VI. "Additional Observations on Hydrogenium." By Thomas
Graham, F.R.S., Master of the Mint. Received June 10, 1869.

From the elongation of a palladium wire, caused by the occlusion of
hydrogen, the density of hydrogenium was inferred to be a little under 2.
But it is now to be remarked that another number of half that amount
may be deduced with equal probability from the same experimental data.
This double result is a consequence of the singular permanent shorten-
ing of the palladium wire observed after the expulsion of hydrogen. In
a particular observation formerly described, for instance, a wire of 609·14
millims. increased in length to 618·92 millims. when charged with hy-
drogen, and fell to 599·44 millims. when the hydrogen was extracted.
The elongation was 9·78 millims., and the absolute shortening or retrac-
tion 9·7 millims., making the extreme difference in length 19·48 millims.
The elongation and retraction would appear, indeed, to be equal in
amount. Now it is by no means impossible that the volume added to
the wire by the hydrogenium is represented by the elongation and re-
traction taken together, and not by the elongation alone, as hitherto
assumed. It is only necessary to suppose that the retraction of the
palladium molecules takes place the moment the hydrogen is first ab-
sorbed, instead of being deferred till the latter is expelled; for the
righting of the particles of the palladium wire (which are in a state of
excessive tension in the direction of the length of the wire) may as well
take place in the act of the absorption of the hydrogen as in the ex-
pulsion of that element. It may indeed appear most probable in the
abstract that the mobility of the palladium particle is determined by the
first entrance of the hydrogen. The hydrogenium will then be assumed
to occupy double the space previously allotted to it, and the density
of the metal will be reduced to one half of the former estimate. In
the experiment referred to the volume of hydrogenium in the alloy will
rise from 4·68 per cent. to 9·36 per cent., and the density of hydro-
genium will fall from 1·708 to 0·854, according to the new calculation.
In a series of four observations upon the same wire, previously recorded,
the whole retractions rather exceeded the whole elongations, the first
amounting to 23·99 millims., and the last to 21·38 millims. Their
united amount would justify a still greater reduction in the density of
hydrogenium, namely to 0·8051.

The first experiment, however, in hydrogenating any palladium wire
appears to be the most uniform in its results. The expulsion of the hy-
drogen afterwards by heat always injures the structure of the wire more
or less, and probably affects the regularity of the expansion afterwards in
different directions. The equality of the expansion and the retraction in
a first experiment appears also to be a matter of certainty. This is a
curious molecular fact of which we are unable as yet to see the full
import. In illustration, another experiment upon a pure palladium wire

may be detailed. This wire, which was new, took up a full charge of hydrogen, namely 956·3 volumes, and increased in length from 609·585 to 619·354 millims. The elongation was therefore 9·769 millims. With the expulsion of the hydrogen afterwards, the wire was permanently shortened to 600·115 millims. It thus fell 9·470 millims. below its normal or first length. The elongation and retraction are here within 0·3 millim. of equality. The two changes taken together amount to 19·239 millims., and their sum represents the increase of the wire in length due to the addition of hydrogenium. It represents a linear expansion of 3·205 on 100, with a cubic expansion of 9·827 on 100. The compositon of the wire comes to be represented as being,

In volume.

Palladium	100·000 or	90·895
Hydrogenium	9·827 or	9·105
	109·827 or	100·000

The specific gravity of the palladium was 12·3, the weight of the wire 1·554 grm., and its volume 0·126 cub. centim. The occluded hydrogen measured 120·5 cub. centims. The weight of the same would be 0·0108 grm., and the volume of the hydrogenium 0·012382 cub. centim. (100 : 9·827 : : 0·126 : 0·01238). The density of the hydrogenium is therefore

$$\frac{0·0108}{0·01238} = 0·872.$$

This is a near approach to the preceding result, 0·854. Calculated on the old method, the last experiment would give a density of 1·708.

It was incidentally observed on a former occasion that palladium alloyed with silver continues to occlude hydrogen. This property is now found to belong generally to palladium alloys, when the second metal does not much exceed one half of the mixture. These alloys are all enlarged in dimensions when they acquire hydrogenium. It was interesting to perceive that the expansion was greater than happens to pure palladium (about twice as much), and that, on afterwards expelling the hydrogen by heat, the fixed alloy returned to its original length *without any further shortening of the wire.* The embarrassing retraction of the palladium has, in fact, disappeared.

