As has been pointed out in our preveious paper, the hydrocarbons, due to the well-defined valences of carbon and hydrogen, lend themselves admirably to an investigation of molecular compound formation, as it is possible to compare their relative tendency with one another. In benzene and acetylene the symmetry of the molecule leaves apparently no secondary valence due to unsaturation by means of which an attraction is exerted upon hydrobromic acid molecules, whereas in the case of alkyl substitutions such an attraction exists. This has an important bearing on the question of subsequent atomic compound formation, as is possible in the case of acetylene and allylene. It has been proposed that atomic compound formation is always preceded by molecular compound formation. The behavior of acetylene and allylene towards hydrogen bromide supports this idea to a modified extent inasmuch as acetylene which does not form a molecular compound does not combine readily (when pure and freed from the presence of catalysts) with hydrogen bromide to form the bromide, while allylene which forms a molecular compound will readily react with hydrogen bromide to form the atomic compound. That is, it is not unreasonable to suppose that the velocity of a chemical reaction is affected by the forces of attraction between the molecules as evidenced by molecular compound formation similar to the effect a catalyst would have on the velocity of a reaction.

An investigation of this is possible by quantitative measurements. Such an investigation, together with a study of systems of hydrobromic acid and chlorine with ethylene, propylene and other hydrocarbons, is now being carried out.

Summary

The details of the preparation of pure allylene have been described. It was shown that, contrary to the behavior of acetylene, allylene forms a molecular compound with hydrogen bromide, and at higher temperatures combines with it to form an atomic compound.

MONTREAL, CANADA.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM. V.

The Electrolytic Determination of Cadmium in Cadmium Sulfate.

BY GREGORY PAUL BAXTER AND CARL HENRY WILSON.

In confirmation of recent determinations of the atomic weight of cadmium completed in this laboratory,[1] the analysis of cadmium sulfate by the electrolytic precipitation of its metallic content has been carried out. Although cadmium sulfate is not particularly well suited for exact work,[2] owing to the danger of included mother liquor in the hydrated salt, and to the difficulty of freeing the anhydrous sulfate entirely from moisture owing to decomposition at high temperatures, yet this salt can at any rate be expected to give a minimum value for the constant in question. The

[1] Baxter and Hines, THIS JOURNAL, 27, 222 (1905); Baxter, Hines and Frevert, *ibid.*, 28, 770 (1906); Baxter and Hartmann, *ibid.*, 37, 113 (1915); Baxter and Grose, *ibid.*, 28, 857 (1916).

[2] Richards, *ibid.*, 33, 890 (1911).

value found is, however, in close accord with the result of the earlier determinations in this laboratory.

Purification of Materials.

Water, acids, alcohol and mercury were purified by distillation as described in previous papers.[1]

In the purification of cadmium salt, advantage was taken of the fact noted by Baxter and Hartmann[2] that cadmium bromide may be very rapidly and efficiently freed from salts of other metals by crystallization from aqueous solution. About 400 g. of crude cadmium, after being covered with dil. hydrobromic acid in a flask, was dissolved by the gradual addition of commercial bromine. The solution was then heated for some time with an excess of metallic cadmium to precipitate more strongly electropositive metals. After filtration through a platinum-sponge crucible into a platinum dish, the solution was evaporated until nearly saturated while hot, and was then allowed to cool, eventually to 0°. The resulting crystals of bromide were then subjected to a process of fractional crystallization similar to that described by Baxter and Hartmann.[3] Centrifugal drainage and rinsing of the crystals was employed to increase the efficiency of the crystallization.

The purified bromide was converted to nitrate in a quartz dish by means of aqueous nitric acid at boiling temperature, and then a small excess of sulfuric acid was added and the nitric acid was expelled by evaporation. In order to do this it was necessary repeatedly to separate the solution from the crystals of sulfate which formed. The crystals were then several times dissolved in water and the solutions evaporated in the same way, in order to make sure of the expulsion of traces of included nitric acid. After removal of the excess of sulfuric acid by drainage, the crystals of sulfate were completely dissolved in water in a platinum dish and the solution was allowed to crystallize slowly under a bell jar containing conc. sulfuric acid. Two additional crystallizations in the same way followed. Since the material had already been crystallized as bromide and since Retgers[4] and Perdue and Hulett[5] claim that crystallization of the sulfate is an effective method of purifying cadmium salt, there seemed to be every reason to hope that this salt was exceptionally pure. Spectrographic examination of this material in a Féry quartz spectrograph bore out this expectation, for no impurities whatever could be detected in this way.

