

Summary.

1. The vapor pressures of saturated aqueous solutions of potassium chloride, potassium nitrate, ammonium chloride, ammonium sulfate, ammonium nitrate, ammonium dihydrogen orthophosphate, sodium nitrate, urea, and a mixture of ammonium chloride and potassium nitrate have been measured at temperatures between 20° and 30°.

2. The relation of the vapor pressures of saturated aqueous solutions to the hygroscopic properties of soluble substances has been briefly discussed.

3. The theory relating the vapor pressure of a saturated solution to the temperature and solubility of the solid has been indicated.

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THE PURITY OF ATOMIC WEIGHT SILVER. I. GASES IN PURE SILVER AND IODINE

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In a series of articles published in 1916 and subsequent years¹ entitled "Contributions to the Study of Sources of Error Affecting the Determinations of Atomic Weights," Ph. A. Guye and his collaborators have discussed critically and in much detail the various sorts of experimental evidence upon which atomic weight ratios depend. The most important sources of error to which attention is drawn are those resulting from impurities in the substances weighed. Under this head special emphasis is laid upon (1) gaseous impurities included in the interior of solids, (2) gaseous impurities condensed on the surfaces of solids, and (3) solid impurities.

Since metallic silver is a very important reference substance in the gravimetric determination of combining proportions, this substance has received especial attention at the hands of the Swiss scientists, and on the basis of experimental evidence doubt has been thrown on the purity of the silver which has served in the past as the standard of comparison. Unfortunately the evidence upon which the speculations of Professor Guye have been based has been obtained almost entirely from material the purification of which, if any, was far less complete than is essential in the most accurate work. It is much to be regretted, therefore, that, although realizing the desirability of repeating his own experiments using

¹ Guye, *J. chim. phys.*, **14**, 25, 55, 83, 195, 204 (1916); **15**, 360, 405 (1917); **16**, 46 (1918).

the best material, he has seen fit to place great emphasis upon the necessity for corrections² of a highly questionable nature and magnitude.

The three suggestions mentioned above are by no means novel. All three sources of error have in the past repeatedly been the subjects of investigation both in the Harvard chemical laboratories and elsewhere. So far as silver is concerned, in general the evidence obtained has led to the conclusion that the proportion of impurities in the best material is too small to have an appreciable effect on the results.³ Nevertheless, in view of the importance of the question, the subject has been further studied. The outcome of our study confirms the earlier conclusion that the best metallic silver, while in the strictest sense not chemically pure, does not contain sufficient impurity to affect the result of the most accurate work within the limit of experimental error.

The first subject to be investigated was the possible gas content of silver and iodine. In a recent paper by Guye and Germann⁴ a method for the analysis of very small quantities of gas⁵ has been applied to the analysis of gases disengaged from iodine during sublimation in a vacuum, and from silver by conversion to silver iodide in a vacuum. In a single experiment with 3 g. of iodine they obtained 30 mm.⁴ of gas which, on the assumption that it has the density of air, represents 0.0013% of the weight of the iodine. They performed five experiments with silver. In three, metal of 99.8% purity was used without preliminary treatment. In two, a purer specimen⁶ was fused in a quartz test-tube in a current of pure dry hydrogen which was bubbled through the molten metal for some time in order to sweep out gases. The less pure material was found to contain about 170 cu. mm. of gas per gram, $\frac{4}{5}$ of which was oxygen and $\frac{1}{5}$ carbon monoxide. The purer silver proved to be almost entirely free from oxygen but to contain 27 cu. mm. of carbon monoxide and 10 cu. mm. of water vapor per gram. Converted to percentages by weight these figures represent 0.0034% of carbon monoxide and 0.0008% of water, a total of 0.0042%. In another experiment⁷ in which silver wire which had been heated in a vacuum was converted to chloride by means of chlorine, evidence was obtained that the gas content of the metal was greater in the inner than in the outer layers of the wire.

On the basis of these results Guye and Germann⁸ make a preliminary

² See in particular, Guye and Germann, *J. chim. phys.*, **14**, 229 (1916). Guye, *ibid.*, **15**, 549 (1917).

³ Richards and Wells, *Carnegie Inst. Pub.*, **23**, 16 (1905). *THIS JOURNAL*, **27**, 459 (1905).

⁴ Guye and Germann, *Compt. rend.*, **159**, 225 (1914); *J. chim. phys.*, **14**, 204 (1916).

⁵ *Compt. rend.*, **159**, 154 (1914); *J. chim. phys.*, **14**, 195 (1916).

⁶ "Extra-pur a 1000/1000." Both samples were provided by the Société g n rale de d grossage d'or.

⁷ *J. chim. phys.*, **14**, 227 (1916).

