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PASSIVITY OF IRON AND NICKEL

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"Protection Against Corrosion"
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Passivity of Iron and Nickel

Technical Report No. 8

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I. INTRODUCTION

Even though much work has been devoted to the phenomenon of passivity of a metal (1,2), our knowledge of the subject is still very incomplete. This situation should be remedied as soon as possible, because (a) it is essential to have a reliable theory of how to protect against corrosion and (b) it is in many cases desirable to know precisely how best to remove a passive layer, so that subsequent electrodeposition can be carried out under the most favorable conditions (see article by Graham (3)).

Graham states "if we could quantitatively define the degree of passivity on metals by tests, we could prescribe more specifically the precise cycles required to control the degree of passivity in preparing a metal master which is to be separated from an electroform subsequently. Information should be obtained on nickel and nickel-iron alloys, and perhaps also on high nickel alloys such as Hastalloy, Monel, and Inconel."

The most sensitive, rapid, and powerful method for studying the passive layer is, in our opinion, the determination of its electrical behavior under various experimental conditions. We have applied this method to passive iron (4,5,6), have found how the layer thickens and thins, and have learned exactly what is necessary for removal of the layer from the surface. Iron may be made passive very quickly by making it an anode in an acid solution and passing a high current through the cell. The adherent, invisible layer which is thus formed seems to be an oxide of thickness less than 10^{-6} cm. In

sulphuric acid, it may be removed rapidly by cathodic reduction or by shorting across the cell.

The results have been analyzed in terms of an electrical model of the layer on the surface, and the bulk of this work has been written up in Technical Report No. 7, which summarizes our knowledge up to September, 1961. Since then, however, further refinements in technique have enabled us to study the subpassive region (7), i.e., the region just below that where the steady-state current is constant. Also, further work on anodic reduction and on concentration effects has been carried out. The claim of Sukhotin (8) that a second plateau exists for an open-circuit break at low concentrations has not been substantiated, despite a careful search (see Fig. 4). We surmise that his second plateau occurred because his acetate buffer acted as a complexing agent.

The electrical behavior of passive nickel is essentially unknown at the present time, and the literature is meager (9-16).

A preliminary investigation of passive nickel has been made, and it turns out that this system is quite amenable to experimental study. It is more complicated, apparently, than iron, for there are important changes with time and the transition from the passive state to the active state is in some cases not very noticeable. Still, it is possible to cycle the system, to passivate readily, and to reclean. We intend to make a more thorough study of passive nickel, and present the following results just as a sample of what may occur, and with the remark that much more needs to be done before one can attempt an interpretation with any degree of assurance.

II. CURRENT IN THE SUBPASSIVE REGION (IRON)

In the region between -0.2 v and $+0.1$ v the current drops from 45 ma to around $3 \mu\text{a}$. This region will be called the subpassive region. Actually -0.175 v is the minimum voltage which can be maintained without activating the anode because of decreasing stability. Fig. 1 shows the dependence of the logarithm of steady-state current on steady-state voltage in this region. These data were taken at 23°C in $2\text{N H}_2\text{SO}_4$.

III. OPEN CIRCUIT PLATEAU POTENTIAL

If the steady-state current is interrupted while the anode is passive, a potential transient (see Fig. 8, Technical Report No. 7) is observed. This transient exhibits a rapid "exponential" drop to a plateau which decays gradually until activation occurs. The method used to study the nature of the plateau as a function of passivating potential involves the extrapolation of the plateau slope back to zero time and forward in time to the point of activation. This essentially separates the entire decay transient into three components which overlap to some degree: the rapid "exponential" decay, the plateau, and the abrupt activation.

Figure 2 shows the dependence of the extrapolated potentials at zero time, and at activation, on the passivating potential. In the true passive region ($V > 0.1$ v), the plateau as defined by the extrapolated potentials is independent of passive voltage. However, the duration of the decay plateau increases with time of passivation and also with passive potential.

Below the true passive region ($V_{ss} < 0.1$ v), the decay plateau defined by the extrapolated potentials shifts to lower transient

voltages as the passive potential is decreased. In this region the decay plateau is of decreased duration although the voltage drop along the plateau is nearly constant.

IV. ANODIC REDUCTION

Anodic reduction studies have been performed in the subpassive region ($v_{ss} < 0.1$ v) to determine the amount of charge necessary to activate the anode.

A potential transient similar to the open circuit transient is observed when an anodic current i_c , less than the steady-state current i_{ss} , is impressed on the anode. The charge necessary to activate the anode is defined as

$$Q = (i_{ss} - i_c) t$$

where i_{ss} represents the dissolution current and time t is the length of the decay transient to activation.

The results are shown in Fig. 3 as a function of passive potential. Q depends exponentially on the initial potential in the subpassive and passive regions below 0.3 v. Bartlett and Ord (6) found a linear dependence at higher passive potentials.

V. SUBPASSIVE v_o

Bartlett and Ord (6) found that the initial part of the open-circuit potential transient was such that

$$v' = v_o \ln(t + \theta)$$

where v' is the potential measured relative to the open circuit plateau. The parameter v_o may be determined from the slope of the line v' vs. $\log(t + \theta)$. It is found to be constant at approximately 22 mv in the subpassive region, but rises linearly with higher steady-state potentials.

The plateau potential V_{plateau} at any time is defined as the extrapolated open circuit potential. Over most of the passive region the plateau potential is almost constant during the initial part of the transient. Since only the slope of the v' vs. $\log(t + \theta)$ curve is of interest, in all previous calculations no distinction was made between v and v' . When the steady-state potential is in the subpassive region, the slope of the plateau is appreciable and must be considered. It is then found that v_0 in the subpassive region is 22 mv instead of 38 mv as previously reported.

VI. DEPENDENCE OF CAPACITY ON ACID CONCENTRATION

The capacity was determined from the initial portion of voltage transients associated with open circuit potential decays and galvanostatic potential changes, for various acid concentrations.

Its reciprocal, in the passive region, is shown in Fig. 5. This suggests a linear change in layer thickness as a function of anode voltage, if we adopt a parallel plate capacitor model. The behavior of $1/C$ with voltage is somewhat similar to the behavior of the v_0 parameter.

Both $1/C$ and v_0 curves shift toward lower potentials as the acid concentration is decreased. The lines do not extrapolate to the same point on the potential axis, as might be expected if they were a measure of the same physical thickness.