The Electrolytic Method.

The analysis of cadmium sulfate was carried out by electrolytic deposition of the cadmium in pure mercury in a weighed cell of the type used by Baxter and Hartmann[1] and Baxter and Grose,[6] into which both electrodes were permanently fused. During the analysis of cadmium sulfate the accuracy of the process was further tested by blank experiments in which known quantities of cadmium were deposited in mercury. Because these experiments

[1] See especially, Baxter and Hartmann, THIS JOURNAL, 37, 120 (1915).

[2] Loc. cit. p. 119.

[3] Loc. cit., p. 119.

[4] Retgers, Z. physik. Chem., 16, 590 (1895).

[5] Perdue and Hulett, ibid., 15, 1579 (1911); Hulett and Quinn, THIS JOURNAL, 37, 1997 (1915).

[6] Loc. cit.

brought to light certain difficulties not noted in the earlier analyses of the cadmium and zinc halides, they will be discussed first.

Previous to an experiment the cell was prepared for the initial weighing by adding a suitable charge of pure mercury, usually about 100 g., and sufficient dil. sulfuric acid to cover the anode, and then passing a current somewhat less than one ampere through the cell for from 2 to 3 hours. The electrolyte was then displaced while the current was flowing by adding pure water at the surface of the electrolyte while the solution was drawn away at the surface of the mercury. When the current had apparently ceased to flow the water was drawn off as completely as possible.

In order to remove residual water, small portions of alcohol were added and the mercury was gently rolled around the bulb of the cell before the removal of each portion in order as far as possible to displace electrolyte trapped between the mercury and the glass. The cell was dried by inserting the stopper and placing it in a tubular desiccator which could be exhausted by an efficient Geryk oil–pump. Care was taken not to lower the pressure too rapidly, so as to avoid spattering and loss of mercury by violent evaporation of alcohol trapped between the mercury and the glass. Ultimately the mercury was gently rolled around the exhausted cell so as to expose any alcohol held underneath the mercury.

For the blank experiments metallic cadmium was fractionally distilled in a good vacuum from one portion of a hard glass tube, separated into parts by constrictions, to another. During the distillation the pump was operated continuously to remove the small amount of gases liberated during the distillation. Two or more distillations were necessary before the resulting button was perfectly bright. No other attempt was made to free the cadmium from traces of metallic impurities.

The button, contained in a platinum-gauze basket, was supported on the anode of the cell containing the dried mercury. Both cell and counterpoise were then wiped with a cloth moistened with alcohol and placed together in a desiccator, which was exhausted and left near the balance for at least 2 hours before the weight of the system was determined.

After covering the button with dil. sulfuric acid the cadmium was electrolytically transported to the cathode by passing a current of about 0.5 ampere for 18 hours or more. At the end of this time the voltage was raised to the maximum (about 17 v.) for 5 minutes, and the electrolyte was displaced with pure water without interrupting the current. Rinsing with alcohol and drying of the cell followed as described above, even greater pains being taken to prevent spurting of the amalgam during the evaporation of the alcohol.

In the meantime the electrolyte, together with the aqueous and alcoholic washings, was evaporated to small volume in a quartz dish over an electric

stove, and then was transferred to a weighed platinum crucible and evap-orated to dryness over an electric stove.   Finally the slight residue was heated to very dull redness over a small flame.   Although this residue, be-sides cadmium sulfate, contains small quantities of material extracted from the glass of the cell,[1] the assumption that it is cadmium sulfate in calculat-ing the correct weight of recovered cadmium cannot be far in error, since bases extracted from the glass are weighed as sulfates in the residue.

In general after the first electrolysis of a cadmium button the weight of the cell containing the amalgam corrected for the residue was from 0.2 to 0.3 mg. heavier than the cell containing the mercury and the cadmium but-ton.   This excess seemed to be independent of the weight of the original button.   Since Baxter and Grose found that the amalgam at first obtained in the analysis of cadmium bromide frequently lost slightly in weight if made, the cathode during a second electrolysis under sulfuric acid, the amalgams obtained in these blank experiments were similarly treated.   Frequently the results of the first and second electrolyses were essentially identical, but beyond this point a series of disturbing losses was apt to begin.   In some of these experiments the residues from the evaporation of the elec-trolyte were returned to the cell, before a new electrolysis.   In others the residues were allowed to accumulate in the crucible.   No systematic differ-ence in the result could be traced to variation in this procedure.

