To obtain this quantity of material about 200 kilos of euxenite, ytter-spar, gadolinite, fergusonite and yttrotitanite were employed; and in addition the yttrium earths derived from large quantities of monazite, supplied by the Welsbach Light Company through the courtesy of Dr. H. S. Miner, to whom many thanks are due.

Thulium bromate is more soluble than erbium bromate, but less soluble than the corresponding compound of ytterbium.

Thulium salts are of a pale bluish green color, best seen in artificial light. However, this tint is very readily destroyed by minute amounts of erbium, the solution becoming first yellowish green, then yellow, color-less, and lastly pink as the erbium content increases.

The material is still undergoing fractionation so as to make sure of the non-complexity of this element.

In addition to the above, it may be as well to state that the more soluble portions are being carefully studied, since the most soluble frac-tions are colored pale yellowish green when in solution while the inter-mediate fractions between these and thulium are colorless.

It is expected that early in May the determination of the atomic weight will have been completed and a study of the compounds commenced. All these fractions are being examined by means of a quartz spectrograph and Sir William Crookes has kindly offered to investigate the spark spec-tra of thulium and erbium with the unequaled instruments at his dis-posal. This latter element has also been obtained in a high state of purity.

NEW HAMPSHIRE COLLEGE, DURHAM, N. H.,
            February 15, 1910.

THE MARSH TEST AND EXCESS POTENTIAL.

(FIRST PAPER.[1])

THE QUANTITATIVE DETERMINATION OF ARSENIC.

BY W. D. HARKINS.
Received May 14, 1909.

Introductory.

The most widely used method for the determination of small quantities of arsenic is the separation as arsine suggested by Marsh,[2] together with the decomposition of this gas in a heated glass tube as recommended by Liebig.[3] An excellent review of the history of the development of this method has been given by Lockemann.[4]

[1] Presented at the New York meeting of the American Chemical Society, December 28, 1906, and in part at the December, 1905, meeting of the Stanford Chemical Society.

[2] *Ann.*, **23**, 207 (1837).

[3] *Ibid.*, p. 217.

[4] *Z. angew. Chem.*, **18**, 416 (1905).

In the year 1902 the writer attempted to utilize the Marsh method for the direct determination of the arsenic contained in the acid extracts from soils, but found that the amounts of arsenic recovered were entirely too small. This was explained by the work of Parsons and Stewart[1] and other investigators[2] as due to the retentive effect of the iron present in the solution. According to Headden and Sadler[3] a successful determination by this method can be made only in the absence of iron, copper, platinum and their salts.

In spite of the evidence cited above, and that of other observers,[4] A. H. Allen[5] recommends that zinc should always contain a certain amount of iron to insure a regular evolution of hydrogen, and Gautier[6] advises that platinic chloride be added in order to make the zinc active. Even in what he claims to be his most delicate method,[7] he precipitates the arsenic together with ferric hydroxide and adds the solution of this precipitate, containing about 0.1 gram of iron, directly to the Marsh generator.

Retention of Arsenic by Iron and Other Metals.

In view of these facts it was thought advisable to repeat a portion of the work of Parsons and Stewart. The experiments confirmed their work in every respect, showing that approximately the same percentages of arsenic were held back by the iron as those given in their paper. The results obtained, together with a few of the data given by Parsons and Stewart, are appended in Table I:

TABLE I.—RETENTION OF ARSENIC BY IRON.

Wt. Zn.	Reagent.	Wt. Iron.	Arsenic. Taken.	Found.	Per cent. Found.	Time. Hrs.
35 g.	H_2SO_4	0.160 g.	1.88	1.00	53	6
35	HCl	0.400	1.88	0.72	38	5
35	H_2SO_4	7.000	1.88	0.30	16	6
35	HCl	7.$FeCl_2$	1.88	0.25	13	6
35	H_2SO_4	0.150	0.80	0.52	65	6
35	H_2SO_4	0.150	0.93	0.55	59	4

Parsons and Stewart.

