VIII.—*On the Physical Constants of Hydrogenium.* By JAMES DEWAR.
(Plate XII.)

(Read January 20, 1873.)

In March 1869 I communicated to the Society a paper entitled “Motion of a Palladium Plate during the Formation of GRAHAM’S Hydrogenium,” which appears in the Proceedings for Session 1868–69. When engaged with this subject many points of interest regarding the behaviour of palladium containing occluded hydrogen, suggested themselves for investigation, and in concluding the paper I remarked “that careful determinations must be made of the electromotive force, latent heat, &c., of hydrogenium” before we could arrive at any conclusion regarding the condition of the absorbed hydrogen. Subsequently Professor TAIT made a series of determinations on the “Electrolytic Polarisation of Palladium Electrodes,”* devising a new and ingenious method for the purpose. Although at different times subsequent to my first communication, the problem of determining the physical constants of hydrogenium recurred, as my attention was in the meantime directed to the specific heat of carbon at high temperatures, no progress was made with the investigation until September 1872, when the results of my preliminary experiments were communicated to the “Philosophical Magazine,” under the title, “Note on the Specific Heat of Hydrogenium.” In that note it is stated that by means of a specially constructed calorimeter the specific heat of hydrogen in palladium is found to be 3·1 per atomic weight, nearly identical with that of gaseous hydrogen. The present paper deals with some of the physical constants of hydrogenium, more especially with the specific gravity, specific heat, and co-efficient of expansion.

GRAHAM, in his celebrated paper on hydrogenium, made many determinations of the specific gravity of the occluded hydrogen by observing the increase of length of palladium wire after being fully charged, thus finding the cubical expansion, and from it deducing the weight of unit volume of the absorbed hydrogen.

From experiments made in this way he found the specific gravity to be nearly 2. Afterwards he discovered the value was about three times what it ought to be from a contraction of length occurring when palladium wire is used. This he confirmed by the use of alloys of palladium that resist this contraction, and finally regarded the specific gravity as 0·733. No determinations were made when the palladium was partially saturated, and he rejected the ordinary

* Proceedings of the Royal Society of Edinburgh, Session 1868–9.

process of taking specific gravities because of the continual evolution of gas preventing exact weighings being taken in water.

In the experiments to be detailed a cubical mass of the metal was charged with hydrogen by electrolysis, taken at different times during the progress of the saturation, and weighed in air and in water. If the mass was allowed free exposure to the air for several hours little difficulty arose from the evolution of gas when immersed in water, and accurate results could be obtained.

From the experimental numbers the specific gravity of the absorbed hydrogen was calculated by the well-known formula—

$$\frac{w_1 + w_2}{\frac{w_1}{S_1} + \frac{w_2}{S_2}} = S;$$

when w_1 and w_2 are the weights of the substance, S_1 and S_2 the specific gravities, and S the mean specific gravity found by experiment. This formula assumes that no condensation takes place in the palladium.

TABLE I.—SPECIFIC GRAVITY OF BAR PALLADIUM AT DIFFERENT TIMES DURING SATURATION WITH HYDROGEN. WEIGHT OF ORIGINAL PALLADIUM, 31·802.

Experiments.	Weight of Palladium and Hydrogen in air.	Weight of Palladium and Hydrogen in water.	Specific gravity of substance.	Specific gravity of Hydrogen (calculated).	Weight of Hydrogen.
1	31·8748	29·1150	11·5488	0·6215	0·0728
2	31·9230	29·0860	11·2520	0·6230	0·1210
3	31·9425	29·0715	11·1259	0·6150	0·1405
4	31·9715	29·0615	10·9867	0·6081	0·1625
5	31·9860	29·0500	10·8944	0·6270	0·1840
6	31·9955	29·0455	10·8459	0·6299	0·1935
7	32·0040	29·0450	10·8158	0·6388	0·2020
8 (after some days)	31·9940	29·0325	10·8033	0·6024	0·1920

When the calculated values of the specific gravity of the hydrogen in the eight determinations of Table I. are examined it will be observed no material alteration can be said to take place in the specific gravity during the course of the saturation, regard being paid to the difficulty of getting accurate weighings immediately after removal from the electrolytic cell. All the above determinations were made as quickly as possible after the palladium was taken from the pole of the battery. The mean of the results gives a specific gravity of 0·620 for the hydrogen. The atomic volume of this condition of hydrogen is therefore

1.6, and the alteration of volume is equivalent to saying in the formation of this condition 7 litres of gas are condensed into 1 cubic centimetre. The maximum charge of hydrogen the palladium would take was given to No. 7 experiment, and this very nearly accords with the composition Pd_3H_2 . In treating masses of palladium the above proportion was never exceeded.