A search for an explanation of these losses revealed two causes of the difficulty.   Although a cell containing dry amalgam shows no change in weight when repeatedly exhausted, the situation is different when the amalgam is wet with a volatile liquid, for the mercury evaporates into the rather large volume of vapor formed during the volatilization of the liquid under reduced pressure.   This was detected by repeatedly pouring a small quantity of alcohol (about 0.5 cc.) upon a weighed amalgam, and, after evaporating the alcohol, reweighing the amalgam.   In four such treatments one cell lost successively 0.04, 0.06, 0.06, 0.03 mg. respectively.   On the assumption that the 0.5 cc. of alcohol evaporated at an average tempera-ture of 10° and at its vapor pressure, 24 mm., the loss to be expected if the alcohol vapor were saturated with mercury (v.p. = 0.0008 mm. at 10°) would be approximately 0.07 mg.   An exactly quantitative agreement between theory and experiment is not to be expected, for the alcohol vapor was undoubtedly not wholly saturated with mercury.   Since the quantities involved are not much larger than the error of weighing the cells, further evidence was secured by substituting water for alcohol in similar experiments.   In one series the losses were successively 0.16, 0.15, 0.28, and 0.12 mg., and in another, carried out by Dr. J. H. Hodges, they were 0.11 and 0.13 mg., while the loss to be expected with 0.5 cc. water at

[1] See following paper, p. 1246.

10° is approximately 1.0 mg. Even if there were no other reason, the low molecular weight and low vapor pressure of water thus make it far less suited for the final rinsing than alcohol. Ether was found to give no perceptible changes in weight, as is to be expected from its higher molecular weight and greater volatility. With alcohol the difficulty is not serious, however, although in a long series of experiments with the same amalgam the total weight of evaporated mercury may become appreciable.

The effect noted above is insufficient to account entirely for the losses in weight sometimes observed when the amalgams were repeatedly made the cathode under sulfuric acid. The fact that if the amalgams are violently agitated, rusting and turbidity in the washing liquid are produced, especially with alcohol, led to a suspicion that in spite of the gentlest handling traces not only of cadmium but also of mercury might thus be transferred to the washings of the cell. These washings invariably contain cadmium and although a part of this material probably results from incomplete electrolytic deposition, a part undoubtedly originates in the rusting. If the washings are merely evaporated to dryness and the residue heated the mercury ultimately is lost by volatilization. The procedure was therefore modified by first "fixing" the mercury by passing chlorine into the electrolyte before evaporation, then, after evaporation of the solution to small bulk, hydrogen sulfide was passed into the solution to saturation. The sulfuric acid contained in the electrolyte was sufficiently concentrated to prevent the precipitation of cadmium sulfide. Frequently, although not invariably, a precipitate of mercuric sulfide resulted. This precipitate was collected on a weighed platinum-sponge crucible, washed and dried, and then extracted with distilled carbon disulfide to remove sulfur, before the final drying at 110° and weighing. The filtrate from the mercuric sulfide, which had come into contact only with quartz, was evaporated and the residue weighed as before. The effect of this modification in the method was very satisfactory, for the total weight of material recovered as amalgam, residue, and mercuric sulfide, in most cases remained constant within the limit of error of the experiment.

The following table shows the effect of a typical series of repeated electrolyses upon a cell containing mercury only. In each case the residue was returned to the cell for the succeeding electrolysis.

TABLE I.

Weight of cell. G.	Weight of residue. G.	Gain or loss. G.
0.42674		
0.42671	0.00015	+0.00005
0.42663	0.00024	+0.00002
0.42662	0.00032	+0.00005
0.42659	0.00039	+0.00006
0.42655	0.00047	+0.00006

Table II gives the results of blank experiments with cadmium buttons. In Expts. 5 and 6 the cadmium was deposited in an amalgam resulting from a previous experiment.

Since the volume of liquid cadmium amalgam is slightly less than the sum of the volumes of the components a very small correction for the different buoyant effect of the air is necessary, as the figures for a 5 % cadmium amalgam show.

