CRYSTAL AND SOLID CONTACT RECTIFIERS.

By Alan E. Flowers.

Contents.

In the Physical Review for March, 1909, there appeared an account of tests made by G. W. Pierce on a number of rectifiers, consisting of points resting on crystals. The crystals used were anastase, brookite and molybdenite. Of these the molybdenite was by far the most sensitive and possessed the largest current carrying capacity. In the accounts given of these experiments, and in the accounts published elsewhere, no definite and final conclusions were drawn as to the cause of the phenomenon, though various possible causes were investigated. Wishing to determine if possible the cause of this action a series of experiments was carried out and a description of these experiments and their results follows.

1. Search for and Selection of a Rectifier of Large Capacity.

It seemed that the first and most important thing to do was to find a rectifier of large current carrying capacity, as the rectifiers previously described were capable of delivering, at most, but a few milliamperes of rectified current.

Believing that high resistance was not necessary, the crystals having high conductivity were selected for study. The sulphides appear to be particularly high in conductivity and iron, zinc and lead sulphides were tried for current carrying capacity and rectifying properties.

Of these, lead sulphide, galena, has by far the highest conductivity, and fortunately it showed in several samples not only large current carrying capacity, but very appreciable rectification. Single crystals showing sometimes 150 to 200 milliamperes of rectified direct current with a 3-volt (effective) alternating current supply. The crystals studied appeared to rectify about half the alternating current, though here it is well to emphasize the fact that different samples and different places on the same sample give widely varying results.

The samples of molybdenite examined required roughly a 21-volt effective alternating current supply to give 20 to 30 milliamperes of rectified direct current, and in such cases the alternating current ammeter indicated sometimes 500 or more milliamperes.

Believing that still larger capacities might be desired, two rectifiers were made by setting eight to ten samples of rectifying crystals in a little metal trough containing melted lead.[1] The lead on hardening made an absolutely certain contact with the body of the crystal and the metal trough constituted one electrode.

Pointed copper wires, in parallel, attached to a common return were set so that each touched a rectifying spot on one of the crys-

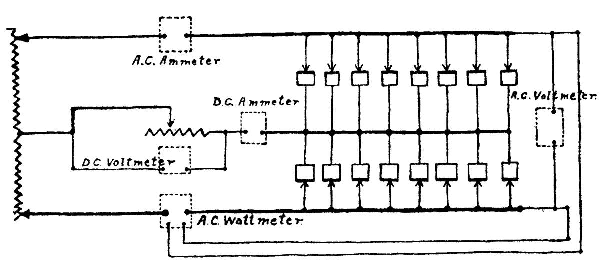


Fig. 1.

tals. (It is not essential to have but *one* point in contact with any one crystal, for if the rectifying surface be large enough, as many additional points may be used as there is room for on the rectifying surface.) See Fig. 1.

[1] Later I found that a similar method, using solder, had been used by L. W. Austin. Bulletin Bureau of Standards, Vol. 5, No. 1, p. 133, 1908.

These two rectifiers were connected in series-opposition across the secondary of a small transformer. One terminal of the direct current circuit was connected to the mid-point of a transformer and the other to the interconnection between the two rectifiers.

This rectifying set was left on the circuit all day without showing much change in its performance. A set of readings taken is shown in Table I.

From these results it was concluded that galena was the most promising crystal to study in order to find out the characteristics and cause of the rectification.

Table I.

Galena Crystal Rectifiers on Alternating Current. Frequency 60 Cycles.
Observer A. E. F. Rectifiers A_{1-8} and B_{1-9}. Date of Test, April 10, 1909.

Time.	Alternating Current Input.			Direct Current Output.			
	Total Volts.	Total Amperes.	Total Watts.	Volts.	Amperes.	Watts.	Efficiency.
3:12 P. M.	3.75	.555	1.75	.56	.493	.276	15.7
10:12 P. M.	3.82	.560	1.75	.56	.483	.270	15.4

Note that B_7 was disconnected.
See Fig. 1 for diagram of connections.

2. Characteristics of the Galena Rectifier.

In order to analyze the action of the crystal it seemed best to try the effects on a direct E.M.F.

(*a*) *Volt Ampere Characteristics.*— A large number of observations were taken on different crystals. Of these the set of readings given in Table II. and plotted Fig. 2 are characteristic.

Discussion of Volt Ampere Characteristic.— The values given in Table II. and shown in Fig. 2 are fairly representative. A large number of other runs were made which showed similar results. In some cases 4.2 volts would give a current of .850 or more amperes from crystal to copper and only .025 amperes in the opposite direction.

