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THE OCCLUSION OF HYDROGEN BY A PALLADIUM CATHODE.

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The occlusion of hydrogen by palladium, whether from the gas directly or during electrolysis, has been the subject of numerous investigations. In particular, the changes in the electrical resistance of the metal brought about by this occlusion have been studied by Graham,[1] Dewar,[2] Knott,[3] Bruchietti,[4] Krakau,[5] McElfresh,[6] Fischer,[7] Sieverts[8] and Wolf.[9]

As a result of these investigations it has been established that an increase in the specific resistance of the metal results from the occlusion and that, at least between thirty and about nine hundred and eighty volumes, the increase in resistance is approximately proportional to the hydrogen taken up.

With regard, however, to the relation between the resistance and the

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[1] *Proc. Roy. Soc. London*, **17**, 212 (1869).

[2] *Proc. Camb. Phil. Soc.*, **3**, 207 (1878).

[3] *Proc. Roy. Soc. Edinb.*, **12**, 181 (1884).

[4] *L'Elettricista*, Nov., 1893.

[5] *Z. physik. Chem.*, **17**, 689 (1895).

[6] *Cont. Jeff. Phys. Lab.*, **1**, 305 (1903).

[7] Dissertation, Leipzig, 1906; *Ann. Phys.*, [4] **20**, 503 (1906).

[8] *Internat. Zeits. Metallog.*, **3**, 36 (1912).

[9] *Z. physik. Chem.*, **87**, 575 (1914).

quantity of occluded gas, which obtains for the high degrees of occlusion reached in palladium cathodes when electrolysis is long continued, we have only the observations of Fischer.[1] These are remarkable in that the last portions of gas, which, since they are again spontaneously evolved as soon as the current is interrupted, he termed "supersaturation" hydrogen, produce no effect upon resistance, although they cause an expansion of the metal proportionally greater than that produced by the occlusion in its earlier stages. Since the increased effect of the "supersaturation" hydrogen upon the volume was also found by Thoma,[2] this lack of effect upon resistance raises certain questions as to the nature of the states of "saturation" and "supersaturation."

In order, if possible, to obtain further information upon these questions and upon the phenomena of occlusion generally, the following experiments were undertaken. They consisted in observing the changes in the electrical resistance and in the cathode potential of palladium wires during their cathodic occlusion of hydrogen from 2 *N* sulfuric acid. As a control of the conditions of electrolysis, the applied voltage and the current were also observed, and occasional measurements were made of the anode potential.

Experiments.

The electrolytic cell consisted of separate cathode and anode vessels, the former of which is shown in Fig. 1. Here A is the inlet for the electrolyte and B the outlet. The palladium wire *e*, *f*, *g*, *h*, about 10 cm. long, is fused at each end to two other palladium wires, X and Y, which pass through the rubber stoppers C, C and are soldered outside to copper wires of 3.26 mm. diameter, which form the leads of a Kelvin bridge. D is a siphon which connects through an intermediate vessel with the reference electrode. To make possible the observation of the cathode potential during electrolysis, without the introduction of an error due to the ohmic fall of potential, this siphon terminates in a small orifice held directly against the cathode. The principle is that of the capillary-tip siphon of Luggin and Haber,[3] and the modifications necessary to keep the wire cathode in place during its expanison with absorption of hydrogen will be clear from Fig. 1*a*. To make the distribution of current at the cathode symmetrical the latter is connected to battery through the branched lead *j*, *j*.

In order to diminish changes in the temperature or composition of the electrolyte in the constricted cathode chamber, the liquid was made to flow through the cell during electrolysis at the rate of about four liters in twenty-four hours, while to guard against its depolarizing influence,

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[1] Dissertation, Leipzig, 1906; *Ann. phys.*, [4] **20**, 503 (1906).

[2] *Ibid.*, 3, 69 (1889).

[3] Haber, *Z. physik. Chem.*, **32**, 207 (1900).

all air was displaced by nitrogen from the closed system of vessels through which the electrolyte circulated. The cell and a glass coil through which the electrolyte first passed were contained in a large oil thermostat which maintained a termperature of 25 ± 0.01°. The platinum anode was enclosed in a porous cup to preclude the possibility that platinum might find its way to the cathode.[1]

The measurements of electrical resistance had an accuracy of about one part in 6000 for the higher resistances encountered in the later portions of the experiments with small palladium wires, where alone results of interest were obtained, while the measurements of e. m. f. were made with the potentiometer. Potentials refer to a mercurous sulfate electrode with 2 *N* sulfuric acid, which varied during the investigation by less than one millivolt.

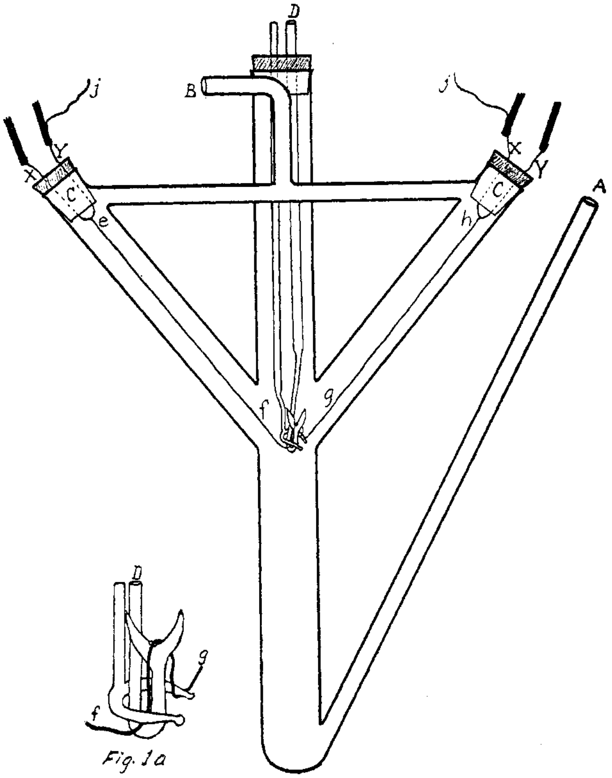

Fig. 1.—Cathode vessel.

