluorine was similar to that employed by Jones[34]. The copper vessel C, four inches in diameter, served as cathode, and was wrapped with nichrome wire as heating coil. The wire was insulated from the cathode pot by two layers of asbestos paper. Several layers of asbestos paper were placed outside the heating element to prevent excessive loss of heat. The cathode pot contained a thermometer inside a copper well which was immersed in the electrolyte, and a copper vessel H to prevent the mixing of the hydrogen and the fluorine generated at the respective electrodes; through the top of vessel H passed a large copper wire lead threaded to a graphite rod A, which served as anode. The wire was insulated at K with mica and held in place with

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[34] Jones, Jour. Phys. Chem., 33, 801 (1929).

alundum cement. The bottom of the anodic diaphragm was covered with a copper sheet to prevent the cathodic hydrogen from entering from below. The diaphragm was pierced with several 1/4 inch holes near the bottom to allow free circulation of the electrolyte, and was suspended in the electrolyte in such a way that it touched neither the sides nor the bottom of the cathode pot.

A 1/4 inch copper tube leading from the anode compartment connected a copper U-tube by means of a copper flange. The U-tube, which was closed with copper plugs P, was made to hold sodium fluoride for removing the hydrogen fluoride gas passing over in the process of generating fluorine. This U-tube however, was used merely for connecting the apparatus, because the sodium fluoride pellets in previous experiments stopped the passage way for the fluorine. Vessel S was an ordinary wide-mouthed bottle of 400 cc. capacity, lined with ceresin, and served as a safety contrivance. This bottle, as well as the U-tube, was kept wrapped with cold towels, while the gas was being generated, in order to keep the fluorine from reacting with the ceresin. On one occasion, during the electrolysis of the fused potassium bifluoride, a small explosion and fire occurred in vessel S. The fluorine was passed into the 500 cc. copper vessel E, which contained the arsenate solution at 0°. An ammeter A, and water-cooled rheostat R were used in the 220-volt alternating-current heating circuit. A series of storage

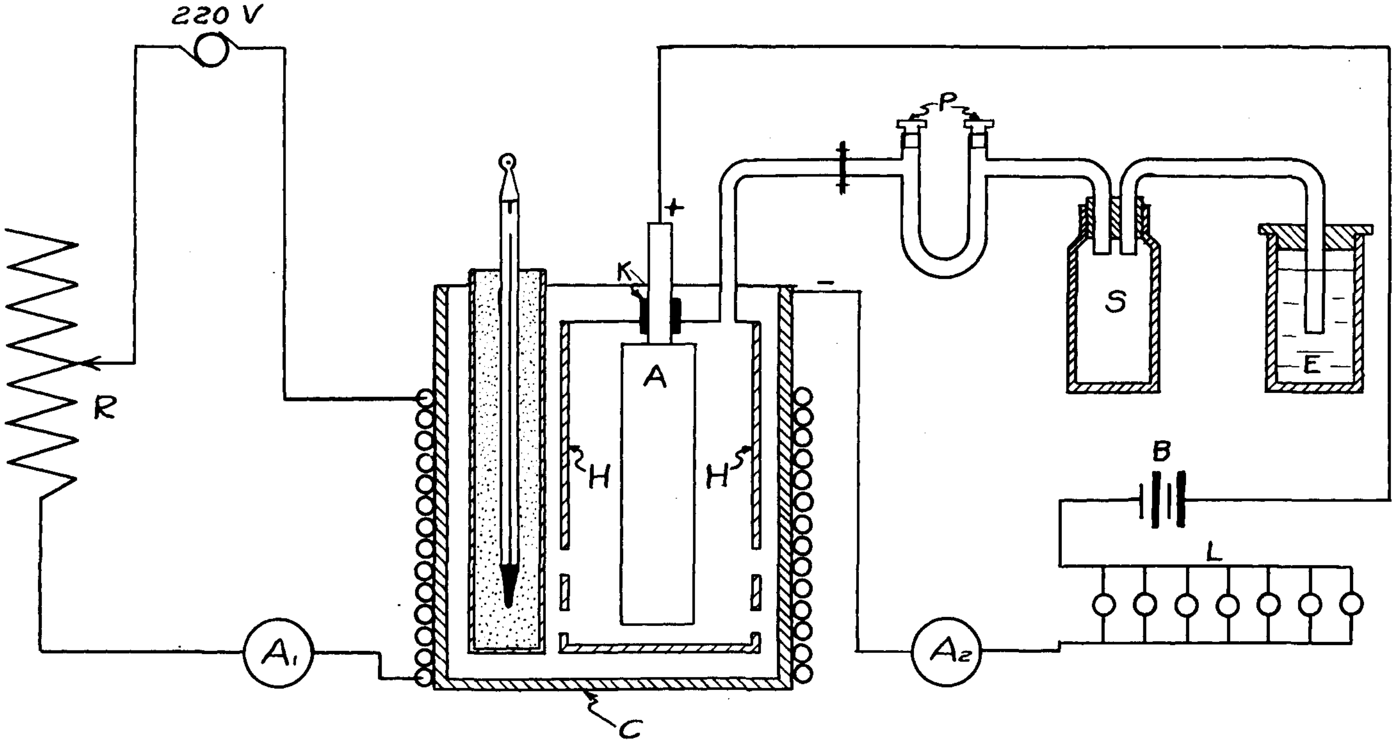

Fig 2.