⁸ *Compt. rend.*, **159**, 992 (1914); Ref. 2.

calculation of the effect of this gas upon the atomic weights of silver and of other elements which have been referred to silver, and find that while the effect upon the atomic weight of silver is small, -0.0045 unit, the effect upon those of other elements may amount to several hundredths of a unit, e. g., $+0.005$ in the case of chlorine, -0.031 in the case of tin.

The original investigation by Guye and Germann is an interesting one, although the outcome is not surprising in view of the questionable quality of the material examined. Certainly the matter is one demanding investigation. Under the circumstances we felt warranted in preferring to carry out this investigation ourselves, rather than to subject our material to Professor Guye for examination.

In outline we have followed closely the method of analysis used by Guye and Germann.⁹ So far as possible we have examined material remaining from atomic weight researches. While it was impossible to investigate every specimen of iodine and silver which has been used in the past, a considerable variety of samples was available, and, since the specimens still remaining have already been compared with many others, there can be little question that the ground has been sufficiently covered.

Purification of Iodine and Silver

Iodine.—Of the different samples of iodine examined in the course of the work, one consisted of commercial material which had merely been resublimed in a current of pure dry air, in a hard glass tube constricted at 3 points. The iodine was sublimed from porcelain boats into the portion of the tube included between the first 2 constrictions, where it was first melted to liberate moisture, and then sublimed into the next compartment where the process of melting and subliming was repeated. Finally, the product was sublimed a fourth time from the tube into a hard glass receiver from which it was transferred to the quartz tube. This sample (A) was prepared in an identical fashion for Expts. 3 and 5 (Table II).

A second sample of iodine was prepared by Baxter and Grose¹⁰ for work upon the vapor pressure of iodine, and by Baxter and Harris¹¹ for an investigation on the atomic weight of arsenic. This material was distilled from aqueous potassium iodide and reduced to hydriodic acid by treatment with hydrogen sulfide under water. A possible impurity of cyanogen was eliminated as hydrocyanic acid by prolonged boiling of the solution and, after removal of sulfur by filtration, potassium permanganate was added and the iodine liberated was distilled from the residual solution of potassium and manganous iodides. A second reduction with hydrogen sulfide and oxidation of the hydriodic acid followed, and the

⁹ This is a modification of that used by Guichard. *Compt. rend.*, 153, 272 (1911).

¹⁰ Baxter and Grose, *THIS JOURNAL*, 37, 1061 (1915).

¹¹ Not yet published.

final product, after being rinsed, was dried over sulfuric acid. This sample is designated Sample B. An essentially similar method was used by Baxter¹² in earlier work upon the atomic weight of iodine, so that this specimen represents closely one sample of material involved in the question under discussion. Preparatory to examination for gaseous impurity it was sublimed in the manner already described (Expts. 1, 2 and 6) and part of the material was subjected to a second series of sublimations in exactly the same way (Expt. 4). The second series of sublimations apparently was without effect.

A third sample of iodine was made from iodic acid by first dehydrating the acid to the pentoxide and then decomposing the pentoxide into iodine and oxygen at a high temperature. This method also was used by Baxter.¹³ One specimen of iodic acid had been made by Mr. P. C. Voter by acting on iodine with fuming nitric acid, and fractionally crystallizing the product many times. Since the material remaining consisted of fractions of intermediate purity, the fractional crystallization was continued for three more series of fractions. Although this material had been prepared and crystallized in quartz vessels, this point is of minor significance for the present purpose. The powdered crystals were carefully dehydrated in a current of pure dry air at gradually increasing temperatures up to 275°. Finally, the hard glass tube which had been used during the dehydration was heated until decomposition of the pentoxide took place, the iodine first being condensed and then thrice sublimed through the series of compartments of the tube as described above. The product was again sublimed through the hard glass tube before use (Sample C). The material used in Expt. 10 consisted of that used in Expts. 7, 8 and 9 after further sublimation in air. The material used in Expt. 17 was subjected to three series of sublimations in a quartz tube, the vapors passing over a roll of incandescent platinum gauze once in each series as described under Sample D. In Expt. 11 it is probable but not certain that Sample C was used.

Sample D of iodine was made from iodic acid prepared from potassium iodate through the barium salt, and subjected to a series of fractional crystallizations. This material also had been used by Baxter¹³ in finding the ratio of silver to iodine. In Expt. 12 it was converted to iodine as described above. In Expts. 13 and 14 a quartz decomposition and sublimation tube was employed and the first constriction in the tube was filled with platinum gauze heated to redness. This served to decompose any iodine pentoxide which might have been blown along in the current of gas and also to facilitate the oxidation of the vapors of organic substances

¹² Baxter, *Proc. Am. Acad.*, **40**, 419 (1904); **41**, 73 (1905); *THIS JOURNAL*, **26**, 1577 (1904); **27**, 876 (1905); **32**, 1591 (1910).