The $1/C$ measurements in $2N \text{ H}_2\text{SO}_4$ are reproducible in the passive region but have scatter at lower voltages where the steady-state current begins to rise. In lower acid concentrations there is also appreciable scatter in the data taken so far.

VII. RESPONSES TO ACID CONCENTRATION CHANGE

In Fig. 11 of Technical Report No. 7, the v_o versus potential curves for 0.1N and 2N H_2SO_4 are parallel. The potential separation of these curves is approximately equal to the difference in open-circuit plateau potentials associated with the two solutions. These facts suggested the following experiment to throw light on the mechanisms which govern rates of layer formation and dissolution.

An iron anode passivated in 0.1N H_2SO_4 acquires a steady-state current and a value of v_o characteristic of the passive voltage, supposedly just of the height v' above the open-circuit plateau. Let the concentration be changed to 2N H_2SO_4 , holding anode-cathode voltage constant. The calomel-cathode potential will be displaced immediately by an amount corresponding to the pH change, and so should the anode-calomel potential. If the open-circuit plateau also has this same change, v' and hence v_o should be constant.

Actually, v_o changes according to preliminary results shown in Fig. 6 and Fig. 7.

The iron anode was initially passivated in 0.1N H_2SO_4 + 0.9N K_2SO_4 at 0.3 v, with $i_{ss} = 0.15 \mu a$ and $v_o = 157$ mv. Immediately following the change of solution to 2N H_2SO_4 , the potential rose to 0.365 v and remained constant. The current, shown in Fig. 6, increased gradually from 0.15 μa to a value characteristic of the higher acid concentration. Figure 7 indicates the rather rapid change in v_o with time after the acid has been changed. v_o does not remain constant but decays to a value of 127 mv. Since the observed current is less than the dissolution current, the layer is being reduced and getting thinner.

VIII. PASSIVATION OF NICKEL

A preliminary study of the passivity of nickel has been made in 2N H₂SO₄ using the same equipment and experimental technique as was used in the study of the electrical behavior of passive iron (6).

The nickel electrode was prepared from spectrographically standardized nickel rods obtained from Johnson, Matthey and Co., 75/83, Hatton Garden, London, England. The electrode has a diameter of 5 mm and a surface area of 0.196 cm² uncorrected for a roughness factor. The nickel rod is pure to within 17 parts per million as determined by spectrographic methods. The method of anode preparation is the same as that used by Bartlett and Ord (6) in the study of iron except that CENCO Sealstix, a De Khotinsky cement, was used as a coating compound because it gives a more adherent coating. The cell components and electrical accessories were the same as for the iron experiments, except for the adoption of a Keithley Model 200 B DC VTVM electrometer and a Keithley 414 micro-microammeter.

When the electrode is placed in solution the open-circuit potential exhibits a value of -0.74 volts. (All potentials are measured with respect to the sulfate electrode unless otherwise specified.) When the circuit is closed and the potential is raised to a new value of -0.4 volts, an initial current of the order of 0.5 ma flows. This current remains constant for one or two minutes and then starts slowly to increase. This increase accelerates with time until a maximum current of 66 ma is reached in about 10 minutes. After the current has risen above 1 ma, etching becomes visible as pitting. The pits grow in diameter and have a direct effect on the current. This indicates that some kind of resistive layer is being

removed as the current increases. All currents are given as measured with no correction for roughness. The roughness factor is estimated to be approximately 2.5, giving an actual area of 0.5 cm^2 .

After a current of 66 ma is reached, the anode is left to etch until all evidence of the cold worked surface is removed. Upon re-opening the circuit, the potential drops to -0.83 for the very clean surface. This potential is well defined and is stable as long as the electrode remains in solution under open circuit conditions. When the potential is raised above -0.39 volts the anode becomes passive, with a minimum current of 1.63 microamps at +0.1 volts. The passive current varies by less than a factor of two between -0.2 volts and +0.4 volts. The current-potential curve (taken starting with a clean, well etched anode) is plotted in Fig. 8. A correction was made for the potential drop across the 3.5 ohm solution resistance at all currents above 1 ma. The electrode potential, ϵ , is equal to $V_{a\text{-cal.}} - ir$, where $V_{a\text{-cal.}}$ is the measured anode-calomel potential, i is the steady-state current and r is the solution resistance. At potentials above +0.4 volts the steady-state current becomes dependent on potential and attains a value of 180 μa at +0.7 volts. Above +0.4 volts the current rises exponentially with potential to a value of 5 ma at 1.0 volts. At currents above 1 ma in the passive region H_2 evolution at the cathode and O_2 evolution at the anode become visible as tiny bubbles going off into solution.

IX. TRANSIENT MEASUREMENTS

Current interruptions were made (1) for different passivating potentials after the electrode had been passive for 30 minutes, and

(2) for different times passive at a constant negative potential +0.5 volts. The open-circuit potential decays are shown in Figures 9 and 10, respectively. From Fig. 9 we see that the shape of the potential decay has a significant dependence on passivating potential after the initial capacitive transient is completed. From Fig. 8, the electrode is in the active state for all potentials below -0.39 volts. However, on the open circuit transient (Fig. 9), we find no significant activation point for passivating potentials of 0.0 and -0.2 volts. At a passivating potential of +0.2 volts a point of inflection is noticeable at -0.36 volts and becomes more pronounced for higher passivating potentials. An experiment was performed to see if the knee indicated that an activation reaction takes place. The experiment consisted of reapplying the steady-state current at various times along the open circuit break. If i_{ss} is reapplied at any time before the activation knee, it is found that the potential undergoes a capacitive-type rise and eventually returns to the original steady-state value. On reapplying i_{ss} at any point below the knee there is an insignificant potential change by comparison and the potential is only arrested for a few seconds before it continues in the negative direction with the same slope as in the open circuit case. Within 2 to 5 minutes (depending on the time of passivation) the open circuit potential becomes constant at -0.74 volts. This indicates that we have returned to the original open circuit condition after activation rather than to the clean surface active state. The clean surface active state can now be reached by cathodic reduction with 15 mcou. of charge, and hence only a portion of the passive layer is removed under open circuit conditions. The

clean surface state may also be attained at this time by applying -0.4 volts and allowing the anode to etch until the current attains a steady value of 66 ma. Much higher currents than 66 ma can be attained by applying a step potential to a clean surface anode since only the circuit resistance and solution resistance r are present to limit the current. If a potential step of 0.7 volts is applied, 140 ma current will flow for about 10 seconds, after which the anode will become passive. The total effective resistance of external circuit and solution is about $700/140 = 5$ ohms. However, when the surface has not been made clean, such as when we have passivated the electrode and then activated by opening the circuit, the imposition of a step voltage of 0.4 volts results in a current of the order of two or three ma, indicating that the layer resistance is of the order of 100 ohms.

