

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## A REVISION OF THE ATOMIC WEIGHT OF ZINC. II.

### The Electrolytic Determination of Zinc in Zinc Chloride.

By GREGORY PAUL BAXTER AND JAMES HALLETT HODGES.

Received March 18, 1921.

In a recent paper Baxter and Grose<sup>1</sup> have described the electrolytic determination of the zinc in zinc bromide by deposition in a weighed mercury cathode. The atomic weight of zinc calculated from the results of this work, 65.388, agrees very well with the outcome of Richards and Rogers's<sup>2</sup> comparison of zinc bromide and silver, 65.376. Since zinc composes very nearly one half of zinc chloride, the latter substance is better suited than zinc bromide for the purpose in question. On the other hand the preparation of zinc chloride in an anhydrous condition and free from basic chloride is an unusually troublesome process. The difficulty was overcome, however, by first preparing anhydrous zinc bromide, and then converting this salt into the chloride by heating it in a current of chlorine. The result of the electrolytic analysis of the salt is in accord with the atomic weight of zinc as determined by the analysis of the bromide.

### Purification of Reagents.

Water, nitric acid, sulfuric acid, alcohol and mercury were purified as described by Baxter and Hartmann.<sup>3</sup> Bromine was freed from impurities by the processes used by Baxter and Grover,<sup>4</sup> and from the pure bromine, hydrogen bromide and its solution were prepared by synthesis with pure electrolytic hydrogen in the same way and with the identical apparatus employed by Baxter and Grover.

### The Preparation of Zinc Bromide.

Since the zinc chloride was prepared from the bromide, the purification of the various samples of the latter substance will be described first.

Sample A.—This specimen was prepared by the method used by Baxter and Grose.<sup>5</sup> Crude stick zinc was electrolytically transported through a concentrated solution of zinc bromide. The resulting crystalline sponge was washed many times with water and then leached for a week in a very dilute solution of hydrobromic acid. After another thorough washing the metal was dissolved by covering it with dil. hydrobromic acid in a quartz flask and slowly adding pure bromine. During this operation the flask was cooled with running water to prevent undue rise of temperature.

Since Baxter and Grose found electrolysis effective in removing iron, but not cadmium and lead, the solution was allowed to stand with an excess of zinc for 3 months with occasional shaking, in order to precipitate, in part at least, the above metals as well as others of smaller solution tension than zinc.

<sup>1</sup> Baxter and Grose, *THIS JOURNAL*, **38**, 868 (1916).

<sup>2</sup> Richards and Rogers, *Proc. Am. Acad.*, **31**, 158 (1895).

<sup>3</sup> Baxter and Hartmann, *THIS JOURNAL*, **37**, 120 (1915).

<sup>4</sup> Baxter and Grover, *ibid.*, **37**, 1029 (1915).

<sup>5</sup> *Loc. cit.*

After removal of the excess of zinc and the very considerable amount of basic salt which had formed during the long standing, by filtration through a platinum-sponge crucible supported in a platinum funnel, the solution was subjected to a prolonged process of fractional crystallization. Only platinum vessels were used and the crystals were centrifugally drained in platinum Gooch crucibles.

Zinc bromide prepared in this way, after fusion in a dry atmosphere containing pure hydrogen bromide, yields a small quantity of black insoluble matter, chiefly carbon and silica;<sup>1</sup> hence in order to eliminate this impurity the purest fractions of salt were fused in platinum boats contained in a quartz tube, in a current of nitrogen and hydrogen bromide gases. Solution and filtration through a platinum-sponge crucible removed the insoluble residue. The filtrate was slightly yellow but a second series of fractional crystallizations removed the color rapidly. The final product was preserved in a quartz dish over fused sodium hydroxide. Baxter and Grose found material prepared in a similar way to contain only the merest trace of cadmium.<sup>2</sup>