¹³ Baxter, *THIS JOURNAL*, **32**, 1591 (1910).

which may have been present. Baxter¹³ used this same precaution. Before testing for gases this iodine was twice more sublimed through the silica tube (Sample D).

For Expts. 15 and 16 the iodine used in Expts. 12, 13 and 14 was twice sublimed in air through the silica tube with the incandescent platinum gauze. The iodine used in Expt. 18 was a mixture of residues from earlier experiments which was thrice sublimed through the silica tube containing the hot platinum gauze.

For purposes of comparison the treatment given iodine preparatory to weighing by Baxter in work on the atomic weight of iodine is summarized here. In the first investigation¹⁴ carefully purified iodine was sublimed once from a crystallizing dish to a cool surface, and once from a hard glass tube into the weighing tube in a current of dry air. In the second investigation¹⁵ the iodine was sublimed from one part of the hard glass sublimation tube to another and then again into the weighing tube, all in a current of pure dry air. In the third investigation¹⁶ iodine pentoxide was decomposed at about 350° in a current of dry air. Then the iodine was fused, and finally was sublimed into the weighing tube and again fused. Another specimen was made in the same way in a quartz tube, but the iodine vapor was passed through hot platinum gauze. Still a third specimen of iodine which had been carefully purified in another way was twice sublimed in the quartz tube, once through the platinum gauze, and then a third time into the weighing tube where it was fused.

The material designated Sample D in this paper resembles most closely that used by Baxter in the latest and most satisfactory determinations of the ratio of silver to iodine, in that it was made from iodine pentoxide, was sublimed through platinum gauze in a current of air and oxygen, and was fused. The material used by Baxter had, however, been subjected to fewer sublimations than Sample D.

Silver.—All the silver examined consisted of specimens of material which had already been employed in determining atomic weight ratios. One group of samples had been prepared in a similar way by Baxter, Moore and Boylston,¹⁷ Baxter and Grover,¹⁸ and Baxter.¹⁹ After an elaborate preliminary purification, crystals of metal which had been deposited electrolytically were fused in a current of hydrogen on a support of the purest lime. The adherent lime was removed by etching, and finally

¹⁴ *Proc. Am. Acad.*, **40**, 428 (1904); *THIS JOURNAL*, **26**, 1587 (1904); *Z. anorg. Chem.*, **43**, 25 (1905).

¹⁵ *Proc. Am. Acad.*, **41**, 77 (1905); *THIS JOURNAL*, **27**, 879 (1905); *Z. anorg. Chem.*, **46**, 40 (1905).

¹⁶ *Ref. 13*, p. 1597; *Z. anorg. Chem.*, **70**, 41 (1910).

¹⁷ Baxter, Moore and Boylston, *THIS JOURNAL*, **34**, 260 (1912).

¹⁸ Baxter and Grover, *ibid.*, **37**, 1030 (1915).

¹⁹ Baxter, *ibid.*, **28**, 1329 (1906). Sample E.

the buttons were washed, dried and heated in a vacuum at about 400°. (Sample I).

Another specimen, prepared by Richards and Hall,²⁰ had been finally precipitated as metal by ammonium formate, and the product was fused, etched and dried as stated above (Sample II).

As all the material had been standing for some years in desiccators, most of it was again slightly etched with nitric acid, dried and again heated in a vacuum, although this last process was omitted in Expts. 2 and 3.

Description of Apparatus

The apparatus resembled very closely that used by Guye and Germann for the determination of small amounts of gases except that when first constructed no provision was made for analysis of the gas, and later, because the quantity of gas was found to be very small, it was not considered necessary to make the analysis. We have found the apparatus very satisfactory for the purpose.

The transparent quartz tube *AB*, in which the reactions were carried out was connected by a carefully ground joint *C* to the all-glass measuring apparatus. The tube *F* contained copper amalgam to prevent iodine vapor from reaching the mercury in *H* and *J*. Measurements of pressure were made in the McLeod gage *H*, which magnified the pressure 50 times. In order to dry the gas, *L* was filled with phosphorus pentoxide which had been freshly sublimed in a current of pure dry oxygen. A spectroscopic examination of the gas was made possible by the Plücker tube *R*, which was partially protected from mercury vapor by gold leaf in the tube *S*. The whole system could be exhausted by an automatic Töpler pump of the Maass²¹ type. By means of the leveling bulb *W* the gas content of the apparatus could be largely transferred to *L* or back again to *AB*. Ground joints and stopcocks were made tight with Ramsay grease, especial pains being taken in the ground joint *C* to prevent contact of the grease with gases in the tube.

