

THE EFFECT OF VARIOUS SUBSTANCES
ON THE ELECTROLYSIS OF ZINC

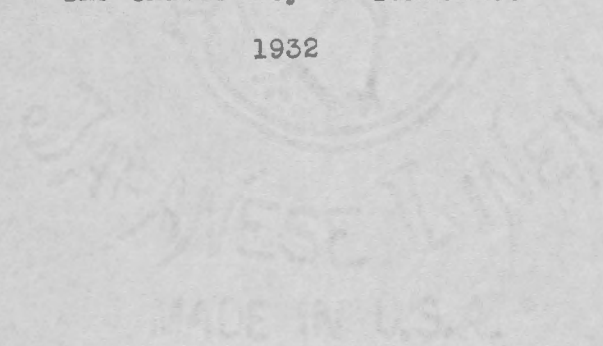
by

C. S. Quillen

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OUTLINE OF PAPER

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INTRODUCTION

The determination of zinc electrolytically is a common method when the percentage of zinc in the sample is small, in which case the method gives accurate results. When the amount of zinc is large, the method of electrolysis has some disadvantages. One disadvantage is that the zinc falls off the electrode after it has been deposited. In an analytical chemistry class at the University of Tennessee, the method of estimating zinc by electrolysis is used. In many cases, even when the percentage of zinc is small, it is difficult to deposit the zinc on the electrode so that it will not fall off before it can be weighed. To improve the situation it is not merely a problem of finding conditions which will result in a firm deposit of the zinc, but the deposition must be quantitative, which means that all the zinc and no interfering substances must deposit.

The purpose of this thesis was to study the electrical deposition of zinc with the view of finding some conditions in which the metal could be made to deposit in a firm, compact form on the electrode.

One method used in electrolysing a zinc solution is to deposit the metal from a solution of double ammonium oxylate.¹ The zinc separates quickly from this solution but it will not adhere to the electrode. The author found that as much as ten

¹ Classen, Quantitative Chemical Analysis by Electrolysis. P 62

per cent of the zinc fell from the electrode after it was deposited.

Beilstein and Jawein precipitated zinc from a solution of potassium zinc cyanide. The solution is treated with NaOH until a precipitate is formed and potassium cyanide is added until it dissolves.¹ The solution is then electrolysed. This method is inconvenient since the solution is heated by the strong electric current which is necessary for reduction and must be kept cool.

Parodi and Mascozzini have a method in which they electrolyse a zinc sulphate solution to which has been added sodium acetate and citric acid.¹ The author found that the zinc deposited with this method was spongy and some of it fell from the electrode.

In the method used at the University of Tennessee, rochelle salts is added to the solution to improve the deposit. This is the method used in various technical laboratories.² The author found that rochelle salts also improved the deposit but that much of the zinc failed to stick to the electrode.

Other methods of electrolysing zinc solutions were not convenient enough for ordinary laboratory procedure. What is needed is a simple procedure which can be carried out in an average laboratory without special equipment or expense. The present study has resulted in finding some conditions which are excellent for the deposition of zinc in a compact form on the electrode.

¹ Classen, Quantitative Chemical Analysis by Electrolysis. P 63

² Petty, C. L. , Commercial Laboratory Notes.

FACTORS AFFECTING THE DEPOSIT

The theory upon which this thesis was worked was that the presence and concentration of certain ions such as SO_4^{--} , Cl^- , Br^- , NO_3^- , CN^- , Na^- , NH_4^- , H^- , OH^- , and K^- will influence the condition and amount of zinc that will deposit on the electrode. The presence of some ions, such as SO_4^{--} , Cl^- , Br^- , and H^- , in the solution ~~to~~ prevents the zinc from depositing on the electrode, while still other ions, such as, CN^- , CH_3COO^- , and ClO_3^- will prevent the zinc from depositing in a firm form. The presence of still other ions, for example, OH^- , Na^- , and K^- , will increase the amount of zinc electroplated and will make the deposit firm and compact. The concentration of zinc ions also affect the form and quantity of the deposit.

When the zinc is in solution, it is partly in the form of zinc ions with a positive charge. When a current is made to pass through this solution which is placed between two electrodes, the zinc ions will migrate to the negative electrode and there, upon coming in contact with the negative pole, give up their positive charge and collect on the electrode as molecules of zinc. All of the zinc in the solution will be deposited in this manner.

The condition of the deposit depends upon several factors besides the presence of other ions. These factors are, temperature, volts and amperes of the current passing through the solution, the acidity and alkalinity of the solution, the concentration of the solution and the size of the electrodes.