Sample B was prepared in exactly the same manner as Sample A except that the black residue was eliminated by distilling the zinc bromide from the residue shortly before use. This was done by first drying the salt by fusion in hydrogen bromide as described above. Next the boat with the dried salt was removed from the quartz tube and the tube thoroughly cleaned. Then the boat and contents were replaced in the tube and the bromide was distilled from the boat into the tube. Finally the salt was melted in the tube to facilitate removal. Salt prepared in this way was free from black residue and remained so if fused again preparatory to analysis, provided the salt had not in the meantime been exposed to even extremely dilute vapors of organic substances. Sample B, for instance, which was preserved in a highly exhausted desiccator for several months, upon fusion yielded traces of black residue, although when prepared it must have been free from this impurity. One specimen of Sample C was kept in a desiccator for 4 days only, but yielded traces of the impurity. The grease used for making the desiccators tight was composed of three parts of vaseline to one of beeswax. While dust may account for a part of this difficulty, the above evidence, together with somewhat similar experience with other substances, leads us to the opinion that the desiccator grease is, in part at least, responsible.

Sample C of zinc bromide was purified in quite a different fashion. Crude metal was distilled in a high vacuum in a hard glass tube divided into sections by constrictions. First, about ninety per cent. of the crude material was distilled from the end section of the tube to the second section. Spectroscopic examination of the residue and distillate in a Féry quartz spectrograph showed that all the iron and the greater part of the lead remained in the residue, while the cadmium and a trace of lead were contained in the distillate. Without opening the tube the distillate was heated until about a quarter had evaporated. Nearly all the cadmium was thus removed. The residual button was then heated in a clean tube until about a quarter had evaporated, and with some samples the latter process was repeated. Spectrograms made with this material did not show the cadmium line  $\lambda$  3610, although the line  $\lambda$  2288 could be faintly seen. Finally the button was distilled with rejection of the least volatile tenth in order to eliminate traces of lead.

To convert the metal to bromide the button was placed in a quartz boat contained in a quartz tube and was heated, in a current of hydrogen bromide, to a temperature slightly above the melting-point of zinc. At this temperature zinc bromide formed and distilled rapidly from the metal. Although the boat was badly etched in this process, possibly by the action of basic salt, the tube remained unattacked. Neverthe-

<sup>1</sup> Baxter and Hartmann, *loc. cit.*, p. 121; Baxter and Grover, *loc. cit.*, p. 1040.

<sup>2</sup> *Loc. cit.*, p. 869.

less the salt was a second time distilled from a platinum boat into the quartz tube. Because it was inconvenient to carry on the above processes with large quantities of material, a new preparation was made for each analysis.

### The Preparation of Zinc Chloride.

Since zinc chloride hydrolyzes very readily to form basic salt, and since the latter substance cannot be converted to neutral chloride by heating or even fusion in an atmosphere of hydrogen chloride, a method of preparation is necessary which protects the salt from moisture from the time it is formed. To be sure Lorentz<sup>1</sup> and Czepinski<sup>2</sup> claim to have prepared neutral anhydrous salt by electrolysis of fused material. Baxter and Lamb<sup>3</sup> overcame the difficulty by heating the anhydrous double ammonium chloride,  $ZnCl_2 \cdot 3NH_4Cl$ , until the ammonium salt was vaporized. A large portion of the zinc chloride is, however, lost by evaporation during the prolonged heating which is necessary. Displacement of the bromine in anhydrous zinc bromide by fusion in a current of dry chlorine<sup>4</sup> proved to be a somewhat better solution of the problem, although the loss of material by this method also is considerable.

The chief difficulty met in the conversion of the bromide to chloride lay in the fact that the zinc chloride is considerably less dense than the bromide, and that as soon as a considerable quantity of the chloride has been produced it constitutes a protective layer above the unchanged bromide, thus retarding the progress of the conversion. This difficulty was obviated by stirring the fused salt during the operation. To do this one end of the fusion tube was attached to a peg located on the rim of a slowly revolving wheel, so that the end of the tube was alternately raised and lowered. The flow of the liquid from one end of the boat to the other accomplished the desired end. Three hours, fusion in chlorine was found sufficient to convert from 10 to 20 g. of bromide to chloride.

The complete fusion process was as follows. A quartz boat was filled with bromide and placed in a quartz fusion-tube, which formed part of a Richards and Parker bottling apparatus, together with the weighing bottle and stopper in which the boat had been initially weighed. After the tube had been swept out with nitrogen which had been charged with hydrogen bromide by bubbling through a nearly saturated solution of the gas,<sup>5</sup> the boat was gradually heated until the bromide was fused, and the temperature was maintained at this point for 10 minutes. Without allowing the bromide to cool, the current of hydrogen bromide was cut

<sup>1</sup> Lorentz, *Z. anorg. Chem.*, **10**, 85 (1895).

