

January 22, 1891.

THE ASTRONOMER ROYAL, V.P.R.S., in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "On the Unsymmetrical Distribution of Terrestrial Magnetism." By HENRY WILDE, F.R.S. Received November 20, 1890.

[Publication deferred.]

- II. "The Passive State of Iron and Steel. Part II." By THOS. ANDREWS, F.R.S.S.L. and E., M.Inst.C.E. Received October 24, 1890.

In Part I of this research ('Roy. Soc. Proc.,' vol. 48, p. 116), the author showed the influence of magnetisation on the passive state of iron and steel, and he has now the pleasure of communicating to the Royal Society the results of a further study of certain temperature and other conditions affecting the passivity of these metals in concentrated nitric acid. The experiments of Series III, in this paper, relate to the effect of temperature, and the observations of Series IV refer to the influence exerted by nitric acids, of varied concentration, on the passive condition of iron and steel.

SERIES III.

Effect of Temperature on the Passivity of Iron and Steel.

The bars selected for these observations were unmagnetised polished rods, which had been previously drawn cold through a wire-die; a pair of bars of each metal were cut adjacently from one longer bar, and then placed securely in the wooden stand, W; each bar was $8\frac{1}{4}$ inches long, 0.261 diameter. The U-tube containing $1\frac{1}{4}$ fluid oz. of nitric acid, sp. gr. 1.42, was rigidly placed in an arrangement as shown on fig. 3. One limb, A, was surrounded by a tank containing water, the other limb, B, by a tank of the same capacity, containing powdered ice; the arrangement was such that the water-tank could be heated by a

Bunsen burner, and its temperature slowly raised, whilst the ice-tank was kept full of powdered ice. A non-conductor of wood was put between the ends of the two tanks so as to prevent the melting of the ice; the bottom or bent portion of the U-tube was also enclosed in a thick non-conductor of wood. A thermometer, T, was placed in the water-tank. The bars were in circuit with the galvanometer, and soon after immersing them in the nitric acid heat was applied to the water-tank, and the temperature of the nitric acid in that limb of the U-tube slowly raised to the temperatures required, whilst the acid in the other limb of the U-tube was meanwhile maintained at a temperature of 32° F.

The arrangement will be understood on reference to fig. 3, and the electro-chemical results obtained are graphically recorded on Diagram I.

FIG. 3.

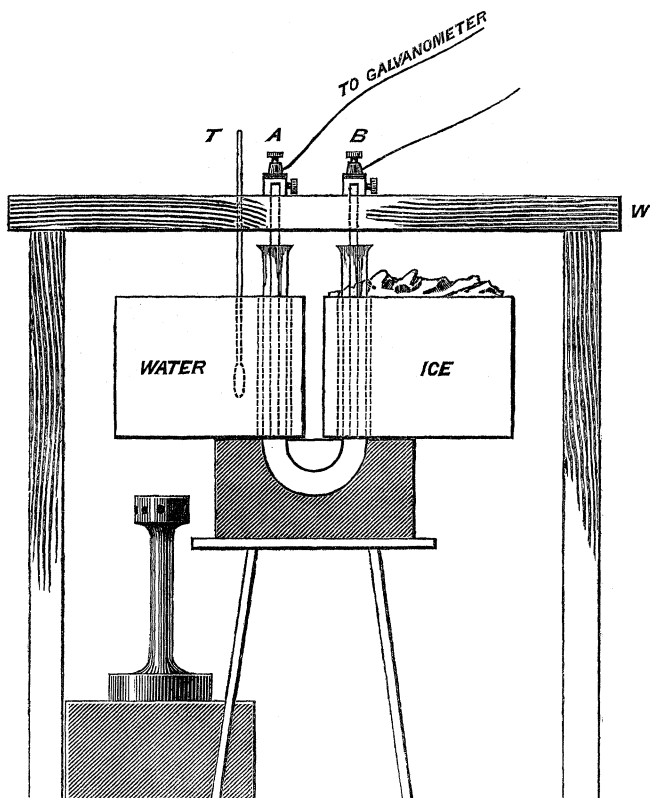
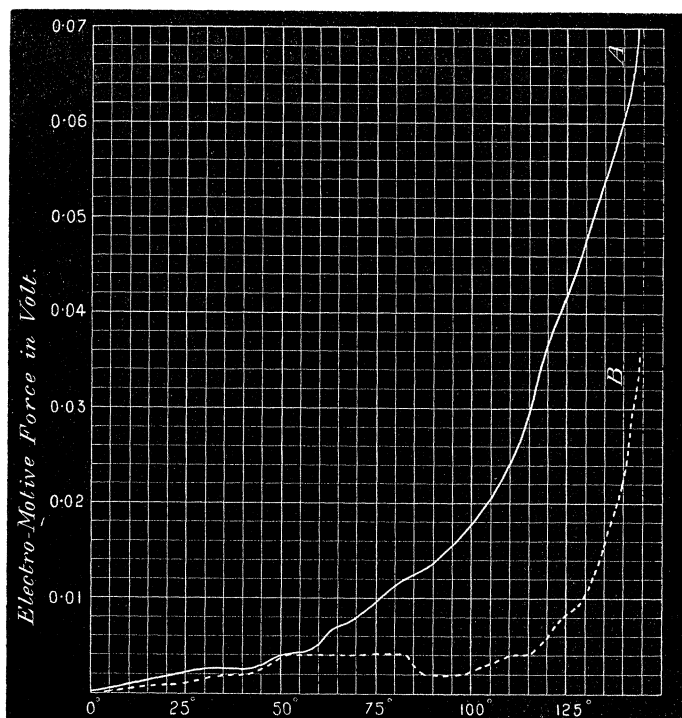