The most important thing about these characteristics is that they show a point at which breakdown occurs. This point occurs at a fairly definite *current* for any *given set* of conditions of *setting*. In general, however, each crystal and each setting will have its own breakdown point. This point may be 15 or more volts with 30 to 40 milliamperes flowing from point to crystal on fresh rectifying spots and may be as low as 5 volts and 90 milliamperes after several breakdowns. In general the higher breakdown voltages are reached when the current is small.

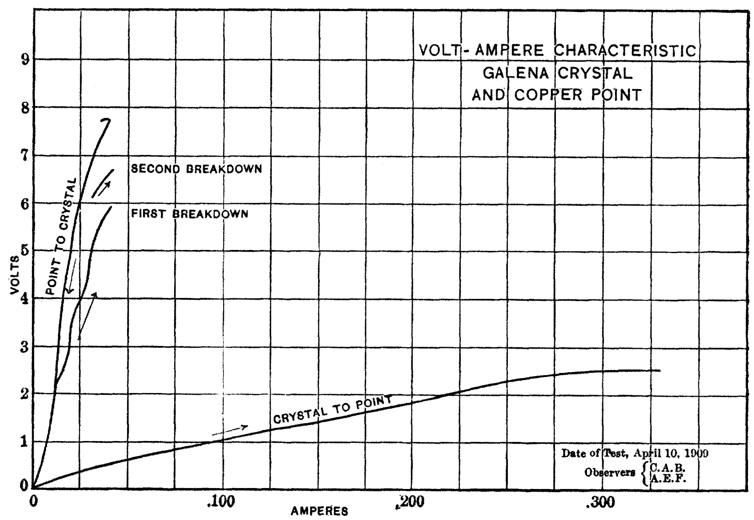


Fig. 2.

This breakdown point may occur at a higher voltage (and the same current) if the circuit be broken at the instant of partial failure and the crystal allowed to recover; while if the current is allowed to continue to flow after breakdown, partial or permanent destruction of the unidirectional conductivity or rectifying property will result.

The rectifying property is however not destroyed by the passage of considerable currents in the direction of crystal to point. In the case just cited 850 milliamperes did not destroy the rectifying property of the crystal.

Excessive current in *either* direction will break down and partially or permanently destroy the rectification, and breakdown occurs at a lower voltage when the current is reversed at each value of impressed voltage than it does when the voltage is simply increased in the direction of least current, *i. e.*, with the point as anode.

Table II.

Volt Ampere Characteristic of Galena Rectifier. Rectifier C, Copper Point Anode. Observers A. E. F. and C. A. B. Date of Test, April 10, 1909.

Time.	Volts.	Amperes.
2:35 P. M.	.824	.005
	1.492	.010
	2.230	.013
	2.500	.016
	2.704	.018
	3.060	.019
	3.288	.020
	3.804	.023
	3.900	.024
	4.008	.025
	4.292	.028
	4.472	.029
	4.780	.030
	4.960	.031
	5.180	.032
	5.308	.033
	5.468	.035
	5.940	.039

At this point the crystal resistance seemed to break down, allowing several hundred milliamperes to pass.

The voltage was reduced till resealing occurred and then raised.

Time.	Volts.	Amperes.
	6.104	.031
	6.36	.034
	6.44	.035
	6.58	.037
	6.66	.039
	6.66	—

Breakdown occurred again and the voltage was reduced till resealing occurred and then raised again.

The following readings were taken to prove that the passage of current in the previous runs had not spoiled the rectifying properties of the crystal.

Time.	Volts.	Amperes.
	1.92	.005
	5.80	.020
	6.36	.023
	7.17	.028
	7.48	.030
	7.64	.030
	7.78	.032
	7.93	.033
	7.98	.033
	0	0

Current was off for a short time while arranging for higher voltage.

Time.	Volts.	Amperes.
2:35 P. M.	6.98	.026
	7.58	.028
	7.86	.030
	8.36	.034
	8.57	.039
	8.96	.039 — Breakdown occurred at this point.
	6.64	.055
	4.16	— ?

Breakdown occurred again.
Resealing began at this voltage.

Time.	Volts.	Amperes.
	7.72	.035
	7.76	.039
	7·72	.039
	7.38	.035
	6.90	.030
	5.69	.026
	5.39	.020
	3.36	.015
	1.83	.010
	.72	.005

Copper Point Kathode.