In this thesis a study was made of effect of foreign ions, and the acidity and alkalinity of the zinc solution.

APPARATUS

The equipment which was used for this thesis was a variable resistance, a ringstand for holding the electrodes and two sets of platinum electrodes, the surface area of the negative electrode being 6.2832 square inches and perforated with small holes and the positive electrode being a spiral of very heavy platinum wire two inches long and one-fourth inch in diameter. Direct current at two volts was used.

PROCEDURE

We prepared several sample solutions of ZnCl_2 of such strength that each sample had in solution a known weight of zinc. To one sample was added 5 c.c. of HCl in excess. The solution was then diluted to 250 C.C. and electrolysed. A current that evolved 10 c.c. of gas per minute was passed through the solution for five hours, the cylindrical electrode being the negative pole. After electrolysis was completed, the electrodes were raised nearly out of the solution and washed with water with the aid of a wash bottle while the current was still flowing. If the current had been stopped before the electrodes were taken from the solution, some of the zinc would have dissolved from the electrode. After thoroughly washing the negative electrode (on which the zinc had been deposited) with distilled water, it was dried. The appearance of the zinc, as to firmness, compactness, and hardness was noted and the electrode then weighed. The results are given in Table I.

To another sample of known zinc content, we added 110

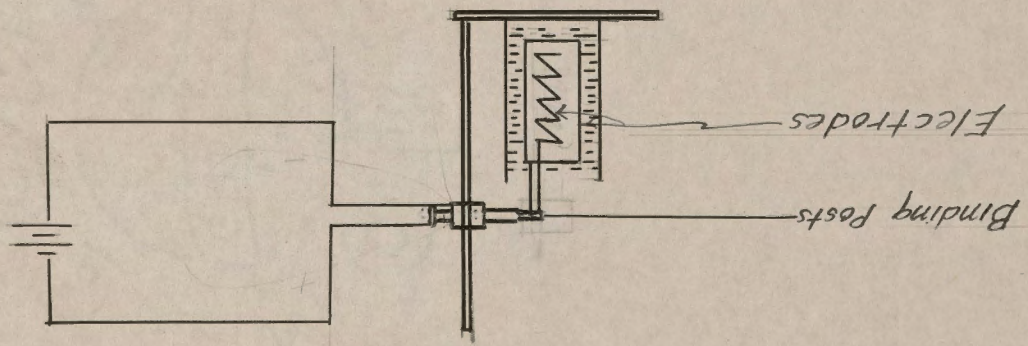


Fig. 1. - Apparatus for Electrolysis of Zinc

c.c. of HCl and electrolysed as before, tabulating all results. To each of eight similar samples there were added respectively 15, 20, 25, 30, 35, 40, 45, 50 c.c. of excess .1N. HCl and the results tabulated as before in Table I. This table shows that as the excess of HCl was increased, the per cent of zinc which deposited on the electrode decreased. A curve was drawn showing the relation between the weight of zinc deposited and the concentration of the acid. A few samples were run in the same way using H_2SO_4 and HNO_3 . These results were tabulated in Table Ib.

Another series of samples was prepared, in which there was a known weight of zinc in each sample. To one sample was added 5 c.c. of concentrated NH_4OH solution and the solution electrolysed as before. The weight of zinc deposited, per cent of zinc and the appearance are given in Table II. To another sample 10 c.c. of NH_4OH was added and the solution electrolyzed, and to each of several other samples the excess of NH_4OH added was increased 5 c.c. for each following sample. Samples were electrolyzed until the per cent of zinc deposited was beginning to decrease with increase in NH_4OH concentration. Figure III shows the relation between the per cent of zinc deposited and the concentration of NH_4OH .

The next work was to determine the effect of other substances on the deposition of zinc. Many substances were recommended by various writers but for different reasons proved to be unsatisfactory. For example Parodi's and Mascazzini's method as explained in the introduction. The effect of Rochelle salts in the solution was first studied. Various weights of Rochelle salts were used and the zinc deposited on the electrode

TABLE I

Effect of HCl on Deposition of Zn

Am't HCl In Excess:	Am't Zn In Sample:	Ions in Sample	Am't Zn Deposited:	Percent: Zn Dep- osited	Appearance of Zn -Remarks
5 cc N	.1 g in 250 cc	ZN,H,Cl	.0980	98	Spongy-Stuck to Electrode
10 cc N	.1 g in 250 cc	"	.0921	92	Spongy- Did not Stick Well
15 cc N	"	"	.0843	84	Loose and Spongy Fell Off Plate
20 cc N	"	"	.0810	81	Loose and Spongy Increase,Falling
25 cc N	"	"	.0750	75	" "
30 cc N	"	"	.0623	62	"
35 cc N	"	"	.0521	52	Very Loose
40 cc N	"	"	.0438	43	"
45 cc N	"	"	.0321	32	"
50 cc N	"	"	.0548	54	"

In every case, all the Zn was removed from the
sample, but it would not stick to the electrode.

