member of equation (10) becomes zero, and we have

$$dT = \frac{RT^2}{Q} dn, \qquad (11)$$

which is equation (2).

In the same way it may be proved that Raoult's law for the raising of the boiling-point applies to any constant boiling mixture, of any number of constituents.

In deriving equation (11) we have implicitly made use of two assumptions. The first is contained in equation (8) and is merely the assumption that the solute dissolves to form an ideal solution. The second is contained in equations (8) and (9). It is the assumption that the vapor obeys the gas laws. Now while the first assumption is fundamental and necessary, it is possible by a somewhat more general method than the one here adopted to dispense with the second assumption, and thus to show that equation (11) applies to all solvents, even to those whose vapors behave abnormally.

Our general conclusions are therefore as follows:

(1) The law of Raoult for the lowering of the vapor-pressure is applicable to an ideal dilute solution in any constant boiling mixture whose vapor obeys the gas laws.

(2) The law of Raoult for the raising of the boiling-point is applicable to an ideal dilute solution in any constant boiling mixture whatever.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

BY GREGORY PAUL BAXTER, MURRAY ARNOLD HINES AND HARRY LOUIS FREVERT.

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(SECOND PAPER.)

FROM a recent investigation of the atomic weight of cadmium[1] the value 112.469 (Ag = 107.930) for this constant was obtained, by analysis of cadmium chloride. Since this value is nearly one-tenth of a unit higher than the results of recent prior determinations by other investigators, in order to confirm or disprove the higher value, the analysis of cadmium bromide was undertaken.

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[1] Baxter and Hines: This Journal, 27, 222 (1905).

PURIFICATION OF MATERIALS.

In the previous investigation the cadmium material was purified by fractionally precipitating cadmium sulphide with hydrogen sulphide from an acid solution of cadmium chloride. Two small fractions were rejected, and the next three, which included very nearly all the remainder of the cadmium, were preserved separately. Each one of these three fractions was first thoroughly washed, then dissolved in hydrochloric acid and reprecipitated. Next the precipitates were again dissolved, in nitric acid, the nitric acid was expelled by heating with an excess of sulphuric acid, and the sulphate was recrystallized thrice from pure water. Fraction I and a portion of Fraction II were converted into chloride and were analyzed in the earlier work, while Fraction III and a second portion of Fraction II were converted into bromide.

The method employed for this purpose was that of depositing metallic cadmium electrolytically, dissolving the metal in bromine under water in a quartz dish, and recrystallizing the bromide in platinum vessels. In the first experiments electrolysis was carried on in a solution of the sulphate in pure water, between two electrodes of platinum foil. A sponge of extremely small crystals was thus produced. These crystals contained occluded sulphate in considerable quantities, and no amount of washing with water was sufficient completely to leach out this occluded material. Hence the bromide made from this metal was seriously contaminated with sulphate, which was finally eliminated with difficulty by repeated crystallization. This bromide was used only in preliminary experiments. More satisfactory results were obtained by depositing the metal upon a platinum dish which had been covered with a very thin film of soft paraffine, so that the deposit could be readily separated from the dish.[1] The cadmium was first washed with water, then with ether, next with alcohol, and finally with water again. This treatment effectually cleansed the metal from paraffine. In order to convert the cadmium into bromide, it was covered in a quartz dish with water slightly acidified with hydrobromic acid to prevent the formation of basic cadmium salts, and the purest bromine was added in small quantities until the metal was almost wholly dissolved. The solution was heated with the residual metallic cadmium upon a

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[1] Richards: Pr. Am. Acad. 25, 200 (1890).

steam-bath until every trace of bromine had disappeared. Then it was filtered with a platinum funnel into a platinum dish, and was recrystallized three times, with centrifugal drainage in the platinum funnel after each crystallization.[1] The original solution contained only traces of sulphate, and, when tested with barium hydroxide, the mother-liquors of the third crystallization gave absolutely no test for sulphate, hence the crystals themselves must have been pure (Samples II*a* and III*a*). From the mother-liquors of each fraction, by three crystallizations, similar samples were obtained (Samples II*b* and III*b*). The crystals were dried over potassium hydroxide in a vacuum desiccator.

