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June 14, 1948

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Chemistry Division

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Pentavalent Manganese

H. H. Miller and L. B. Rogers

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June 14, 1948

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Pentavalent Manganese

By

H. H. Miller and L. B. Rogers

Oak Ridge National Laboratory

In fused alkaline melts, the lower oxides of manganese react with oxygen until an oxygen-to-manganese ratio of about 2.5 is established (4). For aqueous media reliable evidence pointing to the existence of pentavalent manganese has not been reported. The present paper will show that such a valence state can be detected polarographically in strongly alkaline solutions.

A solution containing 1.00×10^{-3} M potassium permanganate and 0.10 M sodium hydroxide was deaerated with nitrogen and then polarographed using a stationary platinum electrode (5) and an outside saturated calomel electrode (S.C.E.). The resulting curve is shown in Figure 1.

The first step of the reduction ($E_{1/2} = +0.33$) has a diffusion current corresponding to a one-electron change and a formal oxidation potential of -0.58 V. versus the normal hydrogen electrode. Since the permanganate reaction has a normal potential of -0.54 V. (2), the first wave can definitely be assigned to this reaction. The second ($E_{1/2} = +0.13$ V.) and third steps ($E_{1/2} = +0.01$ V.) also have diffusion currents corresponding to one-electron changes. Hence the reactions taking place must be $Mn^{VI \rightarrow V}$ and $Mn^{V \rightarrow IV}$. The fourth (and last) step beginning close to -0.2 V. must be due to the reduction of Mn^{IV}. Its irregularity can easily be explained by the fact that the electrode is covered with a visible layer of precipitated manganese dioxide.

There is indirect evidence that the lifetime of pentavalent manganese in 0.1 M hydroxide is not more than a few minutes. The polarographic half-wave potentials and diffusion currents appeared to be independent of the rate

at which the motor-driven slidewire changed the voltage. On the other hand, a current-voltage curve obtained by a manual method (1) resulted in a single broad wave. It was not surprising, therefore, when an attempt to produce pentavalent manganese by electrolysis of manganate at a suitable potential (3) produced a large amount of manganese dioxide. The solution had a bluish color (similar to chromous sulfate) which might be attributed either to pentavalent manganese or to a mixture of manganate and colloidal dioxide. The question will be studied using a spectrophotometer.

Preliminary studies have also been made in other concentrations of sodium hydroxide. In a 1.0 M solution, the polarogram is very similar to the one described for a 0.10 M solution; but in a 0.010 M solution, the manganate is reduced directly to manganese dioxide in a single two-electron step. A more complete study of changes in halfwave potentials with the concentration of hydroxide will be necessary before the Mn^{V} ion and its reactions can be described accurately. The results of such a study will be helpful in predicting the behavior of technetium ions.

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This work was performed under contract No. W-35-058 eng. 71 between the Atomic Energy Commission and the Monsanto Chemical Company.

Figure I.

Polarograms Obtained with a Stationary Platinum Microelectrode for Millimolar Potassium Permanganate in 0.10 M Sodium Hydroxide Solution.