<sup>2</sup> Czepinski, *ibid.*, **19**, 228 (1899).

<sup>3</sup> Baxter and Lamb, *Am. Chem. J.*, **31**, 229 (1904).

<sup>4</sup> Baxter and Hartmann used a similar method for preparing cadmium chloride, *loc. cit.*, p. 122.

<sup>5</sup> The apparatus used by Baxter and Grover was employed. *Loc. cit.*, p. 1035.

off and a stream of dry chlorine together with a small proportion of hydrogen chloride was admitted. Although visible evidence of bromine in the gaseous products ceased after about half an hour, fusion in hydrogen chloride was continued for about one-half hour more in order to eliminate dissolved chlorine from the salt. The chloride was allowed to solidify in an atmosphere of hydrogen chloride, then the latter gas was displaced by nitrogen and this in turn by air before the boat was transferred to the weighing bottle and weighed. On account of the strongly hygroscopic nature of the salt it was always weighed within 2 hours of the time it was transferred to the desiccator, although there never was any evidence that it was absorbing moisture. If the fused salt was cooled rapidly it was glassy in appearance, but if cooled slowly it became crystalline.

The apparatus for generating and purifying the gases used during the fusion was constructed almost entirely of glass with fused or ground joints, and was connected through grids of glass tubing which furnished the necessary flexibility. A few short rubber connections were used at the beginning of the apparatus for preparing hydrogen and nitrogen. Hydrogen bromide was prepared synthetically from the elements as described by Baxter and Grover.<sup>1</sup> Chlorine was generated by the action of conc. hydrochloric acid on manganese dioxide, and after scrubbing with water was dried by conc. sulfuric acid and resublimed phosphorus pentoxide.<sup>2</sup> Hydrogen chloride was formed by dropping conc. sulfuric acid into conc. hydrochloric acid in the usual way and was dried by means of conc. sulfuric acid only. Nitrogen was prepared from air and ammonia by the Wanklyn process, and was purified and dried as described by Baxter and Grover.<sup>3</sup> Air was purified and dried as described by the latter. The different parts of the system could all be swept out thoroughly before the gases were admitted to the fusion tube. Grease was used only on the stoppers of the air apparatus. Sulfuric acid was used to lubricate the stoppers of the sulfuric acid purifying columns, but stopcocks were selected for tightness and were used dry.

Zinc chloride prepared in this way dissolves without turbidity. A solution of the fused material was compared with that of a similar solution of salt which had been three times recrystallized from a solution containing a slight excess of hydrochloric acid, by adding methyl red and methyl orange to different portions. The two solutions appeared to be identical in acidity. Comparison with standard solutions of different hydrogen-ion concentrations showed this quantity to be between  $10^{-5}$  and  $10^{-4}$ , but this absolute value has little significance, since the concentration of the solution was not recorded.

Occasionally samples were obtained which when dissolved and electrolyzed obviously contained unchanged bromide, for bromine was liberated in the process. In general such material was rejected. One specimen which contained a barely perceptible amount of bromide, upon analysis yielded a value for the atomic weight of zinc 0.03 unit lower than the

<sup>1</sup> *Loc. cit.*, pp. 1030, 1036.

<sup>2</sup> Baxter and Moore, *THIS JOURNAL*, **34**, 1645 (1912).

<sup>3</sup> *Loc. cit.* p. 1037.

average. There is no positive evidence, however, that the average is not somewhat affected from the same cause.

### The Electrolytic Method.

The type of electrolytic cell devised by Baxter and Hartmann<sup>1</sup> was used throughout the work. The method and new precautions necessary in using such a cell are discussed in the paper preceding this one by Baxter and Wilson on the electrolytic analysis of cadmium sulfate. In fact the two researches were carried on side by side for a large portion of the time and were mutually helpful. The procedures in the two cases differed only in minor details, and similar irregularities were observed.