The fusion of the alloys employed was kindly effected for me by Messrs. Matthey and Sellon, when the proportion of palladium was considerable, by the instrumentality of M. Deville's gas-furnace, in which coal-gas is burned with pure oxygen—or by means of a coke-furnace when the metals yielded to a moderate temperature. The alloy was always drawn out into wire if possible, but if not sufficiently ductile, it was extended by rolling into the form of a thin ribbon. The elongation caused by the addition of hydrogenium was ascertained by measuring the wire or ribbon stretched over a graduated scale, as in the former experiments.

1. *Palladium, Platinum, and Hydrogenium.*—Palladium was fused with platinum, a metal of its own class, and gave an alloy consisting, according to analysis, of 76·03 parts of the former and 23·97 parts of the latter. This alloy was very malleable and ductile ; its specific gravity was 12·64. Like pure palladium, it absorbed hydrogen, evolved on its surface in the acid fluid of the galvanometer, with great avidity.

A wire 601·845 millims. in length (23·69 inches) was increased to 618·288 millims., on occluding 701·9 volumes of hydrogen gas measured at 0° C. and 0·76 barom. This is a linear elongation of 16·443 millims. (0·6472 inch), or 2·732 on a length of 100. It corresponds with a cubic expansion of 8·423 volumes on 100 volumes ; and the product may be represented—

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In volume.

Fixed metals .... 100·000 or 92·225
Hydrogenium ....   8·423 or 7·775

108·423 or 100·000
</div>

The elements for the calculation of the density of hydrogenium are the following, the assumption being made as formerly, that the metals are united without condensation :—

> Original weight of the wire 4·722 grms.
> Original volume of the wire 0·373 cub. centim.
> Volume of the hydrogen extracted 264·5 cub. centims.
> Weight of the hydrogen extracted, by calculation, 0·0237 grm.

The volume of the hydrogenium will be to the volume of the wire (0·373 cub. centim.) as 100 is to 8·423—that is, 0·03141 cub. centim. Finally, dividing the weight of the hydrogenium by its bulk, 0·0237 by 0·03141, the density of hydrogenium is found to be 0·7545.

On expelling all hydrogen from the wire at a red heat, the latter returned to its first dimensions as exactly as could be measured. The platinum present appears to sustain the palladium, so that no retraction of that metal is allowed to take place. This alloy therefore displays the true increase of volume following the acquisition of hydrogenium, without the singular complication of the retraction of the fixed metal. It now appears clear that the retraction of pure palladium must occur on the first entrance of hydrogen into the metal. The elongation of the wire due to the hydrogenium is negatived thereby to the extent of about one half, and the apparent bulk of the hydrogenium is reduced to the same extent. Hydrogenium came in consequence to be represented of double its true density.

The compound alloy returns to its original density (12·64) upon the expulsion of the hydrogen, showing that hydrogen leaves without producing porosity in the metal. No absorptive power for vapours, like that of charcoal, was acquired.

A wire of the present alloy, and another of pure palladium, were charged

with hydrogen, and the diameters of both measured by a micrometer. The wire of alloy increased sensibly more in thickness than the pure palladium, about twice as much; the reason is, that the latter while expanding retracts in length at the same time. The expansion of both wires may be familiarly compared to the enlargement of the body of a leech on absorbing blood. The enlargement is uniform in all dimensions with the palladium-platinum alloy; the leech becomes larger, but remains symmetrical. But the retraction in the pure palladium wire has its analogy in a muscular contraction of the leech, by which its body becomes shorter but thicker in a corresponding measure.

The same wire of palladium and platinum charged a second time with hydrogen, underwent an increase in length from 601·845 to 618·2, or sensibly the same as before. The gas measured 258·0 cub. centims., or 619·6 times the volume of the wire. The product may be represented as consisting of

	By volume.
Fixed metals	92·272
Hydrogenium	7·728
	100·000

The density of hydrogenium deducible from this experiment is 0·7401. The mean of the two experiments is 0·7473.

2. *Palladium, Gold, and Hydrogenium.*—Palladium fused with gold formed a malleable alloy, consisting of 75·21 parts of the former and 24·79 parts of the latter, of a white colour, which could be drawn into wire. Its specific gravity was 13·1. Of this wire 601·85 millims. occluded 464·2 volumes of hydrogen with an increase in length of 11·5 millims. This is a linear elongation of 1·91 on 100, and a cubic expansion of 5·84 on 100. The resulting composition was therefore as follows :—

	In volume.	
Alloy of palladium and gold	100 or	94·48
Hydrogenium	5·84 or	5·52
	105·84	100·00

The weight of the wire was 5·334 grms.