The electrolyte used throughout was 2 *N* sulfuric acid, for the preparation of which chemically pure acid was redistilled in quartz and diluted with water of conductivity between 1.0 and $1.2 \cdot 10^{-6}$. The concentration, which corresponded to a specific gravity of 1.0605 at 21°, was occasionally controlled by titrating against normal hydrochloric acid, obtained by the method of Hulett and Bonner.

During the course of the experiments palladium from three different sources was employed. One sample, G, of Table II, was a piece of foil obtained from a German dealer and drawn into wire for the present purpose; another lot, A, was obtained ready-drawn from an American dealer

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[1] See J. Tafel, *Z. physik. Chem.*, 50, 641 (1905); J. Tafel and B. Emmert, *Ibid.*, 52, 349 (1905).

and the third variety, P, was prepared in this laboratory from commercial palladium by employing in succession the customary methods for the separation of this metal, precipitations with hydrogen sulfide, ammonium thiocyanate and mercuric cyanide being repeated.

Before use each wire, from whatever source, was ignited *in vacuo* at 830° for from four to ten hours to expel any occluded gas and to anneal the metal. Evacuation to a pressure of 1 mm. of mercury, or less, was effected by means of a lift pump, a vessel of finely divided silver being interposed between the pump and wire in order to guard against the vapor of mercury, which Ramsay[1] has shown to exert an inhibitive action upon the occlusion of hydrogen by palladium. Except in one instance a new wire was taken for each experiment.

The initial reading of resistance was made as soon as possible after the cell had filled with electrolyte, and before electrolysis had begun. It was found that no change occurred even in the course of several days, until the charging circuit had been closed. The other measurements were made at such intervals as may be seen from Table I, in which are given in full the observations taken in one of the six experiments with varied charging current. In four other experiments a constant current was employed. Saturation was in general considered to have been attained when the curve of resistance as a function of current-time (see Fig. 3), had become horizontal within the limits of measurement, but in several instances the charging was much prolonged, and in Expt. 5, electrolysis was continued for six days after the attainment of apparent constancy, without causing any further change.

TABLE I.

Experiment No. 5.

			Cathode potential.		
Time.	Applied[2] voltage.	Current.	C. F.[3]	C. S.[4]	Resistance.
8.50 A.M., Jan. 18	1.82 volts	0.2 mil. amps.	0.6150	0.5950 volt	.....
9.00 A.M., Jan. 18	....	stopped	....	....	1.446 ohm.
9.25 A.M., Jan. 19	....	started	....	....	1.446
9.30 A.M., Jan. 19	1.82	0.2	0.6300	0.5850	1.514
10.00 A.M., Jan. 19	2.26	0.2	0.6800	0.6100	1.528
10.20 A.M., Jan. 19	2.15	0.2	0.6810	0.6120	1.536
10.35 A.M., Jan. 19	2.35	0.3	0.7040	0.6100	1.552
10.50 A.M., Jan. 19	2.57	0.5	0.7160	0.6110	1.588
11.05 A.M., Jan. 19	2.82	0.6	0.7270	0.6120	1.630
11.20 A.M., Jan. 19	3.63	0.8	0.7470	0.6100	1.688
11.35 A.M., Jan. 19	3.98	0.9	0.7474	0.6100	1.756
11.50 A.M., Jan. 19	4.46	1.0	0.7615	0.6100	1.832

[1] *Phil. Mag.*, [5] 38, 209 (1894).

[2] In this column is given the potential difference between the poles of the electrolytic cell, properly termed applied voltage until the interruption of the current.

[3] "Current flowing."

[4] "Current stopped."

TABLE I (*continued*).

Time.	Applied voltage.	Current.	Cathode potential.		Resistance.
			C. F.	C. S.	
12.05 P.M., Jan. 19	5.18	1.2	0.7740	0.6385	1.924
2.30 P.M., Jan. 19	2.00	0.2	0.7030	0.6350	2.034
2.45 P.M., Jan. 19	2.07	0.2	0.7100	0.6330	2.041
3.00 P.M., Jan. 19	2.17	0.3	0.7180	0.6340	2.047
3.15 P.M., Jan. 19	2.34	0.3	0.7300	0.6420	2.063
3.30 P.M., Jan. 19	2.61	0.4	0.7420	0.6470	2.080
3.45 P.M., Jan. 19	2.84	0.5	0.7520	0.6500	2.096
4.00 P.M., Jan. 19	3.69	0.8	0.7720	0.6700	2.183
4.15 P.M., Jan. 19	4.00	0.9	0.7770	0.6700	2.207
4.30 P.M., Jan. 19	4.48	1.0	0.7840	0.6790	2.248
4.45 P.M., Jan. 19	5.19	1.2	0.7950	0.6840	2.270
10.00 A.M., Jan. 20	2.08	0.2	0.7650	0.6665	2.466
10.15 A.M., Jan. 20	2.15	0.2	0.7710	0.6660	2.466
10.30 A.M., Jan. 20	2.24	0.3	0.7790	0.6690	2.466
10.45 A.M., Jan. 20	2.39	0.3	0.7910	0.6720	2.466
11.00 A.M., Jan. 20	2.63	0.4	0.8050	0.6750	2.466
11.15 A.M., Jan. 20	2.87	0.5	0.8170	0.6820	2.466
11.30 A.M., Jan. 20	3.69	0.8	0.8410	0.6920	2.462
11.45 A.M., Jan. 20	4.01	0.9	0.8475	0.6990	2.460
12.00 A.M., Jan. 20	4.49	1.0	0.8550	0.7050	2.464
12.15 P.M., Jan. 20	5.19	1.2	0.8690	0.7100	2.464
12.20 P.M., Jan. 20	....	0.2	....	....	2.472
2.15 P.M., Jan. 20	2.08	0.2	0.7685	0.6670	2.504
2.30 P.M., Jan. 20	2.15	0.2	0.7750	0.6675	2.502
2.45 P.M., Jan. 20	2.24	0.2	0.7800	0.6710	2.502
3.00 P.M., Jan. 20	2.39	0.3	0.7900	0.6720	2.502
3.15 P.M., Jan. 20	2.64	0.4	0.8130	0.6780	2.498
3.30 P.M., Jan. 20	2.88	0.5	0.8240	0.6830	2.496
3.45 P.M., Jan. 20	3.72	0.8	0.8510	0.6950	2.486
4.00 P.M., Jan. 20	4.07	0.9	0.8600	0.7035	2.478
4.15 P.M., Jan. 20	4.59	1.0	0.8665	0.7050	2.476
4.30 P.M., Jan. 20	5.24	1.2	0.8800	0.7050	2.462
5.00 P.M., Jan. 20	....	0.2	....	....	2.484
7.15 P.M., Jan. 21	2.15	0.2	0.8330	0.6750	2.467
8.20 A.M., Jan. 22	2.17	0.2	0.8510	0.6750	2.470
9.10 A.M., Jan. 22	....	0.8	....	....	.....
9.15 A.M., Jan. 22	....	0.8	....	....	2.458
9.20 A.M., Jan. 22	3.81	0.8	0.9480	0.6750	2.430
9.50 A.M., Jan. 22	3.82	0.8	0.9480	0.6710	2.420
10.20 A.M., Jan. 22	3.82	0.8	0.9480	0.6650	2.428
10.50 A.M., Jan. 22	3.83	0.8	0.9475	0.6580	2.422
11.20 A.M., Jan. 22	3.83	0.8	0.9500	0.6525	2.416
12.00 A.M., Jan. 22	3.84	0.8	0.9480	0.6450	.....
1.15 P.M., Jan. 22	....	1.0	....	....	.....
2.15 P.M., Jan. 22	4.59	1.0	1.0185	0.6570	2.416
3.30 P.M., Jan. 22	4.58	1.0	0.9970	0.6450	2.414
4.40 P.M., Jan. 22	....	0.3	....	....	.....
4.45 P.M., Jan. 22	....	0.3	....	....	2.434