30		0.060	5.00	3.45	69	
30		0.300	5.00	2.70	54	
30		1.500	5.00	2.95	59	
30		6.000	5.00	1.60	32	

[1] THIS JOURNAL, 24, 1005 (1902).

[2] Wöhler, Ann., 23, 217 and 223 (1837). Santermeister, Chem.-Ztg., 15, 1021. J. Thiele, Chem. News, 67, 125 (1893).

[3] Am. Chem. J., 7, 341.

[4] O. Hehner, J. Chem. Soc. Ind., 20, 194 and 200. Chapman, "Reports of the Royal Commission on Arsenical Poisoning," Vol. II, page 84.

[5] J. Soc. Chem. Ind., 21, 94 (1902).

[6] Bull. soc. chim., 27, 20–21, 1030–34 (1902). Ann. chim. phys. (5), 8, 384 (1876).

[7] Compt. rend., 137, 158–63. Bull. soc. chim. (3), 29, 859–863.

In addition to these results it was found that mercury, platinum, silver, palladium, nickel, cobalt, and their salts were injurious in their action, particularly mercury;[1] and that copper is injurious when added in large amounts as copper sulphate to the solution. The following table gives the results of four experiments upon copper:

TABLE II.

Grams Zn.	Grams Cu.	Time. Hrs.	Arsenic.	
			Found. Mg.	Added. Mg.
35	0.037	6	1.88	1.88
35	0.184	6	1.80	1.88
35	0.368	6	1.79	1.88
35	7.000	6	0.22	1.88

The addition of tin, bismuth, cadmium, lead, or their salts to the generator did not cause the retention of any arsenic, except in cases where their addition diminished the rapidity with which the zinc was dissolved.

The Separation of Arsenic from Iron by Heating the Marsh Generator.

It was observed early in the course of the experiments upon the retention of arsenic by iron, that even after the arsenic had almost stopped depositing in the tube, a sudden increase in the rapidity of the evolution of hydrogen would cause a considerable evolution of arsine. It was found impossible to obtain a quantitative separation by merely increasing the rate of evolution of the hydrogen, but, when the generator was heated to 100° in a water bath, excellent results were obtained. The apparatus is shown in Fig. 1.
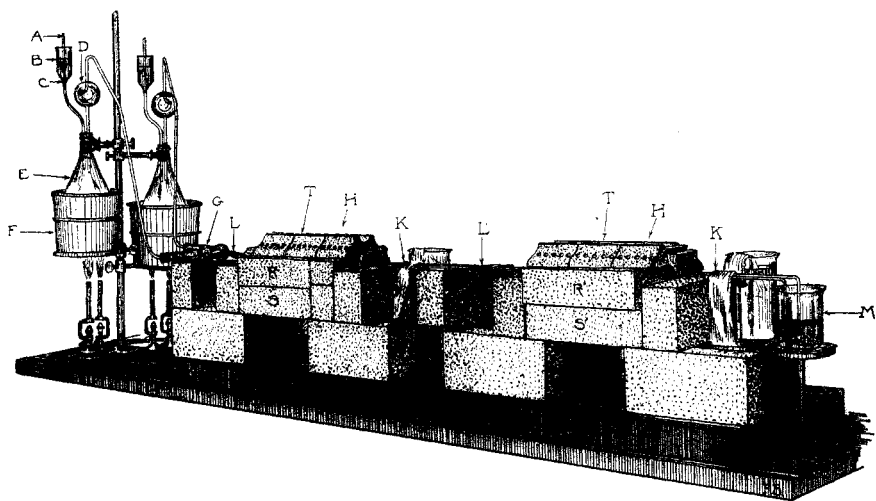

Fig. 1.—Apparatus for the determination of arsenic.

