

THE ELECTROLYTIC OXIDATION OF POTASSIUM ARSENITE

BY

MARION VAUN ADAMS

#d 19

T378
Ad19e
1924

A Thesis Submitted for the Degree of
MASTER OF ARTS
Arts and Sciences

UNIVERSITY OF ALABAMA

1924

ACKNOWLEDGMENT.

On completion of the present work I wish to acknowledge the assistance of Dr. Stewart J. Lloyd, who has offered many valid suggestions and aided materially in making the work a success. I also wish to thank the Department of Chemistry of the University of Alabama for making the research possible.

Marion Vaun Adams

University, Ala.

May 1, 1924.

THE ELECTROLYTIC OXIDATION OF POTASSIUM ARSENITE.

Potassium arsenate is a comparatively unknown compound, that is, very little experimental work has been done with it, and since no important use has been found for it no attempt has been made to produce it in large quantities.

Several arsenic compounds are very useful in destroying insects which have proven themselves enemies to the life of economic plants. Probably the first of these was the well-known Paris Green which contains copper and acetic acid as well as arsenic. As copper was a fairly expensive metal, and since the acetic acid served no useful purpose, this was followed and to a certain extent replaced by lead arsenate, which does the same work at a considerably less cost. The users of Paris Green usually associated the green color, due to copper, with its effectiveness, so that arsenate of lead, which is white, had a strong prejudice to overcome at first.

Another member of the arsenic family to come into prominence is calcium arsenate. It was primarily intended to cope with the boll weevil, though other uses are constantly being found for it.

Potassium arsenate will probably never be commercialized as the caustic potash is too expensive, and because it offers no apparent advantage over sodium arsenate.

The essential raw material from which all these arsenic insecticides are made is white arsenic - As_2O_3 . It happens that when any of the numerous ores of iron, copper, cobalt, nickel, lead and zinc, which contain a small amount of arsenic, are roast-

ed in the air, the arsenic attaches to itself some oxygen and sublimes over as white arsenic. Copper and lead smelters are in most places forbidden by law to allow this material to escape into the air as it is very poisonous. In the past very few smelting companies refined and marketed the white arsenic as there was very little demand for it, but, since the consumption of the arsenic insecticides has begun to increase, the mines have begun to collect the arsenic as well as the precious metals, gold and silver. One of the common gold carriers, arsenopyrite, contains when pure about forty-six per cent of arsenic.

Until recently As_2O_3 was converted into As_2O_5 , which was used for insecticides, by oxidation with nitric acid, - HNO_3 . The process was essentially as follows: the white arsenic is placed by hand in large kettles and concentrated nitric acid added in small amounts, till the requisite quantity has been added. The kettles are then heated externally and the nitric acid gives up some of its oxygen to the white arsenic, (which now becomes As_2O_5), and is itself reduced to the oxides of nitrogen. These oxides are drawn through an elaborate series of towers and converted back to nitric after which the latter is concentrated by evaporation and returned to the circuit to be used again. The arsenic, now in the form of hard massive pentoxide, is chipped out of the kettles by hand after it has cooled and is then dissolved in water. Later lime is stirred with it and the basic calcium arsenate is formed.

Within the last year a method of electrolytic oxidation has been worked out and patented. This process differs from the nitric acid process in that the oxygen needed to carry the As_2O_3 to As_2O_5

is provided by the action of an electric current upon caustic soda solution. The white arsenic is dissolved in caustic soda solution, the latter is placed between iron electrodes and a current is passed through. The oxygen produced by the action of the current on the solution adds itself to the white arsenic and in the presence of caustic soda turns it into sodium arsenate. Some of the As_2O_3 is precipitated as metallic arsenic and is filtered off. When the white arsenic has been completely oxidized the sodium arsenate solution is drawn off and mixed with lime whereby calcium arsenate is produced and the caustic soda regenerated. The solid calcium arsenate is filtered off, washed, dried and packed.

A plant for making calcium arsenate by the method outlined above has been recently constructed in Montgomery, Ala., operation of which has just commenced. This plant is owned by the Gulf States Chemical Refining Company and is operated under the direction of Dr. Stewart J. Lloyd, professor of chemistry at the University of Alabama, and Mr. A. M. Kennedy, a well-known research chemist.