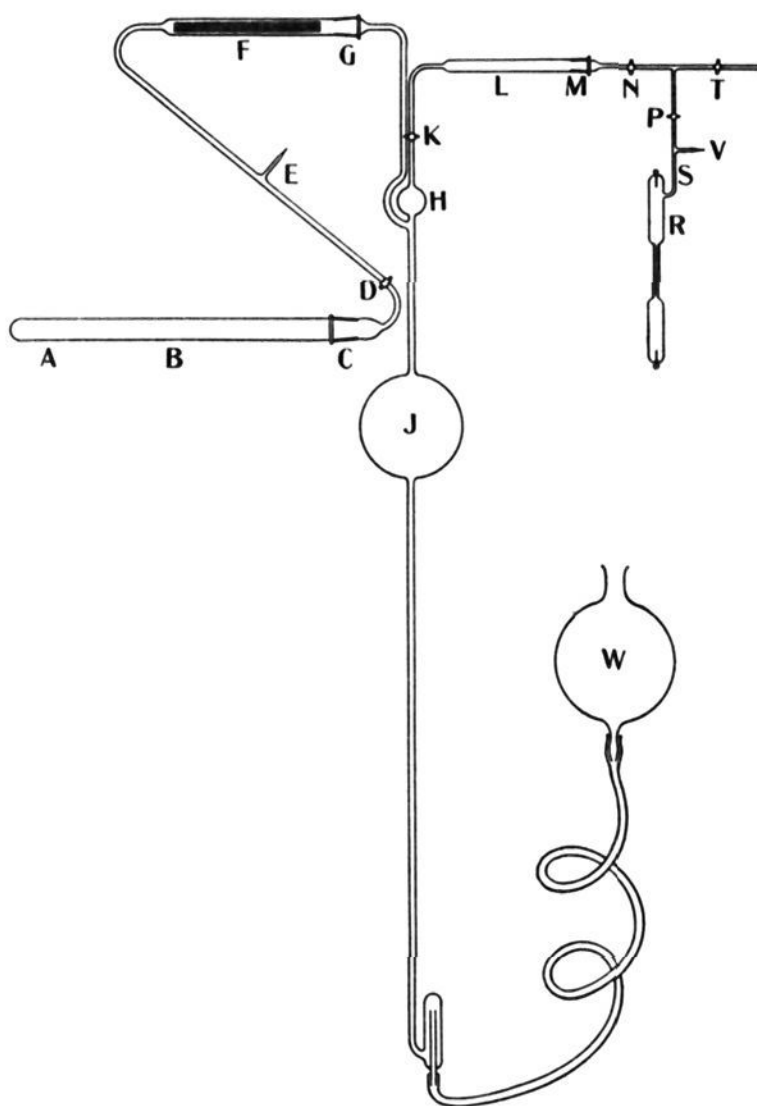
The method of procedure was in general as follows. The whole apparatus was exhausted through *T* and the stopcock *K* was closed. By raising the leveling bulb *W* the mercury was introduced into the gage *H* and the reading of the gage was taken. Then the stopcock *D* was closed and the reaction was carried out in *AB*. When the reaction was complete and the tube *AB* was cold, the stopcock *D* was opened and after the pressure had been given time to adjust itself, the reading of the gage *H* was taken. If it was desired to dry the gas, it was forced into *L* by filling *J* with *D* open, then closing *D* and by raising *X*, forcing all the gas through *K* into the drying tube. After closing *K* the process was repeated four times. When the gas was dry it was allowed to diffuse back again into *AB* and the pressure was remeasured. Although this method of determining the proportion of water vapor is obviously not highly exact, in view of the small quantities of gas ultimately found, the process is

²⁰ Richards and Hall, *THIS JOURNAL*, **39**, 531 (1917).

²¹ Maass, *ibid.*, **37**, 2654 (1915).

amply accurate for the purpose. In a similar fashion the gas could be collected in *L* and then admitted to the Plücker tube *R*.

The quantity of gas was estimated from the difference between the gage readings before and after the experiment, and the volume of the system as far as the gage, and is expressed in terms of weight of gas per gram of material on the assumption that the density of the gas is as large as that of air. Since a portion of the gas was certainly water vapor and a portion of it was undoubtedly hydrogen, and as the other gases likely to be present,—carbon dioxide, carbon monoxide, oxygen and nitrogen,—with the exception of carbon dioxide possess nearly the same density as air, the above assumption seems to be a safe one.



The Determination of Gases in Iodine

Since the determination of the gases in silver involved the reaction of silver with iodine, the first step in the problem was the determination of the gases in iodine. This was carried out by placing the iodine at *A* and then, after exhausting the tube, subliming the iodine from *A* to *B*

by warming the tube very gently at *A* and cooling it at *B* by means of a cloth wet with alcohol and with the assistance of a blast of air.