DIAGRAM I.

Current between two bright "passive" bars of the same composition, one in warm, the other in cold, nitric acid sp. gr. 1.42.

The electro-chemical position of the bar in the warm nitric acid was positive.



Difference of temperature between the nitric acid in Tubes A and B, see Fig. 3, in degrees Fahrenheit.

Curve A gives the E.M.F. between two wrought iron bars, and Curve B gives the E.M.F. between two cast steel bars under the conditions recorded.

The above experiments indicate that the wrought iron was less passive in the warm nitric acid than the soft cast steel; the average E.M.F. of 94 observations with wrought iron was 0.030 volt; whereas, in the case of the 94 observations on cast steel, the average E.M.F. was only 0.010 volt.

It will be seen from the above diagram that the behaviour of the steel, under the conditions stated, was more irregular than that of the wrought iron.

In the whole of the above series of experiments on Diagram I the nitric acid was raised to a temperature of 175° F.; the cold nitric acid in the limb of the U-tube A remained perfectly colourless, and the steel or iron therein absolutely passive; but the steel or iron in the warm nitric acid in tube A commenced to be gradually acted upon as the temperature increased, a pale yellow tint beginning to appear in

the solution in the tube A shortly after commencement. When the temperature of about 170° to 175° F. was reached a faint evolution of gas in the form of bubbles was manifest, adhering to the steel, in the warm tube only. No powerful solvent action or violent evolution of nitric oxide gas, however, occurred in any of these experiments even up to the temperature of 175° F., and these experiments were not continued beyond this temperature. These results show that iron or steel does not fully lose its passivity up to a temperature even of 175° F., though the passivity is shown to have been considerably modified by temperature only. The critical point of temperature of transition from the passive to the active state is therefore higher than 175° F., and is shown in the experiments of Part I, Series II, Table II, to have been about 195° F.

SERIES IV.

The Passivity of Iron and various Steels increases with the Concentration of the Nitric Acid.

Schönbein considered that, "by immersing an iron wire in nitric acid 1.50 sp. gr., it became likewise indifferent to the same acid of 1.35 sp. gr.," and to all outward appearance this is so.

