EFFECT OF ABSORBED HYDROGEN AND OF OTHER GASES ON THE PHOTO-ELECTRIC ACTIVITY OF METALS.

By V. L. Chrisler.

SKINNER'S experiments[1] indicate that in a glow current through rarefied gases hydrogen atoms probably serve as carriers between the cathode and the gas atmosphere. This suggests that the photo-electric current from metals may also be carried, in part at least, by hydrogen atoms freed from their surface. That the presence of hydrogen in the metal probably increases its photo-electric current was shown by Wulf,[2] who found that after platinum had been allowed to stand in hydrogen for some time, there was a marked increase in current over that obtained in air and again a decrease in the current after the platinum had been exposed to air. Holman[3] obtained a series of results which showed that use as cathode with a glow current in hydrogen reduced the photo-electric activity of zinc, and use as anode increased it; but he could not corroborate these observations in further tests.

The present investigation was undertaken with the same object in view. The plan followed was a modification of Holman's, the only important difference being that all tests of the photo-electric current were made in the same atmosphere as that which served for the glow current and immediately afterward, while Holman first evacuated after passing the glow current before testing the photo-electric activity. The advantage of the present plan over his was two-fold. There was less chance for a "time" change in the metal — which in hydrogen was always large — before the activity was measured. Further the time saved was considerable, since it was possible to take an entire set of readings without evacuating the system.

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[1] Phys. Rev., XXI., p. 1, 1905.

[2] Ann. d. Physik, 9, p. 946, 1902.

[3] Phys. Rev., XXV., p. 81, 1907.

The effect of use as cathode in a glow current is first to clean the metal and thus increase its activity under the action of light, and then by continued use, to decrease it, probably by reducing the supply of negative carriers in its surface. The effect of use as an anode is first to charge up the metal with negative carriers, but if continued the activity is generally rapidly reduced, presumably by a layer of tarnish which always makes its appearance on the metal surface under prolonged use as anode. The effect produced by contact of the metal with the conducting gas is very similar to that of using it as anode; it first charges the metal with negative carriers — though not as rapidly as when used as anode — but continued exposure is very likely to decrease its activity.

Apparatus.

A diagram of the system is shown in Fig. 1. The source of ultra-violet light was a high potential arc between iron electrodes

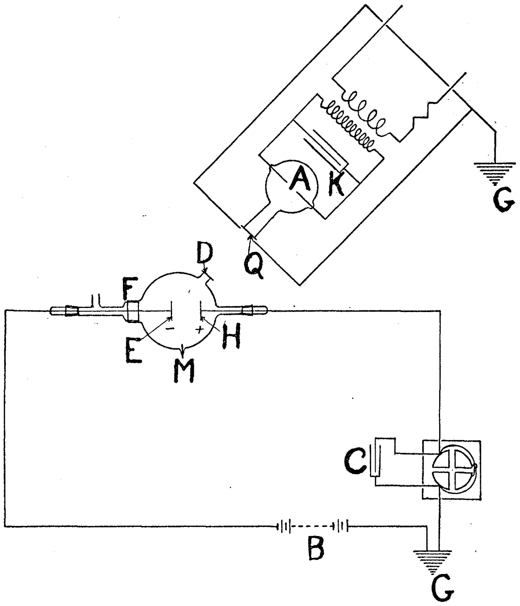

Fig. 1.

in hydrogen, operated in parallel with a capacity *K*, by an induction coil fed from an alternating-current circuit. A Kipp generator connected through a drying tube to the bulb containing the arc maintained a fresh supply of hydrogen. The light passing through the quartz plates *Q* and *D* fell at an angle of about 45 degrees on *E*, the metal tested. This was connected to the negative pole of a battery *B*, the positive being earthed. The negative electricity freed from *E* by the action of the light passed to the collecting electrode *H* which was connected to one plate of a condenser, the other plate being earthed. The current was measured by the potential to which the condenser was charged in a given time. A Thomson quadrant electrometer was used for measuring this potential, 53 scale divisions deflection corresponding to a difference of potential of one volt. The electrometer, condenser, arc system and wire leading from the collecting electrode to the condenser and electrometer were all enclosed in earthed metal cases.