Figure 10 shows open-circuit interruptions from +0.5 volts for various passivation times, and we see a wide variation in the time required to activate the electrode. In curve (A) the passivation time was 28 minutes and the time to activation was less than 7 seconds. Curve (B) was taken after a passivation time of 119 minutes. The time to the activation knee has become less pronounced. Curve (C) was taken after a passivating time of 234 minutes and the activation knee is missing entirely. The time constant for decay increases with time of passivation, but it is at present premature to attempt an explanation of this behavior.

Fig. 11 shows the initial portion of the same data that is contained in Fig. 9. In Fig. 11 the time axis is only 2 seconds total and the amplification of the Y axis is increased by a factor of 4. The curves are shifted to a common starting point for comparison but the

curves start from passivating potentials ranging from -0.2 volts for (a) to +0.6 volts for curve (e). No significant change in the potential decay is noted for breaks in the low current region indicating little or no change in the v_0 parameter used in the analysis of iron by Ord and Bartlett (6).

The open circuit transient at 0.6 volts exhibits a much more rapid initial decay than is found for the lower potentials. After the initial decay, however, this transient appears to parallel the others. Above 0.4 volts the current-voltage curve rises rapidly, possibly indicating that a new reaction is occurring. This may also account for the change in the open circuit transient at high potential.

An experiment was performed to determine dependence of activation time on cathodic reduction current. Fig. 12 shows a plot of activation charge Q vs. current, where $Q = (i - i_{ss})t$, i being the applied cathodic current, i_{ss} the original steady-state current, and t the time interval to the activation knee. The charge to activate is constant for currents greater than $40 \mu\text{a}$. This result is very similar to that found for iron (6).

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FIGURE CAPTIONS

- Fig. 1 Steady-state current versus potential. Subpassive region. (Iron anode, 2N H_2SO_4).
- Fig. 2 Decay plateau potential versus passivation potential. (Iron anode, 2N H_2SO_4).
- Fig. 3 Anodic reduction. Charge to activation versus passivating potential. (Iron anode, 2N H_2SO_4).
- Fig. 4 Open circuit potential transient prior to activation. (Iron anode, 0.01N H_2SO_4).
- Fig. 5 Reciprocal transient capacity versus passivating potential. (Iron anode, 2N H_2SO_4 ;
iron anode, 0.1N H_2SO_4 ;
iron anode, 0.01N H_2SO_4).
- Fig. 6 Current versus time. Acid change 0.1N to 2N H_2SO_4 at $t = 0$. (Fe/ H_2SO_4).
- Fig. 7 v_o versus time. Acid change 0.1N to 2N H_2SO_4 at $t = 0$. (Fe/ H_2SO_4).
- Fig. 8 Steady-state current versus potential. (Ni/2N H_2SO_4).
- Fig. 9 Open circuit potential decay from different passivating potentials. One-half hour passive time. (Ni/2N H_2SO_4).
- Fig. 10 Open circuit potential decay from +0.5 v, different passivation times. (Ni/2N H_2SO_4). Passive time: curve A (28 min), curve B (120 min), curve C (234 min).

Fig. 11 Open circuit potential decay versus time. Passive time 30 min. Initial passivation potential: Curve a), -0.2 v; curve b), 0.0 v; curve c), +0.2 v; curve d), +0.4 v; curve e), +0.6 v. (Ni/2N H₂SO₄).

Fig. 12 Cathodic reduction. Charge to activation versus reduction current. (Ni/2N H₂SO₄).