Commercial bromine was freed from chlorine by two distillations from a concentrated solution of a bromide, the bromide in the second distillation being almost free from chloride. The bromine was covered with water, and hydrogen sulphide, which had been thoroughly washed with water, was passed into the solution until reduction of the bromine was complete. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was filtered. Iodine was eliminated by boiling the hydrobromic acid with several small portions of potassium permanganate and rejecting the bromine set free. By heating the remainder of the hydrobromic acid with an excess of permanganate, over half of the bromine was obtained in the free state. The process of reduction with hydrogen sulphide and oxidation with permanganate was then repeated with the resulting bromine, and the final product was redistilled shortly before use.

One sample of silver was purified especially for this research. The processes to which it was subjected were essentially those which have been repeatedly used in this laboratory for the purification of silver. The commercial metal was dissolved in nitric acid, and the solution was filtered and precipitated at considerable dilution with hydrochloric acid. After thorough washing, the precipitate was reduced with invert sugar and sodium hydroxide, and the metallic silver was fused with a blowpipe on a crucible of the purest lime. In order to cleanse the buttons from surface impurities, they were first scrubbed with moist sand, and then the surface was removed with dilute nitric acid. Next the buttons were dissolved in nitric acid and the solution was reduced

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[1] Richards: This Journal, 27, 110 (1905).

with ammonium formate.[1] The precipitated silver was thoroughly washed and again fused in a lime crucible. The final process of purification consisted in electrolyzing the silver, with a solution of silver nitrate, made from a portion of the silver, acting as electrolyte, while the anode was a pile of the pure silver buttons and the cathode a bar of the purest silver. The electrolytic crystals were washed, dried, and fused in a current of pure hydrogen on a lime boat. The buttons were cleansed with dilute nitric acid, and, after drying at 200°, they were cut into fragments with a clean chisel and anvil. Then they were again treated with fresh portions of dilute nitric acid until free from iron, washed, dried, and finally heated to about 400° in a vacuum. This silver was employed in analyses 4 to 8.

In the first three analyses a mixture of two specimens of silver was employed, both of which had already been used in an investigation upon the atomic weight of iodine by one of us.[2] One was prepared from silver nitrate which had been seven times recrystallized from nitric acid, five times recrystallized from water, and finally precipitated with ammonium formate. The other was precipitated once as silver chloride, electrolyzed once, and finally reduced with ammonium formate.

Water was purified by double distillation with tin condensers, first with alkaline permanganate, finally with a trace of sulphuric acid. Nitric acid was twice distilled with a platinum condenser, the first third of the distillate being rejected in both distillations. The product of the first distillation contained only the merest trace of chlorine.

METHOD OF ANALYSIS.

The method of analysis was essentially that already frequently employed in this laboratory for the analysis of metallic halides. Weighed portions of the bromide, after fusion in nitrogen and hydrobromic acid gases, were first titrated against weighed portions of silver. Then the precipitated silver bromide was collected and weighed.

The apparatus used for the fusion of the salt in hydrobromic acid gas was employed in the preparation of ferrous bromide

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[1] Richards: Publications of the Carnegie Institution, No. 28, p. 19 (1905); This Journal, 27, 475.

[2] Baxter: Pr. Am. Acad. 41, 73 (1905).

by one of us,[1] and is a modification of apparatus used for a similar purpose in the determination of the atomic weights of cobalt,[2] nickel,[3] and uranium[4] in this laboratory. A mixture of air and ammonia was passed over heated rolls of copper gauze and the excess of ammonia was removed by means of sulphuric acid. The gas was then conducted into an apparatus constructed wholly of glass, with ground joints, which consisted of a tower filled with beads moistened with silver nitrate solution to remove sulphur compounds, two similar towers containing dilute sulphuric acid to eliminate last traces of ammonia, and two towers filled with sticks of fused potassium hydroxide to absorb moisture and carbon dioxide. The partially dried gas, after bubbling through bromine in a small flask, passed into a second flask containing concentrated hydrobromic acid solution in which washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes containing beads moistened with concentrated hydrobromic acid only, served to eliminate phosphorus compounds which were found, in the investigation upon ferrous bromide,[5] to accompany the hydrobromic acid if the phosphorous acid in the reduction flask was allowed to become very concentrated. Finally, the mixture of nitrogen and hydrobromic acid gases was thoroughly dried, first by pure fused calcium bromide, and then by resublimed phosphorus pentoxide.