TABLE I_b
EFFECT OF ACIDS

Am't of Acid	Am't of Zinc	Ions in Sample	Am't of Zn De- posited	Per cent of Zn Deposited	Appearance of Zinc
10 cc N HNO ₃	.05	Zn, Cl, H, NO ₃	.0341	68.2	Soft and Spongy
20 cc N HNO ₃	.05	"	.0219	43.8	"
30 cc N HNO ₃	"	"	.0198	39.6	Most of Zn fell off
10 cc N H ₂ SO ₄	"	Zn, Cl, H, SO ₄	.040	80	Spongy
20 cc N H ₂ SO ₄	"	"	.0376	75.2	"
30 cc N H ₂ SO ₄	"	"	.0339	67.8	"

UNIVERSITY OF TENNESSEE

LABORATORY

DATE

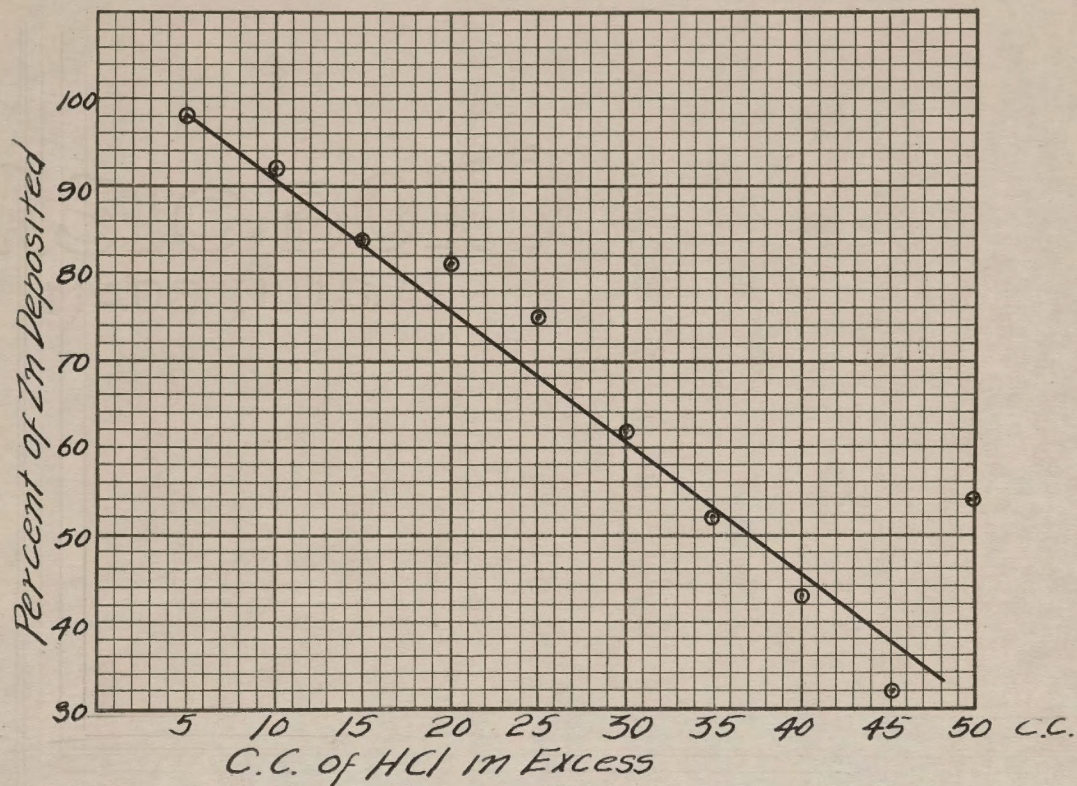


FIG. NO. 1

TITLE:-

*Curve Showing Relation Between C.C. of HCl
and Percent of Zn Deposited*

INTERPRETATION OF CURVES

TABLE II

Effect of Ammonia on Deposition of Zn

Am't HCl In Excess cc	Am't Zn :In Sample:	Ions in Sample	Am't Zn : Deposited:	Percent Zn Dep- osited :	Appearance of Zn - Remarks
5	: .05 g in: 250 cc :	OH, Zn, Cl: NH ₄ :	.0392	78.2	Spongy
10	"	"	.0381	76.2	Slightly Spongy