Time.	Volts.	Amperes.
	.16	.009
	.272	.018
	.32	.020
	.416	.030
	.60	.049
	.72	.052
	.944	.090
	1.12	.110
	1.28	.130
	1.408	.143
	1.68	.179
	1.792	.196
	1.872	.203
	2.065	.229
	2.25	.241
	2.275	.257
	2.41	.276
	2.52	.310
	2.56	.329

Breakdown seems to be due to the heat produced. When viewed under a high-power microscope the point can be seen to sink into the body of the crystal, the surface bending and cracking like thin ice over mud, and little globules of molten material ooze through the crevices.

The point leaves a hole in the surface visible to the naked eye and breakdown carried to this extent is permanent.

Even before the final breakdown is reached one can perceive partial breakdown occurring and immediate resealing, resulting often in a decreased current. This is shown admirably in the varying curvature of the volt-ampere characteristic from point to crystal in Fig. 2.

The fact that the reactions are taking place at the surface or in a surface film is shown strikingly by measuring the potential difference between the copper point and the surface of the crystal near the point. It is found that practically the whole E.M.F. impressed on the rectifier is required for the potential difference between the copper point and the crystal. For example, a drop of 5.95 volts was measured between the copper point and the nearest spot on the crystal surface when the total voltage impressed on the rectifier was 5.98 volts.

(*b*) *Effect of the Material of the Point.* — Having found a crystal that was capable of rectifying large currents the next thing done was to try to determine whether the effects observed were in any way dependent on the material of the point used. Volt-ampere characteristics were taken with points of copper, steel, platinum, lead, zinc, aluminum, brass, solder and graphite.

The characteristics were similar to the ones illustrated in Fig. 2 and Table II., and apparently the material of the point made no difference in the rectification. Small differences, however, such for instance as those which might be caused by variation in heat conductivity of the points, might easily be masked by the considerable variations in the volt-ampere characteristics of different crystals.

(*c*) *Effect of the Shape of the Point and the Ratio of Contact Areas.* — The rectification did not seem to be affected in any way by change of shape of point. The steel needle, point end, seemed to show the same results as the eye end and sharp and blunt ends of copper wire points seemed to give equally good results. Even the substitution of a globule of mercury about 3 mm. in diameter or of melted lead dropped on the crystal surface and allowed to harden in place so that it made intimate contact with a large area of the surface gave good rectification. It is unusual to find a large surface showing uniformly good rectification, and if any *part* of the globule touches a spot that does not rectify the effect of the rectifying surface is masked or lost.

For comparison a copper point was set on the rectifying surface near the globule of lead; the other contact to the crystal being made by a lead setting such as has already been described. The results of these tests are given in Table III.

Table III.

Comparison of Point Contact and Large Area of Contact on Rectification.
Observer A. E. F. Date of Test April 30, 1909.

Volts. Crystal to Point.	Amperes.	Resistance, Ohms.	Ratio of Resistance.	Remarks.
– 4.00	.003	1333		
+ 4.00	.190	21.05	.01577	Copper point under very light pressure.
– 4.00	.012	333		
+ 4.00	.192	20.8	.0625	
– 1.00	.023	43.5		Connection made to globule of lead.
+ 1.00	.186	5.38	.01236	
– 1.00	.049	20.2		Readings taken after several reversals.
+ 1.00	.216	4.63	.229	
– 2.00	.100	20		Current decreasing.
+ 2.00	.600	3.33	.1663	Current increasing.
– 3.00	.210	14.28		Current increasing.
+ 3.00	.980	3.06	.214	Current increasing. Breakdown finally.
– 1.00	.044	22.7		Contact made with crystal by a globule of mercury.
+ 1.00	.118	8.57	.373	
– 1.00	.039	25.6		Mercury globule contact on rectifying surface and copper wire point on non-rectifying crystal for the other connection.
+ 1.00	.088	11.36	.443	

The use of a large area of contact to the rectifying surface of the crystal does not destroy the rectification.

When the lead or mercury globule was used to make connection to the rectifying surface the substitution of a copper wire point in contact with the non-rectifying surface of the crystal instead of the usual lead setting had no very great effect on the rectification.

Finally a crystal was selected which showed good rectifying properties. This was mounted in a lead setting and the crystal cut down to a point. This pointed crystal was then set in contact with a large block of metal and also in contact with another crystal and it was found that rectification was produced as before.

The results of this test are given in Table IV.

TABLE IV.