The cadmium bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen until a small quantity of residual crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen and this in turn by dry air. The boat was then transferred to the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus which has been

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[1] Baxter: Pr. Am. Acad. 39, 246.

[2] Richards and Baxter: Ibid. 33, 117.

[3] Richards and Cushman: Ibid. 33, 99.

[4] Richards and Merigold: Ibid. 37, 378.

[5] Loc. cit.

frequently described in papers from this laboratory.[1] The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

Next the boat was transferred to a flask and the salt was dissolved in about 300 cc. of the purest water. The weighing-bottle was rinsed and the rinsings were added to the solution. Then the solution was filtered into the glass-stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited at a low temperature in a weighed porcelain crucible. This residue, which usually amounted to less than 0.1 mg. and was never as much as 0.2 mg., did not contain detectable quantities of cadmium, and probably consisted of silica and a trace of platinum removed from the boat during the fusion, for the boat, when reweighed, in most cases was found to have lost a few hundredths of a milligram. No change in weight could be found when the boat was first dried and weighed, then ignited and reweighed. The difference between the weight of the residue and the loss in weight of the boat was subtracted from the weight of the cadmium bromide.

From the corrected weight of the cadmium bromide very nearly the requisite quantity of pure silver was calculated. This silver was weighed out and dissolved, in a flask provided with a column of bulbs to prevent loss of silver by spattering, in redistilled nitric acid diluted with an equal volume of water. After the silver was dissolved, the solution was diluted to twice its volume and was heated until free from nitrous fumes. Then it was still further diluted until not stronger than 1 per cent., and was slowly added, with constant stirring, to the 1 per cent. solution of cadmium bromide in the precipitating flask. In three analyses (4, 5 and 8), this procedure was varied by adding the bromide to the silver nitrate. After being shaken for some time, the solution was allowed to stand several days, with occasional shaking, until the supernatant liquid was clear. 30 cc. portions of the solution were then tested with hundredth normal solutions of silver nitrate and sodium bromide in the nephelometer[2] for excess of bromide or silver, and, if necessary, either standard silver nitrate or sodium bromide solution was

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[1] Richards and Parker: Pr. Am. Acad. 32, 59.

[2] Richards and Wells: Am. Ch. J. 31, 235 (1904).

added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of dissolved silver bromide; otherwise they were returned to the flask and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about 4 centigrams of silver nitrate in excess were added, to precipitate dissolved silver bromide, and the flask was again shaken and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after it had been washed by decantation about eight times with pure water. Then it was heated in an electric air-bath, first for several hours at 140°, finally for an hour at 200°, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small covered crucible, contained in a large crucible, and again weighed. After fusion the silver bromide was light yellow, with only a trace of darkening, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible, together with a minute quantity of silver bromide which occasionally escaped the crucible, were collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of this substance. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions. Finally, the weight of silver bromide was corrected for the sodium bromide introduced.