Most of the iodine could then be sublimed back to the point *A*, if desired, and the whole process could be repeated. Some iodine unavoidably reached the joint *C*, and even as far as the stopcock *D*, but the greater part remained in the quartz tube.

Because of the desirability of duplicating so far as possible the conditions used in preparing iodine for weighing for atomic weight work in the Harvard laboratory, and because in this work the iodine was always weighed after fusion in the weighing tube, the iodine was usually melted into the quartz tube and allowed to solidify in a fairly thin layer over the closed end of the tube. Thus, most of the material formed a compact mass, although of course a small proportion evaporated and condensed as crystals. In some cases a small amount of air apparently was trapped between the iodine and the glass, for the tube, after the preliminary exhaustion, showed a slight gain in pressure on standing. When this occurred the apparatus was allowed to stand exhausted until the pressure had become constant and remained so for some hours before the iodine was sublimed. In order to find out whether the surface exposed by the iodine plays an important part in the gas retention, in Expts. 3 and 6 the iodine was wholly in the form of loose crystals. The weight of iodine used in each experiment was found from the gain in weight of the reaction tube.

After Expt. 4 had been completed, a test was made to determine whether the quartz sublimation tube was perfectly tight. The empty quartz tube was exhausted and after the pressure had been read, the tube was heated as in an experiment with iodine. No change in pressure resulted. On further heating to a much higher temperature (about 500°), however, the interior pressure increased 0.054 mm. Since this increase might have been due to gases dislodged from the interior surface of the tube at the higher temperature, it was again exhausted and heated. The increase in pressure, 0.016 mm., though smaller, was disquieting. Therefore the whole tube was fire polished with an oxy-gas flame. Upon exhausting and heating to about 500° the pressure rose 0.014 mm., and after two days had increased only 0.010 in addition. Two later experiments of the same sort yielded still smaller gains, of 0.004 mm. in each case. Although it seems likely, therefore, that a small part of the increase in pressure in the experiments with iodine is not to be attributed to the iodine, this uncertainty is too small to be of importance in the final outcome.

In several experiments the iodine was subjected to repeated sublimation as described above (this page). The results of these experiments are collected in Table I. In accordance with the observations of Guye and Germann,²² these results indicate clearly that gas evolution is essentially over in most

²² *Compt. rend.*, 159, 226 (1914).

cases after one sublimation in vacuum and that two sublimations are invariably sufficient. Consequently in many of the later experiments only one sublimation was carried out.

TABLE I
EFFECT OF REPEATED SUBLIMATION
Increase in pressure in mm.
Sublimation

Expt.	I	II	III	IV
2	0.146	0.020		
3	0.054	0.024	0.020	
4	0.154	0.106	0.000	0.004
5	0.446	0.020		
6	0.152	0.000		
8	0.144	0.020		
12	0.068	0.086		
14	0.070	0.006		

In Table II are given the results of all the experiments. In Expts. 1 to 9 the vacuum apparatus contained only iodine, in the remainder the examination of iodine was combined with that of silver, the iodine being first sublimed to free it from gases and then allowed to react with silver in a separate part of the experiment.

The following experiments indicate conclusively that the proportion of gas obtained is very largely dependent upon the purity of the iodine. In Expts. 13 to 18 not only was the material from which the iodine was prepared more carefully purified than for the previous experiments but the iodine was also passed over hot platinum gauze to ensure complete combustion and elimination of carbon compounds. Although these last six experiments yielded less than half as much gas as the general average of all the experiments and less than $\frac{1}{3}$ as much as the crude iodine, even the crude material yielded considerably less than half as much gas as Guye and Germann obtained,²³ while our purest iodine, which was essentially identical with that used by Baxter in his last determination of the ratio of silver to iodine except that it had been subjected to a larger number of sublimations, was found to yield only 0.00015% of gas, slightly more than $\frac{1}{10}$ that found by Guye and Germann. This proportion is far smaller than the experimental error of the process in which iodine was compared with silver.

Spectroscopic examination of the gases obtained in Expts. 3 and 9 showed the presence of hydrogen and carbon monoxide (besides mercury). The hydrogen spectrum may have had its origin in water held either by the iodine or the interior surfaces of the apparatus, and incompletely removed from the gas. The carbon spectrum undoubtedly is due largely

²³ Guichard in a similar experiment found 0.45 cc. of gas, per 100 g. of iodine. The percentage calculated as air is 0.0005, a proportion identical with ours obtained with crude iodine. *Compt. rend.*, 153, 272 (1911).

TABLE II
GASES IN IODINE
Volume of Apparatus = 180 cc.

