

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

ATOMIC WEIGHT OF CADMIUM.

By G. A. HULETT AND E. L. QUINN

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In an article on the atomic weight of cadmium, Baxter and Hartman¹ obtained the value 112.417 and call attention to the disagreement between this result and that obtained by Perdue and Hulett², Laird and Hulett,³ and Quinn and Hulett,⁴ where the value 112.3 was obtained by three independent methods.

Baxter and Hartman have pointed out some possible sources of error in our work which we think should receive some attention. In the last article we analyzed cadmium chloride by depositing the cadmium electrolytically in a mercury cathode. This was done in order to avoid the inclusions which are always present in electrolytic deposits and very pronounced in the case of cadmium—we have found as much as 0.085%—but when the metal was dissolved in a mercury cathode, there were no inclusions.

Baxter and Hartman have also analyzed cadmium chloride by depositing the cadmium electrolytically in a mercury cathode which was in a glass cell with a sealed-in platinum anode. These workers were unable to obtain all of the cadmium in a weighable form in their cell, and so made a correction for the cadmium in the electrolyte and wash-waters. Therefore, they suspected that we overlooked cadmium in our electrolyte and wash-water. We concentrated our electrolyte and wash-water to a small volume, but were unable to find cadmium, but Baxter and Hartman make the objection that we must have had a strong acid solution in our test. This, however, was not the case, as we evaporated the electrolyte and wash-waters in a platinum dish and heated until the fumes of sulfuric acid ceased; the residue was then taken up with a very little water and tested in a volume of 1 cc. with hydrogen sulfide. Comparisons were made with known amounts of cadmium in the same volume. There may, however, have been a trace of acid in our tests, as we did not endeavor to expel the last trace of acid. So some special tests have been made by one of us (Quinn), in regard to this point. A volume of liquid equal to the electrolyte and wash-water and containing 1½ cc. of strong sulfuric acid was evaporated with known amounts of cadmium sulfate, and the acid expelled just as in our previous work. The following amounts were taken:

1. 0.0002; 2. 0.0001; 3. 0.00005; 4. 0.00001 g. of cadmium.

¹ THIS JOURNAL, 37, 113.

² J. Phys. Chem., 15, 1579.

³ Trans. Am. Electrochem. Soc., 22, 385.

⁴ J. Phys. Chem., 17, 780.

The first three tests showed cadmium at once, and smaller amounts in time. In addition to this, some tests were made with known amounts of acid present. On using an 18% solution of sulfuric acid with known amounts of cadmium, as follows:

1. 0.00007; 2. 0.00006; 3. 0.00005; 4. 0.00004 cadmium in 1 cc. acid.

The first three were detected at once, by the aid of hydrogen sulfide and smaller amounts in time. We conclude, therefore, that we could not have overlooked a weighable amount of cadmium in our experiments. We weighed from 4 to 6.5 g. of cadmium in analyzing the cadmium chloride so there could not have been a loss greater than one part in 100,000 due to this cause.

Baxter and Hartman used a glass cell with a mercury cathode for decomposing their cadmium chloride, and always found cadmium in their electrolyte and wash-water; this corresponds with our earlier experience in using this kind of a cell, and is the reason for developing the cell we finally used. Our observation was, that the difficulty was not inability to deposit all the cadmium in the mercury, but rather in the subsequent manipulations due to removing the layer of electrolyte which is always found between a mercury cathode and the glass part of a cell. In order to remove this layer of electrolyte and satisfactorily wash the amalgam it must be disturbed and there is danger not only of oxidation but also of loss of finely divided amalgam. We found that this could be avoided by using a platinum cup amalgamated internally, so that the mercury cathode wet the cup and it was therefore impossible for either electrolyte or water to get underneath the mercury. It was only necessary to wash the upper surface of the amalgam which was not disturbed during the process. The amalgam and cup were strongly cathode during the process of replacing the electrolyte with water. The final wash-water was removed with a pipet so that only a drop or two remained on the surface. Then the cup and amalgam were placed in a vacuum desiccator over a dehydrating agent, where the last traces of water rapidly disappeared and there was no layer of water between the amalgam and cup to cause spurting. We took precaution to avoid any loss of mercury by evaporation, and convinced ourselves that the method was reliable by means of blank tests as follows: We started with weighed pieces of our purest cadmium, dissolved these in hydrochloric acid, changed them to the sulfate, electrolyzed in our cell, and weighed the cadmium in the mercury cathode, following every detail of the manipulation used in analyzing the cadmium chloride. Five such tests were carried out. Two showed a gain, and three a loss, the probable error of a single determination was ± 0.00004 g., so that our method of determining cadmium in cadmium chloride gave us results which we think can be relied upon to two or three parts in 100,000, and we conclude that the percentage of cadmium in the

cadmium chloride we had was 61.217, with a probable error of not over two in the last decimal place. We question whether any method of analysis has been tested as rigidly as we have tested the method we used.