Although in our analyses of cadmium chloride no evidence could be obtained of appreciable occlusion of either cadmium or silver salts by silver chloride, especial precautions were taken to avoid any possibility of such a difficulty in this research. In the first place both the cadmium bromide and the silver nitrate solutions were extremely dilute during precipitation, each one having a volume of about one liter. In the second place the method of precipitation was varied by sometimes adding the silver nitrate to the cadmium bromide (analyses 1, 2, 3, 6 and 7), and sometimes adding the bromide to the silver (analyses 4, 5 and 8). And in the third place the solutions were allowed to stand varying lengths of time before the titration was completed, so that occluded substances might have opportunity to be dissolved. Analysis 1, in which the largest quantity of bromide was employed, over 11 grams, which is to be expected to give the most marked evidences of occlusion, was not tested for five days after precipitation, and the titration was completed eight days later. In the other analyses the period between precipitation and the completion of the titration varied from seven days in analysis 4 to three days in analysis 8. Furthermore, in some cases, after the end-point had been reached, the solutions were allowed to stand some days longer with occasional testing. No change in end-point with standing was observed. In spite of these differences in the method of procedure, the variations in the final results do not exceed the experimental error to be expected, except in the case of analyses 4 and 12. Evidently, occlusion of any sort must have been very slight if it existed at all. Analyses 4 and 12, performed with the same bromide, differ so markedly from the others that, although no reason for the difference is known, they are rejected in computing the final average.

The gold-plated brass weights were carefully standardized to hundredths of a milligram. Vacuum corrections of +0.000090 for cadmium bromide,[1] of +0.000046 for silver bromide and of —0.000031 for silver were applied. All weighings were made by substitution with counterpoises as nearly like the objects to be weighed as possible. The atomic weight of silver is assumed to be 107.930 and that of bromine to be 79.955.

The analytical work was performed wholly by Mr. Hines.

The ratios of silver used to silver bromide obtained in the same analyses afford sufficient proof of the purity of the bromine and silver, as well as confirmatory evidence of the absence of appreciable occlusion by the silver bromide.

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[1] The specific gravity of cadmium bromide has recently been found to be 5.192. Baxter and Hines: Am. Ch. J. 31, 220 (1904).

THE ATOMIC WEIGHT OF CADIMUM.

Ag = 107.930 Br = 79.955.

Series I. $CdBr_2 : 2Ag$.

Number of analysis.	Sample of $CdBr_2$.	Weight of $CdBr_2$ in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of $CdBr_2$. Grams.	Corrected weight of Ag. Grams.	Atomic weight of cadmium.
1	II*a*	11.46220	0.00008	0.00004	9.08409	—0.00030	11.46216	9.08379	112.468
2	II*b*	6.82294	0.00018	0.00006	5.40734	—0.00010	6.82282	5.40724	112.461
3	II*a*	6.75435	0.00011	+0.00004	5.35297	—0.00020	6.75420	5.35277	112.465
4	III*a*	7.08590	0.00006	0.00004	5.61567	+0.00030	7.08588	5.61597	112.449
5	III*a*	5.13867	0.00008	0.00000	4.07236	—0.00010	5.13859	4.07226	112.473
6	III*a*	5.84328	0.00008	0.00004	4.63092	—0.00020	5.84324	4.63072	112.471
7	III*a*	5.99712	0.00008	0.00000	4.75269	—0.00010	5.99704	4.75259	112.472
8	II*a*	5.90811	0.00017	0.00002	4.68200	0.00000	5.90796	4.68200	112.472
							Average rejecting analysis 4		112.470

Series II. $CdBr_2 : 2AgBr$.

Number of analysis.	Sample of $CdBr_2$.	Weight of $CdBr_2$ in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of AgBr. in vacuum. Grams.	Loss on fusion. Gram.	Weight of asbestos from filtrate. Gram.	Weight of AgBr from wash-waters. Gram.	Corrected weight of $CdBr_2$. Grams.	Corrected weight of AgBr. Grams.	Atomic weight of cadmium.
9	II*a*	11.46220	0.00008	0.00004	15.81286	0.00024	0.00024	0.00033	11.46216	15.81319	112.466
10	II*b*	6.82294	0.00018	0.00006	9.41251	0.00028	0.00044	0.00000	6.82282	9.41267	112.469
11	II*a*	6.75435	0.00011	+0.00004	9.31815	0.00028	0.00043	0.00000	6.75420	9.31830	112.460
12	III*a*	7.08590	0.00006	0.00004	9.77557	0.00013	0.00053	0.00052	7.08588	9.77649	112.444
13	III*a*	5.13867	0.00008	0.00000	7.08897	0.00007	0.00043	0.00000	5.13859	7.08933	112.461
14	III*a*	5.84328	0.00008	0.00004	8.06076	0.00005	0.00033	0.00026	5.84324	8.06130	112.467
15	III*a*	5.99712	0.00008	0.00000	8.27321	0.00012	0.00020	0.00031	5.99704	8.27360	112.463
16	II*a*	5.90811	0.00017	0.00002	8.15022	0.00015	0.00037	0.00026	5.90796	8.15070	112.463
									Average rejecting analysis 12........		112.464
									Average of Series I and II, ...		112.467