The discharge chamber consisted of a glass bulb with a ground joint at *F* for convenient removal of the electrodes. In addition to the two electrodes mentioned a third was inserted at *M*. The quartz plate *D* was sealed on with de Khotinsky's laboratory cement. In the vacuum system all ground joints and stop-cocks were lubricated with a mixture free of hydrocarbons. P_2O_5 was used as a drier. Evacuation was produced by a Barr and Stroud mercury pump. The pressure was measured by a McLeod gauge. Small storage batteries served as a source of potential, and also for the glow current. *C* was a plane air condenser (capacity 3,360 centimeters) consisting of tin-foil pasted on glass plates and insulated by quartz.

The gases used were hydrogen, nitrogen, oxygen and helium. Hydrogen obtained from aluminum in a solution of potassium hydrate, was after careful drying by P_2O_5 stored in a flask which had stood evacuated for a time sufficient to free it of occluded gases. Nitrogen was obtained by passing air through phosphorus vapor, through a wash bottle containing KOH, and finally through a tube containing P_2O_5. After complete drying it was also stored in a flask freed of occluded gases. Oxygen obtained from manganese dioxide and potassium chlorate was first passed through a solution of KOH then through concentrated H_2SO_4, and finally past two electrodes between which was maintained a spark discharge for reducing any hydrogen to H_2O. It was then passed through a tube containing P_2O_5 and stored in a flask after perfect drying. The helium used was obtained from Messrs. Thomas Tyrer and Co.

Experimental Results.

1. *Platinum in Hydrogen.* — The following detailed series of results were obtained with platinum in an atmosphere of hydrogen. The metal was first carefully cleaned and polished, and then placed in the electrode chamber and this immediately evacuated and flushed out at least once with hydrogen before using, so that when filled to 1.2 mm. pressure with hydrogen, not more than two tenths of one per cent. of the gas present was air. For photo-electric measurements the metal was charged to a negative potential of 40 volts, and the collecting electrode started at zero potential. The most uniform results were obtained by breaking the arc after each reading.

By exposing the metal to the light for two seconds each time the following electrometer deflections were obtained from the metal in its initial state: 15, 16, 16 — equivalent to a current of 4.2×10^{-10} amperes. This represents the photo-electric activity of the freshly polished metal.

A glow discharge of moderate intensity was then sent from the platinum as cathode for about one minute, after which, returning to the original conditions, the following deflections were obtained from the photo-electric current: 85, 80, 78 — equivalent to 22.4×10^{-10} amperes. In these tests the metal was used as cathode just before each observation, otherwise it showed some recovery, as seen later, by exposure to the gas. Compared with the results above this shows the cleaning effect of use as cathode.

Immediately following these observations the platinum was used as anode in a glow discharge (during a fraction of a second only) after which the photo-electric effect tested as before gave the following deflections: 135, 160, 150, or 41×10^{-10} amperes. This shows the increased effect caused by use as anode, care having been taken not to operate it for a time sufficient to tarnish the metal. It is about double that obtained after using as cathode.

After again using the metal as cathode in a glow discharge (which reduced the photo-electric current to approximately 22.4×10^{-10} amperes given above) it was then allowed to stand disconnected while a discharge was sent between the two electrodes *H* and *M*. Following this the photo-electric activity was again tested giving the deflections 140, 115, 114 — equivalent to a mean value of 34×10^{-10} amperes. This shows also a marked increase in activity by exposure of the metal to the conducting hydrogen. After an hour's use as cathode the following values were obtained, which are in their relative effects a repetition of those already given:

	Amps. $\times 10^{10}$.
After use as cathode,	12
After use as anode,	30
After use as cathode,	12 (approx.)
After standing in conducting gas	27.3

After standing thirteen hours in the same atmosphere the following values were obtained:

	Amps. $\times 10^{10}$.
After use as cathode,	46
After use as anode,	136
After use as cathode,	46 (approx.)
After standing in conducting gas,	91

2. *Platinum in Helium.* — Similar tests were made with freshly polished platinum in an atmosphere of helium, care being taken to have pure gas and to rid the surface of the electrodes as far as possible of their supply of hydrogen. To this end, while flushing out with helium, the metal to be tested and also the collecting electrode were used as cathode in a glow discharge.