TABLE I (*continued*).

Time.	Applied voltage.	Current.	Cathode potential.		Resistance.
			C. F.	C. S.	
9.00 A.M., Jan. 24	2.40	0.3	0.9735	0.6065	2.440
11.00 A.M., Jan. 24	2.40	0.3	0.9735	0.6065	2.440
2.00 P.M., Jan. 24	2.40	0.3	0.9590	0.5920	2.440
2.10 P.M., Jan. 24	....	0.6	....	....	.....
7.00 P.M., Jan. 24	3.48	0.6	1.0530	0.6050	2.408
8.45 A.M., Jan. 25	3.52	0.6	1.092	0.6170	2.402
8.50 A.M., Jan. 25	....	1.0	....	....	.....
2.40 P.M., Jan. 25	4.63	1.0	1.1370	0.6140	2.388
7.10 P.M., Jan. 25	....	0.4	....	....	.....
7.15 P.M., Jan. 25	2.99	0.4	0.9950	0.5870	2.424
9.30 A.M., Jan. 26	3.10	0.4	1.0900	0.5870	2.414
9.35 A.M., Jan. 26	....	stopped	....	....	.....
9.50 A.M., Jan. 26	1.37	000	....	0.5650	2.456
10.05 A.M., Jan. 26	1.33	000	....	0.5570	2.472
10.30 A.M., Jan. 26	1.29	000	....	0.5400	2.482
10.45 A.M., Jan. 26	1.27	000	....	0.5380	2.490
11.00 A.M., Jan. 26	1.26	000	....	0.5350	2.494
11.15 A.M., Jan. 26	1.25	000	....	0.5450	2.496
11.30 A.M., Jan. 26	1.23	000	....	0.5700	2.498
11.45 A.M., Jan. 26	1.06	000	....	0.5590	2.500
12.00 A.M., Jan. 26	1.03	000	....	0.5540	2.502
12.30 P.M., Jan. 26	0.97	000	....	0.5560	2.504
1.00 P.M., Jan. 26	0.93	000	....	0.5490	2.508
1.30 P.M., Jan. 26	0.90	000	....	0.5650	2.508
2.00 P.M., Jan. 26	0.86	000	....	0.5610	2.508
2.30 P.M., Jan. 26	0.80	000	....	0.5440	2.508
3.00 P.M., Jan. 26	0.75	000	....	0.5430	2.508
3.30 P.M., Jan. 26	0.68	000	....	0.5425	2.512
4.00 P.M., Jan. 26	0.68	000	....	0.5470	2.512
4.30 P.M., Jan. 26	0.68	000	....	0.5435	2.512
5.00 P.M., Jan. 26	0.70	000	....	0.5500	2.512
5.30 P.M., Jan. 26	0.71	000	....	0.5800	2.512
6.00 P.M., Jan. 26	0.72	000	....	0.5670	2.512
7.00 P.M., Jan. 26	0.73	000	....	0.5700	2.512
8.00 P.M., Jan. 26	0.73	000	....	0.5750	2.512
9.00 P.M., Jan. 26	0.74	000	....	0.5750	2.514
10.00 P.M., Jan. 26	0.73	000	....	0.5750	2.514
8.00 A.M., Jan. 27	0.73	000	....	0.5790	2.514
10.00 A.M., Jan. 27	0.73	000	....	0.5890	2.514
12.00 A.M., Jan. 27	0.75	000	....	0.5910	2.515
2.00 P.M., Jan. 27	0.75	000	......	0.5930	2.516
4.00 P.M., Jan. 27	0.76	000	....	0.5930	2.516
8.00 A.M., Jan. 28	0.73	000	....	0.5820	2.520
9.30 A.M., Jan. 28	0.73	000	....	0.5830	2.520
9.31 A.M., Jan. 28	....	started	....	....	.....
9.32 A.M., Jan. 28	3.22	0.6	0.9040	0.5290	2.518
2.15 P.M., Jan. 28	3.39	0.6	1.0200	0.6350	2.390
7.00 P.M., Jan. 28	3.46	0.6	1.0540	0.6220	2.382

TABLE I (*continued*).