[1] Wm. Thompson, *Chem. News*, **85,** 173 (1901) and 86, 179 (1902). The action of the mercury is very different from that of the other injurious metals, since it lessens the rapidity of the solution of the zinc, while the other metals increase its rate of solution.

At A is connected an apparatus giving arsenic-free hydrogen, which is passed through the tube $A\,C$ into the flask E, until the air in the apparatus is completely displaced. Then, by turning A, acid may be dropped into the flask upon the zinc. The arsine and hydrogen pass through a Kjeldahl bulb, D, and a drying tube of calcium chloride, G, into a Jena hard-glass tube which lies in the fire-brick furnace $R\,S$. A second tube and furnace are always used to test the completeness of the decomposition of the arsine. The tubes are cooled at K by a strip of wet filter paper, or better by water flowing through a metal trough. Except where large quantities were determined, the glass tube was four millimeters in internal diameter, but drawn out to a smaller diameter where the arsenic was to be deposited. For all amounts greater than one-half milligram, the tube was enlarged to a bulb at K. The tube was finally cut at a and c (Fig. 2) and wiped by a slightly moist cloth. The

Fig. 2.

tube was then left in the balance case for a considerable time and weighed by substitution against a tube of the same size and shape and made from the same glass. The arsenic was then dissolved in nitric acid and the tube washed with distilled water, dried in air, and finally weighed exactly as before on a balance sensitive to 0.005 mg. To avoid errors in a weighing care must be taken to deposit the arsenic in as small a tube as possible. Most of the weighings were made at a high altitude, where the air is light and very dry. The tubes were handled by forceps with flexible platinum tips, and by platinum wires.

For each analysis about forty grams of arsenic-free zinc were used. The determination was begun by dropping a cold hydrochloric acid solution of the arsenic at such a rate that all of the arsenic was added during a period of one-half hour. Then the solution was heated gradually by boiling, and when the action had subsided somewhat more hydrochloric acid (sp. gr. 1.1) was added,[1] 100 to 150 cc. of acid in all. Finally 25

[1] All of the methods for the purification of hydrochloric acid described in chemical literature were tried, and in addition some others which seemed to give promise of success. The only method which always gave perfectly arsenic-free hydrochloric acid was a modification of that described by Otto ("Ausmittelung der Gifte," p. 159). Either mercuric chloride or copper sulphate was added to hydrochloric acid of a density of 1.10, in the proportion of ten to twenty grams to six liters of acid. Hydrogen sulphide was then passed until the salts were completely precipitated as sulphides, the bottle stoppered, and the solution allowed to stand for four or five days. At the end of this time it was filtered and the filtrate distilled, the first quarter of the distillate being rejected.

cc. of concentrated sulphuric acid mixed with 25 cc. of water were added to the generator. At once, when all the zinc was dissolved, the burners of the fire-brick furnaces were extinguished, the tile lifted from the furnaces, and the tubes cooled as quickly as possible. If this is not done, air will draw back into the apparatus and water vapor be formed and condensed, thus spoiling the determination. In cases where time is an object, the generator should be heated from the beginning.

After a series of preliminary experiments the results given in Table III were obtained:

TABLE III.—EFFECT OF HEAT UPON THE RETENTION OF ARSENIC BY IRON.

Wt. zinc. Grams.	Time cold. Hours.	Iron added. Gram.	Time 100°. Hours.	Arsenic found. Milligrams.	Arsenic taken. Milligrams.
35	8	0.0	0.0	1.87	1.88
30	5	0.0	0.0	1.84	1.88
30	5	0.075	1.5	1.85	1.88
50	1	0.400	6.5	1.82	1.88
30	3.5	0.300	4.5	1.87	1.88
35	4.0	0.160	2.5	1.87	1.88
40	1.0	0.160	3.0	1.86	1.88
40	0.5	0.400	2.5	1.86	1.88
40	0.5	0.400	4.0	1.89	1.88
40	0.5	0.400	4.0	1.90	1.88
40		0.400	2.0	1.80	1.88
40		0.400	2.0	3.76	3.76
40		1.000	2.0	3.70	3.76