The purpose of the present work was to see if a similar result could be obtained by using caustic potash in place of caustic soda and in addition to study the potassium arsenate produced.

EXPERIMENTAL.

To carry out the work the following solutions had to be made. It was necessary to standardize them very accurately.

Potassium Arsenite Solution.

206 grams of As_2O_3 were dissolved in 321.8 grams of caustic potash, which had previously been dissolved in water. The solution was then diluted to 2000 c.c. and found to be approximately 0.52 Normal.

Iodine Solution.

It was desirable to have the two solutions of approximately the same normality, therefore a 0.5 Normal solution of iodine was made up. The operation consisted of dissolving 126.97 grams of iodine in 166 grams of potassium iodide, which had been dissolved in water, and then diluting the solution to 2000 c.c.. Both the arsenite and the iodine solutions were placed in acid bottles and kept in the dark as much as possible.

The object of the experiment was to oxidize the arsenite to the arsenate form, the oxygen being provided by the action of an electric current upon caustic potash solution and water. After the potassium arsenate was made and dried it was studied and the exact formula was calculated. This process is continuous and goes on very smoothly.

The apparatus needed to carry on the work consisted of a direct current, a large beaker, two sheet-iron electrodes, and a solution of potassium arsenite. The larger the distance between the electrodes the higher the voltage will be.

Electrolytic oxidations may be divided into several classes, but the one in which we are most interested is the process in which the oxygen content of a substance is increased. The materials in the beaker were potassium hydroxide, water and white arsenic. The OH ions were first discharged to oxygen, two OH ions giving oxygen and water. The influence of the OH concentration was twofold, as it determined the potential at which the oxygen evolution began and secondly it altered the nature of the substance submitted to oxidation. A rise in temperature probably increases the velocity of the diffusion of the AsO_2^- ions to the electrode and is therefore favorable if the oxidation is desired to be complete.

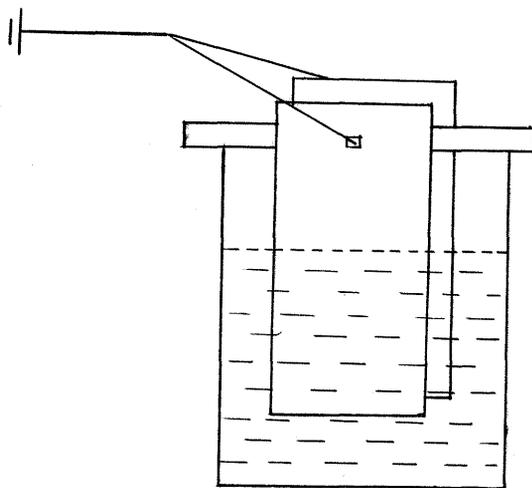


Fig. 1.

PROCEDURE AND EXPERIMENTAL DATA.

The preceding diagram will give the reader an idea as to the

outward appearance of the apparatus used. A large beaker was nearly filled with a stock solution of potassium arsenite and the iron electrodes immersed in the liquid. The wooden bar holding the electrodes apart rested on the edges of the beaker and kept the electrodes from touching the sides. The wires were then connected and the current turned on. Very soon the solution in the beaker began to heat and bubbles of oxygen were seen to rise from the anode while hydrogen was coming from the cathode. The bubbles around the cathode came off much faster than those at the other pole. After the current had been on for several hours, 25 c.c. of the solution were drawn off with a pipette, which had a rubber bulb at one end for sucking the liquid up into the pipette, and titrated with iodine. The percentage which had changed from the arsenite to metallic arsenic and the arsenate was then calculated. This was done at different times until practically all of the arsenite had been converted. The results were:

c.c. solution	Hours run	c.c. iodine	% change
25	0:00	111.8	0.0
25	1:10	91.3	18.2
25	2:40	67.3	39.7
25	3:40	55.0	50.8
25	5:00	39.1	65.0
25	6:30	30.2	73.0
25	9:00	17.5	84.0
25	11:00	4.0	92.0
25	12:00	1.5	98.0

