

transversely to the line of the cold crystallising force, and from my former experiments in this direction ('Roy. Soc. Proc.,' vol. 40, 1886, p. 544), I think there appear substantial indications that ice may expand unequally in different directions. Messrs. McConnell and Kidd have shown, in their experiments with glacier ice, that "ordinary ice, consisting of an irregular aggregation of crystals, exhibits plasticity, both under pressure and under tension at temperatures far below the freezing point, down to -9° at least, and probably much lower." The experiments recorded on Diagram I now practically demonstrate the latter supposition, and I found the plasticity at the lower temperature to be very considerably reduced. Mr. J. Y. Buchanan, F.R.S., in his paper on "Ice and Brine" ('Edinburgh Roy. Soc. Proc.,' vol. 14, 1888, p. 129), has expressed notions of the plasticity and flow of glacier ice which tend to confirm the views of Messrs. McConnell and Kidd on this subject. In this direction the experiments on pure ice, Diagram I, compared with those on pond ice, Diagram II, have shown that ice frozen from water containing saline constituents is more plastic than the ice frozen from pure distilled water.

I hope that the experiments of this memoir may help to afford information in connexion with the interesting subject of the plasticity of ice.

Appendix.

Attention has very recently been drawn to the manner in which lake ice has a tendency to crystallise, in a series of interesting letters published in 'Nature,' 1889, by Mr. Thomas H. Holland, Mr. T. W. Backhouse, Mr. T. D. Latouche, Messrs McConnell and Kidd, and others. I have myself also frequently noticed the six-rayed starlike figures and skeleton triangular forms on natural pond ice, and other similar indications of the tendency of lake ice to the hexagonal form of crystallisation.

III. "The Passive State of Iron and Steel."—Part I. By THOS. ANDREWS, F.R.SS.L. and E., M.Inst.C.E. Received May 18, 1890.

The singular metallurgical phenomenon of the passive state of iron presents many features of interest, affording a wide field for original research. The knowledge we possess on this peculiar and obscure subject is not, however, very extensive, owing possibly to the difficulties encountered in devising suitable methods of research in relation thereto. The author, therefore, approached the investigation with considerable diffidence, feeling greatly the difficulties accompanying

a research of this intricate nature. He feels, however, rewarded by the measure of success which has ensued. The general tentative conclusion he has arrived at, as a result of careful experimentation, is that the passive state of iron and steel ought not to be regarded as fixed or static, the electro-chemical observations tending to show that the passivity is a property influenced more or less by various conditions, such as variation of the molecular structure and chemical composition of the iron and steel, different strengths of nitric acid, modification of attendant physical conditions, magnetism, temperature, &c. It is known that when bright iron is immersed in nitric acid of 1·4 sp. gr., the iron is not acted upon, but remains passive in the acid, which appears to exert no perceptible effect upon the metal. "Under certain circumstances iron is not acted upon at all by nitric acid. Iron in this state is termed passive, and this condition is brought about by dipping the metal into concentrated nitric acid and then washing it" ('Treatise on Chemistry,' by Sir Henry E. Roscoe, F.R.S., and Dr. C. Schorlemmer, F.R.S.). The late Dr. Jno. Percy, F.R.S., the eminent metallurgist, referring to the passive state of iron, remarked that "this is a very curious and interesting subject, which may possibly be one day found to admit of valuable practical application." The passive state of iron appears first to have been observed just a century ago by Keir, and brought before the notice of the Royal Society in 1790 ('Phil. Trans.,' 1790, p. 379); he observed that strong nitric acid had no action on iron when the metal was placed therein. Bergman, Scheurer-Kestner, Schönbein, and Buff also made some observations on the passivity of iron previous to the year 1848. Faraday and Beetz were disposed to attribute the passive state of iron to the immediate formation of a very fine envelope or film of oxide on immersion of the metal in concentrated nitric acid, whereas Sir John Herschel ('Annales de Chimie,' vol. 54, 1833, p. 87) considered the phenomenon was due to a certain permanent electric state of the surface of the metal.

Westlar ('Annales des Mines,' vol. 2, 1832, p. 322) observed that when iron or steel had been immersed in nitrate of silver solution it failed to precipitate copper from its solutions.