Expt.	Sample of iodine	Wt. of iodine G.	Initial reading of gage Mm.	Final reading of gage Mm.	Change in pressure Mm.	Water vapor in gas %	Wt. of gas Mg.	Gas %
1	B	2.0	0.5	2.0	0.030		0.0096	0.00044
2	B	10.2	0.2	7.5	0.146		0.0418	0.00041
			1.7	2.7	0.020		0.0057	0.00006
3	A	5.6	0.3	3.0	0.054	7	Total	0.00047
			3.0	4.2	0.024		0.0154	0.00027
			4.2	5.2	0.020		0.0069	0.00012
							0.0057	0.00010
4	B	17.6	0.3	8.0	0.154	55	Total	0.00049
			8.0	13.3	0.106		0.0441	0.00025
			13.3	13.2			0.0303	0.00017
			13.2	13.5	0.004			0.00001
5	A	25.1	0.7	23.0	0.446	36	Total	0.00043
			23.0	24.0	0.020		0.1275	0.00051
							0.0057	0.00002
							Total	0.00053
6	B	8.7	1.2	8.8	0.152		0.0435	0.00050
			8.8	8.8	0.000			
7	C	5.7	2.1	7.0	0.098		0.0280	0.00049
8	C	13.7	0.8	8.0	0.144		0.0412	0.00030
			8.0	9.0	0.020		0.0057	0.00004
9	C	5.8	0.8	4.4	0.072	6	Total	0.00034
10	C	11.8	1.0	8.3	0.146	39	0.0206	0.00036
11	C	17.1	2.5	22.0	0.390		0.0417	0.00035
12	D	14.0	0.5	3.9	0.068		0.1115	0.00065
			3.9	8.2	0.086		0.0194	0.00014
							0.0246	0.00018
							Total	0.00032
13	D	5.9	0.8	1.9	0.022		0.0063	0.00011
14	D	16.5	1.2	4.7	0.070		0.0200	0.00012
			1.0	1.3	0.006		0.0017	0.00001
							Total	0.00013
15	D	12.1	1.2	8.0	0.136		0.0389	0.00032
16	D	15.9	1.0	4.6	0.072		0.0206	0.00013
17	C	16.0	0.8	3.2	0.048		0.0137	0.00009
18	Residues	13.6	0.5	3.1	0.052		0.0149	0.00011
							Av.	0.00035
							Av. of Expts. 13 to 18	0.00015
							Av. of Expts. with Sample A	0.00051
							Sample B	0.00046
							Sample C	0.00038
							Sample D	0.00020

to carbon compounds contained in the iodine, since the proportion of gas obtained was very markedly diminished by the step taken to burn such substances. It is possible that the grease employed on the ground joints was responsible for a part of the gas. However, since the percentage of gas obtained is certainly a maximum and is so small as to be negligible from the standpoint of present atomic weight accuracy, no further attempt was made to discover the exact nature and source of the gas.

The Determination of Gases in Silver

In the conversion of silver into silver iodide, a weighed quantity of silver was placed at the point *B* in the quartz tube with an excess of iodine at the point *A*. After the system had been exhausted, the iodine was once sublimed and the increase in pressure which resulted was used as a measure of the quantity of gases evolved from the iodine as already described. The apparatus was then exhausted a second time and the portion of the tube where the silver was located was heated to a temperature somewhat above the melting point of silver iodide, 530° , so that the product of the reaction flowed away from the residual metal, leaving a fresh surface for attack. The reaction progressed rather slowly, several hours being necessary for even approximately complete conversion of the silver into iodide. In fact in many cases the experiment was stopped while a residue of unconverted silver still remained and, after the gas determination was completed, this residue was cleaned, weighed and the weight was subtracted from that originally taken. When the conversion of silver to iodide was over, the pressure in the apparatus was measured as previously described. In the first four experiments the proportion of water vapor in the gases also was measured.

After the first two experiments with silver had been completed, the suspicion arose that gas might result either by evolution from or diffusion through the quartz tube at the point of heating. Blank experiments in which the empty tube was exhausted and heated at one spot for several hours to the same temperature as in the experiment with silver, showed increases in pressure of 0.038 and 0.030 mm. Although these gains are small, the attempt was made to diminish the uncertainty by again fire polishing the greater part of the tube with an oxy-gas flame. Repetition of the blank experiments showed increases in pressure of 0.020 and 0.016 mm. and a short but intense heating of nearly the whole tube produced an increase in pressure of only 0.008 mm. Preparatory to all subsequent experiments with silver the section of the tube which had been heated in the previous experiment was fire polished. In spite of this precaution it seems likely at any rate that a small part of the observed increase in pressure in the experiments with silver had its source in the tube itself.