Drawing #5347

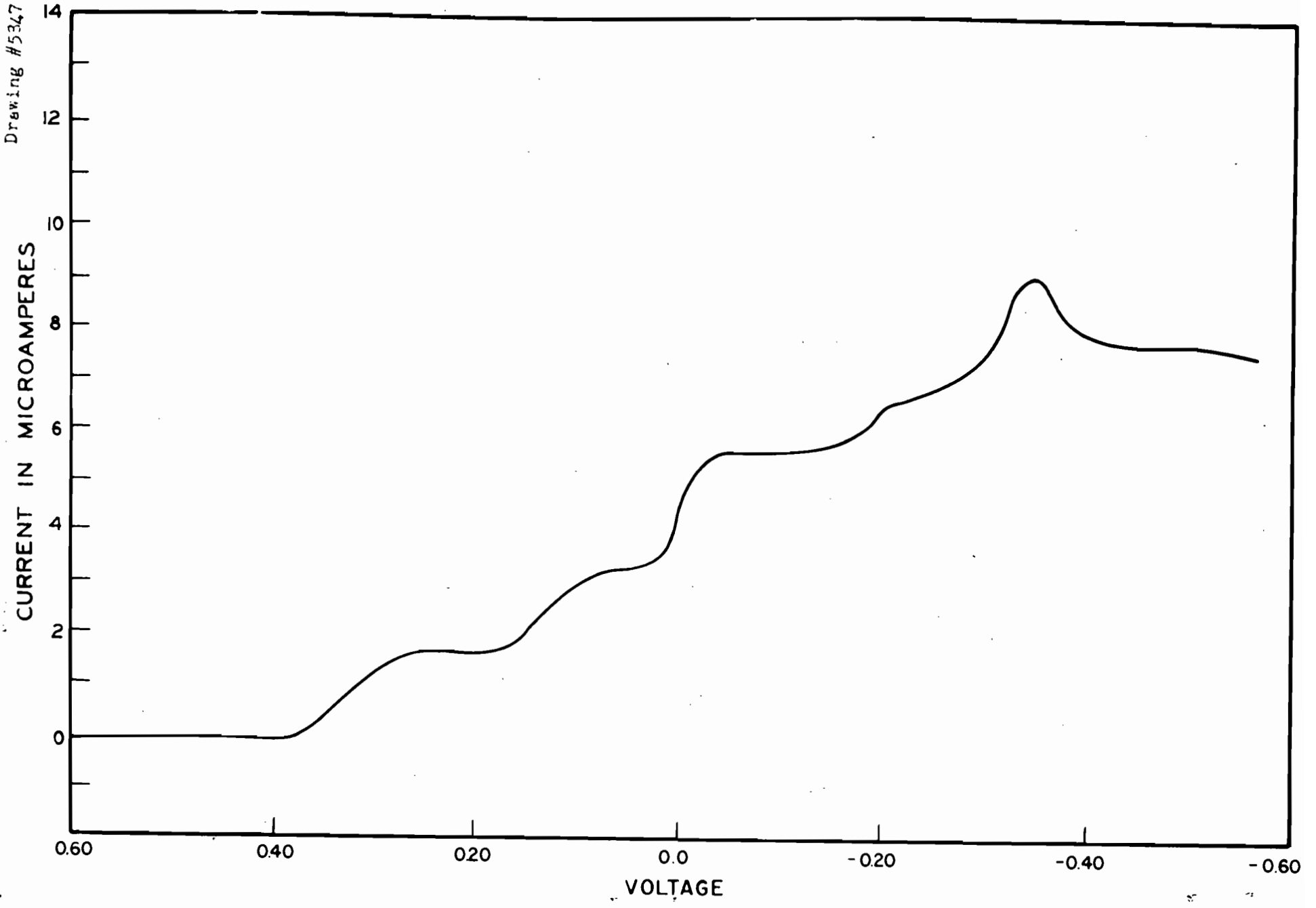


Figure 2.

Polarograms Obtained with a Stationary Platinum Microelectrode for Millimolar Potassium Permanganate in 1.0 M Sodium Hydroxide.