	Ag : AgBr.
Analyses 1 and 9	57.4444
" 2 " 10	57.4464
" 3 " 11	57.4436
" 4 " 12	57.4436
" 5 " 13	57.4421
" 6 " 14	57.4438
" 7 " 15	57.4428
" 8 " 16	57.4429
Average,	57.4437

The most probable value for this ratio has been shown both by Stas and by experimenters in this laboratory to be 57.4445.[1]

In recent experiments in fusing manganous chloride, in a current of hydrochloric acid gas which had been dried by concentrated sulphuric acid and finally by means of phosphorus pentoxide, an insoluble residue of manganous phosphate was invariably obtained when the salt was dissolved in water. The quantity of this residue varied with the amount of moisture contained by the salt when brought in contact with the hydrochloric acid gas, being extremely slight if the salt was very nearly dry, but amounting to several milligrams if the salt still contained much of its crystal water. Although it seemed certain that the phosphorus had its origin in the phosphorus pentoxide, and was volatilized in the form of either phosphorus pentachloride or oxychloride through the action of the hydrochloric acid upon the pentoxide, in order to obtain still more positive evidence that this was really the case, the experiment was tried of passing hydrochloric acid gas which had been dried thoroughly by means of sulphuric acid, first over phosphorus pentoxide which had been freshly sublimed in a current of dry air, and then into water. The aqueous solution, upon evaporation and testing with ammonium molybdate gave a considerable amount of the characteristic ammonium phosphomolybdate. This result confirms that of Bailey and Fowler,[2] who have found that both hydrochloric and hydrobromic acids react with phosphorus pentoxide at ordinary temperatures to form the oxychloride and bromide of phosphorus respectively. The manganous phosphate, then, must have been produced by the action of the volatilized chloride of phosphorus

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[1] Richards: Proc. Amer. Phil. Soc. 43, 119.

[2] Chem. News, 58, 22.

upon the moisture contained by the manganous chloride to form phosphoric acid, and subsequent displacement of hydrochloric acid from the salt by the phosphoric acid.

Although in our previous work with cadmium chloride, where the double cadmium ammonium chloride, $CdCl_2NH_4Cl$, was fused in a current of hydrochloric acid gas which had been finally dried with phosphorus pentoxide, the salt, which contains no crystal water, was essentially free from moisture before coming in contact with the hydrochloric acid, yet it seemed desirable to repeat the experiments with cadmium chloride in such a way that the danger mentioned above could be completely avoided. This result was easily attained by drying the hydrochloric acid gas with concentrated sulphuric acid only, four columns about 30 cm. in length, filled with beads moistened with sulphuric acid, being used for the purpose.

In order to ascertain whether concentrated sulphuric acid is appreciably attacked by hydrochloric acid gas, a large quantity of this gas was conducted through the columns and then into water. The aqueous solution was then evaporated and tested for sulphate with barium chloride. Although a slight precipitate of baric sulphate was produced, the quantity was estimated, by comparison in a nephelometer with a standard solution of a sulphate, to be less than five-hundredths of a milligram. Evidently nothing is to be feared from this source.