Braconnot ('Annales de Chimie,' vol. 52, 1833, p. 288) noticed that filings or plates of iron were not at all affected in strong nitric acid at ordinary temperatures.

In the present memoir are presented the results of a study of certain magnetic, temperature, and other conditions which the author found to affect the passive state of iron and steel, and he is extending the inquiry into the relative passivity of the various modern steels and other aspects of the subject. The author observed, in course of experimentation some years ago, that when bright iron or steel was magnetised whilst immersed in concentrated nitric acid, its passive

condition was to some slight extent modified, magnetism acting through considerable periods of time apparently exerting a measurable influence. For conducting the present investigation he devised, and, after careful consideration, decided to adopt, the delicate electrochemical method of research hereafter described, and by the use of a sensitive astatic mirror galvanometer and other appliances the following results were obtained, which it is hoped may prove of interest and afford an addition to our knowledge of some of the conditions affecting the passive state of iron and steel.

For convenience, the experiments are classified under the following heads:—

Series I, Table I, containing the result of observations on the influence of magnetisation on the passive state of steel in cold nitric acid, sp. gr. 1.42, at temperature of 45° F. or less.

Series II, Table II, treating of the influence of magnetisation on the passive state of steel in warm nitric acid, sp. gr. 1.42, above the temperature of 45° F., the experiments showing that magnetised steel bars were less passive in warm nitric acid than unmagnetised ones.

Chemical Analysis of the Steel Bars.

	per cent.
Combined carbon	0.570
Silicon	0.032
Sulphur	trace
Phosphorus	0.066
Manganese	0.147
Iron (by difference)	99.185
Total	100.000

Physical Properties of the Steel Bars.

Contraction of area at fracture.	Extension.	Breaking strain per square inch of original area.
per cent. 22	per cent. 2.0	tons 55.42

SERIES I.

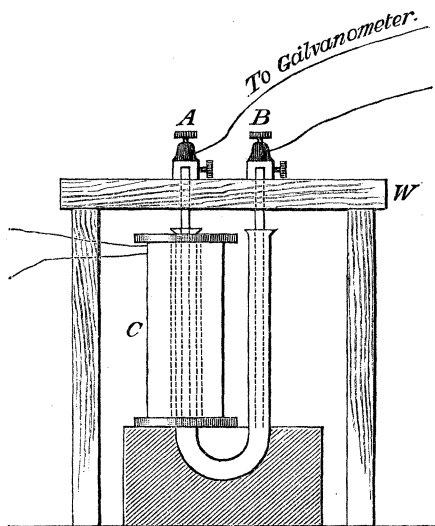
The Influence of Magnetisation on the Passive State of Steel in Cold Nitric Acid.

The method of experimentation for the observations of Series I was as follows:—

For each experiment a pair of polished steel bars, $8\frac{1}{4}$ inches long, and 0.261 diameter, were cut adjacently from a long steel rod to insure practical uniformity of structure and composition. The steel and iron rods were of the chemical composition and physical properties given on previous page.

The apparatus will be understood on reference to fig. 1.

FIG. 1.



A pair of bars, supported in a wooden frame, *W*, were immersed in $1\frac{1}{4}$ fluid oz. of cold concentrated nitric acid, sp. gr. 1.42, contained in the U-tube, *A* being the magnetised bar, and *B* the unmagnetised one, and allowed to remain therein for periods stated on the Table I. The bars were in circuit with a delicate astatic mirror galvanometer, the telescopic observations of the deflections of which were carefully taken. In some cases the bar *A* was previously permanently magnetised by hand, and in other instances the bar was magnetised in the coil *C* for a short time. In the latter instances the subsequent results were due to the residual permanent magnetism. The magnetising coil, *C*, was a powerful one, and was worked in connexion with a bichromate battery in cases where the magnetisation of the metal was made in the coil.

A considerable number of experiments were made in the above manner, those sets recorded on the Table I being selected as average typical ones. In all the following experiments a new wooden stand and a fresh pair of bright polished steel or iron rods were prepared for each set of observations.