Time.	Applied voltage.	Current.	Cathode potential.		Resistance.
			C. F.	C. S.	
8.00 A.M., Jan. 29	3.48	0.6	1.0980	0.6000	2.382
1.00 P.M., Jan. 29	....	1.0	....	....	.....
7.00 P.M., Jan. 29	4.65	1.0	1.1750	0.5980	2.376
7.05 P.M., Jan. 29	....	0.6	....	....	.....
9.00 A.M., Jan. 31	3.54	0.6	1.1550	0.5820	2.390
9.05 A.M., Jan. 31	....	stopped	....	....	.....
9.07 A.M., Jan. 31	1.49	000	....	0.5740	2.406
9.30 A.M., Jan. 31	1.32	000	....	0.5440	2.458
10.00 A.M., Jan. 31	1.27	000	....	0.5170	2.474
10.30 A.M., Jan. 31	1.24	000	....	0.5025	2.486
11.00 A.M., Jan. 31	1.21	000	....	0.5000	2.492
11.30 A.M., Jan. 31	1.19	000	....	0.5070	2.496
12.00 A.M., Jan. 31	1.13	000	....	0.5070	2.500
1.00 P.M., Jan. 31	1.01	000	....	0.5070	2.504
2.00 P.M., Jan. 31	0.88	000	....	0.5070	2.506
7.00 P.M., Jan. 31	0.68	000	....	0.5150	2.512
8.00 A.M., Feb. 1	0.73	000	....	0.5810	2.514
1.00 P.M., Feb. 1	0.72	000	....	0.5740	2.515
8.15 A.M., Feb. 2	0.69	000	....	0.5550	2.516

The principal results with regard to resistance may be summarized as follows:

(1) All palladium wires increased in resistance during electrolysis by more than 56%, finally reaching a value which remained unaltered by prolonged charging, but which appeared to vary irregularly from wire to wire.

(2) Wires of 0.1 mm. diameter or less, and the ribbon of Expt. 12, which was 0.018 mm. thick and 0.57 mm. wide, showed a further increase of resistance after the interruption of electrolysis.

(3) With the small wires and ribbon there was also found a change of resistance whenever the intensity of the charging current was altered either during the later stages of occlusion or after the attainment of saturation.

(4) The larger wire of Expt. 11 could not be made to exhibit the effects noted under (2) and (3).

The variability of the saturation resistance, referred to under (1), is shown in the fifth column of Table II, where the highest resistance attained with each wire is expressed as per cent. increase of the original resistance.

The effect mentioned in (2) may be seen from the last column of Table II, and is further illustrated by Fig. 2, where each curve shows the change of resistance which occurred after the interruption of electrolysis in the case of a wire which had already reached a constant resistance with the current flowing.

The dependence of resistance on current, noted in (3), is displayed by Fig. 3, where are given portions of the curves of resistance, as dependent upon current-time, for four wires. At A on each curve may be seen the drop in resistance induced by an increase of current, while at B occurs an increase of resistance produced by diminution of current. In the case of No. 3 the current was raised at A from 0.8 to 1.1 milliamp. and was reduced at B to 0.2 milliamp.

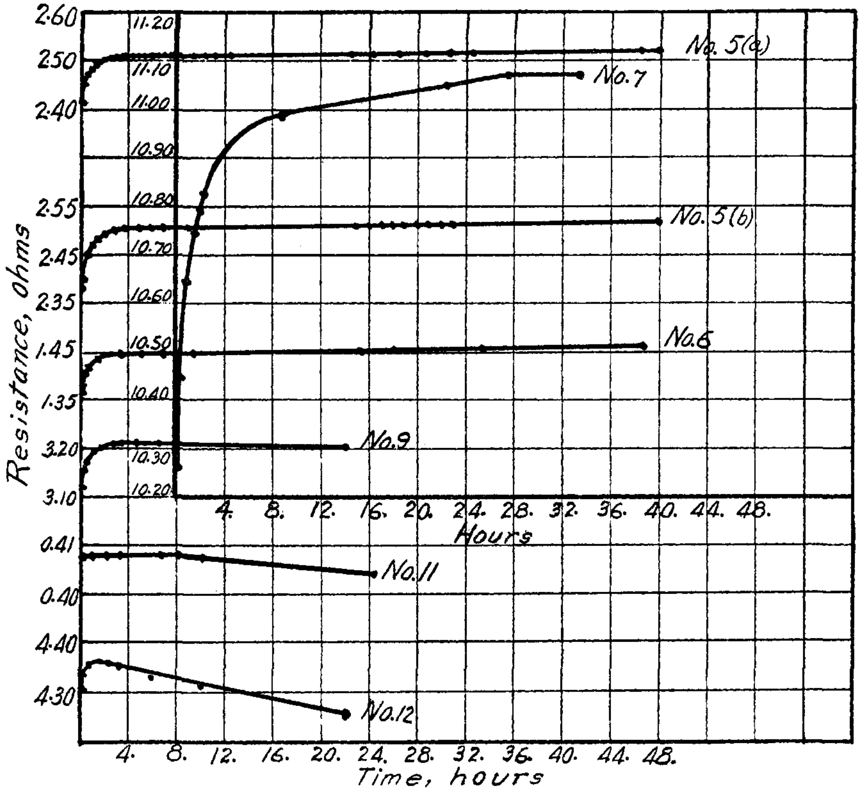

Fig. 2.—Change of resistance after interruption of current.

TABLE II.

Expt. No.	Material.	Diameter.	Current.	Constant resistance.	Increase.
2	G	0.1	0.1	72.4	...
3	P	0.1	0.2	63.0	1.3
4	P	0.1	0.2	57.7	...
5	A	0.1	1.2	>73.2	<0.7
6	A	0.1	1.2	74.7	1.3
7	G	0.05	0.5	56.7	12.6
8	A	0.1	0.2	62.5	2.5
10	A	0.1	0.1	61.9	2.6
11	P	0.32	1.1	56.9	0.0
12	P	ribbon	0.8	57.7	0.5

The conduct of the large wire, mentioned in (4), is shown by Curve 11 of Fig. 2. When this wire was again charged, after the loss of resistance shown in the figure, it recovered exactly its former maximum resistance in six hours and retained it unaltered until the current was again interrupted forty-three hours later. The resistance curve obtained after this second interruption was entirely similar to that shown.