As all the above experiments were made with bar palladium increasing to saturation, it was necessary to find similar values for a mass decreasing from saturation, the hydrogen being expelled by heating. For this purpose a piece of plate palladium was employed. When the plate was fully charged for the first time, and the specific gravity of the hydrogen found as in the previous experiment, the result was a density of 0.621, the plate in this case contained 0.21 grammes of hydrogen. When a portion of the hydrogen was expelled by heat, leaving 0.127 grammes in the plate, the density of the hydrogen was 0.633, and where only 0.0495 gramme was left, the value was 0.615. The mean specific gravity of the three different alloys of plate was 0.623, nearly the same as previously found for the bar. After palladium has been treated with hydrogen, and heated, the metal becomes porous, and often blisters, thus rendering specific gravity determinations very uncertain. The curious discovery of GRAHAM, that the strain on the particles of palladium produced by wire-drawing induces such a curious shrinking in the length after the hydrogen has been expelled, suggests the importance of investigating how a saturated piece of bar would resist the action of sustained pressure or tension. If the formation of the alloy is attended with an increase of volume in excess of the sum of the volumes of the constituents regarded as in the solid state, then partial decomposition ought to occur under great pressure. Experiments on this subject are left over for the present. After palladium has been used in the above experiments, and the last trace of hydrogen is removed by heating, the specific gravity is found to have diminished from 12.0359 to 11.9546. If this final value is taken in calculating the mean density, then the average result of the three hydrides of plate is 0.707 for the specific gravity of the condensed hydrogen. The mean of the first and second series of experiments is thus 0.664. A piece of palladium, weighing 31 grammes, was fused in a lime crucible with the oxyhydrogen flame, and the specific gravity was now found reduced to 10.5549. When this sphere of palladium was hydrogenised for a very long time (twenty-four hours) only 0.0684 grammes of hydrogen were absorbed, and by further treatment nothing was added. The specific gravity of the hydrogen in this case was 0.655, nearly identical with the mean of the values found from the plate experiments.

Specific Heat Observations.

The apparatus devised for this purpose is represented in the plate appended to this paper. The calorimeter used in the experiments had the form (A) shown

in Plate XII. It held conveniently 100 grammes of water, and was inserted in the middle of a stout brass envelope, thoroughly exhausted of air, the whole being placed in the middle of a large cylindrical tin vessel (E), having an outer annular compartment. The tin vessel was filled with water, and a constant current from the town supply was kept circulating by means of a syphon through the outer chamber. To the thermometer a ring of thin sheet india-rubber was attached as a stirrer, and when it was removed before the immersion of the palladium was placed in the little tin tube represented at (B). Immediately before an observation the whole apparatus was moved below the steam bath (C), and the palladium dropped in. This arrangement of the calorimeter is very convenient in a small chemical laboratory, where uniformity of temperature cannot be easily commanded. The constancy of the radiation in the calorimeter makes the correction for cooling very exact.

The same arrangement of the calorimeter is employed for registering very small amounts of heat by placing in (A) bisulphide of carbon or chloroform, packing the middle and outer compartments of the tin vessel full of pounded ice, and covering the exposed surface with sawdust. The thermometer is now provided with a thin sheet copper stirrer, instead of the india-rubber one formerly used. The rate of cooling is in this case determined once for all for a range of 5° above zero, and plotted in a curve. From this curve the correction for the radiation is determined for all subsequent experiments.

Two series of experiments were made. In the first series bar, and in the second plate, palladium was used, three different hydrides* of each. The experimental results are given in Tables II. and III.