	Specific Gravity.	Volume. Cc.
95 g. Hg	13.53	7.02
5 g. Cd	8.64	0.58
Total		7.60
100 g. 5% amalgam	13.23[1]	7.56
Difference		0.04

0.04×1.2 mg. $= 0.05$ mg.

Vacuum correction per gram of cadmium in amalgam $= -0.01$ mg.

TABLE II.

Expt.	Wt. of Cd button. G.	Wt. of cell + mercury + cadmium button. G.	Wt. of cell + amalgam. G.	Wt. of residue. G.	Gain or loss. G.
1	6.7	6.62631	6.62653	0.00057	+0.00053
			6.62639	0.00066	+0.00044
2	8. ±	8.59050	8.59047	0.00042	+0.00020
			8.59051	0.00050	+0.00028
3	4. ±	4.41596	4.41606	0.00037	+0.00030
4	5. ±	6.07287	6.07291	0.00034	+0.00022
			6.07293	0.00048	+0.00032
			6.07272	0.00053	+0.00014
			6.07252	0.00067	+0.00001
5	2.9	7.33992	7.33951	0.00042	−0.00018
			7.33927	0.00035	−0.00046
6	5.0	11.09416	11.09398	0.00031	−0.00001
			11.09394	0.00047	+0.00003
			11.09375	0.00043	−0.00018
			11.09355	0.00081	−0.00017
7	2.7	4.52836	4.52847	0.00031	+0.00028
			4.52812	0.00037	−0.00004
			4.52783	0.00043	−0.00030
8	3.3	4.76680	4.76667	0.00028	+0.00002
			4.76643	0.00056	−0.00007
			4.76625	0.00096	−0.00004
			4.76556	0.00126	−0.00056
9	4.5	5.98637	5.98651	0.00017	+0.00023
			5.98606	0.00046	−0.00006
			5.98579	0.00060	−0.00026
			5.98555	0.00070	−0.00044
10	5. ±	5.32483	5.32488	0.00023	+0.00017
			5.32432	0.00042	−0.00028

[1] Hulett and De Lury, THIS JOURNAL, 30, 1810 (1908).

TABLE II.—(Continued.)

Expt.	Wt. of Cd button. G.	Wt. of cell + mercury + cadmium button. G.	Wt. of cell + amalgam. G.	Wt. of residue. G.	Gain or loss. G.
11	5. ±	5.03096	5.03093	0.00027	+0.00012
12	5. ±	5.31691	5.31685	0.00035	+0.00013
13	6. ±	6.84433	6.84429	0.00045(a)	+0.00020
			6.84395	0.00088(a)	+0.00010
			6.84338	0.00115(b)	+0.00001
			6.84264	0.00126(c)	+0.00018
14	7. ±	7.05940	7.05938	0.00029(a)	+0.00014
			7.05912	0.00056(a)	+0.00002
			7.05858	0.00088(d)	+0.00082
			7.05841	0.00106(e)	+0.00075

The weight of HgS was not determined except in Expts. 13 and 14 where in (a) none was found; in (b) 0.00039 g.; in (c) 0.00135 g.; in (d) 0.00136 g.; and in (e) 0.00136 g.

The evidence furnished by the above table is extended and confirmed by that obtained in the analysis of cadmium sulfate to be described later. In every case but one the initial weight of amalgam corrected for residue from the electrolyte is as high as or higher than any subsequently obtained. If the electrolyte is merely evaporated, a loss in weight of total material recovered appears after one or two repetitions. If, one on the other hand, care is taken to prevent loss of mercury by treating the electrolyte with chlorine and precipitating its mercury content with hydrogen sulfide, the changes in the corrected weight of recovered material are less than the experimental error. On the whole the initial weight of amalgam and residue seems to be the safest starting point for correcting the weight of cadmium thus determined. However, this initial weight is too large; but it is possible to determine the negative correction to be applied by averaging the gains recorded in Table II. This correction is apparently not dependent upon the weight of cadmium involved. Excluding Expts. 5 and 6. in which the cadmium was deposited upon an amalgam instead of upon mercury, so that an excess in weight is hardly to be expected, and omitting Exp. 1, in which experience in the procedure was being acquired, the average initial excess in weight of the products over the factors is 0.18 mg. In the later experiments a negative correction of this magnitude is applied to the initial corrected weight of recovered cadmium. The cause of the excess was not discovered. Possible causes are mentioned in the following paper.

The Preparation of Cadmium Sulfate for Analysis.