In helium there was observed with all the metals a small but definite leak without the light but this was of a magnitude smaller than the photo-electric current. The deflections given are the difference between the magnitudes obtained with and without light. Following are the results with duration of exposure to light, 20 seconds:

	Deflections.	Amps. $\times 10^{10}$.
After use as cathode,	7, 10, 8	.22
After use as anode,	5, 7, 7	.17

There was no increase after use as anode in helium, but immediately after evacuating and admitting *hydrogen*, the following were obtained:

	Amps. $\times 10^{10}$.
Initial photo-electric current,	.16
After use as cathode,	9.7
After use as anode,	10

After standing four hours in hydrogen:

After use as cathode,	23
After use as anode,	28

This shows an increase in the photo-electric current from the value of approximately $.2 \times 10^{-10}$ amperes in a helium atmosphere to 28×10^{-10} in hydrogen, or *140 times as great a current in the hydrogen as in the helium.* Had the platinum been allowed to stand in the hydrogen longer, its photo-electric activity would undoubtedly have increased still further.

3. *Platinum in Nitrogen.* — Similar tests were also made with freshly polished platinum in an atmosphere of nitrogen the same care being taken to insure purity of gas as with helium. In this case also there was a slight leak without light which effect is eliminated from the recorded observations. With a twenty second exposure the results were as follows:

	Deflections.	Amps. $\times 10^{10}$.
After use as cathode,	122, 98, 75	2.6
After use as anode,	106, 61, 61	2.2

showing a *decreased instead of an increased activity by use as anode.* The system was then immediately evacuated and *hydrogen* admitted, giving the following as mean results:

	Amps. $\times 10^{10}$.
Initially,	1.5
After use as cathode,	1.8
After use as anode,	15.5

In this case also the current was increased about *seven times in the hydrogen over that obtained in the nitrogen.*

4. *Platinum in Oxygen.*—Tests were next made in an atmosphere of oxygen. Here again there was a slight leak when the platinum was not exposed to the light. Duration of exposure, 20 seconds:

	Deflections.	Amps. $\times 10^{10}$.
After use as cathode,	4, 3, 2	.08
After use as anode,	0, 1, 2	.03

After evacuating and admitting *hydrogen* the following mean values were obtained:

	Amps. $\times 10^{10}$.
Initially,	.01
After use as cathode,	4.8
After use as anode,	15.7
After standing one hour,	10.8
After use as cathode,	7.3
After use as anode,	36

Taking the last value here we find *the photo-electric current about 1,200 times as large in hydrogen as in oxygen.*

5. *Relative Conductivity of the Gases.*—To test merely the relative mobility of the ions in the different gases, in which case care was taken to see that the activity of the metal should remain unchanged, the following observations were made in the sequence given :

Photo-Electric Current from Platinum.

Gas.	Pressure in mm.	Amps. × 10^{10}.
H	1.25	.83
He	1.27	.92
N	1.23	.97
O	1.18	.97
H	1.16	.83
H	1.93	.69
H	.66	.92

Photo-Electric Current from Nickel.

Gas.	Pressure in mm.	Amps. × 10^{10}.
H	1.06	.66
He	1.07	.78
H	1.04	.67
N	1.06	.61
O	1.07	.69
H	1.03	.69
H	2.19	.50

That the activity of the metals did not change is indicated by the fact that after testing in the other gases hydrogen was again admitted at the same pressure and the photo-electric current was found to approximate its original value. These tests show that the mobility of the ions in the other gases is as great if not greater than in hydrogen, hence the larger effect in hydrogen cannot be ascribed to this factor. The effect of gas pressure on the magnitude of the current is shown in these tables by the last tests in hydrogen. To determine if the photo-electric current was affected by the ionization of the gas, the activity of zinc was tested at a pressure of .0005 mm. giving 17.2×10^{-10} amperes. Hydrogen at a pressure of 1.82 mm. was then immediately admitted and the activity again tested giving 15×10^{-10} amperes. Platinum was also tested at a pressure of .001 mm. giving 3.6×10^{-10} amperes and at 1.2 mm. hydrogen the current was 4.2×10^{-10}. These observations show conclusively that the relatively large magnitudes in hydrogen are not to be ascribed to a greater ionization of this gas over the others because there appears practically no change in the current in passing from a high vacuum to the pressures used.