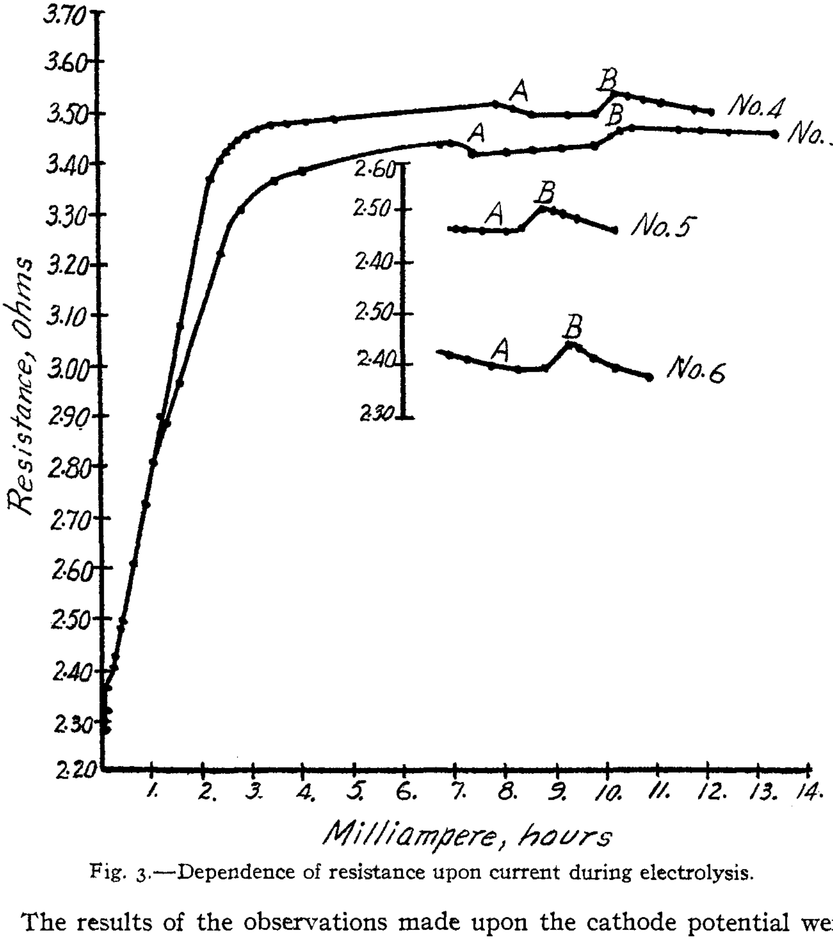

Fig. 3.—Dependence of resistance upon current during electrolysis.

The results of the observations made upon the cathode potential were as follows: The potential, in every case, rose steadily so long as electrolysis was continued. Upon the interruption of the current at the end of the first charging of a palladium wire there always occurred the series of changes shown in the first part of Fig. 4, consisting of a sharp drop, followed by a pronounced recovery and then by a gradual decline. When a wire was repeatedly charged to constant resistance, the recovery of potential became less marked with each succeeding interruption of electrolysis, as may be seen from the eight successive curves for the same cathode given in Fig. 4. The initial drop of potential, preceding the recovery, appeared to consist of two parts. For the first reading, taken as soon as possible after the interruption, instead of corresponding to chance positions upon the falling branch of the curve, showed marked regularity, as may be seen from Fig. 5. Here the points upon Curve *a* represent the first readings for successive interruptions of electrolysis during the first charging of Wire No. 5, while Curves *b*, *c* and *d* correspond to three subsequent chargings of the same wire. The regularity with which these values increase with increasing occlusion, together with the form of the potential-time curves, seen best in Nos. 4, 5 and 7 of Fig. 4, seem to show that the point A of these last is a well-

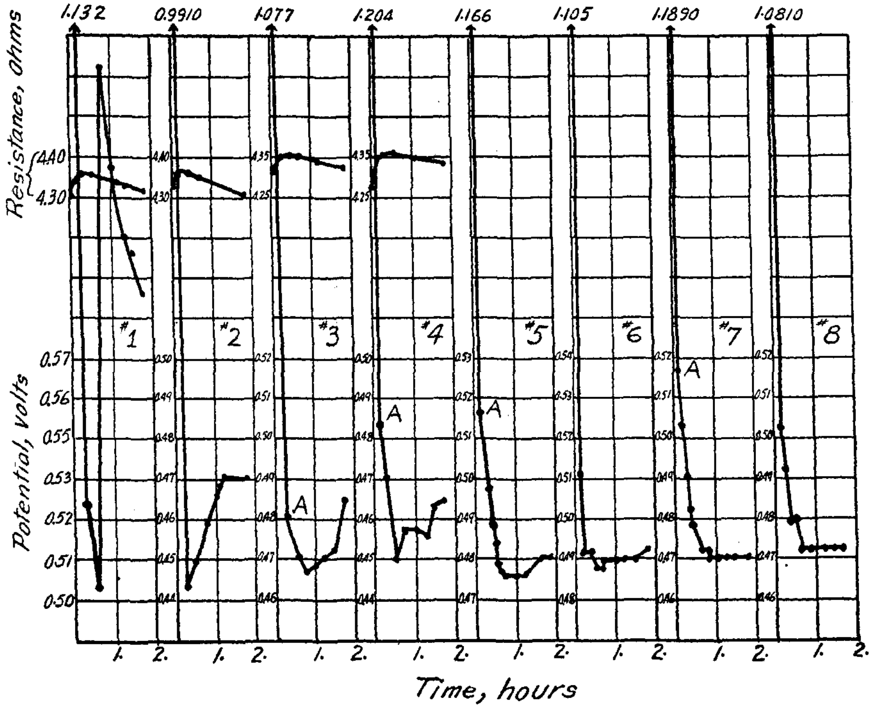

Fig. 4.—Changes of potential and resistance for successive interruptions.

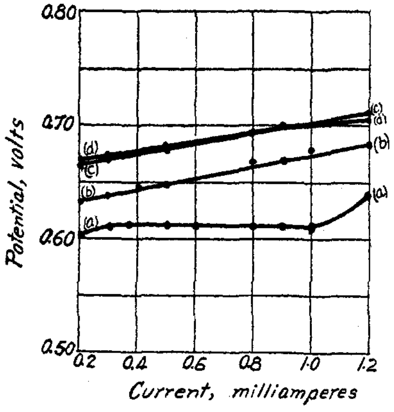

Fig 5.—First readings of potential after interruption of current, Expt. 5.

defined potential, determined by the state of occlusion in the surface of the metal.