15	"	"	.0395	79	Slightly Firm
20	"	"	.0401	80.2	Firm
25	"	"	.0446	89.2	"
30	"	"	.432	96.4	"
35	"	"	.0491	90.2	Smooth and hard
40	"	"	.0459	91.8	"
50	"	"	.0471	94.2	"
55	"	"	.0488	97.6	"
60	"	"	.0491	98.2	"
65	"	"	.0495	99	"
70	"	"	.0481	95.2	"
75	"	"	.0475	95	"
80	"	"	.0469	93.8	"

Specific Gravity of Ammonia was .9 - The Zn stuck to the Electrodes fairly well. In the strongly Ammonical solutions, the Zn deposit was firm, smooth and compact, and none of the Zn fell off. The Solutions were diluted to 250 cc.

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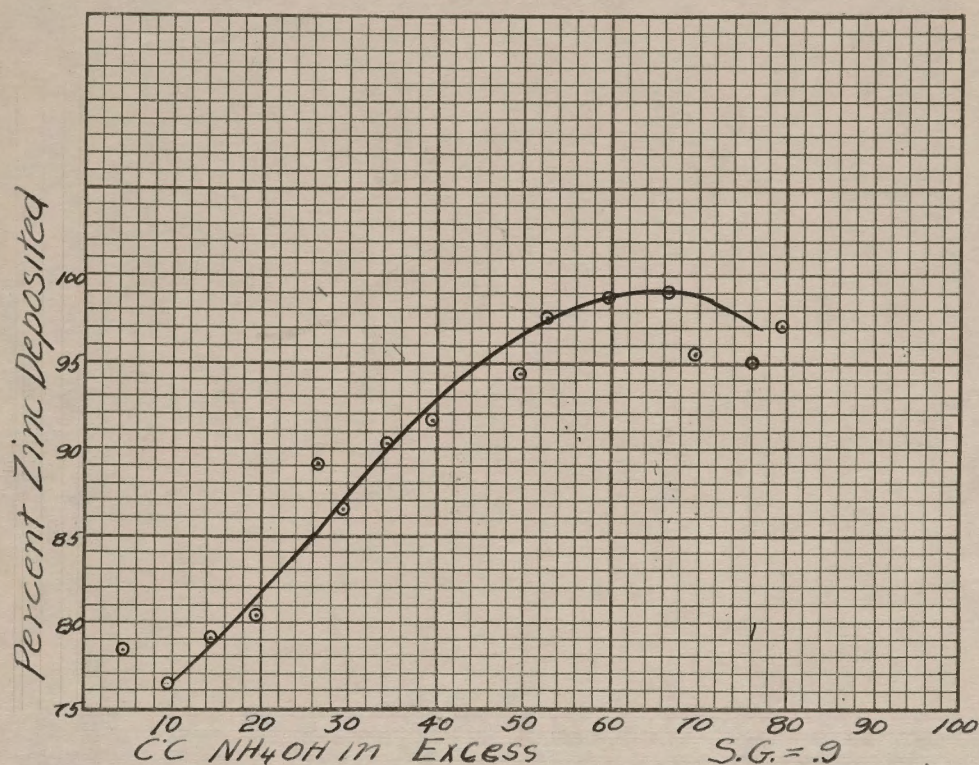


FIG. NO. 3

TITLE:-

Curve Showing Relation Between C.C. NH_4OH in Excess and Weight or Percent of Zn Deposited

INTERPRETATION OF CURVES.

Curve Shows that Highest Percent of Zn Was Deposited With an Excess of 60 C.C. of NH_4OH S.G. = .9