It was found, for instance, that if the cell containing mercury only was used for the electrolysis of a dilute acid solution, a slight loss in the weight of the cell was observed, but the electrolyte upon evaporation with sulfuric acid was found to yield a non-volatile residue. In one experiment a residue somewhat larger than usual, weighing 1.0 mg. was extracted with dil. sulfuric acid, and lost in weight 0.8 mg. No change in weight was observed upon evaporation with hydrofluoric and sulfuric acids. Since the material was extracted from the glass of the cell and apparently contained no silicic acid, it evidently was composed of sodium and calcium sulfates. If a correction is applied upon the assumption that sodium and calcium oxides were dissolved from the glass, only small changes in weight of the cell are observed.

The following table gives the results of experiments in which cells containing mercury only were several times used for the electrolysis of dilute acid. Hydrochloric acid was used in every case and electrolysis was continued until chlorine ceased to be evolved at the anode. The residual electrolyte was then perchloric acid. After each electrolysis the residue was dissolved in hydrochloric acid and returned to the cell for the next electrolysis. About 0.07 mg. of the observed gain in weight in each electrolysis was traced to the use of rinsing water which had been standing for sometime in a resistance-glass bottle, so that the actual gain is no larger than the error of weighing the cells. In all later experiments the rinsing water was freshly distilled into a quartz flask.

TABLE I.

Weight of cell. G.	Weight of residue. G.	Corrected weight of cell. G.	Gain or loss. G.
0.77106	.....	.....	.....
0.77113	0.00049	0.77134	+0.00028
0.77081	0.00069	0.77111	+0.00005
0.97554	.....	.....	.....
0.97549	0.00031	0.97562	+0.00008
0.97552	0.00049	0.97573	+0.00019
0.97545	0.00101	0.97589	+0.00035
0.98006	.....	.....	.....
0.97992	0.00048	0.98013	+0.00007
0.97965	0.00078	0.97999	-0.00007

The electrolytic method for determining zinc was tested in several ways. A clean zinc button was prepared by melting the best c. p. zinc in a current of hydrogen on an alundum boat and allowing it to flow from one end of the boat to the other where it was allowed to solidify. This button was dropped into the mercury in a weighed cell

<sup>1</sup> *Loc. cit.* p. 123.

and the system was weighed. Dil. hydrochloric acid was then added and electrolysis carried on until the hydrochloric acid was completely decomposed. The cell was rinsed and the amalgam dried in vacuum, while the electrolyte was evaporated to dryness and the residue was gently ignited and weighed. The correction for the residue was computed on the assumption that it was zinc sulfate. Since the percentage of sodium oxide in sodium sulfate is very nearly the same as the percentage of zinc in zinc sulfate the fact that the residue consisted in part of material extracted from the glass is of little consequence. (Expt. 1). In another similar experiment (Expt. 2) a piece of c. p. zinc was merely etched and dried. For all succeeding experiments zinc was purified by distillation in a vacuum. Expts. 7 and 8 were like Expts. 1 and 2 except that electrolysis was once repeated, and that the cell and button were weighed together both before and after the button had been dropped into the mercury.

In Expts. 3, 4, 5, 6 and 9 the button was placed in a platinum-gauze basket supported on the anode of the cell preparatory to the initial weighing, then, after the addition of acid, the metal was electrolytically transported to the cathode and the amalgam was washed and dried. This method duplicates most closely the procedure in the electrolytic determination of zinc in the chloride. Alcohol was used in the final rinsing of the cell, except in Expts. 5 and 6 when ether was employed. After the first weighing of the amalgam and residue, hydrochloric or sulfuric acid was added and electrolysis was repeated.

As in the case of similar experiments with cadmium discussed in the previous paper, the weight of the amalgam corrected for the residue is slightly greater than the weight of the components. In general a second electrolysis does not diminish this excess although losses occasionally appear in a second repetition. At the time this work was done the loss of mercury from the cell during the rinsing, described in the preceding paper, was not suspected. This undoubtedly accounts for the later losses. In the experiments with cadmium the first two electrolyses with each button were usually not affected by this loss, so that this is likely to have been the case in the experiments with zinc. At any rate these experiments with zinc buttons are comparable with the electrolytic determination of zinc in the chloride, to be described later, and the latter experiments are unquestionably subject to an error of similar sort and magnitude. On an average in Expts. 3, 4, 5, 6 and 9 the initial excess of products is 0.00023 g. This quantity therefore has been subtracted later from the initial weight of amalgam obtained from the electrolysis of zinc chloride.