For comparison two similar experiments were made with copper wires of 0.1 mm. diameter, drawn from electrolytic copper. In these the initial resistance was observed, and the charging circuit was closed, before the introduction of the electrolyte. No change of resistance was found either during electrolysis or after its interruption, nor did the wires show brittleness or any other change upon their removal from the cell. The potential during electrolysis altered in the manner shown by Curves *a*, *b* and *c* of Fig. 6, which correspond to successive chargings with the same wire. After the interruption of the current the potential fell off in a perfectly regular manner.

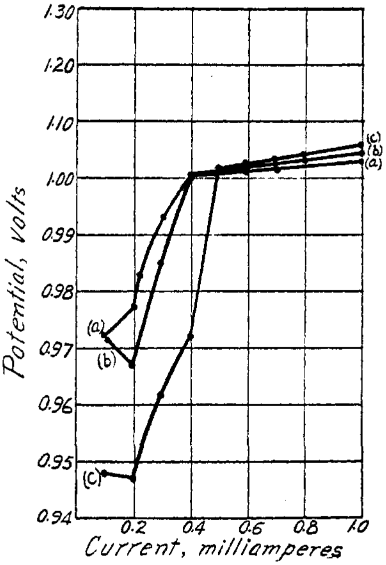

Fig. 6.—Potential of copper during electrolysis.

A wire of commercial nickel of 0.26 mm. diameter also failed to show any change of resistance with currents up to 4.5 milliamperes, and was apparently unaltered in other respects.

Discussion.

The foregoing results confirm those obtained by previous observers in that, with progressing occlusion of hydrogen, the resistance of palladium increases steadily and reaches a constant value. With regard to the proportional increase at saturation the results are, however, extremely divergent. For, while Fischer found increases which varied only between 68 and 69%, and McElfresh obtained the value 67% for both of the wires which he studied, Knott's results run from 63 to 83%, and those here reported from 56.6 to 74.7%. The values found for small wires are undoubtedly too high, owing to the effect mentioned under (2) in the summary of resistance results above, and the circumstance that observations of the saturation resistance had necessarily to be made during momentary interruption of the charging current. Moreover, since it has been shown that the presence of small amounts of alloy-forming impurities exerts a marked influence upon the occlusion[1] of hydrogen by palladium, it is likely that differences of purity between the various wires account in great part for the discrepancies shown, and it may be seen from Table II that the smallest increases of resistance found in the present

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[1] Graham, *Proc. Roy. Soc. London*, **17**, 500 (1869); Berry, *J. Chem. Soc.*, **99**, 463 (1911); Sieverts, *Z. anorg. Chem.*, **92**, 329 (1915).

investigation were obtained with the carefully purified metal, and the largest with that which was probably of poorest quality.

The possibility that the previous history of the palladium used affects its conduct in this matter, which is suggested by the well-known variability in the velocity and extent to which the metal occludes "molecular" hydrogen, should not be overlooked, but the results of these experiments show no indication of such an influence. Indeed, while observations upon this point were only incidental, the conduct of Wire No. 11 suggests rather that such an effect was absent. For this wire, which was of purified metal, and of sufficient diameter to be unaffected by the disturbing factors discussed in the next paragraph, gave reproducible results, the maximum resistance of 0.4080 ohm, which it maintained during two days of electrolysis on first being charged, being exactly recovered and maintained in each of the two subsequent chargings.

The principal new observation of the present experiments is to be found in the change of resistance with change of charging current, which has been noted under (2) and (3) in the summary of resistance results above, and which is further evidenced by a dependence of the saturation resistance upon the current, such as is illustrated by the following observations from Expt. 12: the resistance having become constant at 4.3560 ohms with a current of 0.2 milliamp., fell in the course of an hour and a half to 4.3120 ohms, when the current was increased to 0.8 milliamp., and again became constant. When the current, some eight hours later, was lowered to 0.3 milliamp., the resistance rose to 4.3440 ohms. This inverse response of resistance to current in a saturated wire was found invariably with the small wires and ribbon. It should be noted that, as may be seen clearly from the curves of Fig. 3, an increase of current produced an uninterrupted decline of resistance to a new constant value, while a decrease of current usually caused the resistance to pass through a maximum.

Two possible explanations of these effects suggest themselves. The first is that, during electrolysis, there is formed upon the wire a conducting layer of some product of electrolysis, and that the thickness or conductivity of this layer responds immediately to any change of current or impressed potential.

There are considerations, however, which appear to make this explanation untenable. In the first place, if one regards the change of resistance after interruption of the charging current in connection with the accompanying change of potential, it is evident from the curves exhibited in Fig. 4, which represent the changes of both quantities for successive interruptions with the same cathode, that while the character of the potential curve undergoes great modification between the first interruption and the last, the character of the resistance curve remains unaltered. If the changes of resistance were indeed due to processes occurring in the portion of the electrolyte which immediately surrounds the wire, we should not expect their character to remain the same while the changes of potential suffered such radical alterations.

In the next place, the modification of the potential curves with successive interruptions is alone a sufficient indication of changes occurring in the wire, or in its surface, rather than in the electrolyte. For it is scarcely conceivable that persistent alterations could be produced in the electrolyte.

Finally, if the effect were due to changes in the electrolyte, a similar effect might be expected with copper cathodes, when subjected to the same treatment. Yet none was apparent, the potential of the copper varying regularly, and without the rise and subsequent fluctuations shown by that of palladium, while its resistance remained unaltered.

It seems necessary to conclude, therefore, that the change of resistance observed after interruption of the charging current is produced by changes in the cathode or its surface. It also appears that these changes are not confined to the immediate surface of the metal, which plays a part in determining the potential, for in that case we should again expect some parallel between the variations of potential and those of resistance.

If, then, the change of resistance after interruption of electrolysis is to be explained by processes occurring within the cathode, it is yet evident that these processes cannot be merely a continuation of those which have occurred during charging; for no matter how long or how often the wire has been charged to the attainment of steady resistance, a further increase of resistance takes place when the current ceases. The processes are also immediately responsive to any changes of current, and are evidently reversible.