The material for these experiments was prepared from a portion of fraction II of cadmium sulphide, by first depositing the metal electrolytically from the sulphate as described above (page 771) and then dissolving the washed cadmium in pure hydrochloric acid in a platinum dish. The chloride does not lend itself readily to crystallization from aqueous solution on account of its great solubility even at low temperatures, but by conducting hydrochloric acid gas into the solution the much less soluble double salt with hydrochloric acid, $CdCl_22HCl7H_2O$, was formed. The salt was thus crystallized three times with centrifugal drainage, to free it from the trace of sulphates occluded by the metal during electrolysis. Finally, it was dried and freed from hydrochloric acid as far as possible in a vacuum desiccator containing solid potassium hydroxide.

In analysis 18 the same specimen of silver was used as in analyses

4 to 8. In analyses 17 and 19 a new specimen which had been twice electrolyzed was employed.

The fusion, bottling and analysis of the salt were conducted exactly as described in the previous paper on cadmium chloride and also in this paper. A very slight insoluble residue in the cadmium chloride was determined as in the case of the bromide. The vacuum correction +0.000156 was applied to every apparent gram of cadmium chloride,[1] and of +0.000075 for every apparent gram of silver chloride. The analytical work was performed by Mr. Hines.

The average of these results is almost identical both with that obtained in the previous analysis of cadmium chloride, 112.469, and with that obtained from the bromide, 112.467, hence it is evident that no serious error was introduced in our earlier work by the use of phosphorus pentoxide for drying hydrochloric acid gas. Furthermore, in other analyses of chlorides in this laboratory, where the salts were fused in an atmosphere containing hydrochloric acid, either the salt employed was initially anhydrous, so that it could not have taken up the phosphorus, as in the case of magnesium ammonium chloride,[2] and of strontium chloride,[3] or else the concentrations of hydrochloric acid gas were so low that no error could have been introduced through the use of the hydrochloric acid, as in the case of calcium chloride.[4]

Although Bailey and Fowler attribute to hydrobromic acid an effect similar to that of hydrochloric acid, for several reasons it is certain that in the experiments upon cadmium bromide described in the earlier part of this paper no appreciable amount of phosphorus was introduced into the salt by the action of the hydrobromic acid upon the phosphorus pentoxide. In the first place, the experiment of passing into water hydrobromic acid gas, formed as in our work by passing nitrogen through bromine and then through an emulsion of red phosphorus in concentrated hydrobromic acid solution, and dried first by fused calcium bromide and then by phosphorus pentoxide, was performed in this laboratory some years ago in connection with the analysis

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[1] The specific gravity of cadmium chloride has already been found to be 4.047. Baxter and Hines: Am. Ch. J., 31, 220 (1904).

[2] Richards and Parker: Pr. Am. Acad. 32, 55 (1896).

[3] Richards: Ibid. 40, 603 (1905).

[4] Richards: This Journal, 24, 374 (1902).

THE ATOMIC WEIGHT OF CADMIUM.

Ag = 107.930 Cl = 35.473[1]

$CdCl_2 : 2Ag$.

Number of analysis.	Weight of $CdCl_2$ in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of $CdCl_2$. Grams.	Corrected weight of Ag. Grams.	Atomic weight of cadmium.
17	5.62511	0.00015	0.00004	6.61993	0.00000	5.62500	6.61193	112.472
18	6.81040	0.00026	0.00017	8.01516	0.00020	6.81031	8.01496	112.470
19	5.50097	0.00017	0.00009	6.47393	0.00000	5.50089	6.47393	112.470
							Average,	112.471

$CdCl_2 : 2AgCl$.

Number of analysis.	Weight of $CdCl_2$. in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	Weight of asbestos from filtrate. Gram.	Weight of AgCl from wash-waters. Gram.	Corrected weight of $CdCl_2$. Grams.	Corrected weight of AgCl. Grams.	Atomic weight of cadmium.
20	6.11757	0.00004	+0.00003	9.56432	0.00013	0.00024	0.00147	6.11750	9.56590	112.470
21	6.81040	0.00026	0.00017	10.64731	0.00010	0.00061	0.00136	6.81031	10.64918	112.471
22	5.50097	0.00017	0.00009	8.59940	0.00008	0.00052	0.00190	5.50089	8.60174	112.469
									Average,	112.470

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[1] Richards and Wells: Publications of the Carnegie Institution, No. 28, 1905; this Journal, 27, 459.