A comparison of these results with those given in Table I shows that heating the generator practically doubles the amount of arsenic reduced. It is evident that the directions which usually accompany the description of the Marsh test, namely that the generator be kept cold, are certainly erroneous and just the opposite of the best procedure. The directions should say that the concentration of the sulphuric acid present should be kept small near the beginning of the determination. For this reason hydrochloric acid is the better acid to use at first. The addition of moderately concentrated (1 : 1) sulphuric acid toward the end of the test improves the results, and the acid does not prove injurious by a resulting reduction.

In several cases, where the arsenic was deposited with extreme rapidity, a part of the mirror was a dark brick-red. This was not due to selenium, since the latter metal was not present. It is possible that this red substance was an allotropic modification of arsenic. In these experiments a white crystalline deposit was often obtained between the gas flame and the arsenic mirror. It is much less volatile than the arsenic, and can easily be separated from the latter by cutting the tube at the proper point. In appearance it is somewhat similar to that obtained when aluminium is used in the place of zinc in the generating flask. These de-

posits will be collected until a sufficient amount is obtained for the determination of the composition of the crystals.

The Separation of Arsenic by the Addition of Salts to the Generator.

The purest zinc which can be purchased dissolves in pure sulphuric acid with extreme slowness. If the salt of a metal which lies lower in the electromotive series is added to the acid it is found that in almost all cases the metal precipitates upon the zinc, but in such a way as to leave a part of the zinc surface in contact with the solution. If the metal thus precipitated has a lower excess potential than the zinc, which is the case with all of the metals considered in this paper with the exception of mercury, it would be expected that hydrogen would be liberated more easily from the surface of the second metal. In such cases we find that the zinc dissolves more rapidly than before, except that when salts of iron are added without vigorous stirring a considerable time often elapses before its effect is perceptible.

We may assume that the mechanism of solution of the zinc is now as follows: positively charged zinc ions pass from the surface of the zinc into the solution, and positive hydrogen ions are deposited upon the surface of the other metal, which for convenience we may consider as platinum. Gaseous hydrogen soon escapes from the surface of the platinum, and the mechanism of the reaction is the same as though the zinc and the platinum were connected by a wire, lying outside the solution. The system is a galvanic cell in which the zinc is the negative pole. So far as the platinum is concerned, however, the conditions are practically the same as if it were the cathode in an electrolytic cell containing sulphuric acid as an electrolyte. With such a system the reduction may take place either at the surface of the zinc or of the platinum electrode. If at the latter surface only, we have a case of cathodic reduction similar to that described by Tafel[1] or by Haber,[2] except that the depolarizer is itself a weak electrolyte in the case under investigation.[3] If we assume that the reduction takes place upon the surface of the cathodic metal, the reducing power should be related in some way to the value of the cathode potential. This potential depends upon the current density, the concentration of the oxide of arsenic, and the value of the excess potential for the particular metal. The value of the cathode potential (E) is given by the equation of Haber[4] for the case where no free hydrogen is liberated,

---

[1] *Z. physik. Chem.*, **34,** 197 (1900).

[2] *Ibid.*, **32,** 193 and 271 (1901); **47,** 257 (1904).

[3] Luther and Schilow, *Z. physik. Chem.*, **46,** 777 (1900). This, of course, makes *possible* the direct electrolytic separation of arsenic, provided that the conditions are favorable. That arsenic is precipitated as a metal when the reducing action in the generator is small is well known (Parsons and Stewart, *loc. cit.*).

[4] *Z. physik. Chem.*, **47,** 259 (1904).

$$E = x(\mathrm{RT}/n \ln I/C_M C_H. -- \text{const.}),$$

where I is the current density; C_M, the concentration of the substance to be reduced; C_H, the concentration of the hydrogen ion; x is a number greater than one, whose value depends upon the value of the excess potential for the metal, and the subtractive constant represents the catalytic influence of the cathode metal upon the reduction in question.