In a recent investigation Perdue and Hulett[1] analyzed both hydrated and anhydrous salt; therefore we decided to do the same thing. They se-

[1] Perdue and Hulett, J. Phys. Chem., 15, 1579 (1911).

lected clear crystals which showed no inclusions under high magnification. According to their experience such crystals remain constant in weight upon exposure to air of average humidity.[1] We observed essentially the same behavior, although the same material, when powdered, effloresces rapidly. A crucible containing about 20 g. of crystals, apparently dry, but not specially selected as to freedom from inclusions, in the course of 7 hours lost 2.7 mg., and during the next 17 hours, 1.0 mg. more. After removal of about 8 g. of material the remainder in 3 days lost only 0.4 mg. The salt removed, consisting of 4 large crystals, was weighed in a cell containing mercury, and was then analyzed by electrolysis. A second sample of material, which also had come to essentially constant weight in a platinum crucible, was analyzed in the same way. This material, assuming the formula $CdSO_4 . 8/3 H_2O$, gave as the atomic weight of cadmium 112.03, a value far lower than the one found by Perdue and Hulett, 112.3, from analysis of the hydrated salt.[2] Assuming the atomic weight of cadmium to be 112.4 the crystals must have contained an excess of 0.2 % of moisture. While our material may very well have been inferior to theirs so far as included mother liquor and dissolved moisture[3] are concerned, this evidence that the hydrated salt does under some circumstances contain an excess of moisture makes it extremely probable that under normal conditions of crystallization it always does so to some extent. The hydrated salt, therefore, seemed unpromising material for further work. Aside from one analysis of material which had been powdered and exposed to the air and which had effloresced for some time without coming to constant weight, all further work was carried out with the anhydrous salt. This effloresced material proved to contain 45.65% of cadmium, while the salt with its full quota of water should contain 43.84%, and the anhydrous salt 53.92%.

In one attempt to prepare anhydrous cadmium sulfate by heating in a vacuum, the powdered salt, contained in a quartz boat, was placed in a hard glass tube, connected with a Richards and Parker bottling apparatus,[4] and was heated by means of an aluminum block furnace.[5] The soft glass socket of the bottling apparatus was connected with a Töpler pump, the end of the hard glass tube being closed by a ground joint connected with a stopcock. After heating the salt in a vacuum, dry air

[1] Loc. cit., p. 157; Hulett and Quinn, THIS JOURNAL, 38, 2000 (1915).

[2] In a later paper Hulett and Quinn state that they "did not place much reliance on this value as the determination of an atomic weight by using a hydrated salt is of course questionable" and "merely regard the analysis of the crystals as interesting." ibid., 37, 2000 (1915).

[3] Richards, ibid., 33, 888 (1911).

[4] Richards and Parker, Proc. Am. Acad., 32, 59 (1896).

[5] THIS JOURNAL, 31, 206 (1909).

was admitted through the stopcock. The following table shows the effect of heating the salt in a vacuum at different temperatures.

Period. Hours.	Temperature. °C.	Weight. G.
2	60–70	4.566
3.75	150	4.054
4	250–260	4.034

In the last heating at 250° the salt darkened slightly. Although heated apparently to the point of incipient decomposition, the salt still contained considerable water, for after solution and electrolysis, the apparent atomic weight of cadmium was found to be 111.5.

In a second experiment where the salt was heated to 200° only, in a vacuum, a continuous slow loss in weight was observed, which offered no hope of an early termination; therefore, in all the remaining experiments the salt was heated to a much higher temperature in an atmosphere containing sulfur trioxide. This was the procedure adopted by Perdue and Hulett.[1] In order to avoid condensation of sulfuric acid in the apparatus, the greater part of the water was expelled at 200° in a vacuum in the apparatus described above. The boat with the salt was then placed in a quartz tube connected through a ground joint with a saturating bottle containing fuming sulfuric acid through which dry air could be passed. After being heated in air containing sulfur trioxide the boat was replaced in the bottling apparatus and again heated in a current of pure dry air at 200° for about two hours before being transferred to the weighing bottle.