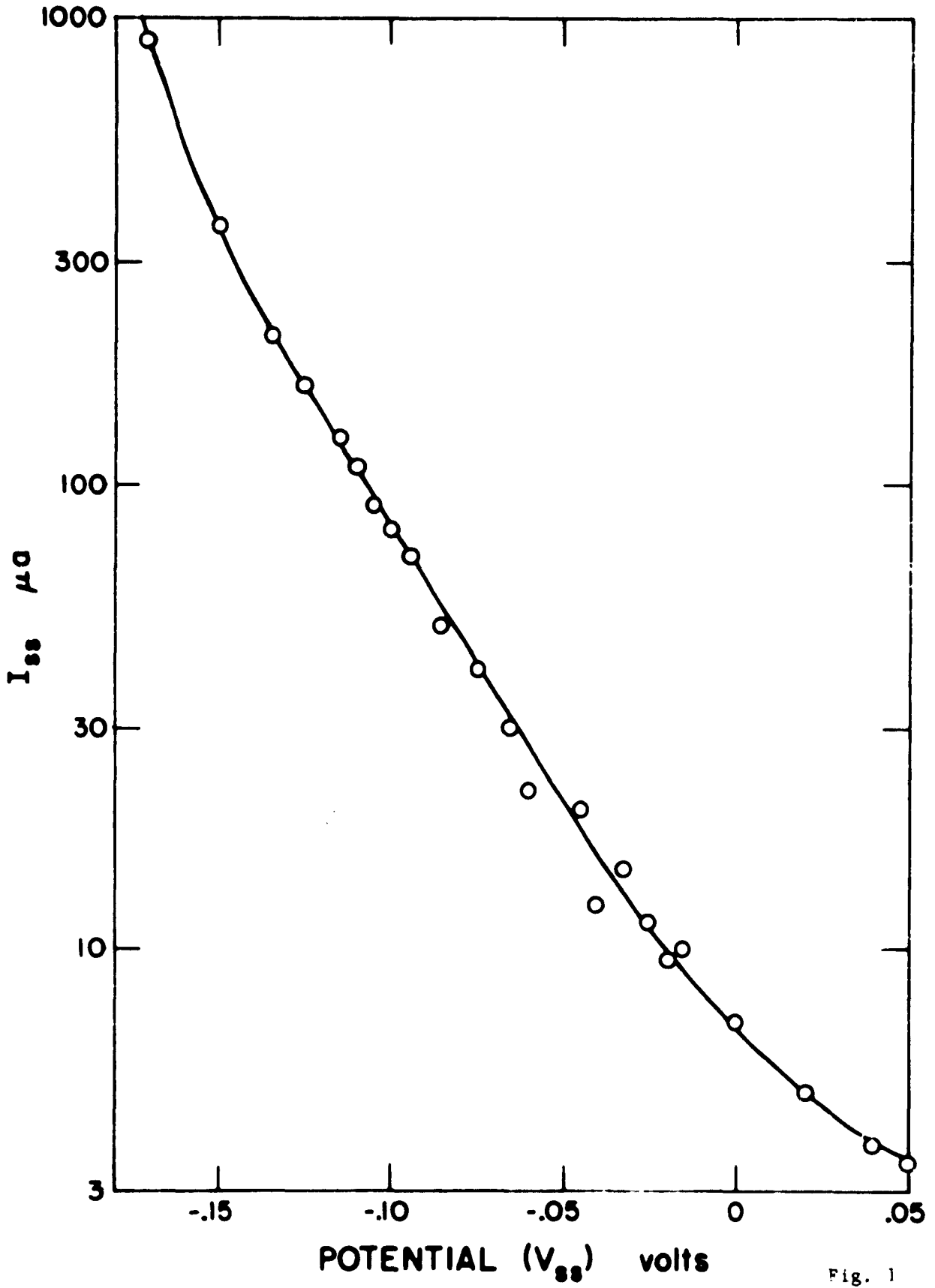


Fig. 1

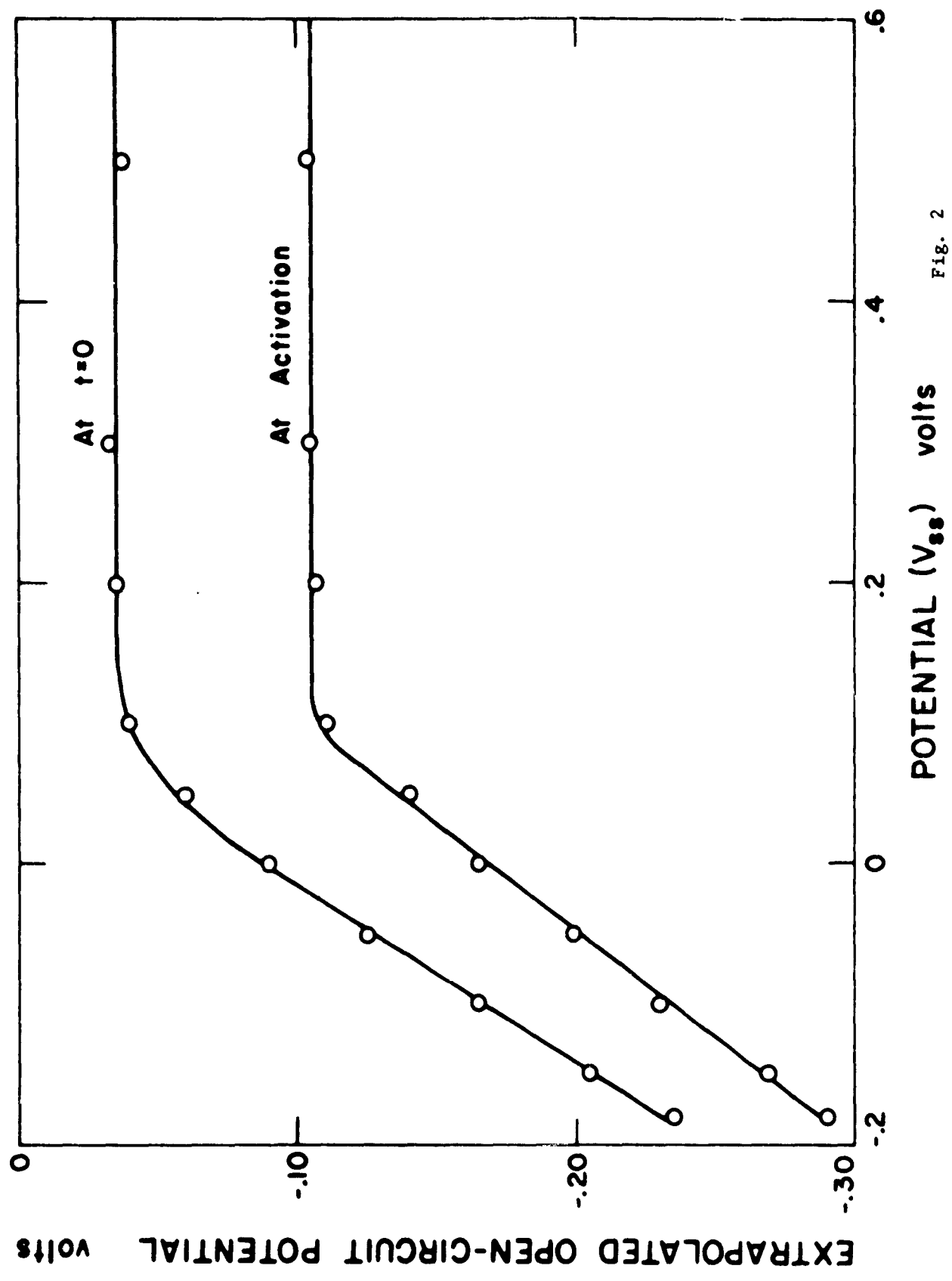