From a theoretical standpoint, the simplest case for investigation would have been the reduction of the oxide of arsenic in an electrolytic cell,[1] with a high concentration of arsenic, vigorous stirring, and a relatively low current density. However, since the work was undertaken at the beginning in order to increase the accuracy of the quantitative determination of small (but still weighable) amounts of arsenic by the ordinary Marsh method, the most favorable conditions for the proof of the theory were not chosen, but instead a much more complicated system was used in which the concentration of the oxide of arsenic was low, and the current density large. Of the factors in the determination of the potential at which the hydrogen is liberated, the excess potential, the current density, and the catalytic action of the metal may be varied; but since nothing is known in regard to catalyzers for this reaction it was decided to work by choosing the first two factors properly and neglecting the last.

That arsenious oxide could be more readily reduced to arsine in the Marsh generator if the salt of a metal other than zinc was added, was suggested in 1893 by Thiele.[2] In trying to determine large amounts of arsenic he found that he could not get a complete reduction of the arsenic unless stannous chloride was added toward the close. Preliminary experiments made upon the basis of these suggestions showed that arsenic can be quantitatively separated from iron or *other injurious metals* by the addition to the solution of salts of bismuth, tin, lead, and cadmium.[3]

In these experiments dilute sulphuric acid was used, of the concentrations advised by Chittenden and Donaldson, though in some instances hydrochloric acid was added to hasten the solution of the zinc. When salts of lead were added to the generator, hydrochloric acid was always used, since in this case sulphuric acid acts slowly upon the zinc. Forty grams of zinc were used for each determination, and enough of the stannous chloride or other salt added to make the zinc active. The arsenical solution, together with the iron and more of the stannous chloride, was then added drop by drop. By the continuous addition of more acid and stannous chloride the action was kept as rapid as was possible without the loss of arsenic from the heated glass tube, until the zinc was almost

---

[1] Thus eliminating any possible reduction by the zinc.

[2] *Chem. News*, **67**, 125 (1893).

[3] Chapman and Low, *Analyst*, Jan., 1906.

all dissolved. In this way it was found that weighable quantities of arsenic could be separated quantitatively from as much as 0.300 gram of iron. It is probable that the separation can be made also from a larger amount, but this was not investigated. It should be remembered that, according to the work of Parsons and Stewart, as little as 0.060 gram of iron is sufficient to prevent the reduction of thirty-one per cent. of the arsenic present.

TABLE IV.—EFFECT OF STANNOUS CHLORIDE AND OTHER SALTS UPON THE RETENTION OF ARSENIC.

No. of exp.	Weight of iron or other element.	Weight of $SnCl_2$ or other salt.	Arsenic taken. Milligrams.	Arsenic found. Milligrams.
1	0.3126 g. Fe	2.0 g. $SnCl_2$	0.75	0.75
2	0.3126	2.0	0.75	0.74
3	0.3126	1.5	0.75	0.75
4	0.3126	1.5	0.75	0.73
5	0.1160	2.0	0.75	0.74
6	0.0600	2.0	0.75	0.73
7	0.3200	4.0	1.86	1.81
8	0.2250	2.0	1.86	1.85
9	0.1550	2.0	1.86	1.84
10	0.1550	2.5	0.93	0.93
11	0.1550	2.5	4.65	4.58
12	0.1550	3.0	0.93	0.91
13	0.1550	2.0	0.93	0.90
14	0.155	4.0	4.65	4.70
15	0.155	No salt	4.65	(3.38)
16	0.155	No salt	93.60	(72.40)
17	0.155	5.0 g. $SnCl_2$	93.60	91.40
18[1]	0.170	5.0	112.40	113.50
19[1]	0.170	5.00	112.40	112.80
20	0.080	3.0 g. $BiCl_3$	0.93	0.92
21	0.155	3.0 "	0.93	0.93
22	0.155	3.0 "	1.86	1.85
23	0.155	1.0 g. $CdSO_4$	0.93	0.95
24	0.155	4.0 g. $CdCl_2$	4.65	4.55
25	0.155	4.0 "	4.65	4.48
26	1.0 g. $PtCl_4 4H_2O$	No salt	2.79	(2.36)
27	1.0 "	2.0 g. $SnCl_2$	2.79	2.77
28	0.300 g. Fe	2.0 g. $Pb(C_2H_3O_2)_2$	0.93	1.90
29	0.300 "	2.0 "	1.86	1.82
30	0.155 "	No salt	1.86	(0.99)