As a tentative explanation, which agrees at least qualitatively with all of the facts observed, the following seems worthy of consideration. The steady rise of resistance observed during the progress of occlusion is due to combination of hydrogen with palladium to form an alloy of higher resistance than the pure metal. When, with steady current and applied voltage, this combination has come to equilibrium, the wire possesses the resistance of the saturated alloy, diminished by a conductance due to the uncombined hydrogen, or to some portion of the latter. Upon the interruption of the current, after this state has been reached, the gradual disappearance of the conducting hydrogen produces an increase of resistance, at first rapid, but diminishing in rate until a constant value has been attained. So long as the charging current continues without variation the loss of conducting hydrogen is made good by further occlusion, but any change of current causes either the rate of supply or the rate of loss to predominate, with corresponding loss or gain of resistance, until a steady state has again established itself. This accords, evidently, with the fact that the lower the current at which the steady state sets in, the higher is the corresponding resistance.

On comparing the conduct, after the interruption of electrolysis, of wires of different sizes, shown in Fig. 2, it appears that the increase of resistance is greatly dependent, both as to magnitude and duration, upon the dimensions of the wire. With the 0.32 mm. wire, No. 11, the effect could not be found. In the 0.1 mm. wires, Nos. 5, 6 and 9, the increase was from 0:10 to 0.15 volt, and was complete in less than four hours, after which the resistance usually remained nearly constant for many hours. In the 0.05 mm. wire, No. 7, the increase amounted to almost 0.9 volt, and required some twenty-eight hours for its completion. With the ribbon of No. 12, however, which was 0.018 mm. thick, and in ratio of surface to volume was equivalent to a wire of 0.035 mm. diameter, the effect again fell to a very small magnitude. Since the form of the ribbon was much more favorable than even that of the smallest wire to rapid escape of hydrogen, it might be supposed that this process made its influence felt in the case of the ribbon before the rise of resistance had come to an end. But doubt is thrown upon this explanation of the behavior of the ribbon by the fact, also apparent from Fig. 2, that a decline of resistance began relatively early also in the large wire, No. 11, and in one of the 0.1 mm. wires, No. 9. Whatever the cause of the divergent conduct of the ribbon, it is at any rate evident that dimensions have a marked influence, and hence the process which is responsible for the rise of resistance must be supposed to take place chiefly near the surface.

If the effect is to be explained as due to conductance by the occluded hydrogen, it seems necessary, in view of this superficial character, to conclude further that the conducting hydrogen is of a form which exists only for a brief time and passes then into a nonconducting form, or one of relatively small conductivity, or else to suppose that a uniform distribution by diffusion had not been attained even in the numerous cases in which the resistance became constant within forty-eight hours, and remained so during days of continued electrolysis. For, unhindered diffusion assumed, a single form of uncombined hydrogen, if there were only one, must have been uniformly distributed through the wire when the steady state was attained, and the loss of conductance on interrupting the current would have been proportionally as great for thick wires as for those of smaller diameter. While there exist many grounds, from the work of other observers as well as from these experiments, for believing that the diffusion of hydrogen in palladium is sufficiently rapid to have insured uniform distribution in all of the experiments under discussion, the conclusion just indicated with regard to the condition of the occluded hydrogen is obviously in need of support by further experiments, and its consequences need not be drawn at present. A particular reason for caution will be found below.

With regard to the observations upon the cathode potential, which have already been summarized, it should be pointed out that the indications as to the initial drop of potential are somewhat doubtful. For if, in any experiment, the electrode wire did not rest closely against the siphon tip of Fig. 1*a*, and in consequence an appreciable ohmic fall was included in the potentials observed before the interruption of electrolysis, the effect must have been to produce such an instantaneous drop upon the interruption of the current as that found, and the magnitude of this drop must have increased with the current, as was the case. Although inspection of the cell before and after each experiment showed the wire to be closely held, it is, therefore, not certain that the first, falling part of the potential curves of Fig. 4, to the point A, corresponds to any process directly related to occlusion. The second, more slowly falling portion of the curve, from A to the minimum, appears to be merely the usual decay of polarization after the cessation of electrolysis.

The recovery of potential, however, seems to warrant further study for its indications as to the diffusion of hydrogen from the interior. It varied greatly in character and magnitude, sometimes showing the regularity seen in Curve 1, Fig. 4, and in other instances consisting of a series of fluctuations, and is probably due to the cause to which Helmholtz[1] attributed irregularities which he observed in platinum cathodes, namely, the existence within the metal of regions of different hydrogen concentration. The explanation agrees qualitatively with many of the observations, such as an exceptionally large and rapid recovery found with the ribbon of Expt. 12, and a very small recovery for the 0.32 mm. wire, and the fact that the recovery seemed to be most regular when a constant current had been employed in charging. But diffusion at a constant rate does not seem to be alone adequate to account for several such observations as may be illustrated by the first interruption of Expt. 7. Here the applied voltage and the cathode potential had risen steadily during the previous electrolysis, and hence possessed, at the time of interruption, values higher than any which had gone before. Yet upon interruption the potential, after falling from 1.2180 volts to 0.4479 volt, or lower, rose in the course of nine hours to 0.4840 volt. Since it would seem that under the conditions mentioned, and with a constant coefficient of diffusion, the concentration of hydrogen at the time of interruption must either have diminished continuously from the electrode surface inward, or must have been uniform throughout the wire, it is not readily seen how a reversal in the course of the potential curve can be explained, unless it is supposed that owing either to local differences in the rate of

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[1] *Pogg. Ann.*, **150**, 494 (1873).

diffusion or to its variation with time, there existed at some depth within the wire concentrations higher than that obtaining immediately within the surface. The occurrence of the recovery in such cases is, therefore, not improbably related to the fact observed by Lessing[1] that the rate of diffusion of hydrogen through palladium declines for some time before becoming constant.

The gradual disappearance of the recovery with repeated interruptions, seen in Fig. 4, is most readily accounted for as due to slow equalization of hydrogen concentrations throughout the metal. If this is the correct interpretation, it can hardly be supposed that saturation had been reached in most of the experiments here recorded, for in the experiment of Fig. 4, which was that conducted with the thin ribbon, conditions were the most favorable to speedy saturation, and yet five repetitions of charging were required before the disappearance of the recovery. On the other hand, if saturation had not been reached in the other experiments, it is difficult to understand the constancy of resistance long maintained in many instances, and particularly the reproducibility of this constant resistance already pointed out in connection with Expt. 11. The reconciliation of these apparently discordant indications must await the completion of further experiments.