Fig. 2

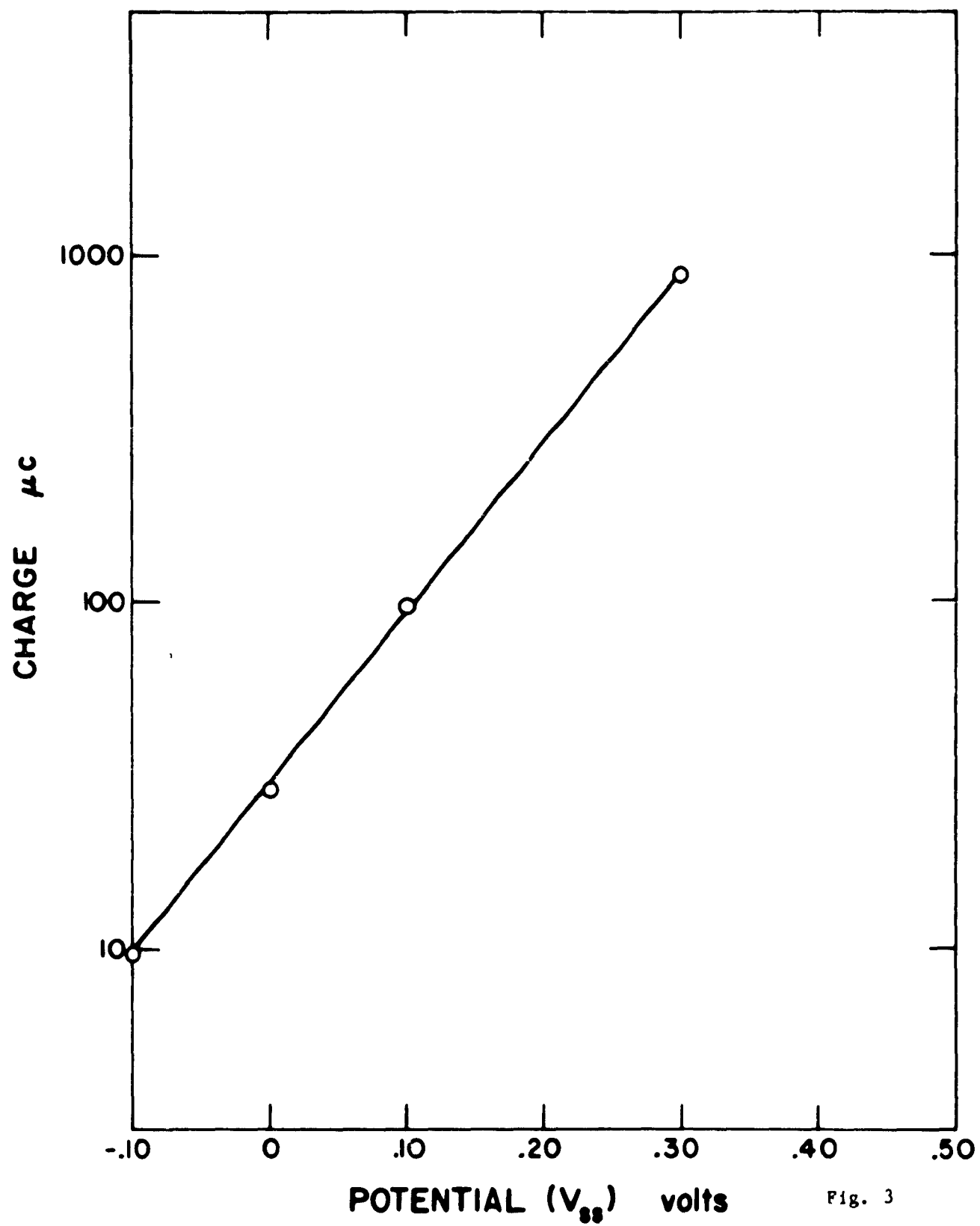


Fig. 3