The volume of the wire was 0·4071 cub. centim.

The volume of hydrogen extracted, 189·0 cub. centims.

The weight of the hydrogen, 0·01693 grm.

The volume of the hydrogenium, 0·02378 cub. centim.

Consequently the density of the hydrogenium is 0·711.

The wire returned to its original length after the extraction of the hydrogen, and there was no retraction.

The results of a second experiment on the same wire were almost identical with the preceding.

The elongation on 601·85 millims. of wire was 11·45 millims., with the occlusion of 463·7 volumes of hydrogen. This is a linear expansion of

1·902 on 100, and a cubic expansion of 5·81 on 100. The volume of hydrogen gas extracted was 188·8 cub. centims., of which the weight is 0·016916 grm. The volume of the hydrogenium was 0·02365 cub. centim., that of the palladium-gold alloy being 0·4071 cub. centim. Hence the density of the hydrogenium is 0·715.

In a third experiment made on a shorter length of the same wire, namely 241·2 millims., the amount of gas occluded was very similar, namely 468 volumes, and was not increased by protracting the exposure of the wire for the long period of twenty hours. There can be little doubt, then, of the uniformity of the hydrogenium combination, the volume of gas occluded in the three experiments being 464·2, 463·7, and 468 volumes. The linear expansion was 1·9 on 100 in the third experiment, and therefore similar also to the preceding experiments.

The hydrogenium may be supposed to be in direct combination with the palladium only, as gold by itself shows no attraction for the former element. In the first experiment the hydrogenium is in the proportion of 0·3151 to 100 palladium and gold together. This gives 0·3939 hydrogenium to 100 palladium ; while a whole equivalent of hydrogenium is 0·939 to 100 palladium [*]. The hydrogenium found is by calculation 0·4195 equivalent, or 1 equivalent hydrogenium to 2·383 equivalents palladium, which comes nearer to 2 equivalents of the former with 5 of the latter than to any other proportion.

To ascertain the smallest proportion of gold which prevents retraction, an alloy was made by fusing 7 parts of that metal with 93 parts of palladium, which had a specific gravity of 13·05. The button was rolled into a thin strip and charged with hydrogen by the wet method. An occlusion of 585·44 volumes of gas took place, with a linear expansion of 1·7 on 100. A retraction followed to nearly the same extent on afterwards expelling the hydrogen by heat.

With another alloy, produced by fusing 10 of gold with 90 of palladium, the occlusion of gas was 475 volumes, the linear expansion 1·65 on 100. The retraction on expelling the gas afterwards was extremely slight. To nullify the retraction of the palladium, about 10 per cent. of gold appears therefore to be required in the alloy.

Another alloy of palladium of sp. gr. 13·1, and containing 14·79 per cent. of gold, underwent no retraction on losing hydrogen, as already stated.

The presence of so much gold in the alloy as half its weight did no materially reduce the occluding power of the palladium. Such an alloy was capable of holding 459·9 times its volume of hydrogen, with a linear expansion of 1·67 per cent.

3. *Palladium, Silver, and Hydrogenium.*—The occluding power of palladium appeared to be entirely lost when that metal was alloyed with much more than its own weight of any fixed metal. Palladium alloys con-

[*] $H=1$; $Pd=106\cdot5$.

taining 80, 75, and 70 per cent. of silver occluded no hydrogen whatever.

With about 50 per cent. of silver, palladium rolled into a thin strip occluded 400·6 volumes of hydrogen. It expanded 1·64 part in 100 in length, and returned to its original dimensions without retraction upon the expulsion of the gas. The specific gravity of this silver-palladium alloy was 11·8 ; the density of the hydrogenium 0·727.

An alloy which was formed of 66 parts of palladium and 34 parts of silver had the specific gravity 11·45. It was drawn into wire and found to absorb 511·37 volumes of hydrogen. The length of the wire increased from 609·601 to 619·532 millims. This is a linear elongation of 1·629 on 100, or cubic expansion of 4·97 on 100. The weight of the wire was 3·483 grms., its volume 0·3041 cub. centim. The absolute volume of occluded hydrogen was 125·1 cub. centims., of which the weight is 0·01120896. The volume of the hydrogenium was 0·015105 cub. centim. The resulting density of hydrogenium is 0·742.