In the case of the bar the specific heat of the occluded hydrogen increased as the charge diminished, the extreme values being 3.79 and 5.05. Similarly with the plate the values are greater, and have a wider range, viz., from 3.93 to 5.88. These results are calculated in each case for the excess of heat given to the calorimeter by the hydride in excess of that of the original palladium. But if a comparison is made between the different hydrides in both series of experiments, then the specific heat is found to exhibit no such regular increase as in the former series. In the bar the extreme values are 3.21 and 3.77, and the mean of the three results is 3.47. The plate, on the other hand, gives a range of from 2.7 to 3.94, the mean value being 3.31. The amount of variation in the plate is very great as compared with the bar, and is clearly due to some secondary action taking place.

The increase of specific heat for small charges of hydrogen, when comparison is made with pure palladium, is clearly due to some regular increase of the spe-

* In this paper the term hydride is not used in its strict chemical sense, but as a convenient abbreviation.

cific heat of the palladium, or of the hydrogen individually or conjointly. The mere fact that we have only a very small weight of hydrogen relatively to the amount of palladium does not explain the anomaly, because a small amount of hydrogen by the second mode of comparison does not yield such high results. The observational errors, although much greater when we are dealing with small quantities, cannot be expected to fall always in the same direction, and thus we are forced to admit there is some regular sequential change taking place in the relations of the hydrogen and palladium.

The palladium, after use, is not found to have increased in specific heat, but rather the reverse, so that the explanation can only rest on some altered condition of the bodies when united. So far as my experiments have led me, I am inclined to regard this alteration as a kind of molecular dissociation that increases with diminished charge of hydrogen. I am led to this conclusion from observing that the rate at which palladium loses hydrogen at constant temperature is dependent on the amount present increasing with diminished charge. In conducting these specific heat experiments, a greater variation in the results has always been observed when small charges were under experiment, especially in the first two or three determinations. This increase of dissociation may be explained in part from the formation of regular cracks or channels in the mass of palladium, together with the effect of pressure resulting from the contraction of the external layers of palladium from the loss of hydrogen. It is, however, premature to discuss the cause of this increase of dissociation until a more extended series of experiments is made, and the behaviour of the alloy to pressure is investigated.

TABLE II.—SPECIFIC HEAT. EXPERIMENTS WITH BAR PALLADIUM. THREE HYDRIDES.
WEIGHT OF BAR, 31.802 GRAMMES. WATER AND CALORIMETER, 107 GRAMMES.

	I.	II.	III.	IV.
Weight of Hydrogen in Palladium,	0.1905	0.103	0.0415	Nothing.
Rise in Calorimeter for a fall of 100° C.,	<div> <div>2.426</div> <div>2.430</div> <div>2.429</div> <div>2.435</div> </div>	<div>2.178</div> <div>2.175</div> <div>2.175</div> <div>2.167</div>	<div>1.944</div> <div>1.958</div> <div>1.958</div> <div>1.967</div>	<div>1.740</div> <div>1.780</div> <div>1.760</div> <div>1.760</div>
Mean rise,	2.436*	2.173	1.956	1.760
Rise due to Hydrogen,	0.676	0.413	0.196	Nothing.
Specific heat of Hydrogen,	3.79	4.29	5.05	
Weight of Hydrogen in—	Increase in Calorimeter due to difference of—		Specific Heat from difference of—	Mean.
I. in excess of II. 0.0875	I. and II.	0.263	I. and II. 3.21	3.47
II. in excess of III. 0.0615	II. and III.	0.217	II. and III. 3.77	
I. in excess of III. 0.1490	I. and III.	0.480	I. and III. 3.44	

* Mean of eight experiments.

TABLE III.—SPECIFIC HEAT. EXPERIMENTS WITH PALLADIUM PLATE. THREE DIFFERENT HYDRIDES. WEIGHT OF PLATE, 37·848 GRAMMES. EQUIVALENT OF WATER AND CALORIMETER, 107 GRAMMES.