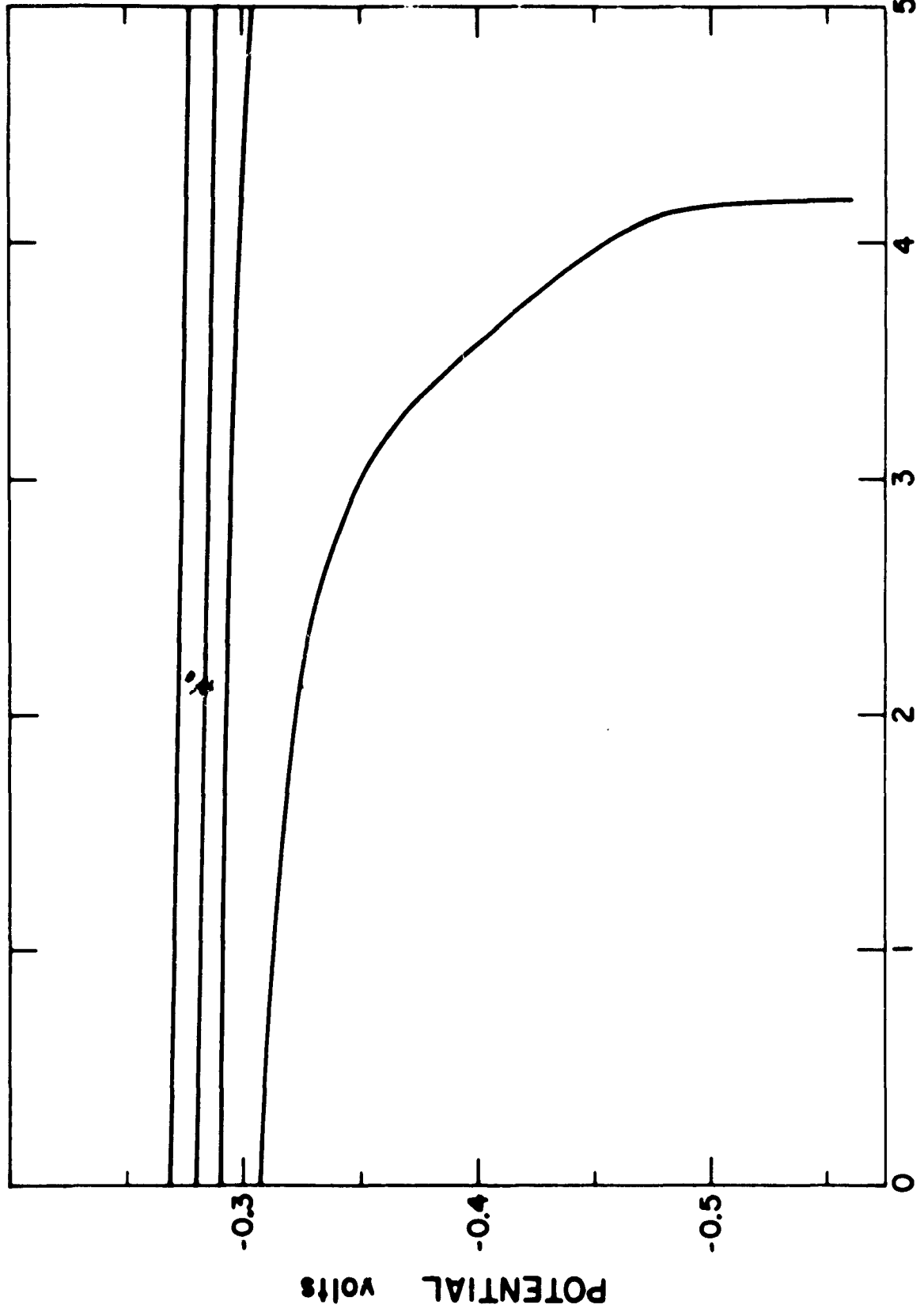


FIG. 4

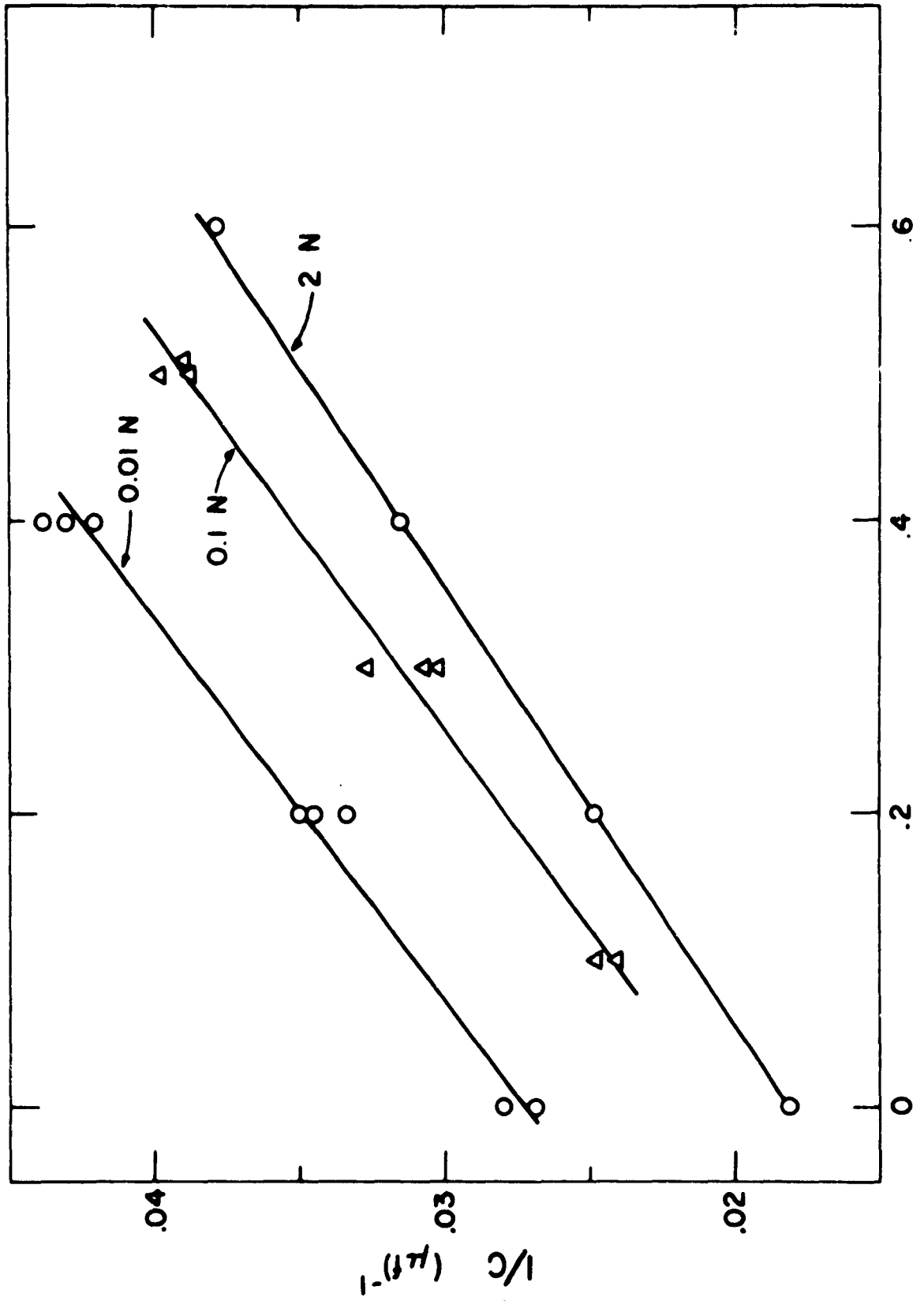


Fig.