6. *Tests of Other Metals.*—The following tables give for a number of metals representative tests similar to those recorded in detail for platinum. Each test designated "after use as anode" and "after standing in the conducting gas" was always preceded by first using the metal as cathode for a moment in order to reduce its activity to the same initial value. Operation as anode as well as exposure to the conducting gas was only momentary. All tests were made at a gas pressure of from one to two millimeters. Quantities in parentheses indicate approximate values. The number of the experiment indicates a freshly polished metal.

Photo-Electric Current in Hydrogen × 10^{10}.

Metal.	Experiment.	Remarks.	Initial.	After Cathode.	After Anode.	After Con. Gas.
Aluminium	1		1.89	.88	4.4	
Antimony	1		2.33	13.9	32.5	
				1.66	35	17.8
				(1.66)	45.5	33.1
	2		2	1.62	21.3	
				2.16		29.5
Bismuth	1		5.6	7	19	12.7
				5.11	18.6	12.2
				5.3	18.9	
	2		4.4	7.77	35.8	15.6
Cadmium	1		6.33	2.03	22.4	18.9
				1.33	23.8	
				1.55	44.1	
	2		.55	3.11	16.9	
				2.33	28.3	
				(2.33)	22	3.5
Copper	1		1.59	24.2	39.3	
				3	19	21.5
	2		1.1	5.77	22	
				7	19.3	
Gold	1		5.55	2.19	18.5	
				2.22	17.9	4.33
Iron	1		.48	5.11	8.56	10.6
		Stood 12 hrs.	3.44	1.81	2.88	
	2		.84	4.7	17.7	

Photo-Electric Current in Hydrogen $\times 10^{10}$.—*Continued.*

Metal.	Experiment.	Remarks.	Initial.	After Cathode.	After Anode.	After Con. Gas.
Lead	1		.58	1.55	30.5	8.34
				6	36.8	11.3
Magnesium	1		.31	1.78	1.55	
				1.89	2.33	.44
Nickel	1		.55	6.55	13.7	
				5.55	12.6	
				6.78	17.1	13.6
Platinum	1		4.24	22.4	41.1	34.1
				15.7	37.9	25.7
		Stood 12 hrs.		46.2	136	91.2
	2			27.7	51.1	
Silver	1		2.77	60.1	83.7	
				59.6	69.9	74.4
				23.3	28.7	34.6
	2		1.1	17.4	53.7	
				11.8	41.2	22.7
				12.1	56.8	31.1
Tin	1		.74	6.33	16.4	
Tin				7.11	16.8	
		Stood 15 hrs.	8.53	1.44	18.1	12
			1.11	6.22	19.9	9.9
Zinc	1		15	2.77	2.2	
		Stood 13 hrs.		41.6	79.5	60.2
		Stood 12 hrs.		3.63	99.8	63

Photo-Electric Current $\times 10^{10}$ *in Helium followed by Test in Hydrogen.*

Metal.	Experiment.	Remarks.	Helium.			Hydrogen.		
			Initial.	After Cathode.	After Anode.	Initial.	After Cathode.	After Anode.
Aluminium	1			.33	.014			
				.27	.019	.33	1.5	1.6
							3.9	10.0
Antimony	1			0	0	0	17.4	17.7
							10.9	39
	2			1.38	.11	1.33	14.6	20.9
							10.2	41.9
Bismuth	1			4.16	3.66			
				3.74	3.18	2.2	12	
							2.6	12.1
		Stood 96 hrs. in H				88		
Cadmium	1			0	0	0	11.6	12.9
							7.22	10
							14.5	24.3
Iron	1			.33	.11			
		Stood 4 hrs.	.12	.27	.13	1.25	3.22	3
		Stood 12 hrs.				1	8.2	10.9
Lead	1			.028	.08			
				0	.08			
		Stood 12 hrs.	.05	0	0	.028	16.9	27.2
							18	31.1
Nickel	1			1.71	.13			
				.27	.36	.33	3.78	8.8
							11	13.4
Platinum	1			.22	.17	.16	9.67	10.5
		Stood 2 hrs.				4	15.9	19.4
		Stood 2 hrs.				5.8	22.8	28.4
Silver	1			.061	.028			
				.055	.028	3.05	1.69	8.9
		Stood 1 hr.				7.9	13.1	20.3
Tin	1			0	0	0	7.55	15.7
							7.89	14.3
Zinc	1			.083	.028			
				.083	.056			