	I.	II.	III.	IV.
Weight of Hydrogen in Palladium,	0·210	0·129	0·0512	Nothing.
Rise in Calorimeter for a fall of 100° C.,	<div style="display: flex; align-items: center;"> { <div style="margin-left: 5px;"> 2·891 2·870 2·856 2·858 </div> </div>	<div style="display: flex; align-items: center;"> { <div style="margin-left: 5px;"> 2·694 2·657 2·646 2·659 </div> </div>	<div style="display: flex; align-items: center;"> { <div style="margin-left: 5px;"> 2·368 2·362 2·375 2·402 </div> </div>	<div style="display: flex; align-items: center;"> { <div style="margin-left: 5px;"> 2·111 2·100 2·082 2·086 </div> </div>
Mean rise,	2·869	2·664	2·337	2·096*
Rise due to Hydrogen,	0·773	0·568	0·281	
Specific heat of Hydrogen,	3·930	4·70	5·88	

Weight of Hydrogen in—	Increase in Calorimeter due to difference of—	Specific Heat from difference of—	Mean.
I. in excess of II. 0·081	I. and II. 0·205	I. and II. 2·70	} 3·31
II. in excess of III. 0·0778	II. and III. 0·287	II. and III. 3·94	
I. in excess of III. 0·1588	I. and III. 0·492	I. and III. 3·31	

Coefficient of Expansion.

As the observations on the coefficient of expansion had to be made with the same pieces of palladium used in the former experiments, the only method that could be employed was to weigh the hydride in distilled water of different temperatures, as MATHIESSEN did in his well-known paper on the expansion of metals and alloys ("Phil. Trans.," 1866), and to deduce the mean cubical expansion from the difference of weights and the known density of water. Experiments made in this way require great care in execution, and when every precaution is taken, are yet liable to considerable variation. Any difference of temperature in different portions of the water in which the alloy is weighed at the time of the observation, causing currents in the fluid, or the condensation of moisture on the fine platinum wire used to suspend the substance, renders the results useless. But in this case the difficulties are greatly increased from the minute bubbles of hydrogen that are apt to accumulate at any angular point of the mass, and must be removed by suddenly depressing or lifting the mass. After making a great many observations in this way, it became clear that the method would not yield results of very great accuracy when applied to the case of palladium containing hydrogen; in the meantime, the results obtained are provisionally stated. Generally a mass of palladium containing hydrogen nearly equivalent to

* Mean for six experiments.

the atomic proportion $\text{Pd}_3 \text{H}_2$, yields the following values for the mean coefficient of cubical expansion :—

Between 0° and 50° ,	.	.	0.000058
Between 0° and 80° ,	.	.	0.000066

The cubical expansion of palladium being 0.000033, we may say the alloy with hydrogen is just twice as great. If the expansion of GRAHAM's alloy is assumed to be equal to the sum of the expansion of the respective volumes of the constituents, then the calculated result for the cubical expansion of hydrogen is 0.000246, a number about one and a half times the coefficient of expansion of mercury.

With a fused mass of palladium containing a small charge of hydrogen, the coefficient of expansion was found to be 0.00048, and the calculated value for the occluded hydrogen became then 0.00059.

Absorption of Hydrogen at a Red Heat.

GRAHAM's theory of the rapid passage of hydrogen through palladium at high temperatures, assumes at first a direct absorption of the gas, and then a transmission of it by a kind of "cementation process." That an absorption of hydrogen takes place with its attendant increase of volume at high temperatures may be shown as follows :—

Take a strip of thin sheet palladium, four or five centimetres long, and about five millimetres in breadth, clamp it firmly by the end in a suitable support, so that the strip is free to vibrate, and insert it edgewise in the middle of a hydrogen flame, burning from a nozzle about a millimetre in diameter. If the palladium is now depressed into the inner dark cone it immediately begins to vibrate, producing a low musical note.

If the flame be extinguished by stopping the current of hydrogen for an instant, or allowing the gas to flow, the vibration commences again, and may be kept up without any actual flame.

The motion in this position in the flame is due to the absorption of hydrogen on the cool side next the inner cone, with its attendant increase of length, producing a bending of the sheet into the hot portion of the flame, where the hydrogen is instantly expelled from the palladium, which is forced to return to its original position from its natural elasticity.

The experiments detailed in this paper have been made with palladium very handsomely placed at my disposal by Messrs Johnson, Matthey, and Co. of Hatton Garden, London, and I gladly avail myself of this opportunity of thanking them for the means of conducting this research.