The E.M.F. recorded in all the following tables was ascertained by using a sensitive galvanometer of known calibration in conjunction with the ascertained resistance of the nitric acid solutions.

Table I.

Influence of Magnetisation on the Passive State of Steel.

Time from commencement of experiment.	Electro-chemical effect between magnetised and unmagnetised steel bars immersed in circuit in cold nitric acid, sp. gr. 1.42. E.M.F. in volt. The electro-chemical position of magnetised bar, positive, except where otherwise specified.					
	Experiments, Set I.	Experiments, Set II.	Experiments, Set III.	Experiments, Set IV.	Experiments, Set V.	Experiments, Set VI.
seconds.						
0		0.022	0.022		0.016	
15		0.013	0.021		0.014	
30		0.011	0.020		0.013	
minutes						
1	0.001	0.008	0.019	0.008	0.013	
4	0.004	0.007	0.009	0.011	0.014	
6	0.004	0.008	0.006	0.011	0.014	
8	0.004	0.008	0.007	0.011	0.015	
10	0.005	0.007	0.008	0.011	0.015	0.006
12	0.005	0.007	0.009	0.011	0.015	0.006
16	0.005	0.007	0.011	0.011	0.015	0.006
20	0.006	0.006	0.011	0.011	0.015	0.006
24	0.006	0.006	0.012	0.010	0.015	0.006
28	0.006	0.006	0.013	0.010	0.015	0.006
30	0.006	0.006	0.013	0.010	0.015	0.006
35		0.007	0.013	0.006	0.015	0.006
50		0.008	0.014	0.007	0.015	0.004
hours						
1		0.010	0.014	0.007	0.016	0.004
2		0.011	0.018	0.007	0.016	0.004
3		0.013	0.020	0.008	0.017	0.005
3½		0.016	0.022	0.008	0.017	0.005
4			0.022	0.008	0.017	0.006
6			0.024		0.017	0.006
8			0.026		0.018	0.007
12			0.030		0.018	0.007
16			0.030		0.018	0.007
18			0.030		0.018	0.008
20			0.029		0.019	0.008
22			0.029		0.019	0.008
24			0.029		0.019	0.008
26						0.007
28						0.007
30						0.007
40						0.013
42						0.013

Table I—*continued.*

Influence of Magnetisation on the Passive State of Steel.

Time from commencement of experiment.	Electro-chemical effect between magnetised and unmagnetised steel bars immersed in circuit in cold nitric acid, sp. gr. 1·42. E.M.F. in volt. The electro-chemical position of magnetised bar, positive, except where otherwise specified.					
	Experiments, Set VII.	Experiments, Set VIII.	Experiments, Set IX.	Experiments, Set X.	Experiments, Set XI.	Experiments, Set XII.
hours						
1		0·0005 N	0·0005 N	0·000	0·000	0·011
3	0·004 N	0·0006	0·001 N	0·000	0·000	0·018
12	0·003	0·011	0·000	0·002	0·002	0·020
20	0·008	0·012	0·001	0·004	0·004	0·021
24	0·012	0·012	0·001	0·002	0·005	0·026
26	0·012	0·012	0·001	0·002	0·005	0·026
28	0·013	0·013	0·002	0·002	0·006	0·026
30	0·013	0·013	0·002	0·002	0·006	0·023
32	0·013	0·014	0·002		0·006	0·028
40	0·016	0·015	0·004		0·007	0·030
42	0·017	0·015	0·004		0·007	0·030
48	0·020	0·016	0·006		0·007	0·032
51	0·020	0·016	0·006		0·008	0·032
64	0·020	0·016	0·007		0·011	0·032
66	0·020	0·017	0·008		0·011	0·032
72	0·023	0·017	0·011		0·011	0·032
days						
3 $\frac{1}{4}$	0·023	0·017	0·011		0·011	0·030
3 $\frac{1}{2}$	0·024	0·017	0·012		0·012	0·027
3 $\frac{3}{4}$	0·025	0·018	0·013		0·012	0·024
4	0·026	0·018	0·014		0·013	0·022
4 $\frac{1}{4}$	0·026	0·018	0·014		0·013	0·020
4 $\frac{1}{2}$	0·027	0·018	0·015		0·013	0·018
4 $\frac{3}{4}$	0·027	0·019	0·015		0·013	0·016
5	0·028	0·019	0·016		0·013	0·013
5 $\frac{1}{4}$	0·028	0·019	0·016		0·013	
5 $\frac{1}{2}$	0·028	0·018	0·017		0·013	
5 $\frac{3}{4}$	0·028	0·018	0·017		0·013	
6	0·028	0·017	0·017		0·013	
6 $\frac{1}{4}$	0·027		0·017		0·013	
6 $\frac{1}{2}$	0·026		0·017		0·013	
6 $\frac{3}{4}$	0·025		0·017		0·013	
7	0·024		0·017		0·013	