In a repetition of the experiment upon another portion of the same wire, 407·7 volumes of hydrogen were occluded, and the wire increased in length from 609·601 millims. to 619·44 millims. This is a linear expansion of 1·614 part on 100, and a cubic expansion of 4·92 on 100. The absolute volume of hydrogen gas occluded was 124·0 cub. centims., and its calculated weight 0·01111 grm. The volume of the hydrogenium being 0·1496 cub. centim., the density of hydrogenium indicated is 0·741. The two experiments are indeed almost identical. The wire returned in both experiments to its original length exactly after the extraction of the gas.

4. *Palladium, Nickel, and Hydrogenium.*—The alloy, consisting of equal parts of palladium and nickel, was white, hard, and readily extensible. Its specific gravity was 11·22. This alloy occluded 69·76 volumes of hydrogen, with a linear expansion of 0·2 per cent. It suffered no retraction below its normal length on the expulsion of the gas by heat.

An alloy of equal parts of *bismuth* and palladium was a brittle mass that did not admit of being rolled. It occluded no hydrogen, after exposure to that gas as the negative electrode in an acid fluid for a period of 18 hours. It seems probable that malleability and the colloid character, which are wanting in this bismuth alloy, are essential to the occlusion of hydrogen by a palladium alloy.

An alloy of 1 part of *copper* and 6 parts of palladium proved moderately extensible, but absorbed no sensible amount of hydrogen. The metallic laminæ which remain on digesting this alloy in hydrochloric acid, and which were found by M. Debray to be a definite alloy of palladium and copper (Pd Cu), exhibited no sensible occluding power.

The conclusions suggested as to the density of hydrogenium, by the compound with palladium alone and by the compounds with palladium alloys, are as follows :—

	Density of Hydrogenium observed.
When united with palladium	0·854 to 0·872
When united with palladium and platinum	0·7401 to 0·7545
When united with palladium and gold	0·711 to 0·715
When united with palladium and silver........	0·727 to 0·742

The results, it will be observed, are most uniform with the compound alloys, in which retraction is avoided, and they lie between 0·711 and 0·7545. It may be argued that hydrogenium is likely to be condensed somewhat in combination, and that consequently the smallest number (0·711) is likely to be the nearest to the truth. But the mean of the two extreme numbers will probably be admitted as a more legitimate deduction from the experiments on the compound alloys, and 0·733 be accepted provisionally as the approximate density of hydrogenium.

I have the pleasure to repeat my acknowledgments to Mr. W. C. Roberts for his valuable assistance in this inquiry.

Could the density of hydrogenium be more exactly determined, it would be interesting to compare its atomic volume with the atomic volumes of other metals. With the imperfect information we possess, one or two points may be still worthy of notice. It will be observed that palladium is 16·78 times denser than hydrogenium taken as 0·733, and 17·3 times denser than hydrogenium taken as 0·711. Hence, as the equivalent of palladium is 106·5, the atomic volume of palladium is 6·342 times greater than the atomic volume of hydrogenium having the first density mentioned, and 6·156 greater with the second density. To give an atomic volume to palladium exactly six times greater than that of hydrogenium, the latter element would require to have the density 0·693.

Taking the density of hydrogenium at 0·7, and its atomic volume equal to 1, then the following results may be deduced by calculation. The atomic volume of lithium is found to be 0·826; or it is less even than that of hydrogenium (1). The atomic volume of iron is 5·026, of magnesium 4·827, of copper 4·976, of manganese 4·81, and of nickel 4·67. Of these five metals, the atomic volume is nearly 5 times that of hydrogenium. Palladium has already appeared to be nearly 6 times. The atomic volume of aluminium on the same scale is 7·39, of sodium 16·56, and of potassium 31·63.

VII. "Spectroscopic Observations of the Sun" (continued). By Lieut. J. HERSCHEL, in a Letter addressed to W. HUGGINS, F.R.S. Communicated by Mr. HUGGINS. Received June 10, 1869.

Bangalore, May 7, 1869.

MY DEAR SIR,—After what I wrote to you last week you will scarcely be surprised to hear again from me on the same subject; and indeed I feel in some measure bound to communicate without delay results of fur-