Effect of Cutting the Rectifying Crystal Down to a Point. Contact Pressure 200 gms.
Observer A. E. F. Date of Test April 25, 1909.

P. D. Volts.	Current, Amperes.	Resistance Ohms.		Ratio of Resistances.	Remarks.
		To Crystal.	From Crystal.		
−4.00	.010	400			Crystal *E*, touching a steel
+4.00	.066		60.6	.151	hack saw blade.
−4.00	.010	400	100		Crystal *E*, touching a zinc
+4.00	.040			.25	plate.
−4.00	.020	200			Crystal *E*, touching lead
+4.00	.105		38.1	.191	plate.
−4.00	.011	363.5			Crystal *E*, touching brass
+4.00	.091		44.0	.1209	plate.
+4.00	.004	1,000			Crystal *E*, touching a recti-
−4.00	.004		1,000	1	fying galena surface.
−4.00	.012	333		.0333	Crystal *E*, touching a non-
+4.00	.360+		11.1		rectifying galena surface.
At this voltage the current continues to increase till breakdown occurs.					
+4.00	.074		54.1		Crystal *E*, touching alumi-
−4.00	.011	363.5		.1486	num plate.
+4.00	.070		57.2	.1715	Crystal *E*, touching brass
−4.00	.012	333			plate.
−6.35	.030	212		—	
−6.18	.074	83.5	—		
At this point breakdown is beginning.					
−5.3	.590				
Breakdown is complete.					

(*d*) *Effect of Mechanical Pressure and Mutilation of Surface.*— When a good rectifying surface has been found the copper point may be pressed against the rectifying surface with very considerable force without impairing the rectification and with a great increase in conductivity (in both directions). However, if the pressure is high and the voltage is carried to the breakdown point the breakdown of the spot touched is likely to be permanent. The point sinks into the crystal, or perhaps a hole is melted in the crystal and the point sinks into this hole.

It was found that a moderate pressure (about 200 grams) was sufficient to give steady contact and in most cases this was the pressure used.

A crystal having a rectifying surface was often found to have other rectifying surfaces underneath and parallel when the layers were split off, but scratching or scarring a rectifying surface usually spoiled more or less completely its rectifying properties.

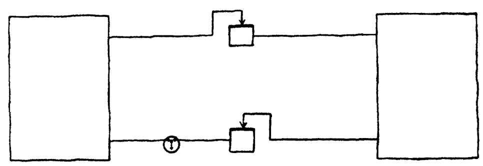
(*e*) *Effects of Frequency.*— No attempt has as yet been made to determine a relation between per cent. rectification and frequency; however, the following significant tests bearing in a general quantitative way on this were carried out. A rectifier consisting of a copper point and galena crystal was connected in series with a fairly sensitive galvanometer and a telephone receiver. Speaking into the receiver caused large deflections of the galvanometer and loud continued vowel sounds would throw the galvanometer off scale. The sensitiveness of this galvanometer is such that $.0286 \times 10^{-6}$ ampere gives 1 mm. deflection, so that the rectified current must have exceeded 7 microamperes.

The frequency of telephone currents is of the order of 1,000 cycles per second.

Another arrangement of the rectifier was tried as a receiver for the electric waves produced by a static machine. The diagram of the connections is given in Fig. 3.

This arrangement gave galvanometer deflections of 3 to 4 cm. corresponding to a current of the order of a microampere with very high frequencies. Similar effects were obtained when using an induction coil as a source for the electric waves.

When using the galena crystal rectifier with a Tesla oscillator large galvanometer deflections were obtained, but here a different type of rectifying effect also occurs between the point and any large conducting surface, such as the lead setting, a piece of brass, etc. That the type of rectification obtained with the Tesla oscillator is entirely different from the type of rectification here studied is made more clear by the results of the tests on the effect of electrical dis-



RECTIFIER AS WIRELESS RECEIVER
Fig. 3.

charges through gases. This type of rectification appears to be similar to the effects observed by

Tamm, Drude's Annalen, VI., p. 259, 1901,

Precht, Wiedemann's Annalen, XLIX., p. 150, 1903,

Himstedt, Wiedemann's Annalen, LXVIII., p. 294, 1899,

which show differences in the minimum voltage for discharge and in the conductivity of the gas between a point and a metal plate. The effects may be due to rectification at the point of connection to the oscillator where both brush discharge and sparking may be occurring and not at all at the point and crystal.