Some of the magnetised bars employed in the experiments on Table I were magnetised by touch, and in other experiments they were magnetised in the coil as previously described.

In some instances on Table I it was noticed that on the first immersion of the metals in the nitric acid an almost instantaneous but steady deflection of considerable extent of the needle of the galvanometer occurred, indicating an electro-positive position for the

magnetised bar; this more extended fling of the galvanometer, however, subsided in a few seconds, and did not interfere with after results due to electro-chemical action.

The results of Series I, in cold nitric acid, were perhaps more perceptible in those experiments extending over the longer periods (see Table I), though even in these, the effect was comparatively small. In a recent research by the author on "Electro-chemical Effects on Magnetising Iron," Part II ('Roy. Soc. Proc.,' vol. 44, p. 152), it was noticed that local currents were set up between the polar terminals and central portions of steel magnets exposed in electrolytes, and this class of local action, together with the slight alteration of the physical structure of the magnet bars consequent on their magnetisation, may possibly be involved in producing the effects due to magnetism on passive steel or iron in concentrated nitric acid. The influence of magnetism of low intensity, whilst modifying to a very limited extent, does not, however, appear sufficient entirely to overcome, the passivity of the metal in nitric acid, and the influence of even a powerful magnetic force, though doubtless slightly modifying (to the extent, possibly, of the slight alteration of physical state in the metals, induced by magnetism), did not destroy the passivity of bright iron or steel exposed to its action in *cold* strong nitric acid.

The whole of the results on Table I afford an indication that magnetisation of comparatively low intensity, acting during considerable periods of time, exerts only a limited modifying influence on the passivity of iron or steel in the cold, or up to a temperature of about 60° F., though the influence is just discernible when employing a delicate galvanometer. Magnetisation, with the nitric acid at a higher temperature, produces a quicker effect, see results in Series II, Table II. The author is pleased to see that somewhat similar conclusions as to the influence of powerful magnetisation on the passive state of powdered iron in *warm* nitric acid have been independently arrived at in America by Messrs. Nichols and Franklin, who, in some recent interesting experiments, have found that powdered iron in nitric acid, 1.368 sp. gr., when placed in a test-tube in a suitable apparatus between the poles of a powerful electro-magnet commenced to be violently acted upon when raised to a temperature of 51° C. Unmagnetised iron usually remains passive in strong nitric acid until a temperature of about 89° C. is reached, when an explosion, consequent on loss of passivity, occurs. Messrs. Nichols and Franklin's experiments, therefore, show that very powerful magnetic action helps to lower the temperature of transition from the passive to the active state. They have also found that "the intensity of the magnetic field necessary to convert passive into active iron at a given temperature increases rapidly with the concentration of the acid."

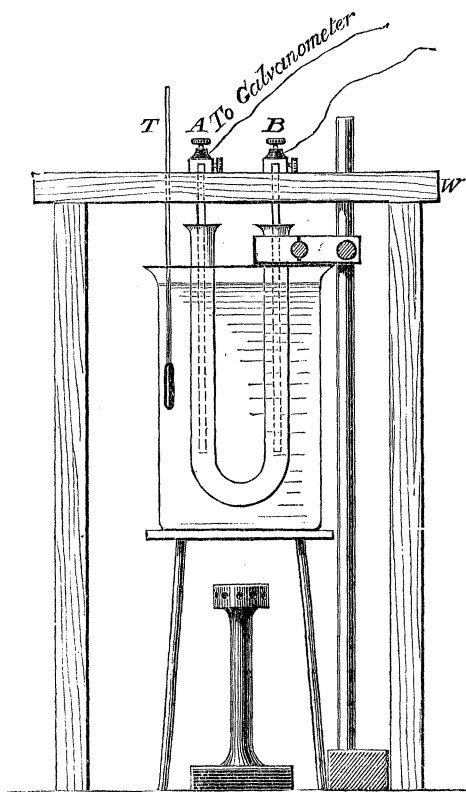
Unknown to each other, we have been simultaneously and independently prosecuting researches having a like object, and it is satisfactory to have arrived at somewhat similar conclusions, though by different methods of experimentation.