POTENTIAL volts

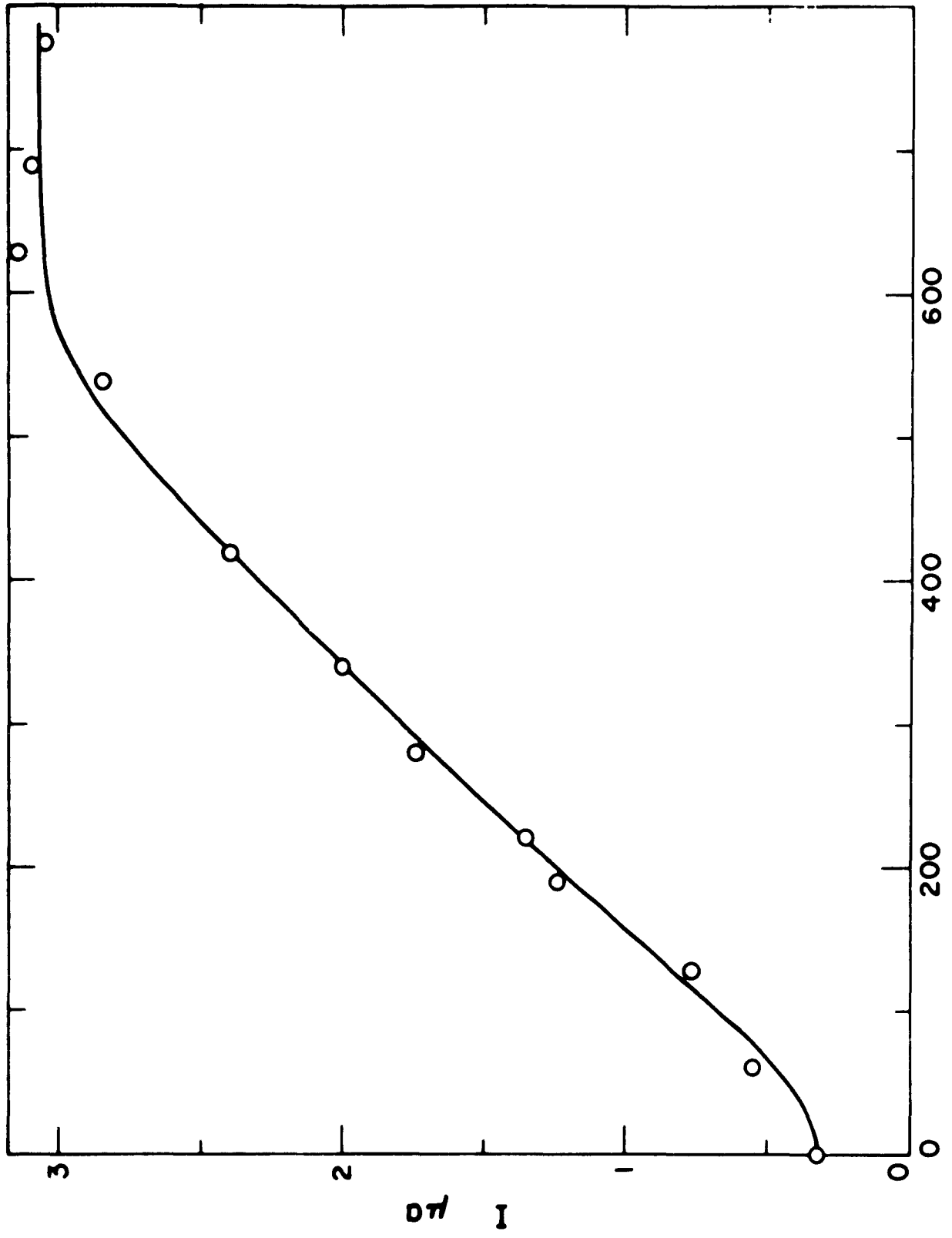


FIG. 9

TIME seconds

I

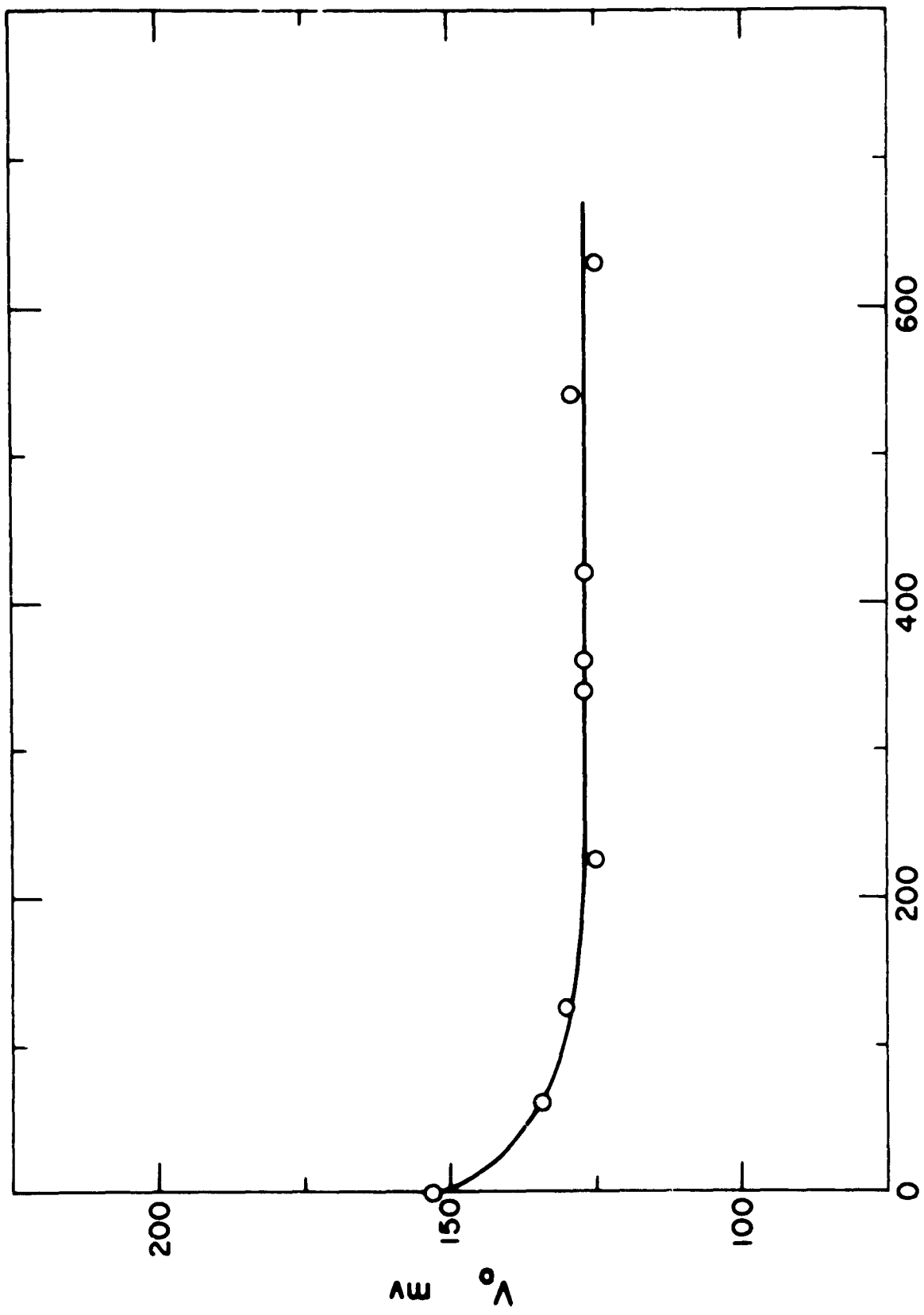