(*f*) *Effect of Electrical Discharges.* — A crystal, D_5, was mounted and connected to a storage battery with meters to measure the voltage impressed on the rectifier and the current flowing from the battery.

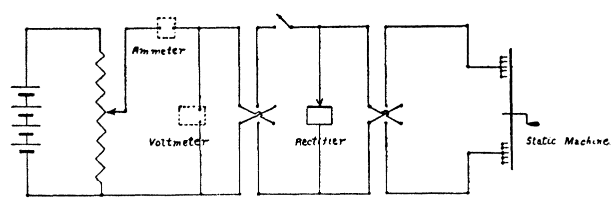


Fig. 4.

A static machine was then so connected that the static discharge could be sent in either direction through the rectifier as illustrated in Fig. 4.

It was found that the static discharge could be passed continuously in either direction through the rectifier, whether the rectifier were connected to or disconnected from the battery, without affecting the conductivity of the rectifier or its rectifying properties. However, it was found that if the static discharge produced a spark anywhere in its path the effect for any connection of battery or static discharge is to increase the conductivity in either direction and to spoil the rectifying property.

(*g*) *Effect of Heat.* — The determination of the effect of heat is complicated by the fact that the current that flows when the determination is being made may cause local heating and so intensify and mask the general effect. There may be also electro-chemical effects.

In general, however, breakdown occurs at a lower voltage with an increase of temperature and the conductivity rises with increase of temperature, but the increase is greater for the direction of least conductivity so that the per cent. of rectification decreases with increase of temperature.

The rectification disappears at a temperature of about 270° C., but is partially regained on cooling, though the parts of the crystal which carried no current are apparently not affected by heating to 270 or 280° C. under oil and then cooling. The effect of the passage of current through the rectifier while it was cooling is given in Table V.

Table V.

Effect of Continued Passage of Current on Rectifier while Cooling.

Volts.	Amperes.	Resistance.		Ratio of Resistances.
Cooling without current.				
— 1	.039	25.68		
+ 1	.074		13.52	.527
Cooling with current flowing from point to crystal.				
— 1	.014	71.5		
+ 1	.051		19.61	.2745
Cooling with current flowing from crystal to point.				
+ 1	.013		77	.539
— 1	.007	142.9		
+ 1	.020		50	
— 1	.008	125		.400

It is worth while noting also that even at 280° C. there is a tendency for the current, if from point to crystal to decrease, and if from crystal to point to increase, if the current is allowed to flow.

It is especially significant that the rectifying property is not entirely destroyed by the continued passage of current in either direction while cooling under oil from this temperature though the rectification is best when the current is allowed to flow from point to crystal.

Heating the rectifier in air in a closed vessel gave similar results up to 270° C., but at slightly higher temperature, 300–320, the difference in conductivity was regained. Here it often appeared that the difference in conductivity was not obtained till an appreciable time had elapsed. At 345° C. the difference in conductivity again decreased, and on cooling there was a continued decrease in conductivity in both directions till the current flowing at 1 volt was less than a milliampere. Parts of the crystal not carrying current were not affected.

After the passage of current in either direction the rectifier if disconnected quickly and connected to a galvanometer, showed a feeble E.M.F. always in the same direction and this direction was always opposite to that required for the difference in conductivity. This appeared to be due to a thermo-electric E.M.F. in the same direction as that which was produced when the *crystal* was gently heated by a flame.

3. Artificial Production of Solid Contact Rectifiers by Chemical and Electro-chemical Treatment.

An attempt was made to produce rectification in samples of galena that did not rectify naturally, by subjecting the crystal to the action of various chemicals. Water and the conducting solutions and acids tried (*i. e.*, nitric acid, alcohol, potassium bichromate), if put on the crystal while the crystal was carrying current, usually increased the conductivity, caused breakdown and spoiled rectification. Although such results did not occur when the chemical treatment was not coincident with passage of current. The non-conducting acids and solutions tried (*i. e.*, conc. H_2SO_4, CS_2 and oils) seemed to have little effect.

The copper point was then covered with burning sulphur, the flame blown out and the remaining sulphur cooled quickly so that it was left in the amorphous state. A point so treated when set on a galena crystal surface that previously showed no rectifying properties would at first show little conductivity, but the passage of current first in one direction and then in the other produced in a few minutes a very fair degree of rectification *but in the opposite direction to that found in native crystals.*

A set of values is given in Table VI.

Table VI.

Rectifier Produced Artificially by Electro-chemical Treatment of Copper Point with Amorphous Sulphur.