SERIES II.

Influence of Magnetisation on the Passive State of Steel in Nitric Acid, 1.42 sp. gr., above the temperature of 45° F.

The experiments for this set of observations were conducted in a somewhat similar manner to those of Series I. The U-tube contain-

FIG. 2.



ing the nitric acid of 1.42 sp. gr., with the magnetised bar A, $8\frac{1}{4}$ inches long, 0.261 inch diameter (permanently magnetised by touch), and unmagnetised bar B, $8\frac{1}{4}$ inches long, 0.261 inch diameter,

were immersed and rigidly supported in a large beaker of water on a sand-bath, and the whole gradually heated to any required temperature, a thermometer, T, being suspended in the beaker. The magnetised and unmagnetised bars were in circuit with a delicate galvanometer throughout each experiment.

The arrangement is shown on fig. 2, and the results are given on Table II.

The nitric acid remained perfectly colourless until a temperature of about 100° to 120° F. was reached, when a very pale-yellow tint began to be perceptible in both tubes, which gradually deepened until the critical point of explosion was reached, at which the passivity of the steel ceased.

During the intervening period, the metal was acted upon but slightly in both tubes; a small evolution of gas showed itself in the form of tiny bubbles adhering to the surface of the steel rod at a temperature of about 170° F. No extensive solvent action, however, occurred until the acid arrived at a temperature of about 190° to 200° F. (the explosion occurred most frequently at an average temperature of 195° F.), when, without any previous warning, a violent explosive evolution of red nitric oxide gas took place, the steel being instantly and vigorously attacked by the nitric acid. After the first explosion the metal again became partially passive for a short time. The explosion and solution of the steel first commenced in the limb of the U-tube containing the magnetised steel bar, and the first intimation of the passivity of the steel having been overcome was a sudden and extensive fling of the galvanometer, positive for the magnet bar. The bars were almost instantly removed from the nitric acid; the solution in the limb of the U-tube which had contained the magnetised bar was of a very dark-brown colour compared with solution in the other limb, thus giving further proof that the magnetised bar had been first attacked.

At the moment of explosion, the E.M.F. was very considerable; in several instances it varied from about $\frac{1}{10}$ th to as high as $\frac{1}{3}$ rd of a volt, the magnetised bar being the electro-positive metal, see Table II.

In the experiment, Table II, col. 9, the temperature was not raised above 185° F., and no explosive evolution of nitric oxide gas, therefore, occurred; the metals were maintained in the nitric acid at a temperature gradually reducing from 185° to 165° F. in course of one hour. The steel did not fully lose its passivity, but was, however, only very slowly and partially acted upon by the nitric acid, even at this high temperature.

Table II.