Photo-Electric-Current × 10^{10} *in Nitrogen followed by Test in Hydrogen.*

Metal.	Experiment.	Remarks.	Nitrogen.			Hydrogen.		
			Initial.	After Cathode.	After Anode.	Initial.	After Cathode.	After Anode.
Aluminium	1			3.86	.92			
				5.82	.94	2.11	1.94	6.65
							1	1.77
Antimony	1			.55	.19			
				10	1.91			
				7.76	2.2			
Bismuth	1			.66	.42			
				5	.61	.14	2.99	5.22
							3.52	7.16
Cadmium	1			2.3	0	.55	4.33	8.22
							4.28	9.22
							.24	9.78
	2			4.5	1			
				2.7	.58			
Carbon	1			.16	.25			
				.17	.28	.042	.44	.25
							.49	.64
Copper	1			.55	.66			
				1.44	1.91			
				1.1	0			
Iron	1			.54	.64			
				.92	.86	1	1.66	6.55
							2.44	13.1
Lead	1			7.88	3.69			
				4.33	2.63	3.52	9.1	25.6
							6.6	11.1
Nickel	1			1	5.83	.55	7	13.3
							3.6	12.5
				9.9	1.38			
Platinum	1			.038	.12			
				2.47	2.48			
				2.63	2.18	1.46	1.89	7.67
							1.83	15.5
Silver	1			.08	2.6			
				.17	2.63			
				.15	.78	1.6	6.33	9.9
	2			1.4	2.8			
				1	2.5			
				.14	5.4	9.88	14.4	27.2
Tin	1			0	0			
Zinc	1			8.87	.12			
				3.2	.06	.05	6.55	11
		Stood 6 hrs.				4.66	4.66	21

Photo-Electric Current $\times 10^{10}$ *in Oxygen followed by Test in Hydrogen.*

Metal.	Remarks.	Oxygen. After Cathode.	Oxygen. After Anode.	Hydrogen. Initial.	Hydrogen. After Cathode.	Hydrogen. After Anode.
Aluminium		.22	0			
		.42	0			
Antimony		0	0			
Bismuth		0	0			
Cadmium		0	0			
Copper		1.85	.83			
		.42	0			
Iron		0	0			
Lead		0	0			
		.05	0			
Nickel		.33	0			
		.28	1.2			
Platinum		.08	0			
		.04	.03	.01	4.77	15.7
					7.3	36.1
	Stood 12 hrs.			12.2	11.1	23.3
Silver		0	0			
Zinc		.055	.014			
		.083	.055	.022	6.1	16.7

From these tables it may be seen that the photo-electric activity of all the metals is increased by use as anode in a glow current in hydrogen while none of them, with the exception of silver in nitrogen, exhibits this property in any of the other gases. This exception makes it probable that there is an absorption of nitrogen by silver or the formation of a chemical compound sufficiently unstable to allow the nitrogen to play with the silver a part similar to that universally played with all metals by hydrogen. To test this supposition carbon, which is known to absorb nitrogen readily, was also tried and found to show a slight increase after use as anode in this gas — which results are given in the foregoing tables.

7. *Change with Time of Exposure.* — Tests were also made of the rate of increase of the photo-electric activity of different metals by simply standing at a given potential in hydrogen. Similar tests were also made to determine the effect of the time of exposure to the conducting gas. The results are embodied in the following tables. Preliminary to each observation the metal was brought to the same

initial condition by use as cathode. The photo-electric effect was then tested as in the foregoing experiments with the metal at a negative potential of 40 volts.

Photo-Electric Current from Platinum in Amperes $\times 10^{10}$.