The uncertainties regarding the attainment of saturation evidently do not affect the observations upon the inverse response of resistance to charging current, and the probability that this is due to conductance by occluded hydrogen, although they have direct bearing upon the question of the form in which this hydrogen is present.

The results with copper and nickel wires seem to show that these metals occlude very little hydrogen, if any, under the conditions of these experiments, although both are known to occlude considerable amounts of "molecular" hydrogen at higher temperatures.

Since the experiments thus far described were all conducted in cells of one type, it seemed desirable to make observations under somewhat different conditions, particularly with regard to the distribution of current at the cathode.

A cell of half-liter volume was employed, in which the cathode wire was supported upon a stirrer which revolved at 100 r. p. m., so that each side of the cathode in turn was presented toward the anode. The platinum points upon the stirrer, to which the cathode was fused, connected with a Wheatstone bridge through mercury seals which served also to close the cell from the air. The resistance of the leads was eliminated by compensating until the original resistance read was that estimated for the palladium wire, so that the observations, while affected with a small constant error, are of high relative accuracy. The arrangements were otherwise

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[1] *Verh. deutsch. physik. Gesell.*, 4, 569 (1906).

the same as those described above, except that provisions for the measurement of potential were omitted.

The electrolyte was 2 N sulfuric acid, prepared as before, and the wires studied were from an American source. They were about 11 cm. long and of 0.05 mm. diameter.

After charging with a steady current of 1.5 milliamp. until the resistance had become constant, electrolysis was interrupted and the observations were made of which the results are displayed in Fig. 7. Here Curve 1 is for a first interruption after 71 hours' charging of Wire No. 1, while the other curves refer to three successive interruptions with Wire No. 2, made after 68, 51 and 22 hours' charging. Curve 1, for which the ordinates are given in brackets, would extend above the figure if drawn to the same ordinates as the other three, to which the unbracketed numbers apply. The rise of resistance in No. 1 was, therefore, greater and much more rapid than any of those observed with No. 2.

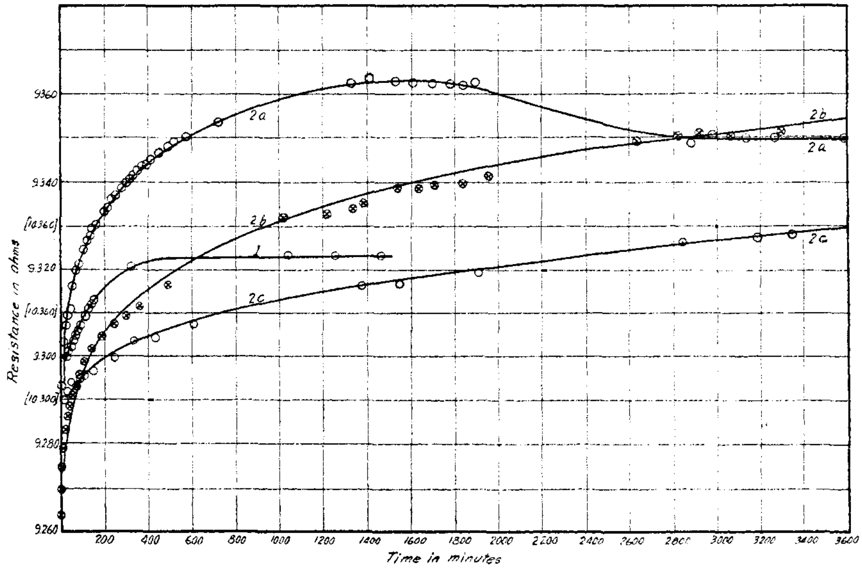

Fig. 7.

The results dispose of the possibility that the supplementary rise of resistance after the interruption of electrolysis might have been due to the peculiar distribution of current at the cathode in the earlier experiments. The differences shown between the first interruptions, Nos. 1 and 2*a*, and between the successive interruptions of No. 2, are much greater than any previously found between wires of the same diameter. This is probably to be attributed to the fact that the preliminary annealing *in vacuo*, to which all of the earlier wires were subjected, was here omitted.

A study of these effects by another method has been undertaken.

Summary.

1. Observations have been made of the changes in the electrical resistance and in the cathode potential of palladium wires, both during their occlusion of hydrogen electrolytically evolved, and after the interruption of electrolysis.

2. The proportional increase of resistance at apparent saturation has been found to vary widely, even with wires from the same lot of carefully purified palladium.

3. The resistance of saturated wire of 0.1 mm. diameter or less, observed during momentary interruptions of electrolysis, has been found to vary in a well-defined manner with the polarizing current; and the resistance after the interruption of electrolysis has been shown to undergo changes which are reversible and reproducible.

4. Saturated wire of 0.32 mm. diameter has been found not to exhibit these changes.

5. Considerations are given which make it probable that the changes of resistance in the smaller wires are due to processes occurring within the metal, and not far removed from its surface.

6. The tentative conclusion is suggested that hydrogen occluded at the cathode surface exists for some time in a transitional state in which it possesses an electrical conductance of its own, and passes gradually into another form which has much less conductance, or none.

7. Characteristic changes have been observed, after the interruption of electrolysis, in the cathode potential of saturated palladium wire, and certain connections have been noted between the manner and magnitude of these changes and the conditions of electrolysis.

8. A few observations have been made upon copper wires which show that this metal does not suffer any measurable alteration of electrical resistance, under the same conditions which produce a high degree of occlusion in the case of palladium.

9. A single experiment has been made upon nickel wire, which appears to show that it too is unable to occlude sufficient hydrogen, under the conditions of these experiments, to produce any perceptible alteration of its electrical resistance.

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THE ACTION OF MAGNESIUM ON SOLUTIONS OF POTASSIUM CHLORIDE.

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It has long been known that metallic magnesium reacts very slowly with distilled water at ordinary temperatures, the products of the reaction being magnesium hydroxide and hydrogen. An apparently similar, though more energetic, reaction has been shown to occur when magnesium