As in the case of cadmium<sup>1</sup> the volume of liquid amalgam is less than the sum of the volumes of the components. Therefore in comparing the amalgam with components a small negative correction must first be applied to the weight of the amalgam.

	Specific Gravity.	Volume.
2.22 g. Zinc.	7.15	0.31 cc.
100.0 g. Hg.	13.53	7.39
		Sum 7.70 cc.
102.22 g. HgZn.	13.34 <sup>2</sup>	7.66
		0.04

$$0.04 \times 1.2 \text{ mg.} = 0.048 \text{ mg.}$$

$$\text{Correction per gram of zinc in amalgam} = - 0.022 \text{ mg.}$$

Since Richards and Lewis<sup>3</sup> found that saturated zinc amalgam has very nearly the

<sup>1</sup> See preceding paper.

<sup>2</sup> Richards and Lewis, *Proc. Am. Acad.*, **34**, 98 (1898).

<sup>3</sup> Richards and Lewis, *Proc. Am. Acad.*, **34**, 98 (1898).

same potential as pure zinc, the solid which separates when excess of zinc is deposited in the amalgam must be nearly if not quite pure zinc and therefore requires no correction. Saturated zinc amalgam contains a little over 2 g. of zinc in 100 g. of mercury, the approximate weight of the latter substance contained in the electrolytic cell; therefore a uniform correction of  $-0.04$  mg. has been applied to the weight of each amalgam.

As in the case of cadmium discussed in the preceding paper the cause of this excess in weight could not be discovered. The water, acid and alcohol used in the course of the experiments were found to be free from non-volatile material. The column of bulbs<sup>1</sup> inserted in the cell during electrolysis to catch spray was weighed before and

TABLE II.

Expt.	Weight of Zn	Weight of	Weight of	Weight of	Corrected	Gain or loss.
	button.	cell + mer- cury + Zn button.	cell + amalgam.	residue.	weight of cell + amalgam.	
	G.	G.	G.	G.	G.	G.
1.	1.8	1.97234	1.97109	0.00142	1.97163	-0.00071
2.	5.0	5.17091	5.17097	0.00038	5.17109	+0.00018
3.	2.7	3.94192	3.94193	0.00058	3.94212	+0.00020
			3.94182	0.00136	3.94233	+0.00041
			3.94126	0.00182	3.94196	+0.00004
4.	5.7	6.78141	6.78133	0.00106	6.78172	+0.00031
5.	2.6	3.95759	3.95773	0.00062	3.95794	+0.00035
			3.95755	0.00096	3.95790	+0.00031
			3.95753	0.00162	3.95815	+0.00056
6.	7.9	8.85610	8.85621	0.00057	8.85640	+0.00030
			8.85597	0.00096	8.85632	+0.00022
			8.85582	0.00093	8.85616	+0.00006
7.	2.7	3.68821	3.68829	not electrolyzed		
			3.68821	0.00023	3.68826	+0.00005
			3.68805	0.00068	3.68829	+0.00008
8.	3.1	4.83118	4.83118	not electrolyzed		
			4.83124	0.00054	4.83142	+0.00024
			4.83081	0.00042	4.83094	-0.00024
9.	2.0	4.24578	4.24564	0.00047	4.24579	+0.00001
			4.24537	0.00067	4.24560	-0.00018
			4.24502	0.00057	4.24521	-0.00057

after one experiment and found to have lost no weight. Moreover the cell when electrolyzed with mercury only shows practically no gain. Oxidation of the amalgam during washing and drying would be a more probable explanation if there were visible evidence of such an effect. But the amalgams possessed a bright appearance which is hardly to be expected if each one contained over a milligram of zinc oxide necessary to explain the excess. Trapping of electrolyte under or in the amalgam is a no more probable explanation, both because the electrolyte was a very dilute acid solution at the close of an electrolysis and because every effort was made to dislodge trapped material by gentle but thorough agitation of the amalgam during electrolysis and washing and during the drying of the amalgam in vacuum.