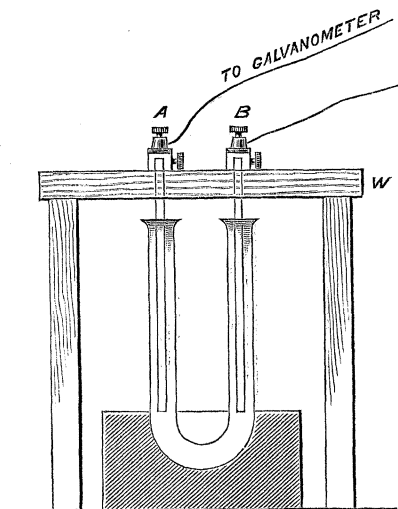
Scheurer-Kestner considered that the passivity of iron was not dependent on the greater or less degree of saturation of the acid. The author, however, ascertained by the delicate electro-chemical mode of experimentation employed, and hereafter referred to, that the passivity is materially influenced according to the concentration of the nitric acid.

The following experiments indicate that the property of passivity in iron is not absolutely fixed or static, but that its passivity is modified to a certain extent in relation to the strength of the nitric acid used. The general *modus operandi* was generally similar to that previously employed. Pairs of unmagnetised polished steel bars 6 inches long, and 0.310 inch diameter, each pair being of the same kind of steel, and cut adjacently from one longer bar, were placed as before in the wooden frame W, fig. 4, and then instantly and simultaneously immersed in nitric acids, of two different degrees of concentration, contained in the U-tube arrangement, one limb of the U-tube containing red fuming nitric acid of sp. gr. 1.50, the other containing nitric acid of sp. gr. 1.42, circuit being made through the galvanometer in the usual manner. The results, the average of repeated experiments in each case, are given on Table III, and show that the passivity of iron increases considerably with the strength of the nitric acid.

Table III.

Time from commencement of experiment.	Current between two bright "passive" wrought iron or various steel bars of the same composition, one in cold nitric acid sp. gr. 1.50, the other in cold nitric acid sp. gr. 1.42. The electro-chemical position of bar in weaker acid positive, except otherwise stated.				
	E.M.F. in volt.				
	Wrought iron.	Soft cast steel, combined carbon 0.57 per cent.	Hard cast steel, combined carbon 1.60 per cent.	Soft Bessemer steel, combined carbon 0.55 per cent.	Tungsten steel, combined carbon 1.75 per cent.
seconds.					
0	0.086	0.041	0.055	0.055	0.038
30	0.077	0.040	0.055	0.052	0.038
minutes.					
1	0.076	0.036	0.054	0.053	0.041
2	0.074	0.036	0.053	0.056	0.043
3	0.073	0.038	0.053	0.058	0.048
4	0.072	0.040	0.052	0.060	0.048
5	0.072	0.041	0.052	0.061	0.049
7½	0.071	0.041	0.050	0.067	0.050
10	0.069	0.041	0.049	0.071	0.050
15	0.066	0.040	0.048	0.074	0.050
20	0.064	0.037	0.046	0.077	0.049
25	0.062	0.035	0.043	0.074	0.049
30	0.060	0.034	0.042	0.072	0.048
35	0.059	0.033	0.040	0.071	0.048
40	0.058	0.031	0.038	0.071	0.047
45	0.056	0.030	0.038	0.070	0.047
50	0.055	0.029	0.036	0.068	0.046
55	0.054	0.029	0.036	0.067	0.046
hours.					
1	0.053	0.028	0.035	0.066	0.045
1½	0.051	0.025	0.034	0.061	0.044
2	0.049	0.022	0.033	0.058	0.043
2½	0.048	0.020	0.033	0.055	0.041
3	0.047	0.019	0.033	0.052	0.041
4	0.046	0.018	0.034	0.050	0.043
5	0.043	0.017	0.034	0.049	0.040
6	0.041	0.016	0.034	0.048	0.038
7	0.041	0.013	0.034	0.047	0.037
8	0.041	0.013	0.034	0.047	0.037
16	0.040	0.009	0.030	0.047	0.037
18	0.040	0.006	0.029	0.046	0.037
20	0.040	0.008	0.029	0.046	0.038
21	0.040		0.029	0.031	0.040
22	0.040		0.024		0.031
24	0.038		0.019		0.013
26	0.038		0.016		0.013
28	0.039		0.013		0.013
29	0.038		0.012		0.013
30	0.040		0.011		0.013
40	0.042		0.006		0.024
45					0.034

FIG. 4.



The steel rods selected for this set of experiments were of the kinds given on Table IV; they were drawn cold through a wortle, and were of the general physical properties and chemical composition given on Tables IV and V.