Salt heated in this way at 650° rapidly came to constant weight within 0.1 mg. One sample of sulfate, weighing 6.2 g. when heated at 720°, after being heated to 650°, lost 0.3 mg., but did not change in weight upon further heating at the same temperature. A second specimen of sulfate gave a similar result, and upon heating even to 800° showed no further loss.[2] In a later experiment, however, salt which had been once heated at 800° showed a considerable loss on a second heating, accompanied by slight discoloration. This may have been caused by an undetected temporary rise in the voltage of the heating current. It seemed safer therefore in general, to heat the salt to constant weight at 700° to 720°, and this was done in the later experiments.

The Electrolysis of Cadmium Sulfate.

After the final weighing of the salt, the boat was placed in a weighed cell containing mercury. The weighing bottle was rinsed and the rinsings added to the cell, into which enough additional water was introduced to cover the boat. Electrolysis with a current somewhat less than one ampere

[1] Loc. cit., p. 157.

[2] Perdue and Hulett state that the salt is stable up to 700° in an atmosphere containing sulfur trioxide. Loc. cit., p. 157.

followed and the remainder of the process was essentially identical with that described for the blank experiments with cadmium buttons.   In order to avoid rusting of the amalgam, washing was carried out with water saturated with pure hydrogen and in many experiments the cell was chilled before the removal of the electrolyte and washing.

The electrolyte was evaporated to small volume in a quartz dish and then to dryness in a weighed platinum crucible which was heated to dull redness for an instant.   The residue was assumed to be cadmium sulfate in calculating the correction, but contained also sulfates of metals extracted from glass of the cell, as Dr. J. H. Hodges has shown by analysis.[1] Since the percentages of sodium and calcium oxides in the sulfates, 43.6 and 41.2, are not very far from the percentage of cadmium in cadmium sulfate, 53.9, and since the weight of residue is usually less than 1.0 mg. no considerable error could be introduced by this assumption.

After the first weighing of amalgam and residue in the later analyses the residue was dissolved and returned to the cell with enough dil. sulfuric acid to cover the anode, and electrolysis was repeated in the same way. As soon as the danger of losing mercury during the rinsing of the amalgam was discovered, before evaporating the electrolyte it was treated with chlorine and then hydrogen sulfide to precipitate the former element, as previously described.

The weights were standardized to hundredths of a milligram by the substitution method described by Richards.[2]   All weighings were made upon a No. 10 Troemner balance.   With the heavier objects, such as the weighing bottle, and the cell containing mercury or amalgam, the balance beam was released some minutes before making observations in order to allow the slight bending of the beam to occur.   The small amount of crude radium bromide was kept in the balance case to prevent the objects weighed from retaining electrostatic charges.   The weighing bottle and cell were always compared by substitution with counterpoises of very nearly the same shape, size and volume in order to avoid variations from changes in atmospheric conditions.

Vacuum corrections of +0.243 mg. per g. of hydrated cadmium sulfate and +0.111 mg. per g. of anhydrous sulfate were applied, the densities of the weights and the salts being assumed to be 8.3, 3.090[1] and 4.691,[3] respectively.   The vacuum correction of cadmium dissolved in mercury computed by Baxter and Hartmann,[4] -0.016 mg., was applied for every apparent gram of dissolved cadmium.

[1] See following paper, p. 1246.
[2] Richards, THIS JOURNAL, 22, 144 (1900).
[3] Perdue and Hulett, J. Phys. Chem., 15, 159 (1911).
[4] Loc. cit., p. 129.

THE ATOMIC WEIGHT OF CADMIUM.

Cd: SO_4.

O = 16.000.   H = 1.008.   S = 32.060.