APPARATUS
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GENERATING FLUORINE

batteries B, which produced an E. M. F. of 96 volts, were connected with an ammeter A, and a number of lamps L in parallel. A direct current of ten amperes could be obtained.

Attempts made to get gaseous fluorine by electrolysis of fused sodium bifluoride proved unsuccessful since the reagent decomposed before fusing. Two kilograms of Kahlbaum's potassium bifluoride were used in the preparation of the gas. Some potassium bifluoride was prepared by treating potassium carbonate with a sufficient quantity of 48% hydrofluoric acid to form the normal potassium fluoride and then adding an equal volume of the hydrofluoric acid of the same concentration as that originally used. The resulting mixture was evaporated on the steam plate and then heated to 240°[35] in the cathode pot C, Figure 2, by means of the alternating current. Experiments showed that the fused reagent, potassium bifluoride, had to be electrolyzed, because of the presence of water, one or two hours, six to eight amperes, before appreciable quantities of elementary fluorine could be detected in vessel E with potassium iodide paper. From two to five amperes were required in the fusion of the electrolyte, and six to nine amperes were used in the electrolysis of the bifluoride. The fluorine, evolved at the rate of approximately 250 cc. per ampere hour, had a rather sweet, sickening, and pungent odor.

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[35] Deming, Lecture on Preparation and Properties of Fluorine, Fort Des Moines Hotel, Des Moines, Iowa, April 18, (1931).

Acid Solution

Experimental

Materials

KBr, C.P., Wilkins-Anderson

$KMnO_4$, Reagent, C.P., Merck and Co.

$(NH_4)_2MoO_4$, C.P., Baker and Adamson.

NaOH, 95%, Baker and Adamson.

Procedure and Observations

A solution of disodium arsenate saturated at 0° was kept at that temperature by means of ice and salt in vessel E, Figure 2, and gaseous fluorine passed into it for three hours at the rate indicated under "The Preparation of Fluorine", page 33. An odor similar to ozone could be detected and potassium iodide paper immediately turned a distinct brown when held in the vapors above the arsenate solution. A small amount of a blue precipitate, probably a copper compound, was formed. Compressed air, washed with a sodium hydroxide solution of pyrogallic acid, was passed for three hours through the solution at 0° to remove most of the ozone, hydrogen peroxide, etc. After filtering with suction, the blue precipitate was dried over concentrated sulphuric acid under reduced pressure, and then over phosphorus pentoxide for three days at room temperature. The colorless filtrate was kept cold in an automatic refrigerator until analyzed.

Analysis of Products

Five cubic centimeters of the fluorine filtrate analyzed by the Mohr method required 26.15 cc. of 0.0986 N. iodine solution, which is equivalent to 0.0967 g. of arsenic.

Five cubic centimeters of the fluorine filtrate analyzed by the Bunsen method required 1.95 cc. of 0.0964 N. sodium thiosulphate solution.

In the analysis for ozone and hydrogen peroxide the method of Rothmund and Burgstaller[36] was used. Briefly the method is: To 0.01 N. acid solution at 0° a sufficient quantity of potassium bromide is added to give about 1% of the salt. More potassium iodide solution is added than corresponds to the ozone present. The iodine set free, which corresponds to the value of the ozone, is titrated with 0.01 N. sodium thiosulphate solution. Then 10 cc. of 0.5 N. potassium iodide solution, 1 cc. of 0.1 N. ammonium molybdate and 15 cc. of dilute sulphuric acid (1:5) are added and the iodine newly set free after the mixture stands for five minutes is titrated with standard sodium thiosulphate solution. This value gives the hydrogen peroxide. The fluorine filtrate contained no ozone, and 5 cc. required 1.40 cc. of 0.0964 N. thiosulphate solution.

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[36] Rothmund and Burgstaller, Sitz. Akad. Wiss., Wien., 122, Abt. IIb, Pt. 1, 75-86, (1913).

A sample of the dried precipitate weighing 0.2906 g., analyzed by the Bunsen method, was equivalent to 0.4 cc. of 0.0964 N. sodium thiosulphate solution.

Explanation of Results

Analysis of a disodium arsenate blank by the Bunsen method showed that 1 cc. of 0.0964 N. sodium thiosulphate solution is equivalent to 0.163 g. of arsenic. Then the 0.0967 g. of arsenic in the 5 cc. of the fluorine filtrate would be equivalent to 0.6 cc. of the thiosulphate reagent. This 0.6 cc., which is the oxidizing equivalent due to the blank, plus the hydrogen peroxide equivalent, which is 1.4 cc., equals 2 cc. Since this checks with the value obtained by analyzing 5 cc. of the fluorine filtrate by the Bunsen method, it is reasonable to conclude that the filtrate contains no active oxygen.