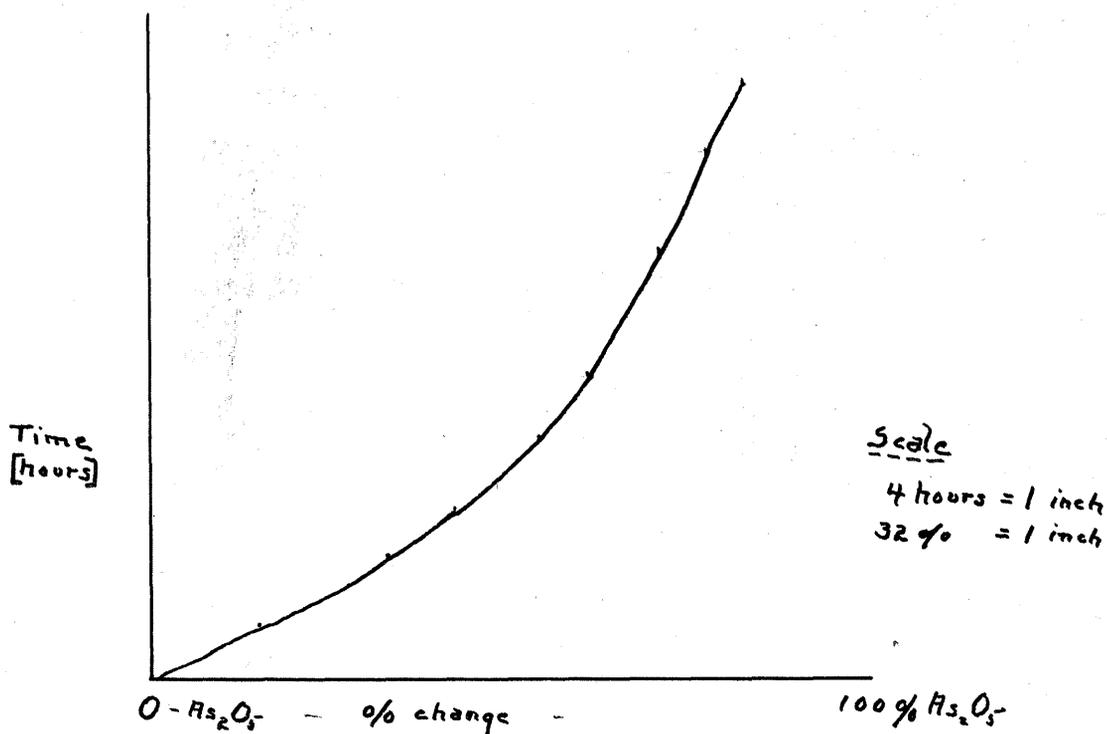


Fig. 2.

The curve drawn above gives the-amount of arsenite converted with respect to the time the current passed through the solution.

When practically all the arsenite had been converted the electric current was cut off and the metallic arsenic was filtered off with a Buchner crucible. The arsenic was then dried and was found to weigh 6.12 grams. Approximately 70 grams of white arsenic were dissolved in the KOH solution and it is estimated that about 10% of the total precipitated as metallic arsenic. As some metallic arsenic was drawn off with each sample titrated the result was very inaccurate but it did show that most of the arsenic was converted to the arsenate.

The solution of supposedly potassium arsenate and water was evaporated and allowed to cool. It was left over night but did not crystallize, so acetic acid was added until it was strongly

acidic and then it was diluted. Potash was then added to the solution until it was slightly alkaline and a fine yellow precipitate was filtered off and thrown away. The solution was again evaporated and allowed to remain overnight. The following morning the bottom of the beaker was covered with yellow rhombic crystals. These were analysed and seemed to have acetic acid in them as they were acidic when dissolved in water and tested with litmus paper. The crystals were probably impure. Arsenic and potassium were found to compose most of the samples. The solution was then evaporated to about one-half its former volume and when it cooled the entire amount crystallized. The crystals could not be readily distinguished.

ELECTRICAL EFFICIENCY OF THE PROCESS.

Data.

Amperes	3.1
Volts	2.0
Time of run(hours)	12.0
Electrode area(sq.dm)	1.13
Current density ,(amp/sq.dm.)	2.75
Theoretical voltage	0.8

Calculations.

Current Efficiency.

The current efficiency of an electrolytic process is defined as the ratio of the yield obtained to the theoretical yield calculated on the basis of Faraday's Law. Consequently the yield of material is nearly always less than that calculated from the quantity of electricity used. Frequently the current efficiency is

the first thing to be considered in an electrolytic process, but at times its importance is modified by other factors.