Analysis.	Temp. of heating. °C.	Wt. of $CdSO_4$ in vacuum. G.	Wt. of Cd from amalgam in vac. G.	Wt. of residue. G.	Wt. of HgS. G.	Corrected[a] Wt. of Cd. from amalgam in vacuum. G.	Ratio Cd: SO_4.	Atomic wt. of cadmium.
1	20	7.79796[b]	3.41058	0.00087		3.41087	0.77748[c]	112.04
2	20	12.20172[b]	5.33693	0.00036		5.33694	0.77744[c]	112.03
3	650	3.65533	1.97007	0.00081		1.97033	1.16934	112.324
4	650	4.59450	2.47708	0.00051		2.47718	1.16996	112.386
5	650	4.12057	2.22155	0.00053		2.22166	1.16997	112.387
6	650	5.34263	2.88065	0.00054		2.88076	1.17015	112.405
7	720	6.19309	3.33910	0.00088		3.33940	1.17020	112.410
8	800	6.55765	3.53564	0.00052		3.53574	1.17004	112.394
9	800	6.04137	3.25714	0.00073		3.25735	1.17002	112.392
10	710	7.52884	4.05941	0.00076	0.00053	4.06010	1.17048	112.437
			4.05856	0.00105	0.00107	4.05987		
			4.05779	0.00139	0.00181	4.05992		
			4.05746	0.00161	0.00181	4.05971		
			4.05746	0.00176	0.00182	4.05980		
11	710	6.58281	3.54848	0.00147	0.00047	3.54949	1.17016	112.406
			3.54892	0.00054	0.00046	3.54942		
			3.54868	0.00084	0.00046	3.54934		
			3.54805	0.00111	0.00046	3.54886		
12	710	6.70646	3.61603	0.00083	0.00023	3.61650	1.17040	112.429
			3.61580	0.00110	0.00023	3.61641		
			3.61580	0.00069	0.00059	3.61650		
			3.61570	0.00110	0.00095	3.61693		
			3.61557	0.00111	0.00119	3.61701		
13	710	6.56059	3.53700	0.00072	0.00010	3.53730	1.17002	112.392
			3.53661	0.00111	0.00041	3.53738		
		Average of Analyses			3 to 13		1.17007	112.397
		Average of Analyses			4 to 13		1.17014	112.404
		Average of Analyses			7 to 13		1.17019	112.409
		Average of Analyses			10 to 13		1.17027	112.416

[a] A negative correction of 0.18 mg. has been applied to provide for the determined excess in weight of the amalgams.

[b] $CdSO_4$. 8/3 H_2O.

[c] Cd : SO_4 8/3 H_2O.

Because the salt used in Analyses 3 to 6 was less thoroughly dried than that subsequently prepared, the average of Analyses 7 to 13, 112.409 is probably more reliable than the slightly lower average of all the experiments with anhydrous salt. The average of the last four experiments in which all the corrections were applied, 112.416, might on this account be considered the most probable value to be derived from these experiments.

It is worth noting that the omission of the correction for excess in weight of the amalgam would raise the average observed atomic weight

by 0.015 unit.   Furthermore, when no corrections whatever are applied in Analyses 4 to 13 the atomic weight of cadmium becomes 112.38.

All things considered, the value 112.41 can be taken to represent a minimum as found by this method, for since the cadmium sulfate could not be fused in preparation for weighing, past experience with other salts leads to the conclusion that this salt was not wholly anhydrous.

The outcome of this investigation is quite different from that of the Analysis of cadmium sulfate by Perdue and Hulett, who found the atomic weight of cadmium to be 112.30.   If their sulfate was anhydrous, this indicates that from every gram of material they recovered a little over 0.2 mg. less cadmium than we did.   A discrepancy of about the same magnitude exists between the experiments of Baxter and Hartmann, and Quinn and Hulett in the analysis of cadmium chloride, although it is erroneously stated to be twice as large by Baxter and Hartmann.

There is every reason to suppose that in the experiments of Baxter and Hartmann, and Baxter, Grose and Hartmann errors occurred, positive as regards the excess in weight of the amalgam, negative as regards the loss of mercury during the washing of the amalgam and evaporation of the electrolyte.   On the assumption that the first error is the same in the analysis of cadmium chloride as in the experiments described in this paper, the corrected atomic weight of cadmium becomes 112.405.   Baxter, Grose and Hartmann's experiments on cadmium bromide cannot be treated in this way since re-electrolysis was necessary there for other reasons.

The following table summarizes the work at Harvard on the atomic weight of cadmium.   The comparison of the halides with silver can apparently be made a more accurate process than the electrolytic method, but even if the five series are given equal weight the average is not far from that of the first two.

Baxter and Hines......................	$CdCl_2 : 2\ Ag : 2\ AgCl$	112.418
Baxter, Hines and Frevert...............	$CdBr_2 : 2\ Ag : 2\ AgBr$	112.417
Baxter and Hartmann (corrected)........	$Cd : Cl_2$	112.405
Baxter, Grose and Hartmann (uncorrected)	$Cd : Br_2$	112.407
This paper...........................	$Cd : SO_4$ (Analyses 7–13)	112.409
Average.........		112.411

The electrolytic analysis of cadmium chloride, bromide and sulfate thus furnishes ample confirmation of the atomic weight of cadmium as determined by comparison of the halides with silver.

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