Numbers inclosed in parentheses ( ) show the retentive effect of salts of iron or platinum, when the salt of another metal is not added.

[1] In experiment 17 the amount of arsenic recovered was slightly lower than it should have been. Since but 40 grams of zinc were used, in experiments 18 and 19 this amount was increased to 100 grams, and the size of the flask to one liter. Under these conditions no difficulty was experienced in the determination of more than a tenth of a gram of metallic arsenic, so this method could be used for the separation of arsenic from iron in ores containing arsenic.

It was found possible to make this separation with either arsenious or arsenic acid when the iron was added either in the ferrous or the ferric state, but the results given above were obtained in experiments where arsenious oxide alone was used.

In the preliminary experiments cadmium salts did not give such good results as when salts of tin were added. This seems due, in part, to the fact that the evolution of hydrogen was much less rapid in the former case. Bismuth salts are less easily purified, and lead salts produce an insoluble sulphate when sulphuric acid is used. For these reasons, most of the experiments were made with stannous chloride. The salts used were purified from arsenic, and all of the other reagents were also purified in cases where arsenic was present.

Good results were obtained by the electrolytic method in the absence of iron when as much as two milligrams of arsenic were present, but the addition of stannous chloride has not produced the same favorable result in the presence of iron as is obtained when the ordinary Marsh generator is used. When zinc electrodes are used in the presence of stannous salts the electrodes dissolve rapidly, so that the conditions are almost the same as those in the ordinary Marsh test.

It was considered possible that a part of the great retentive action of iron salts might be due to a chemical action between the iron salts and the arsine. To test this, the arsine produced in experiments such as those given in Table IV was passed through concentrated solutions of iron salts, with the result that no arsine was absorbed. This, of course, does not prove that compounds are not formed at the surface of the zinc in the generator.

In order to see if there is a connection between the excess potential of the metals and the reducing action of the hydrogen liberated from these metals in the Marsh generator, it was essential to determine a number of excess potentials previously undetermined. These determinations are now in progress, and nearly all of the common and rare metals which can be obtained in a suitable form have been procured for use in this work. The greatest difficulty experienced has been that of keeping the surface of the metals in a proper condition, and at the same time to eliminate the last traces of oxygen from the apparatus.[1]

Approximate determinations of the excess potential were first made by the method of Caspari. The results of these determinations, although made by a method which is only approximate in its results, are of some value in connection with the data presented. It is hoped that more accurate numbers can be presented in the second paper. It is universally recognized that the value of the excess potential of a metal depends

[1] See Lewis and Jackson, *Z. physik. Chem.*, **56**, 199 (1906).

to such an extent upon its surface condition and its previous condition as an electrode that it is impossible to obtain concordant values.

TABLE V.—THE EXCESS POTENTIAL OF THE METALS IN VOLTS AS DETERMINED BY THE APPROXIMATE METHOD OF CASPARI.