In our preliminary work we were unable to fuse cadmium chloride in a platinum tube in an atmosphere of hydrochloric acid gas without a measurable loss of platinum. But we found that with proper precautions this operation could be carried out in a quartz tube. Baxter and Hartman called attention to this part of our work and concluded from a loss in one of our experiments of 2.9 mg. of platinum that we probably had air (oxygen) in our hydrochloric acid gas. We were using a Smith crucible with a much larger surface than an ordinary platinum boat, but aside from this the statements of Baxter and Hartman are quite misleading. They took the value 2.9 from a table recording five experiments. The losses were from 2.9 to 0.6 mg. of platinum. The loss with new platinum was large but decreased with use. This is ten times as large as the figures given in Baxter and Hartman's paper. In our method of preparing the hydrochloric acid we took precaution to exclude air, all of the joints of the apparatus were glass or glass sealed, and that it was gas tight when evacuated was proven in each case. In fusing the cadmium chloride in a quartz tube we found no measurable loss in the weight of the tube.

In the work of Laird and Hulett¹ a cadmium coulometer was developed which used a mercury cathode in an amalgamated platinum cup. There could be no inclusions in the cadmium deposited in mercury, while the washing and handling of the amalgam had the advantages of avoiding the presence of the electrolyte between the mercury cathode and the cup. This coulometer was used in series with a silver coulometer and the cadmium and silver deposited by the same current showed a value of 112.31 as the atomic weight of cadmium if we take the accepted value for silver. Baxter and Hartman remark that it is not easy to obtain a coulometer silver deposit in which the proportion of inclusions is known. We must take decided exception to this statement, as this work was done in conjunction with an extended investigation of the inclusions in electrolytic silver. We developed a direct method for determining these inclusions and in the silver coulometer as used by us at that time the inclusions were 4.6 parts in 100,000 with a probable variation of about 0.5 part. Furthermore we made allowance for the inclusions in our electrolytic silver as stated in the article referred to by Baxter and Hartman. This question of inclusions in electrolytic silver is one which we will take up in detail later, although it is too small to be of significance as far as the atomic weight of cadmium is concerned.

The first work done by us² after we had developed our method of de-

¹ *Trans. Am. Electrochem. Soc.*, 22, 385.

² Perdue and Hulett, *J. Phys. Chem.*, 15, 1579.

termining cadmium deposited in mercury, was an analysis of cadmium sulfate crystals. Cadmium sulfate crystallizes with $8/3$ molecules of water and forms most remarkably perfect and clear crystals. The salt is not isomorphous with other substances and so offers an exceptional method of purifying the substance. The crystals are water-clear and do not show inclusions under highest magnification. They are very stable crystals, neither seeming to effloresce nor deliquesce in ordinary dry air. We observed the weight of a large crystal (5 g.) for a period of several weeks and found no measurable change in weight, although we could have detected 0.01–0.02 mg. The crystal remained in the balance case during this period. This seemed remarkable at first, but it is quite possible that a perfectly pure hydrated salt may not have a definite vapor pressure. This would follow from the phase rule; if we had only vapor and $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ there would be two phases and two components, so it would require the presence of another hydrate or the anhydrous salt for equilibrium. In other words, we would not necessarily be restricted to a particular pressure for a given temperature; in fact the salt appeared to us to behave much like a supercooled liquid. Various samples of this carefully crystallized salt were analyzed by depositing the cadmium in the mercury cathode as described above. The results were very concordant and gave the value 112.3. We did not place much reliance on this value as the determination of atomic weight by using a hydrated salt is of course questionable. Professor Richards¹ has pointed out that there are always inclusions of mother liquor in crystals, also he suggested the possibility of the solubility of water in these crystals. Both of these things are of course possible, but as far as the inclusion of electrolyte is concerned it was impossible to detect its presence by the use of a microscope; furthermore it might be pointed out that cadmium sulfate is a very soluble salt and the percentage of water in the saturated solution is not much over twice that in the crystals so that it would require inclusions amounting to one part in five hundred to affect the atomic weight of cadmium by as much as the amount in question. It is of course possible that there is a certain solubility of water in these crystals, since we must assume that every substance is soluble in every other substance, and there may have been a distribution of water between the solution and the crystals which would tend to give too small a percentage to the cadmium in the crystals. But this argument will also work in the other direction, since we must admit that the solute is also soluble in the crystals, and this would tend to give too great a percentage of cadmium in the crystals. There is, however, no definite information on these points and so we merely regard the analysis of the crystals as interesting.

PRINCETON, N. J.

¹ THIS JOURNAL, 33, 888 (1911).