Time in Gas (Minutes).	Potential of Metal while Standing in Non-Conducting Gas.				
	0	—20	—40	—120	+120
0	7.7	8	7.2	8.3	8.8
1	11.1	17.2	15.8	16.4	16.5
2	17.4	17.4	17	20.5	16.4
4			20.4		
5	21.6	22.2		24.4	23.3
6			22.8		
10	22.2	24.2	24.4	28	24.1
15			23.8		

This shows a marked time effect, approximating a maximum activity in 10 to 15 minutes for all potentials of the metal. No variation with potential is however appreciable.

The next table shows the effect of time of exposure to the *conducting* gas in seconds instead of minutes as above.

Photo-Electric Current from Platinum in Amperes $\times 10^{10}$.

Time in Gas (Seconds).	Potential of Metal while Standing in Conducting Gas.			
	0	—20	—100	+100
.2	22.5	19.4	23.9	23.8
1	23.9	22.2	22.7	25.5
5	25.5	28.9	23.9	28.3
10	22.7	28.3	29.5	31.1
60			36.1	36.6

Here we find the activity of the metal increases far more rapidly in the conducting gas than in the non-conducting, there being very little increase after the first second exposure.

The effect with various metals in non-conducting gas is shown by the next table. All exhibit the quality of increasing toward a maximum activity with time of exposure to hydrogen. A few show a decrease after a certain time is reached.

Increased Activity of Metals by Standing Insulated in Non-Conducting Hydrogen. Current in Amperes × 10^{10}.

Time in Gas (min.).	Aluminium.	Antimony.	Bismuth.	Cadmium.	Copper.	Gold.	Iron.	Lead.	Nickel.	Platinum.	Silver.	Tin.
0	.4	2.2	5.7	.89	2.7	2.8	2.8	7.2	4.8	7.2	31	3.2
1	1.1	2.8	10	5	10	3.1	8.9	9.2	8.6	16	53	4.4
2	—	—	—	—	—	—	—	—	11	17		
5	2	4.2	14	—	26	10	8.9	10	12	—	55	8.9
6	—	—	—	—	—	—	—	—	—	23		
10	—	15	15	—	35	10	—	18	13	24	61	
15	—	20	—	7.2	31	—	—	14	14	24	—	9.4
25	—	24										

CONCLUSIONS.

(*a*) From all of the tests made the indications are that hydrogen is the important factor in the photo-electric current. The relatively small values obtained for the photo-electric activity in helium and oxygen make it probable that if the metal could be entirely freed of hydrogen it would give no photo-electric current. The relatively large values obtained after use as cathode in hydrogen are most naturally ascribed to the fact that there is as shown in § 7 a rapid recovery of the metal by simply standing in this gas. It is likely that an immediate test of the metal after use as cathode in hydrogen, if such were possible, would reveal an activity no greater than that obtained under the same conditions in helium.

(*b*) It was repeatedly noticed that the metal after use as cathode in hydrogen became negatively charged, and that after use as anode it became positively charged by simply standing in the non-conducting gas. This appears to indicate a transfer of negative electricity with hydrogen, in that after use as cathode it absorbs hydrogen and with it negative electricity — after use as anode its surcharge of hydrogen is given off and along with that also negative electricity.

(*c*) The photo-electric activity of silver and of carbon being slightly increased in nitrogen leads to the suggestion that, under favorable conditions, other gases than hydrogen might also play the same part. The increase of the activity of silver by use as anode in nitrogen was however small compared with the increase caused by hydrogen.

(*d*) The tables show that in most cases the photo-electric activity was larger in nitrogen than in either helium or oxygen. Whether this difference arose entirely from the metals being cleaner or in part from the effect of the nitrogen must remain an open question. We are inclined to ascribe it to the fact that more intense cleaning currents with the metal serving as cathode were used in this gas, having observed that the activity was in general much greater after large cleaning currents than after small ones. In the case of nitrogen, this current was in some instances sufficiently intense to melt the solder supporting the electrode. On the other hand it is very improbable that the relatively small values obtained in helium and oxygen were entirely caused by tarnish, since none was visible in any of the tests made in helium, oxygen or nitrogen (with the single exception of silver in oxygen).

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