Potential Difference, Crystal to Point.	Current.	Resistance.		Ratio of Resistances.
		Point to Crystal.	Crystal to Point.	
−1.00	.172	5.88	—	.209
+1.00	.036	—	27.80	

The treatment of a crystal that previously possessed no rectifying properties with amorphous sulphur and then with current, produced rectifying properties similar in all respects to the effect obtained when the copper point was treated.

The effect of the electro-chemical treatment with amorphous sulphur of the point set on metallic lead or the treatment of the lead surface itself was much more marked. Table VII. gives the results obtained with this rectifier.

It is worthy of note that this contact rectifier showed itself far superior in rectifying power to any of the crystal rectifiers so far tried, its resistance in one direction being .3 to .4 per cent. of the resistance in the other direction. Its breakdown point was reasonably high and it showed at one point the partial breakdown and immediate resealing or self-recovery found with the crystal rectifier.

The copper point of a rectifier produced in this way (by electro-chemical sulphur treatment while the point was in contact with a piece of lead) could be removed and set on a block of brass or other metal and be made to exhibit rectifying properties, but the rectifying film had to be produced first in contact with lead.

TABLE VII.

Copper-point Lead-block Contact Rectifier Produced Artificially by Sulphur Treatment.

Potential Difference, Lead to Copper. Volts.	Current, Amperes.	Resistance.		Ratio of Resistances.
		Copper to Lead. Ohms.	Lead to Copper. Ohms.	
−1.00	.002	500		
+ .62	.312		1.986	.00397
−1.00	.002	500		
+ .60	.404		1.485	.00297
−2.00	.003			
−3.00	.004			
−4.00	.022			
−5.00	.004			
−6.00	.008			
−7.00	.009			
−8.00	.010			
Breakdown.				

Attempts to produce the rectifying film by electro-chemical treatment of a copper point with sulphur while in contact with brass, failed to produce definite results, though good results were obtained by setting the copper point, after being treated with sulphur, on a small block of graphite.

4. Applications.

Rectifiers of this type, when perfected, might be used in measuring telephone currents, and sound intensities, in detecting feeble electric waves and in charging small storage batteries.

5. Discussion of the Results and Conclusions.

It is worth while noting that other workers in this field have emphasized the thermo-electric potential difference of the two materials of the contact rectifier or have emphasized the difference in heat and electric conductivity of the two materials.

The rectification cannot be due to thermo-electric forces, since they have neither the magnitude nor the direction necessary. The rectification cannot be due to difference in conductivity of the two materials in contact, because graphite, which has a higher specific resistance than the lead sulphide, could be used for a contact making point. There are only two possible explanations: One is that the film, when once formed, has unidirectional conductivity. This seems improbable in solids. The other explanation is that the film is produced in an infinitesimally short length of time by the passage of a minute quantity of electricity.

The tendency of the resistance to rise when current is flowing to the crystal, the direction of highest resistance, and to fall when the current is flowing from the crystal, seems to give color to this view. The sluggishness of change of resistance sometimes observed at high temperatures and with some crystals also tends to strengthen the probability that the rectifying film is re-formed electro-chemically with each reversal.

If the film is re-formed at each reversal, then there must be a definite quantity of electricity, however small, required for the production of the film, and one should find that the rectification is less perfect for very small currents or for very high frequencies. The facilities for determining this effect are not now at my disposal, but I trust to see this point settled in the near future.

The results of the tests described seem to justify the following conclusions:

1. The rectifying action is produced at the surface, or in a surface film, and is not due to the point employed.

2. The rectification is not an effect of the sharpness of the point or the ratio of contact areas.

3. The rectifying film will break down at a moderate voltage (6 to 15 volts) which is higher the smaller the current.

4. The rectifying film can be destroyed by the action of the electric current.

5. The feeble evanescent E.M.F. existing after the passage of current in either direction through the rectifier is insufficient to account for the rectification, and its direction is opposite to that which would be required for rectification.

6. There is apparently no difficulty in rectifying currents of very high frequency.

7. The rectification disappears at high temperature, *i. e.*, about 270° C., but is partially regained on cooling.

8. The rectifying film can be produced artificially by *electro-chemical* treatment with amorphous sulphur.

9. The rectification is probably due to the electro-chemical formation of a resisting film at each reversal.

It is a pleasure to acknowledge here the assistance rendered in various ways by a number of my colleagues.

UNIVERSITY OF MISSOURI,
June 22, 1909.

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