While there seems to be evidence that at elevated temperatures quartz

is pervious to gases, especially hydrogen,²⁴ we are of the opinion that with our tube a part of the difficulty originally was due to minute striations which were closed by the fire polishing.

Of course, unavoidably the silver buttons were very superficially attacked at ordinary temperature by the iodine during the exhausting of the tube and the determination of the gases in the iodine. The greater part of any gas thus produced must have been included in that evolved during the sublimation of the iodine.

In Expts. 6 to 10 the gas evolved during the early stages of the conversion of the silver to iodide at high temperature was measured. Then the tube was again exhausted and the reaction completed. On an average this gas obtained from the surface of the silver amounts to about one third of the whole. Although the quantities involved are too small to be viewed as positive proof, this result seems to be some indication that the surface of the silver contains a larger proportion of gases than the interior, a conclusion diametrically opposite to that arrived at by Guye and Germann.²⁵

The following table (III) gives the results of all the experiments with silver. In Expts. 6 to 10 the first series of figures in each experiment refers to the gas evolved from the surface of the silver, the second series refers to that subsequently obtained.

It is interesting to note that in Expt. 1 with crude (99.86%), large silver wire, the proportion of gas obtained is slightly greater than that obtained by Guye and Germann from their purer material (0.0042%), but is considerably less than they found in their crude metal (0.024%). So far as the results show there is no difference between silver precipitated electrolytically before fusion (Sample I) and that precipitated with formate (Sample II). On the whole the average of Expts. 4 to 10 seems to give the most reliable estimate of the gas content of the silver, since the material used in Expts. 2 to 3 had been exposed to the atmosphere of desiccators sealed with grease for some years and was not given preliminary cleansing. Furthermore, in Expts. 1 and 2 evidence was secured that slight leakage through the quartz tube had occurred.

As in the case of iodine the final result represents a maximum, both because of the possibility of the evolution of gases from the interior of the apparatus and that of leakage through the quartz tube. The result, 0.00063%, even if real, is almost negligible at the present stage of atomic weight accuracy.

Spectroscopic examination of the gases obtained in Expt. 2 indicated the presence of both hydrogen and carbon monoxide. The gas obtained

²⁴ Villard, *Compt. rend.*, **130**, 1752 (1900). Jacquerod and Perrot, *Arch. sci. phys. chem.*, **18**, 613 (1904); **20**, 454 (1905). Richardson and Richardson, *Phil. Mag.*, **22**, 704 (1911). Mayer, *Phys. Rev.*, **6**, 288 (1915).

²⁵ Ref. 7, p. 228.

in Expt. 3, however, gave only the hydrogen spectrum. This evidence is interesting since it indicates that the gas obtained from silver is at any rate largely composed of this relatively light gas.

TABLE III
GASES IN SILVER
Volume of Apparatus = 180 cc.

Expt.	Sample of silver	Wt. of silver G.	Initial reading of gage Mm.	Final reading of gage Mm.	Change in pressure Mm.	Water vapor in gas %	Wt. of gas Mg.	Gas %
1	Crude	5.2	0.8	56.6	1.132	13	0.324	0.00623
2	I	3.6	0.7	10.0	0.186	30	0.0532	0.00148
3	I	5.2	0.7	17.2	0.330	13	0.0858	0.00182
4	I	4.6	0.7	4.3	0.072	33	0.0206	0.00045
5	I	3.8	1.8	8.2	0.128		0.0366	0.00096
6	I	7.1	1.2	5.0	0.076		0.0218	0.00031
			1.3	7.0	0.114		0.0326	0.00046
							Total	0.00077
7	I	5.6	2.0	3.8	0.036		0.0103	0.00018
			1.0	5.1	0.082		0.0234	0.00042
							Total	0.00060
8	II	6.0	1.2	2.8	0.032		0.0091	0.00015
			1.0	3.5	0.050		0.0143	0.00024
							Total	0.00039
9	I	5.7	5.0	6.8	0.036		0.0103	0.00018
			1.0	5.0	0.080		0.0329	0.00040
							Total	0.00058
10	II	3.4	1.3	2.2	0.018		0.0052	0.00015
			0.5	3.4	0.058		0.0166	0.00049
							Total	0.00064
							Av., excluding Expt. 1	0.00085
							Av., excluding Expts. 1 to 3	0.00063
							Av. of Expts. 4, 5, 6, 7 and 9	0.00067
							Av. of Expts. 8 and 10	0.00052

Since the hydrogen is liberated from the silver in the presence of an excess of iodine, and therefore may have combined in part with the iodine, the question may very well be raised as to whether all the hydrogen originally contained by the silver is eventually recovered. Aside from the possibility of adsorption on the interior surfaces of the system, any hydrogen iodide produced would have exerted twice the pressure of the hydrogen it replaced. It seems reasonable to assume at any rate that one effect compensated the other.