The results obtained from the analysis of the precipitate by the Bunsen method indicate no perarsenate or active oxygen.

Basic Solution

Experimental

Materials

NaOH, 95%, Baker and Adamson.

For other reagents used see materials under hydrogen peroxide method.

Procedure and Observations

Tertiary sodium arsenate was prepared by treating 325 g. of disodium arsenate with 45 g. of sodium hydroxide. A solution of this trisodium arsenate with a slight excess of sodium hydroxide was saturated at 0°. A portion of this filtrate, kept at ± 2° by means of salt and ice in vessel E, Figure 2, was treated with gaseous fluorine for three and one-half hours. The vapors above the arsenate solution quickly turned the potassium iodide paper a distinct brown, showing the presence of fluorine. By addition of a saturated solution of sodium hydroxide, when necessary, the arsenate solution was kept slightly basic, as shown by the litmus test, while the fluorine was passing through it. At the end of the fluorination process, compressed air, passed through cotton to remove dirt and through sodium hydroxide solution to remove oil and carbon dioxide, was bubbled through the mixture at 0° for two and one-half hours to reduce the amount of ozone and hydrogen peroxide in the solution. A bluish gray precipitate, filtered out by suction, was dried over concentrated sulphuric acid under reduced pressure, and then over phosphorus pentoxide. The colorless filtrate was kept cold in an automatic refrigerator until analyzed.

Analysis of Products

Five cubic centimeters of the filtrate analyzed by the Bunsen method required 1.30 cc. of 0.0964 N. sodium thiosulphate solution.

Five cubic centimeters of the filtrate analyzed by the Mohr method required 15 cc. of 0.0973 N. iodine solution, which is equivalent to 0.055 g. of arsenic.

Analysis of 5 cc. of the filtrate by Rothmund and Burgstaller method indicated no ozone, and the hydrogen peroxide was found to be equivalent to 0.05 cc. of 0.0964 N. thiosulphate solution.

A portion of the dried precipitate weighing 1.43 g., analyzed by the Bunsen method, required 0.3 cc. of 0.0964 N. thiosulphate reagent.

Explanation of Results

A blank of disodium arsenate analyzed by the Bunsen method required 1 cc. of 0.0964 N. thiosulphate solution which is equivalent to 0.163 g. of arsenic. From these data the

0.055 gram of arsenic in the fluorine sample would be equivalent to 0.33 cc. of the standard thiosulphate solution. If the 0.33 cc., which is the oxidizing equivalent of the sample as shown by the blank, and the 0.05 cc., which gives the amount of hydrogen peroxide, be subtracted from 1.3 cc., which is the total oxidizing equivalent for the same size sample, the remainder is 0.92 cc. of standard thiosulphate solution. This 0.92 cc. of the standard reagent gives the equivalent of active oxygen in 5 cc. of the fluorine filtrate, and shows about 6% of the arsenic in solution yields active oxygen.

The results obtained from the analysis of the precipitate by the Bunsen method indicate no active oxygen.

GENERAL SUMMARY AND CONCLUSIONS

From the foregoing pages the results of the present study may be summarized as follows:

1. That disodium arsenate with 5% hydrogen peroxide formed a compound which contained 0.15% active oxygen, while the 30% hydrogen peroxide with the same salt gave a preparation yielding 8.45% active oxygen. This would indicate that the better yield could be obtained by using the more concentrated hydrogen peroxide.

2. That arsenic acid treated with barium peroxide did not give a perarsenate. The reaction of barium peroxide on the secondary arsenate gave a product which contained 0.47% active oxygen.

3. That disodium arsenate solution, saturated at 0° and electrolyzed for sixteen hours at 0-8° with a current density of 1.5 amperes per sq. cm., gave a solution in which 2% of the arsenic held active oxygen. Another portion of the secondary arsenate solution electrolyzed under the same conditions, except lower current density, gave no available oxygen. Electrolysis of secondary arsenate solution, to which sodium fluoride had been added, gave no compound containing active oxygen.

4. That a precipitate of trisodium arsenate with peroxide of crystallization was obtained by treating an alcoholic-

aqueous solution of disodium arsenate, at -10°, with sodium peroxide. The following formula was assigned to the preparation: $2Na_2AsO_4.7Na_2O_2.2NaOH.75H_2O$. There was no perarsenate in the precipitate.

5. That a cold solution of disodium arsenate saturated with gaseous fluorine at 0° did not form a product containing active oxygen. But trisodium arsenate, made slightly basic with sodium hydroxide, did react with fluorine to give a compound in which 6% of the arsenic held active oxygen.

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