Weight of As_2O_3 used 69.8 grams.

" " metallic As precipitated 7.0 "

As_2O_3 contains 75.7% As; $.757 \times 69.8 = 51.8 =$ number of grams of As in 69.8 grams of As_2O_3 . $51.8 - 7.0 =$ " "

" " " converted to As_2O_5 .

$51.8 \times 1.54 = 68.90 =$ number of grams of As_2O_5 made.

$51.8 \times 1.32 = \underline{59.13} =$ " " " " As_2O_3 converted.

9.86 = " " " " Oxygen added.

$3.1 \times 12 = 37.2$ ampere-hours run.

$37.2/26.8 \times 8 = 11.04 =$ theoretical yield of oxygen in grams.

$9.86/11.04 = 89.3\%$ current efficiency.

Decomposition Voltage.

The reaction which probably takes place is:



Heat of formation of water is 69,000 cal

" " " " As_2O_3 " 156,400 "

" " " " As_2O_5 " 219,400 "

Using the heats of formation:

$$2 \times 69,000 - 156,400 = 219,400 - (75,000).$$

There is an evolution of 75,000 cal. of heat.

Therefore, according to the Helmholtz - Thomson rule the decomposition voltage is:

$$4.19 \times 75,000/4 \times 96,540 = 0.8 \text{ volts.}$$

This decomposition voltage is theoretical and is somewhat smaller than the actual working voltage.

Energy Efficiency.

The energy efficiency is defined as the ratio of the theoretical quantity of energy to the energy actually used. If the current efficiency is known, it may be worked out as follows:

The energy efficiency is equal to the current efficiency times the theoretical voltage over the actual voltage.

$$\text{E.E.} = \text{C.E.} \times \text{theoretical voltage/actual voltage.}$$

$$= 89.3 \times 0.8/2.0 = 35.72 \%$$

The energy efficiency is always lower than the current efficiency.

ANALYSIS OF THE PURE CRYSTALS.

A few of the white crystals were dissolved in water and tested with litmus paper. The solution was found to be distinctly alkaline. This was expected as the solution from which it crystallized was alkaline, but, the impure crystals were acidic and they also crystallized out of an alkaline solution.

The most important substance supposed to be in the crystals is arsenic and it is necessary to determine the percentage and the form into which it is converted. Acting on the assumption that both arsenite and arsenate were present, the following method was used.

The iodine solution was standardized very accurately by weighing out three samples of pure white arsenic of 0.5 gram each, dissolving them in potassium hydroxide and adding a few drops of methyl orange, followed by a few c.c. of strong hydro-

chloric acid to make the solution acidic, then sodium bicarbonate was added until the solution was alkaline, and an excess was left in the beaker to take up the hydriotic acid as it was formed when iodine was added. About five c.c. of starch solution was added as an indicator and the solution titrated with iodine.

Results.

- (1). 21.1 c.c. of iodine neutralized 0.5 gram As_2O_3 .
 (2). 21.1 " " " " 0.5 " "
 (3). 21.2 " " " " 0.5 " "

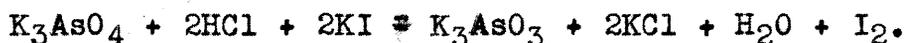
1 c.c. iodine sol. = 0.0237 gram As_2O_3 .

The standard solution should be analyzed for total arsenic, arsenite and arsenate. The arsenate must first be reduced to the arsenite form before the total arsenic can be determined. As we wished to know the amount of arsenic in the arsenite form as well as in the arsenate it was necessary to make a titration for the arsenite before the arsenate was reduced.

One gram of the crystals was very accurately weighed and dissolved in water, made acidic, then alkaline, and starch added. The solution was then ready for the titration with iodine to find the amount of arsenite in the sample. Exactly 0.15 c.c. of iodine was used to reach the end point. The percentage of arsenite was so small that it^{was} considered negligible.

As the percentage of arsenite was negligible, the percentage of total arsenic and arsenate will be the same. The arsenate was reduced by concentrating the solution and adding about fifteen c.c. of hydrochloric acid and about one gram of potassium iodide.