However, the close concordance of the blank runs with zinc metal, with respect to the excess in weight of products, affords a fairly secure basis for correcting the weights of zinc obtained in the analyses of zinc chloride. Therefore a negative correction of 0.23 mg. is applied in all such experiments.

<sup>1</sup> Baxter and Hartmann, *loc. cit.*, p. 123.

In many experiments a loss in weight set in after the first or second electrolysis, the source of which was not easy to detect. Ultimately this loss was found to be due to two different causes. One, discovered in collaboration with Wilson,<sup>1</sup> lay in the evaporation of mercury with the residual alcohol during the drying of the amalgam. Since the amalgam was freed from all but a fraction of a cubic centimeter of alcohol before it was placed in the vacuum desiccator, the difficulty from this source could not have exceeded 0.05-0.07 mg. The other source of loss was found by Wilson to be due apparently to imperceptible emulsification of the amalgam with the washing liquids and volatilization of mercury or mercury salts during evaporation of these washings. Wilson's experiments seem to indicate that this difficulty increases with subsequent electrolyses and that it exists to only a slight extent if at all in the initial electrolysis. In any case, although the experiments described in this paper were completed before the discovery of the last difficulty, since the blank runs with zinc metal were carried out in a fashion identical with the analyses of zinc chloride, the error must have been very nearly compensatory in the two cases.

### The Analysis of Zinc Chloride.

The procedure in the analysis of zinc chloride did not differ materially from that in the comparative experiments with zinc metal. After the salt and cell had been weighed the boat was carefully placed in the cell and was covered with water, usually rinsings of the weighing bottle. Electrolysis followed until chlorine ceased to be evolved. The cell was then rinsed and the amalgam and electrolyte treated as already described.

Table II contains the results of all the analyses of zinc chloride. The usual precautions necessary in exact weighing were taken. Weights were compared by substitution according to Richards,<sup>2</sup> the standardization and all weighings being made with a Troemner No. 10 balance. The weighing bottle with boat, electrolytic cell, and platinum crucibles were all weighed by substitution for similar counterpoises, of very nearly the same weight, shape and size. A vacuum correction of +0.27 mg. is applied for every gram of zinc chloride. This is computed from the density 2.907<sup>3</sup> for zinc chloride, 8.3 for the brass weights and 0.0012 for air. The vacuum correction for zinc dissolved in mercury, computed from the density of saturated zinc amalgam as found by Crenshaw, 13.343,<sup>4</sup> is only +0.003 mg. per gram and is neglected. This amalgam contains 2.22 g. of zinc in 100 g. of mercury. Since about 100 g. of mercury was used as cathode in each experiment, the amalgam never contained more than one g. of solid. If the solid is assumed to be zinc of density 7.15, the correction to vacuum per gram is +0.02 mg. A correction of this magnitude is applied to the weight of zinc in excess of 2.2 g.

<sup>1</sup> See preceding paper.

<sup>2</sup> Richards, *This Journal*, **22**, 144 (1890).

<sup>3</sup> Baxter and Lamb, *Am. Chem. J.*, **31**, 229 (1904).

<sup>4</sup> *Loc. cit.*



In the column headed "Corrected weight of zinc" are given the weights of zinc corrected by adding the weight of residue multiplied by the proportion of zinc in zinc sulfate, and by subtracting 0.23 mg. to allow for excess in weight of the amalgam as determined in the blank experiments with zinc metal. The atomic weight of zinc is computed from the weight of zinc after the first electrolysis, except in Analysis 7 where the initial residue was exceptionally large.

## The Atomic Weight of Zinc.

Zn : Cl<sub>2</sub>.

Cl = 35.457.