Temperature in degrees, Fahren- heit, from com- mence- ment.	Current between bright magnetised and unmagnetised passive steel bars immersed in circuit in warm nitric acid, 1.42 sp. gr. The electro-chemical position of the magnetised bar, positive, except where otherwise specified. E.M.F. in volt.					
	Column No. 1.	Column No. 2.	Column No. 3.	Column No. 4.	Column No. 5.	Column No. 6.
55	0.005				0.004	
60	0.005	0.005	0.003	0.000	0.004	0.004
65	0.005	0.005	0.003	0.0005 N	0.005	0.004
70	0.006	0.005	0.003	0.001 N	0.006	0.004
75	0.006	0.005	0.003	0.001 N	0.008	0.003
80	0.006	0.005	0.002	0.001 N	0.009	0.003
85	0.007	0.005	0.002	0.001 N	0.011	0.002
90	0.009	0.005	0.002	0.001 N	0.011	0.001
95	0.009	0.006	0.002	0.001 N	0.012	0.0005
100	0.009	0.006	0.002	0.0005 N	0.013	0.000
105	0.009	0.006	0.002	0.000	0.012	0.0005 N
110	0.010	0.006	0.002	0.000	0.011	0.001 N
115	0.010	0.006	0.002	0.004	0.011	0.001 N
120	0.010	0.006	0.003	0.009	0.010	0.002 N
125	0.010	0.006	0.010	0.012	0.009	0.001 N
130	0.010	0.006	0.014	0.014	0.009	0.001 N
135	0.011	0.005	0.018	0.014	0.007	0.0005 N
140	0.014	0.004	0.023	0.014	0.006	0.000
145	0.013	0.003	0.023	0.014	0.006	
150	0.010	0.002	0.023	0.014	0.006	0.003
155	0.009	0.001	0.022	0.015	0.006	0.004
160	0.005	0.000	0.020	0.017	0.006	0.009
165	0.007	0.003	0.019	0.018	0.005	0.011
170	0.009	0.006	0.018	0.019	0.004	0.013
173	0.009	0.011	0.017	0.021	0.005	0.013
175	0.009	0.010	0.016	0.024	0.005	0.014
180	0.009	0.010	0.016	0.026	0.006	0.013
185	0.006	0.011	0.014	0.027	0.004	0.010
190	0.006	0.012	0.014	0.027	0.001	0.006
191	0.006*				0.000	
192	0.328	0.189*				
193			0.110*			
195					0.038*	
198						0.072*
200				0.038		
202				0.038		
205				*		
Temperature point of transition from passive to active state.						
	191° F.	192° F.	193° F.	205° F.	195° F.	198° F.

Table II—*continued.*

Temperature in degrees, Fahrenheit, from commencement.	Current between bright magnetised and unmagnetised passive steel bars immersed in circuit in warm nitric acid, 1.42 sp. gr. The electro-chemical position of the magnetised bar, positive, except where otherwise specified. E.M.F. in volt.				
	Column No. 7.	Column No. 8.	Column No. 9.	Column No. 10.	Column No. 11.
45	0.000				
50	0.0005	0.007	0.002	0.002 N	
55	0.001	0.007	0.002	0.003 N	
60	0.001	0.008	0.002	0.003 N	0.004
65	0.001	0.009	0.003	0.002 N	0.003
70	0.001	0.008	0.003	0.002 N	0.003
75	0.002	0.008	0.004	0.000	0.003
80	0.002	0.007	0.005	0.002	0.003
85	0.002	0.006	0.006	0.004	0.002
90	0.002	0.006	0.006	0.006	0.002
95	0.003	0.005	0.005	0.009	0.002
100	0.005	0.004	0.004	0.010	0.002
105	0.005	0.003	0.002	0.011	0.001
110	0.007	0.002	0.001	0.013	0.001
115	0.008	0.003	0.000	0.014	0.001
120	0.009	0.003	0.000	0.014	0.002
125	0.010	0.004	0.000	0.014	0.003
130	0.011	0.004	0.001 N	0.014	0.004
135	0.012	0.006	0.002 N	0.014	0.006
140	0.012	0.009	0.003 N	0.014	0.007
145	0.012	0.011	0.003 N	0.015	0.009
150	0.013	0.011	0.003 N	0.015	0.011
155		0.011	0.002 N	0.016	0.014
160	The temperature of the solution was, in these experiments, maintained at about 150° F. for one hour without explosion occurring, the E.M.F. gradually rising to 0.22 of a volt.		0.000	0.020	0.018
165			0.002	0.027	0.017
170			0.003	0.030	0.011
175			0.004	0.034	
180			0.007	0.038	
185			0.009	0.041	
190				0.072*	
Temperature point of transition from passive to active state.					
				190° F.	

In addition to the observations recorded in Table II, numerous other confirmatory experiments were made which it is not needful to give in detail.