	Excess potential in volts.		
Metal.	Caspari.	New determination.	Tafel.[1]
Mercury.....................	0.78	0.74	1.30
Zinc.........................	0.70	0.71	....
Lead polished...............	0.64	0.62	1.30
Lead rough..................	....	....	1.23
Tin..........................	0.53	0.55	1.15
Cadmium....................	0.48	....	1.22
Arsenic......................	....	0.39	....
Bismuth.....................	....	0.38	1.00
Copper......................	0.23	0.25	0.79
Cobalt.......................	....	0.22	....
Nickel.......................	0.21	0.15	0.74
Silver........................	0.15	0.13	0.93?
Gold.........................	0.02	....	0.95
Iron.........................	0.07	....	....
Platinum....................	0.09	0.07	....
Platinum black..............	0.005	0.002	0.07
Palladium...................	0.48	0.02	....
Palladium black.............	....	0.002	....

Temperature = 20° C.

A study was made of the variation of the excess potentials of bismuth and copper with the current density. The curves of excess potential follow in general the equation

$$E = A + B \log I,$$

in which A and B are constants. From the measurements of Caspari and of Tafel[2] it would seem that the values of B for silver and gold are greater than for nickel and platinum. This shows that it is unsafe to draw too definite conclusions as to the relationship between excess potential and the reducing action of hydrogen in the Marsh generator, until the curves of the variation of excess potential with the current density are more definitely determined. That other factors than current density influence the excess potential is shown by the results of Tafel upon the potential of a silver electrode. When the silver cathode was separated from the anode by a porous cell, the potential value for 0.125 ampere per sq. cm. and 2 N sulphuric acid was about 1.5 volts, while, when there was no separating wall between the anode and the cathode, the potential soon fell to 1.15 volts.

[1] Z. physik. Chem., 50, 712 (1904). The values given are for a current density of 0.1 ampere per square centimeter.
[2] Z. physik. Chem., 50, 712 (1905).

It will be seen by referring to the values for the excess potential of the metals given in Table V, that those metals which were found favorable to the reduction of the oxides of arsenic to arsine are metals of high excess potential, while those which proved unfavorable were metals of low excess potential.

The one seeming exception to this rule, in the case where a salt of mercury was added, was due to the effect of the mercury in decreasing the speed of the solution of the zinc, just as would be expected when the zinc becomes coated with an amalgam whose excess potential is as great or greater than that of the zinc itself.

That the rapidity of the reduction and its completeness depended also upon the speed with which the hydrogen was evolved, and therefore upon the current density, was proved by varying the speed of solution of the zinc and weighing the arsenic deposited for a certain time interval.

The system used was so complicated that the experiments gave little light as to the catalytic effect of the different metals upon the reduction. That the electrolytic method is more favorable for the investigation of this problem is obvious. It is probable that the reduction of arsenious oxide to arsine takes place in two or more stages, and it is possible that an intermediate reduction product other than arsenic may be found.

When the iron was alloyed with the zinc used in the generator, it had the same injurious effect as if it were added to the solution as a salt,[1] and the addition of stannous chloride proved favorable as before.

If we consider the system previously discussed, that of platinum deposited upon zinc, it is to be expected that, on account of the lower excess potential of the platinum, the hydrogen given off will have a low reducing power. That the amount of arsenic reduced to arsine is less than that added to the generator was proved by a number of experiments, only one of which is listed in Table IV (Experiment 26). If a salt of tin is now added, the tin precipitates upon the platinum (and upon the zinc as well) and covers it in such a way that a new surface is substituted. If this new surface has the same excess potential as tin, the reduction should become more rapid than before. That this is the case has been proved in a number of instances.

When a salt of iron is dissolved in the solution the case is more complex, since practically all of the iron remains in solution, together with a part of the arsenic. Whatever may be the cause of the tendency of iron to prevent the reduction, it is probable that the beneficial action of the tin added is due to an increase of potential at the surface from which hydrogen is liberated.

The separation of arsenic from iron is extremely important in work where only traces of arsenic are present, for almost all substances which

[1] Parsons and Stewart, *Loc. cit.*

contain arsenic also contain small amounts of iron, and in no case is the zinc used free from iron. For this reason, whenever the Marsh method is used, the conditions should be such as are favorable to the separation of the arsenic from the iron which is always present.