Anal- ysis.	Sam- ple of ZnCl <sub>2</sub> .	Weight of ZnCl <sub>2</sub> in vacuum. G.	Weight of Zn from amalgam in vac. G.	Weight of residue. G.	Corrected weight of Zn from amalgam in vacuum. G.	Ratio Zn:Cl <sub>2</sub> .	Atomic weight of Zn.
1	A	5.86823	2.81485 2.81499	0.00180 0.00137	2.81536 2.81531	0.92220	65.397
2	A	5.24761	2.51669 2.51671	0.00128 0.00133	2.51698 2.51702	0.92176	65.365
3	A	6.34043	3.04032 3.04092 3.04075 3.04071	0.00273 0.00235 0.00161 0.00184	3.04120 3.04164 3.04117 3.04122	0.92179	65.368
4	B	2.43157	1.16638 1.16631	0.00103 0.00119	1.16657 1.16656	0.92219	65.396
5	B	4.73689	2.27155 2.27143	0.00071 0.00107	2.27161 2.27163	0.92144	65.343
6	C	5.98605	2.87014 2.87013 2.87003 2.86984 2.86976	0.00191 0.00167 0.00169 0.00168 0.00172	2.87068 2.87058 2.87048 2.87029 2.87013	0.92147	65.345
7	C	5.94448	2.84900 2.85138 2.85126	0.00756 0.00053 0.00069	2.85182 2.85136 2.85131	(0.92213 0.92184	65.392) 65.371
8	C	5.80579	2.78351 2.78401	0.00216 0.00073	2.78416 2.78408	0.92141	65.341
9	C	5.87593	2.81859 2.81821 2.81806 2.81781	0.00063 0.00055 0.00054 0.00085	2.81862 2.81820 2.81805 2.81792	0.92193	65.378
10	C	4.00115	1.91965 1.91944 1.91925	0.00081 0.00058 0.00059	1.91975 1.91944 1.91926	0.92234	65.407
11	C	3.51882	1.68790 1.68761	0.00068 0.00045	1.68795 1.68756	0.92194	65.378
Average						0.92185	65.372
Average, rejecting						0.92195	65.379

Analyses 5, 6, 8, 10

In the first two analyses the zinc chloride contained a small quantity of the black insoluble material discussed on p. 1243. This remained chiefly suspended in the electrolyte and was collected on a small weighed platinum-sponge crucible and weighed. The weight was only 0.1 mg. in the first, and 0.7 mg. in the second experiment. In all the succeeding analyses the zinc bromide was initially freed from the residue by distillation. In analysis 8, the solution of the chloride after it had been electrolyzed for an instant, was faintly tinged with yellow, indicating a trace of bromide. The difficulty in detecting this effect leads to the suspicion that Analyses 5 and 6 were similarly affected. In Analysis 10, the quartz boat which remained practically unchanged in appearance and weight through the earlier experiments, was perceptibly attacked, by probably owing to the presence of basic salt. Therefore the average obtained omitting Analyses 5, 6, 8 and 10 is probably more reliable than the average of all the results. The difference is small, however, and judging from the evident difficulty of securing concordant results is within the limit of experimental error.

The agreement of the first average with Richards and Roger's value, 65.376, and with Baxter and Grose's 65.388, indicates very clearly that the atomic weight of zinc cannot be far from 65.38.

The results of this investigation may be summarized as follows.

1. A satisfactory method for preparing pure anhydrous zinc chloride has been devised. This consists in first dehydrating zinc bromide and then converting the bromide to chloride in a current of dry chlorine.

2. The percentage of zinc in zinc chloride has been found to be 47.970, and the atomic weight of zinc 65.38.

We are very greatly indebted to the Bache Fund of the National Academy of Sciences and to the Elizabeth Thompson Science Fund for generous assistance in providing the necessary special apparatus.

CAMBRIDGE 38, MASS.

---

[CONTRIBUTION FROM THE PALMER PHYSICAL LABORATORY OF PRINCETON UNIVERSITY.]

## STATISTICAL MECHANICS AND CHEMISTRY.

BY E. P. ADAMS.

Received March 23, 1921.

In the last few years many attempts have been made to apply the quantum theory to problems of chemical dynamics. Some of these applications have made use of a quantum theory in a rather more definite form than has been found necessary in the physical applications where the theory has had much success. If the laws of chemical dynamics are found to be consistent with the principles of statistical mechanics it would seem to be not only unnecessary, but unjustifiable, to introduce the quantum theory in order to derive these laws. That the quantum theory is of importance in general chemical theory is probable; neither statistical mechanics nor the first two laws of thermodynamics give any information as to the constants which enter into the various thermodynamic functions. These constants depend upon the behavior of systems at or near the absolute zero of temperature, and it is in this region that the quantum theory has