If the gas obtained from the silver is largely hydrogen, as seems likely, from the spectroscopic results, the percentage is 0.00004. Since, however,

a considerable proportion of the gas was found to be water vapor, the real proportion must be somewhat larger than this. For instance, if $\frac{1}{3}$ is water vapor, the percentage of gas is 0.00016.

This proportion of hydrogen is smaller than that obtained by others in the past in silver which had been heated in hydrogen. Graham²⁶ found on an average 0.0005%. Stas²⁷ concluded the proportion to be less than 0.0004%. Mallet's²⁸ result was 0.0003%, and Baxter's²⁹ 0.001%, while Richards and Wells³⁰ found that silver which had been fused in hydrogen produced exactly as much silver chloride as metal which had been fused in a vacuum, within less than 0.001%.

The effect of impurities in iodine and silver upon the results of experiments in which they play a part depends upon the directness with which the calculations may be computed. One of the least favorable cases, used as an example by Guye,³¹ is that of the ratios $I_2O_5:2Ag$, and $I_2:2Ag$, from which the atomic weights of silver and iodine may be computed. Impurity in the iodine alone produces a positive error in the atomic weight of silver. Impurity in the silver alone also produces a positive error. Impurities in both silver and iodine produce an effect depending upon the relative proportions.

In the following table are given the values obtained by applying corrections of the magnitude observed by us, to the results of Baxter and Tilley,³² and Baxter¹³ on the above ratios.

	Uncorrected	Per cent. of gas Ag 0.00063 I 0.00046	Per cent. of gas Ag 0.00016 I 0.00015
At. wt. Ag.....	107.864	107.862	107.864
At. wt. I.....	126.913	126.912	126.913

Only upon the most unfavorable interpretation of the results in this paper are the atomic weights in question affected by as much as 0.002 unit.

Summary

1. Iodine sublimed in air was found to yield small quantities of gas when resublimed in a vacuum. The proportions varied from 0.0005% in the case of crude iodine, to 0.00015% in the case of the purest material. These proportions are far smaller than those found by Guye and Germann.

2. Crude silver, when converted to iodide in a vacuum, was found to yield 0.006% of gas, while the purest material when treated in the same

²⁶ Graham, *Phil. Mag.*, **32**, 503 (1866).

²⁷ Stas, "Oeuvres Complètes."

²⁸ Mallet, *Phil. Trans.*, **171**, 1020 (1880).

²⁹ Baxter, *Am. Chem. J.*, **22**, 362 (1899).

³⁰ Richards and Wells, *Carnegie Inst. Pub.*, **28**, 23 (1905).

³¹ Ref. 7, p. 237.

³² Baxter and Tilley, *THIS JOURNAL*, **31**, 201 (1909).

way yielded $\frac{1}{10}$ as much, 0.00063%. In this case also the proportion of gas found in pure metal is only $\frac{1}{7}$ that found by Guye and Germann.

The foregoing figures are based on the assumption that the iodine and the silver are responsible for all the gas evolved and that the gas is as heavy as air.

The likelihood has been pointed out that a portion of the gas obtained either was liberated from the walls of the apparatus or diffused through the reaction tube. Furthermore in the case of silver at any rate a large portion of the gas was found to be hydrogen. Therefore there is good reason to believe that the real percentages are smaller than those given above.

3. Even when maximum corrections are applied, the atomic weights of silver and of elements referred to silver are affected in the most unfavorable cases by only 0.002 unit.

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THE PURITY OF ATOMIC WEIGHT SILVER. II. SOLID IMPURITIES

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The preparation of silver of the highest purity for purposes of atomic weight comparison has been the subject of many investigations, the most recent of which is that of Richards and Wells,¹ who found that the processes of precipitation as silver chloride, crystallization of silver nitrate, precipitation of the metal from solution by ammonium formate,² and electrolytic transport of the metal from a dissolving anode through a concentrated solution of silver nitrate,³ are all effective in removing metallic impurities. In investigations in the Chemical Laboratories of Harvard University various combinations of these methods have been used both before and since the investigation of Richards and Wells, and the products have been found to yield identical results within the experimental error.⁴

The final treatment of the silver before weighing has consisted almost

¹ Richards and Wells, *Carnegie Inst. Pub.*, **28**, 16 (1905); *THIS JOURNAL*, **27**, 459 (1905).

² Stas, "Oeuvres Complètes," vol. 3, p. 40.

³ Abrahall, *J. Chem. Soc.*, **61**, 660 (1892).

⁴ Guye has recently questioned the freedom of such material from metallic impurities. *J. chim. phys.*, **15**, 554 (1917).