* At these temperatures the first violent explosive ebullition of red nitric oxide gas occurred consequent on the loss of passivity of the metal. The average critical temperature point of transition from the passive to the active state was about 195° F.

The observations show that the magnetised steel bars were less passive in warm nitric acid than the unmagnetised steel bars.

FIG. 1.

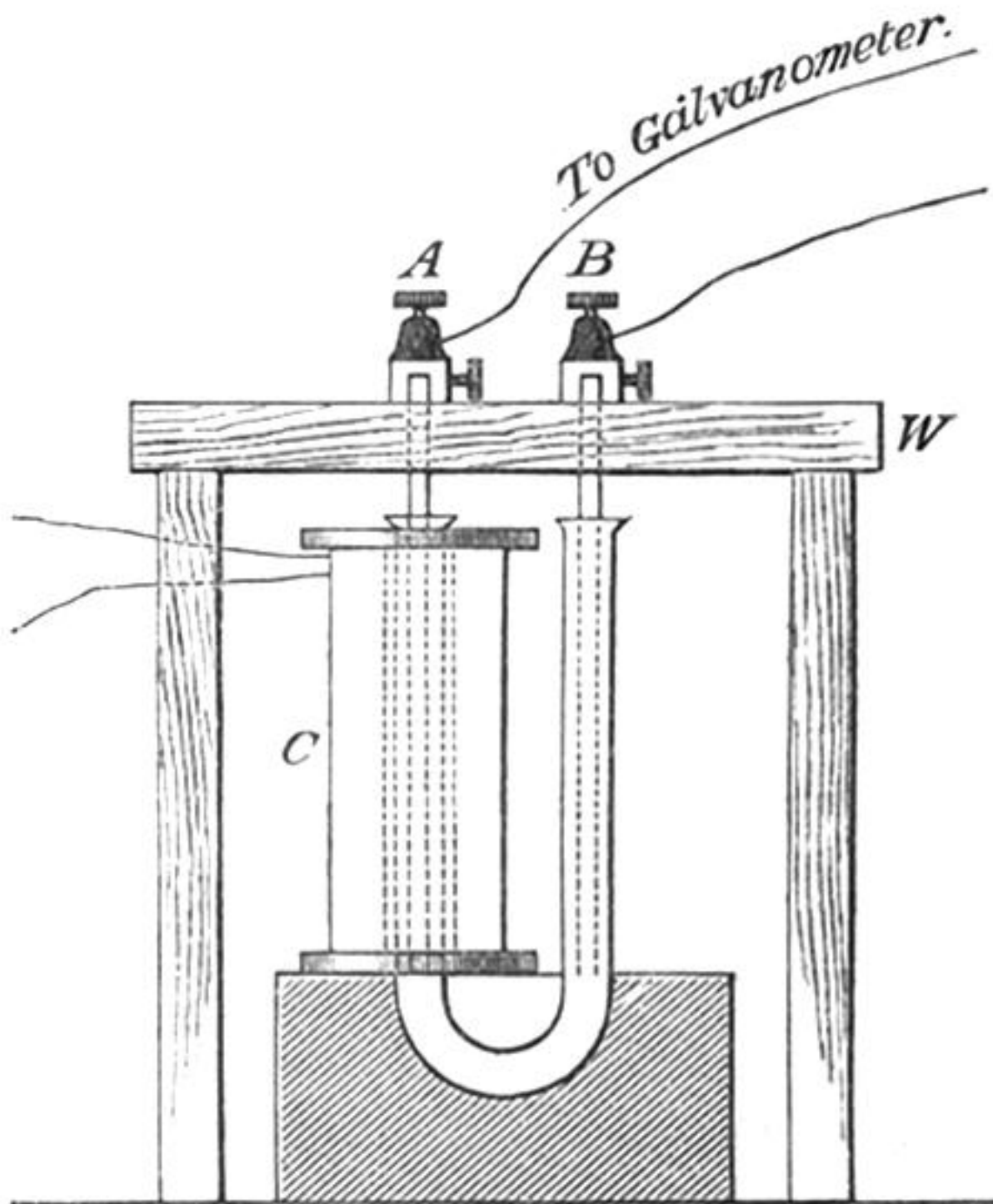


FIG. 2.