The results of this work should not be understood to mean that the excess potential alone is the determining factor in the reduction, but only that it is one factor. A study of the electrolytic reduction of arsenic and arsenious acids will undoubtedly prove that certain metals of lower excess potential are more efficient cathodes for purposes of reduction than certain other metals of higher excess potential.

It is interesting to note that arsenic itself is a metal of moderately high excess potential, so that, if any arsenic were precipitated upon the zinc, the reducing action of the system would not be materially lessened. The addition of a solution of arsenic to the Marsh generator makes the zinc "active" without the addition of the salt of any other metal.

The fact that the value of the excess potential of the metal added to the generator has an influence upon the reduction, proves that at least one step in the reduction takes place at the surface of this metal, and that at least this part of the reduction is due, therefore, to the hydrogen and not to the zinc.

Summary.

1. The addition of salts of tin, cadmium, lead, or bismuth to the liquid in the Marsh generator makes the zinc "active" without the decrease in reducing power which comes from the platinum or iron commonly added as salts, or as alloys with the zinc.

2. Arsenic may be separated quantitatively from iron and determined in one process by either heating the generator or by adding a salt of one of the metals named above.

3. So far as has been investigated, metals of low excess potential hinder the reduction in the Marsh generator, while metals of high excess potential do not have any injurious action. However, it is not claimed that this will be a perfectly general relation, since the variation of other factors will undoubtedly be great enough to cause exceptions to the general rule.

4. The speed of the reduction of an oxide of arsenic increases with the rapidity of evolution of hydrogen, provided that the latter effect is not due to the addition of a metal of low excess potential; or the speed of reduction depends upon the current density. This is to be expected, since the current density is one factor in determining the electrode potential.

5. The determination of arsenic is made more accurate by the use of a special form of furnace for heating the glass tubes in which the arsenic is decomposed.

6. Since as much as 0.1 gram of metallic arsenic may be separated

from iron and determined quantitatively, this method is applicable to the analysis of ores and other substances containing large amounts of arsenic.

7. The method may also be used for amounts of arsenic as small as 0.001 milligram, but the apparatus must be made much smaller than that described.

STANFORD UNIVERSITY AND THE UNIVERSITY OF MONTANA.

ELECTROLYTIC DETERMINATION OF ZINC.

BY ELLWOOD B. SPEAR, EDWARD E. WELLS AND BRAINERD DYER.

Many methods have been proposed for the electroanalysis of zinc,[1] but unfortunately other experimenters have not always been able to get the degree of accuracy that the advocates of a particular method claim it is capable of giving. One of us, while doing some electrolytic determinations of zinc, invariably got high results by several methods. About the same time a paper appeared by Price[2] in which he stated that the values obtained by all electrolytic methods for zinc are too high. The object of this and the succeeding article was to determine, if possible, the magnitude and cause of the error.

The following methods were investigated:

1. The sodium acetate method.
2. The potassium oxalate method.
3. The sodium, or potassium hydroxide method.

The endeavor was made to follow the directions given in the literature as closely as possible while testing each method. Unfortunately, the instructions are sometimes incomplete, especially with regard to the factors, current density, current in amperes and area of cathode surface. It is not sufficient to give the current density, or the current in amperes alone. Two of these factors should be given from which the third can be calculated.

Over 200 determinations with the above methods have been made and it has been found that when the zinc was completely precipitated the results were invariably too high.

The effect of varying the following factors was also investigated:

1. Nature and concentration of the electrolyte.
2. Form and material of the cathode.
3. Current density.

[1] "Electro-analysis," E. F. Smith. Elektroanalytische Schnellmethoden, Fischer, "Die Chemische Analyse," Band 4–5.
[2] *Chem. News*, **94,** 18 (1906), and **97,** 89 (1908).