TABLE III

Effect of Rochell Salts and NH_4Cl

Am't Base; or Acid	Am't of :Other Salts:	Am't Zn In: Sample	Am't of Zn :Deposited	Per Cent : of Zn	Appearance of :Zn - Remarks
5 ccN HCl	3.0 g Rochell	.0500 ^g	.0241	48.2	Spongy and soft
10 ccN HCl	5.0 g Rochell	"	.0219	42	"
5 ccN HCl	3.0 g NH_4Cl	"	.0056	11.2	"
5 ccN HCl	5.0 g NH_4Cl	"	None		
Neutral	5.0 g NH_4Cl	"	.0328	75.6	Loose
5 ccN NH_4OH S.G. 9	3.0 g NH_4Cl	"	.0442	88.4	"
10 cc NH_4OH	3.0 g NH_4Cl	"	.0446	93.2	Firm
15 cc NH_4OH	5.0 g NH_4Cl	"	.0481	96.2	"
20 cc NH_4OH	8.0 g NH_4Cl	"	.0483	96.6	"
25 cc NH_4OH	5.0 g NH_4Cl	"	.0482	96.4	"
30 cc NH_4OH	"	"	.0476	95.2	"
5 cc NH_4OH 1	5.0 g Rochell	"	.0491	98.2	"
10 cc NH_4OH 15 cc	5.0 g Rochell	"	.0499	99.8	"
NH_4OH	5.0 g Rochell	"	.0472	94.4	Compact
20 cc NH_4OH	5.0 g Rochell	"	.0479	95.8	"
25 cc NH_4OH	5.0 g Rochell	"	.0486	97.2	"
30 cc NH_4OH	5.0 g Rochell	"	.0471	94.2	"

as before. From a study of the data collected. It was seen that the highest per cent of zinc was deposited when the weight of the Rochelle salts was 5 grams for .05 grams of zinc in the sample.

Samples were now run with different weights of NH_4Cl . in various concentrations of NH_4OH . We found that the best results were obtained when eight grams of NH_4Cl and 20 c.c. of NH_4OH were used for a sample containing .05 grams of zinc.

The next work done was on solutions containing a mixture of NH_4Cl and Rochelle salts. Samples with various weights of these two salts and with various concentrations of NH_4OH (S.G. .9) were electrolyzed. The results are tabulated in Table IV. From a study of this table it is seen that the best results were obtained with a mixture of 6 grams NH_4Cl and 12 grams of Rochelle salts. In the table it will be seen that gum arabic, which was recommended by some writers, was used but under the conditions in which we used it, the results were unsatisfactory.

CONCLUSION

From a study of the data collected for this thesis, it will be seen that alkalinity and acidity, and the presence of various substances have a marked effect upon the deposition of zinc. The results show that for .05 grams of zinc in solution that 6 grams of Rochelle salts, 12 grams of NH_4Cl and 30 c.c. of NH_4OH (S.G. .9) will give the best and most complete deposition of zinc of the various conditions studied. In quantitative analysis then when the solution contains these substances the estimation of zinc by electrolysis will be accurate for all practical purposes.

TABLE IV

Effect of Various Substances on Deposition of Zn

Am't NH_4OH : Am't of : W't of Zn : W't of Zn : Per cent : Appearance
 In Excess : Other Sub.: in Sample : Deposited: of Zn : of Zn.
 S.G - .9

25 cc	3 g NH_4Cl 3 g Rochell	.0500	.0482	96.4	Compact
25 cc	5 g NH_4Cl 5 g Rochell	.0500	.0489	97.8	"
30 cc	10 g NH_4Cl 10 g Rochell	.0500	.0472	94.4	"
30 cc	10 g NH_4Cl 5 g Rochell	.0500	.0482	96.4	"
30 cc	5 g NH_4Cl 10 g Rochell	.0500	.0492	98.4	"
30 cc	6 g NH_4Cl 12 g Rochell	.0500	.0499	99.8	"
30 cc	6 g NH_4Cl 12 g Rochell	.0500	.0492	98.4	"
35 cc	6 g NH_4Cl 12 Rochell	.0500	.0499	99.8	"
45 cc	6 g. NH_4Cl 12 Rochell	.0500	.0487	97.4	"
10 cc	2 g Gum - Arabic	.0500	.0412	82.4	Firm and Compact
10 cc	3 g Gum- Arabic	.0500	.0314	72.8	Firm
20 cc	5 g Gum- Arabic	.0500	.0216	43.2	Firm
10 cc	3 g $(\text{NH}_4)_2\text{SO}_4$	.0500	.0481	96.2	"
20 cc	5 g $(\text{NH}_4)_2\text{SO}_4$	.0500	.0494	98.8	"

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Results from Parodi's and Mascazzini's Method

Weight of Zn in Solution	.05
Weight of Zn Deposited	.0427
Appearance of Zinc	Soft and Spongy
Per Cent of Zinc Deposited	85.4

APPROVAL

The foregoing thesis is hereby approved as a credit-
able study of an engineering subject, carried out and pre-
sented in a manner sufficiently satisfactory to warrant
its acceptance as a prerequisite to the degree for which
it has been submitted. It is to be understood that by
this approval the undersigned does not necessarily en-
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only for the purpose for which it is submitted.

Name

Judson H. Robertson

Title

Prof. of Chemistry