Drawing # 5545

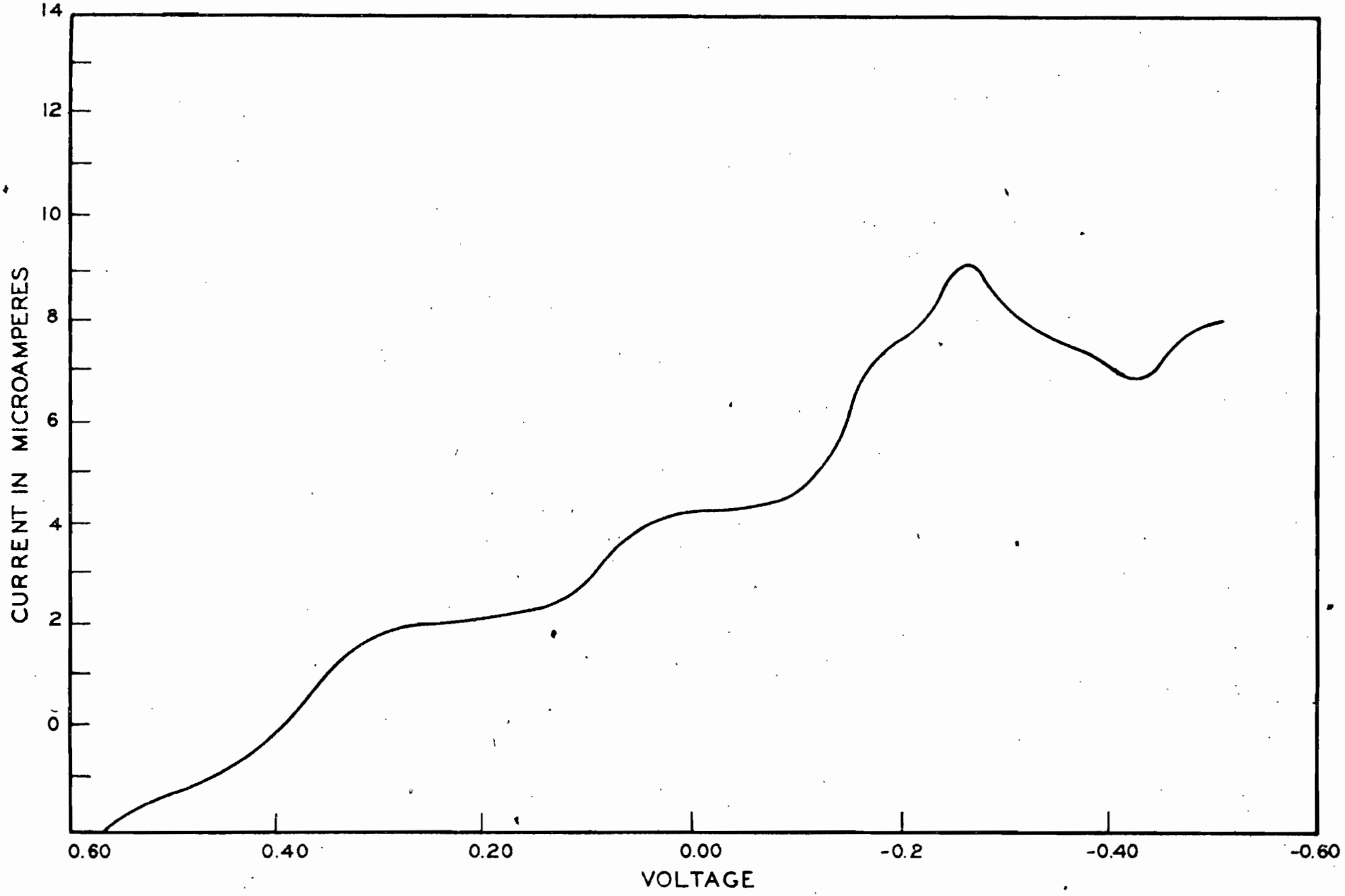
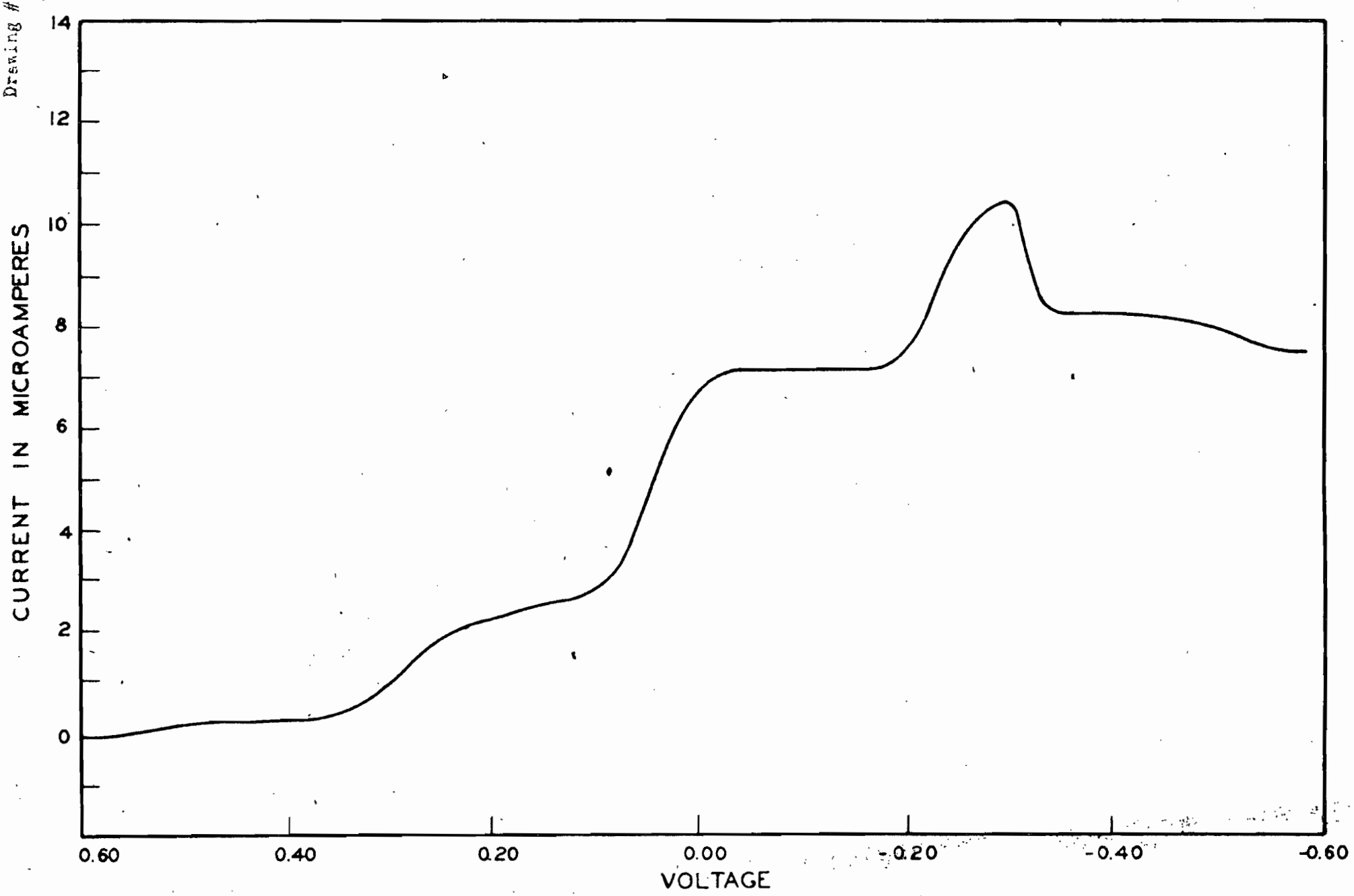


Figure 3.

Polarograms Obtained with a Stationary Platinum Microelectrode for Millimolar Potassium Permanganate in 0.010 M Sodium Hydroxide.

Drawing # 5-49


CURRENT IN MICROAMPERES
14
12
10
8
6
4
2
0
0.60
0.40
0.20
0.00
-0.20
-0.40
-0.60
VOLTAGE