The reduction of E.M.F. towards the close was probably owing to partial diffusion between the two acids of different concentration.

The above results show that wrought iron was less passive in the weaker acid than most of the steels, the soft Bessemer steel being found similar in passivity to the wrought iron.

The average E.M.F. was as follows:—With wrought iron, 0·054 volt; soft cast steel, 0·028 volt; hard cast steel, 0·036 volt; soft Bessemer steel, 0·059 volt; tungsten steel, 0·039 volt.

FIG. 3.

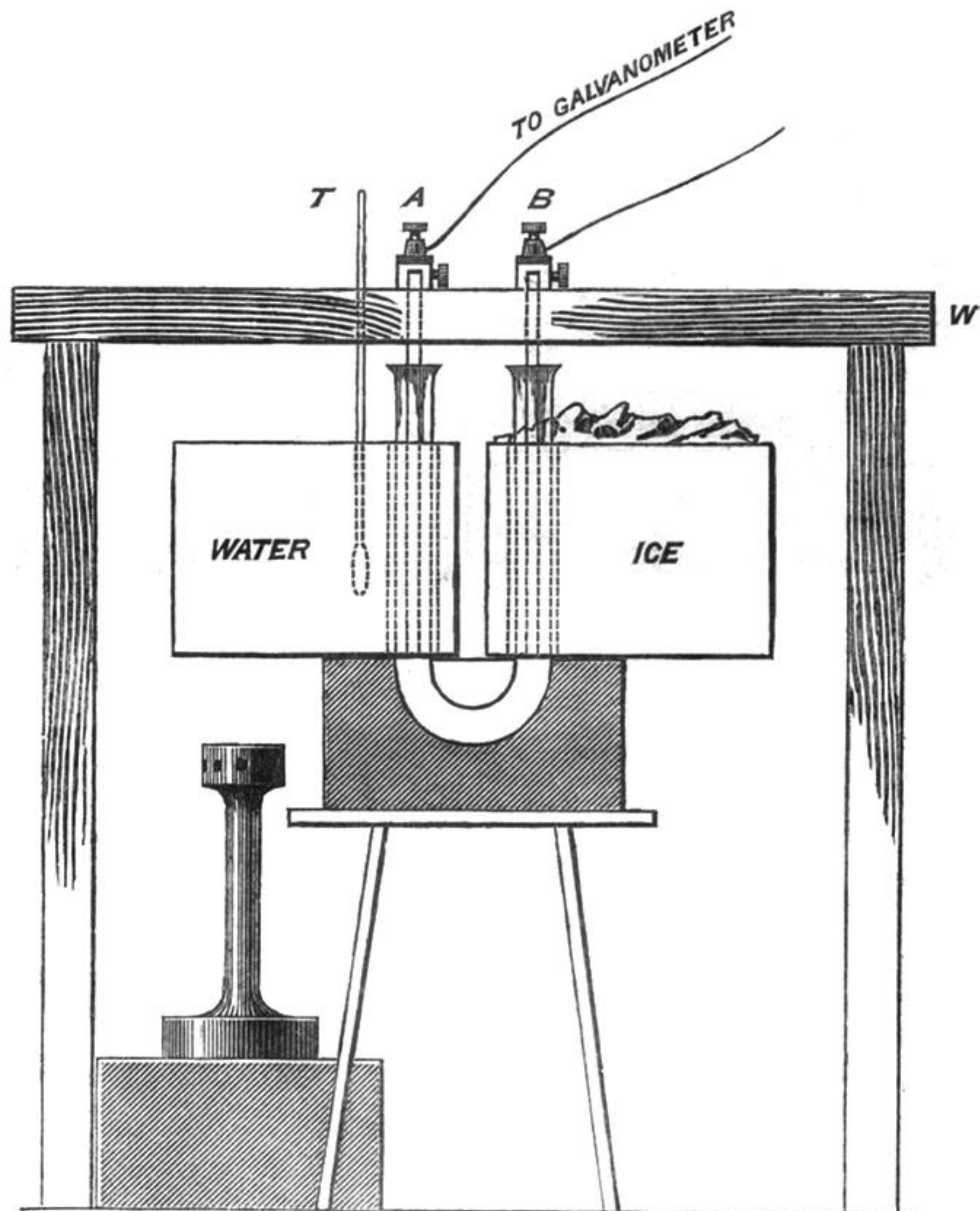
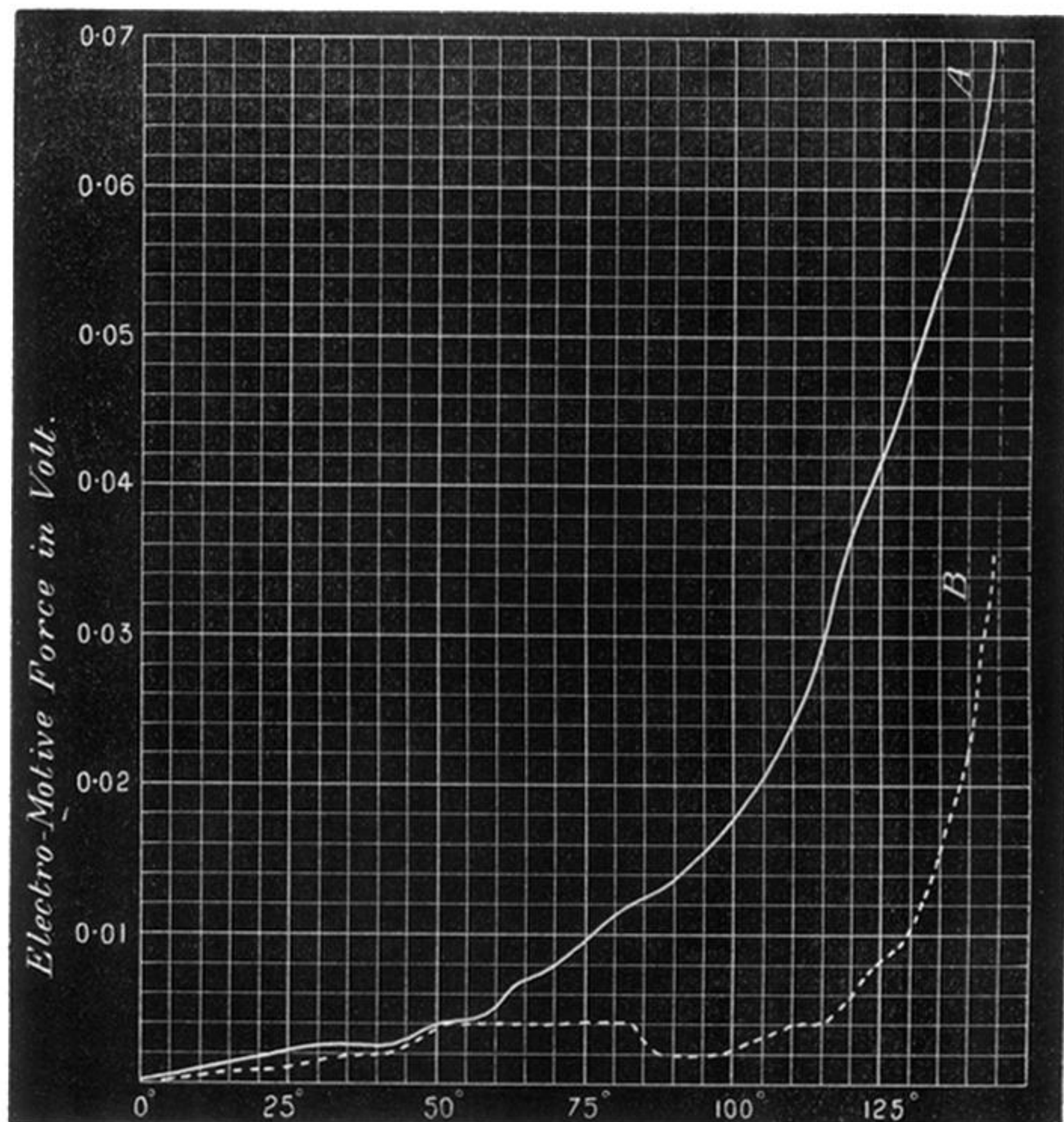


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FIG. 4.