of cobalt and nickel bromides.[1] In this experiment no phosphorus could be discovered in the aqueous solution. In the second place, in two analyses of bromides which had been heated in hydrobromic acid gas, the filtrates from the silver bromide precipitates were evaporated to small bulk and tested for phosphoric acid, with negative results, while the slight residues obtained by filtering the aqueous solutions of the original bromides also showed in one case the complete absence of phosphorus, and in the other the presence of only a minute trace of this substance, although in the latter case the salt had been sublimed in a current of hydrobromic acid and therefore contained maximum amounts of phosphorus.[2] This result was to be expected from a consideration of the fact that the hydrobromic acid gas used in these experiments was diluted with at least twice its volume of nitrogen. In the light of this evidence it seems safe to assume that in the numerous analyses of bromides which have been carried out in this laboratory in recent years, no error was introduced by the use of phosphorus pentoxide as a drying agent for the hydrobromic acid gas. Nevertheless, with more concentrated hydrobromic acid, doubtless it would be unwise to use this drying agent.

It is interesting to compare the results of the analyses of the different fractions of material.

Fraction.			Average.
I	$CdCl_2 : 2Ag$	112.468	112.470
I	$CdCl_2 : 2AgCl$	112.471	
II, Series 1	$CdCl_2 : 2Ag$	112.456	112.469
II, Series 1	$CdCl_2 : 2AgCl$	112.481	
II, Series 2	$CdCl_2 : 2Ag$	112.471	112.471
II, Series 2	$CdCl_2 : 2AgCl$	112.470	
II	$CdBr_2 : 2Ag$	112.467	112.466
II	$CdBr_2 : 2AgBr$	112.465	
III	$CdBr_2 : 2Ag$	112.472	112.468
III	$CdBr_2 : 2AgBr$	112.464	
	Average......	112.469	112.469

The close agreement of the results from fraction II by different methods and of the results from all three fractions leaves no doubt of the identity of the different specimens of material.

No matter how the results are averaged, the same conclusion

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[1] Richards and Baxter: Pr. Am. Acad. 34, 361 (1899).

[2] Baxter: Pr. Am. Acad. 39, 248 (1903).

is reached as in the preliminary paper, *i. e.*, that the atomic weight of cadmium lies very near the value 112.47 (Ag = 107.930).

It is interesting to compare the results of our work with those obtained by other experimenters. From the following list[1] of

Stromeyer: Schweigger's Jour. **22**, 366 (1818).	Cd : CdO	111.5
	Cd : CdS	113.8
	Cd : Cl_2	112.8
	Cd : I_2	111.7
von Hauer: J. pr. Chem. **72**, 350 (1857).	$CdSO_4$: CdS	111.94
Lenssen: J. pr. Chem. **79**, 281 (1860).	CdC_2O_4 : CdO	112.0
Dumas: Ann. Chem. Pharm. **113**, 27 (1860).	$CdCl_2$: 2Ag	112.43 111.95
Huntington: Pr. Am. Acad. **17**, 28 (1881).	$CdBr_2$: 2Ag	112.24
	$CdBr_2$: 2AgBr	112.23
Partridge: Am. J. Sci. (3) **40**, 377 (1890).	CdC_2O_4 : CdO	111.80
	$CdSO_4$: CdS	111.73
	CdC_2O_4 : CdS	111.67
Morse and Jones: Am. Ch. J. **14**, 261 (1891).	Cd : CdO	112.07
	CdC_2O_4 : CdO	112.02
Lorimer and Smith: Z. anorg. Chem. **1**, 364 (1892).	CdO : Cd	112.04
Bucher: Doctoral Dissertation, Baltimore, Md. (1895).	CdC_2O_4 : CdO	111.88
	CdC_2O_4 : CdS	112.15
	$CdCl_2$: 2AgCl	112.37
	$CdBr_2$: 2AgBr	112.39
	Cd : $CdSO_4$	112.35
	Cd : CdO (porcelain)	112.08
	Cd : CdO (platinum)	111.89
Hardin: This Journal, **18**, 1016 (1896).	$CdCl_2$: Cd	112.12
	$CdBr_2$: Cd	112.06
	Cd : Ag	111.99
Morse and Arbuckle: Am. Ch. J. **20**, 536 (1898).	Cd : CdO	112.38
Baxter and Hines: This Journal, **27**, 222 (1905).	$CdCl_2$: 2Ag	112.462
	$CdCl_2$: 2AgCl	112.476