Iodine was set free by this reaction. The equation for the reaction is as follows:



Sodium thiosulphate was then added to the solution and it removed the iodine set free by the reaction above. The reaction formula for sodium thiosulphate and iodine is as follows:



(Note: The exact removal of iodine was determined without the aid of starch, for in strong acid solutions the starch is partly inverted, dextrine being one of the intermediate products and dextrine forms with iodine a deep red color which is not later removed and which interferes in the titration of the iodine solution.)

The first equation represents a reaction that can be quantitatively reversed at will. In the second reaction the end point was apparently reached but when allowed to stand for a few minutes the iodine color would reappear and more thiosulphate had to be added, until finally the solution remained clear. Sodium bicarbonate was then poured into the beaker until the solution was alkaline. Starch was added and the solution was titrated with iodine.

It was necessary to find the percentage of potassium in the crystals which were supposed to be potassium arsenate. One gram of the crystals was weighed out very accurately and dissolved in water. Hydrogen sulphide was generated and passed through distilled water and then into the solution which had been concentrated with hydrochloric acid. The temperature was raised to about 60 degrees as the reaction will proceed much faster at a high temperature. For quite a while there was apparently no change in the sol-

ution but the As_2O_5 was gradually being reduced to As_2O_3 . Finally the arsenic was precipitated out as arsenic sulphide, (As_2S_3). When all of the As_2S_3 had been precipitated it was filtered off and a clear solution was left. As the solution was composed of potassium, hydrochloric acid, and water it was evaporated to dryness so that all the water and acid fumes would vaporize and leave only white potassium chloride. On the bottom of the beaker As_2S_3 could be seen mixed with the KCl crystals, therefore the residue was dissolved again and the solution filtered several times to remove the remainder of the arsenic sulphide which was present. The solution was again evaporated to dryness and the pure KCl was accurately weighed.

Results.

(Percentage of K_2O and As_2O_5).

Samples of the crystals weighed 1 gram each.

As_2O_5 -- 22.1 c.c. iodine to neutralize total arsenic in a one gram sample of the crystals.

1 c.c. of iodine is equivalent to 0.0237 grams As_2O_3 . Therefore $22.1 \times 0.0237 = 0.5237$ grams of arsenic. Then $0.5237/1 \times 100 = 52.37\%$ arsenic.

Potassium Oxide.

Weight of KCl and beaker	98.965 grams.
" " beaker	<u>98.275</u> "
" " pure KCl.....	0.690 "
Molecular weight of KCl	75.6
" " " K	39.1

Then by proportion:

$$75.6 : 0.690 :: 39.1 : X$$

$$X = 0.3607 \text{ grams K.}$$

The potassium comes out in the crystals as K_2O therefore the percentage should be in the same terms.

$$\text{Mol. Wt. of } K_2O = 94.2$$

$$\text{" " " } K_2 = 78.2$$

By proportion:

$$94.2 : 78.2 :: X : 0.3607$$

$$X = 0.4345$$

Then:

$$0.4345/1 \times 100 = 43.45 \% K_2O.$$

DETERMINATION OF THE FORMULA OF THE CRYSTALS.

The crystals were found to contain arsenic, potassium and water. The following table gives the three constituents for the three possible formulae of the crystals analyzed:

		As_2O_5	K_2O	H_2O
$K_2O-2H_2O-As_2O_5$	(1)	63.52%	26.15%	10.33%
$2K_2O-H_2O-As_2O_5$	(2)	52.40%	43.41%	4.19%
$3K_2O - As_2O_5$	(3)	44.87%	55.13%	0.00%

The experimental results were:

$$52.37\% \quad 43.45\%$$

The formula marked (2) corresponds almost identically with the experimental results and should be the correct formula.

(2) $2K_2O - H_2O - As_2O_5$ --	As_2O_5 52.40%	K_2O 43.41%
Experimental	52.37%	43.45%

From the above the formula appears to be K_2HAsO_4 and the substance is evidently di-potassium arsenate.

SUMMARY.

White trivalent arsenic may be smoothly oxidized to the pentavalent condition by dissolving it in caustic potash solution and electrolyzing with direct current. The use of KOH solution does not however, seem to offer any advantages over the less expensive NaOH.

The arsenate produced by such a process does not crystallize so readily as does the corresponding sodium salt, but when it is obtained is undoubtedly K_2HAsO_4 .

Approved May 6. 1924

Steward J. Boyd

Jack P. Montgomery

Apparently a good piece of work, but not well written

A. B. Moore