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[1] The greater portion of this list is to be found in Clarke's "Recalculation of the Atomic Weights," Smithsonian Misc. Coll. 1897.

investigations upon the atomic weight of cadmium it can be seen that this subject has attracted considerable attention, especially in recent years. The following atomic weights are assumed: O = 16.00; C = 12.00; S = 32.06; Cl = 35.47; Br = 79.96; Ag = 107.93; I = 126.98.

The relative value of many of these determinations has already been several times discussed,[1] and since it is invariably a difficult matter intelligently to criticize experimental work without an actual repetition of the experiments, for frequently some constant source of error is so securely hidden that it may be detected only by the most careful investigation, no attempt at criticism is made here.

Furthermore the uncertainty which now exists as to the relation between several fundamental atomic weights, *e. g.*, silver and oxygen,[2] makes it a matter of considerable doubt whether, when this uncertainty is removed, some of the discrepancies in the foregoing table will not disappear.

Attention should be called to the agreement with ours of the results of Bucher's painstaking work upon the halogen compounds of cadmium. The values from cadmium chloride vary between 112.26 and 112.46, with an average of 112.37, but if the first seven of his twenty-one experiments are rejected, his average becomes 112.40, and six of his results are as high as 112.43. His analyses of the bromide vary between 112.30 and 112.46, with an average of 112.39.

The results of this investigation are then as follows:

(1) The value for the atomic weight of cadmium previously found by analysis of cadmium chloride, 112.47 (Ag = 107.930), is supported by the analysis of cadmium bromide and by new analyses of cadmium chloride.

(2) Phosphorus pentoxide is found to be attacked by pure hydrochloric acid gas, and hence is unsuited for drying this gas, thus confirming the results of Bailey and Fowler.

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[1] Clarke, Partridge, Morse and Jones: Loc. cit.; Richards: Am. Ch. J. 20, 547 (1898).

[2] Richards: Publications of the Carnegie Institution, No. 28, page 67; Report of the International Committee on Atomic Weights, This Journal, 28, 1 (1906).

(3) It is shown that no appreciable error is introduced from this source, if a *dry* salt is fused in a current of hydrochloric acid which has been dried by phosphorus pentoxide.

(4) It is pointed out that in the case of hydrobromic acid diluted with twice its volume of nitrogen no similar effect is produced.

We are deeply indebted to the Carnegie Institution of Washington with whose generous aid this investigation has been completed, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

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ON THE CHEMICAL ACTION OF ULTRA-VIOLET LIGHT.

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THE work herein described was undertaken with a view to making especially some quantitative measurements on the chemical action of light. Since in the majority of chemical changes the greatest effect is produced by ultra-violet light, it was thought advisable to work with a source of light rich in these rays. Such a source was obtained by causing an oscillatory spark to pass between aluminium terminals joined in the secondary circuit of a large induction coil used as a transformer. In the secondary circuit was also joined in parallel a large Leyden jar. Through the primary circuit was passed an alternating current of 110 volts having a strength of 3.4 amperes. To obtain a constant source of light proved a matter of considerable difficulty. However, by arranging an apparatus as thus described and having in the primary circuit an ammeter and resistance boxes, the resistance could be changed at will and the strength of the current thus kept constant. When a uniform current was in this way maintained, the amount of energy given out by the spark during intervals of ten minutes was practically constant. This was shown to be the case by the fact that the same amount of iodine was set free from equal volumes of a potassium iodide solution, when exposed to the light under exactly the same conditions for equal intervals of time. After every observation the aluminium terminals were sharpened, and then placed the same distance