Fig. 7

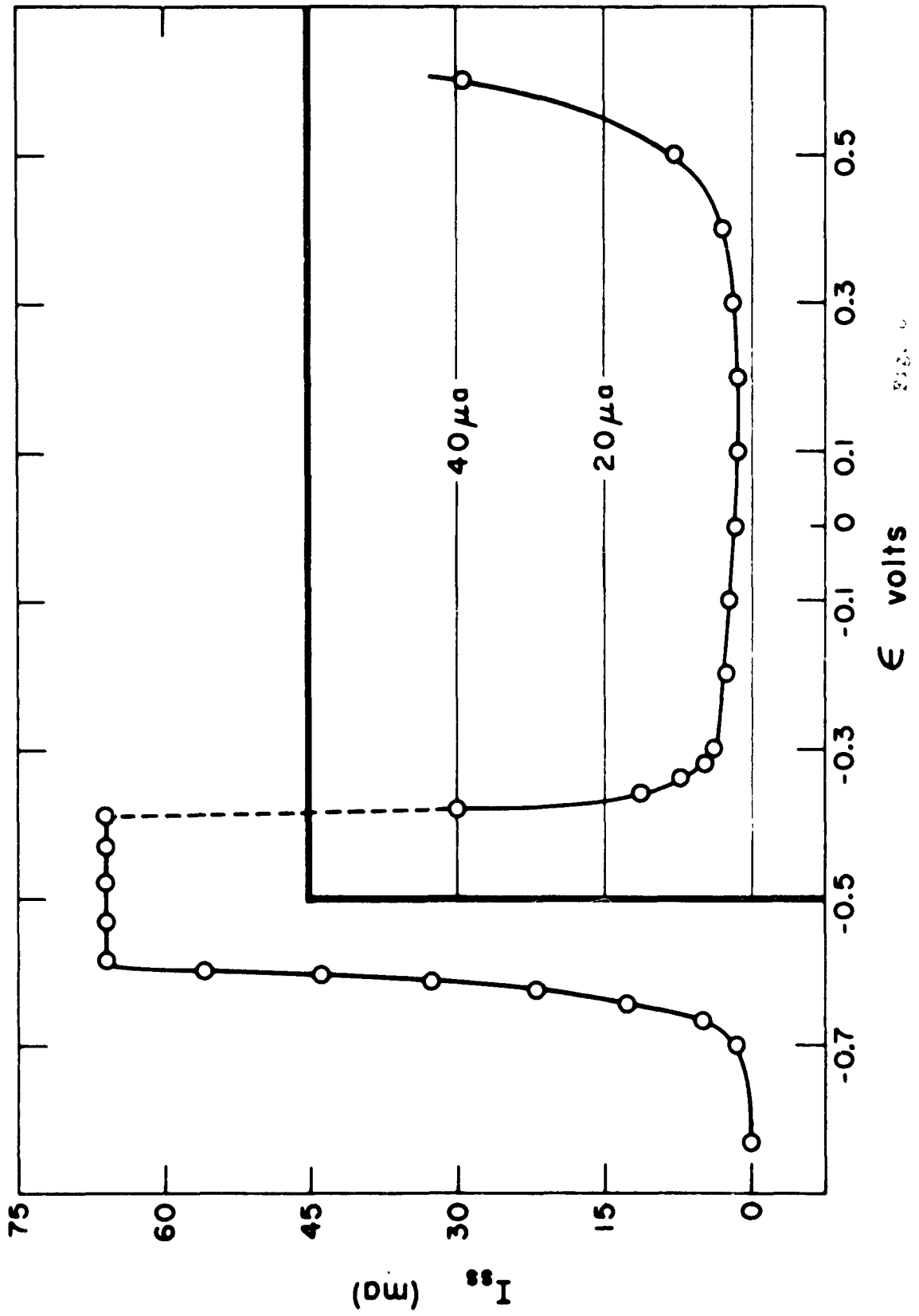


Fig. 6

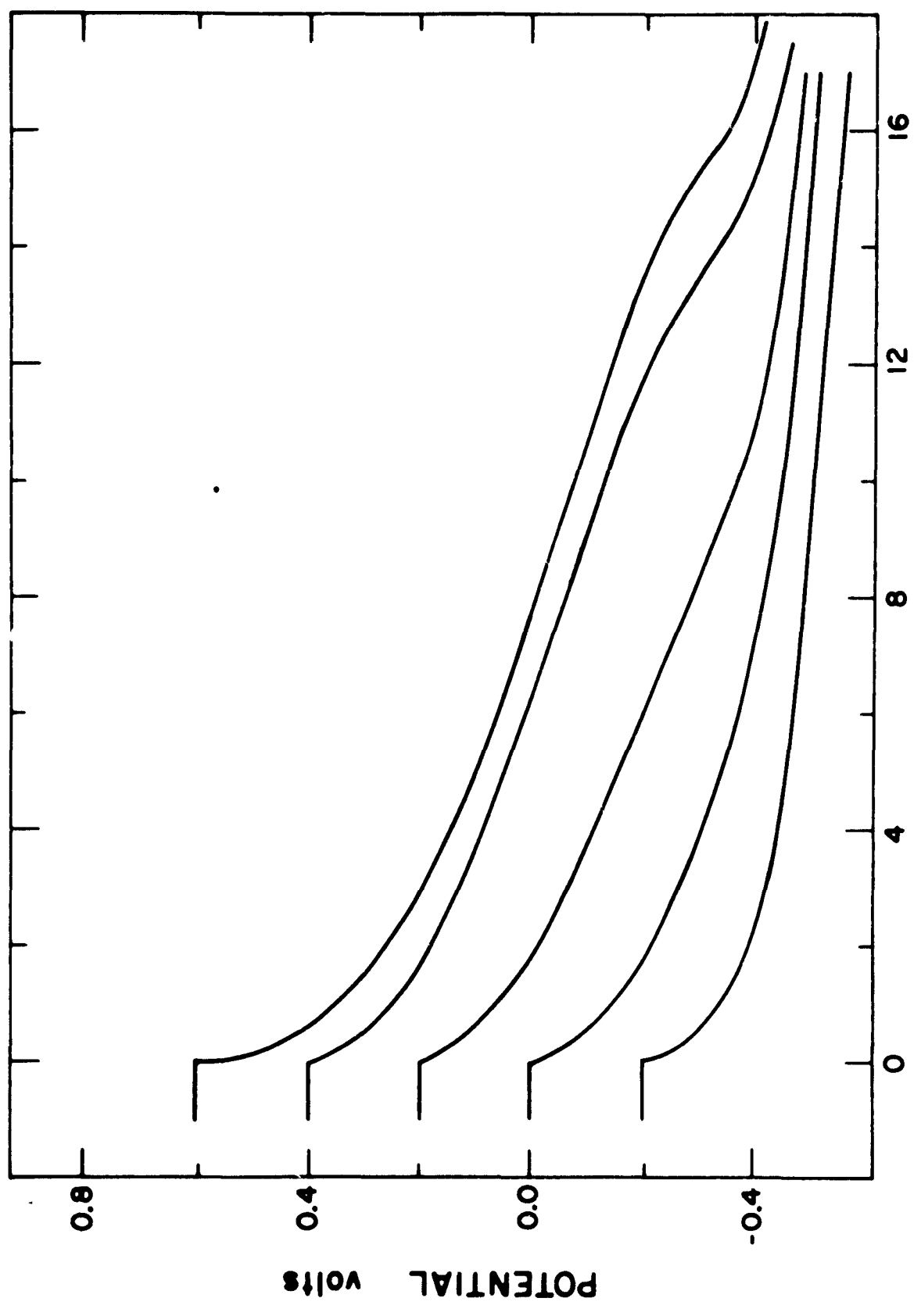
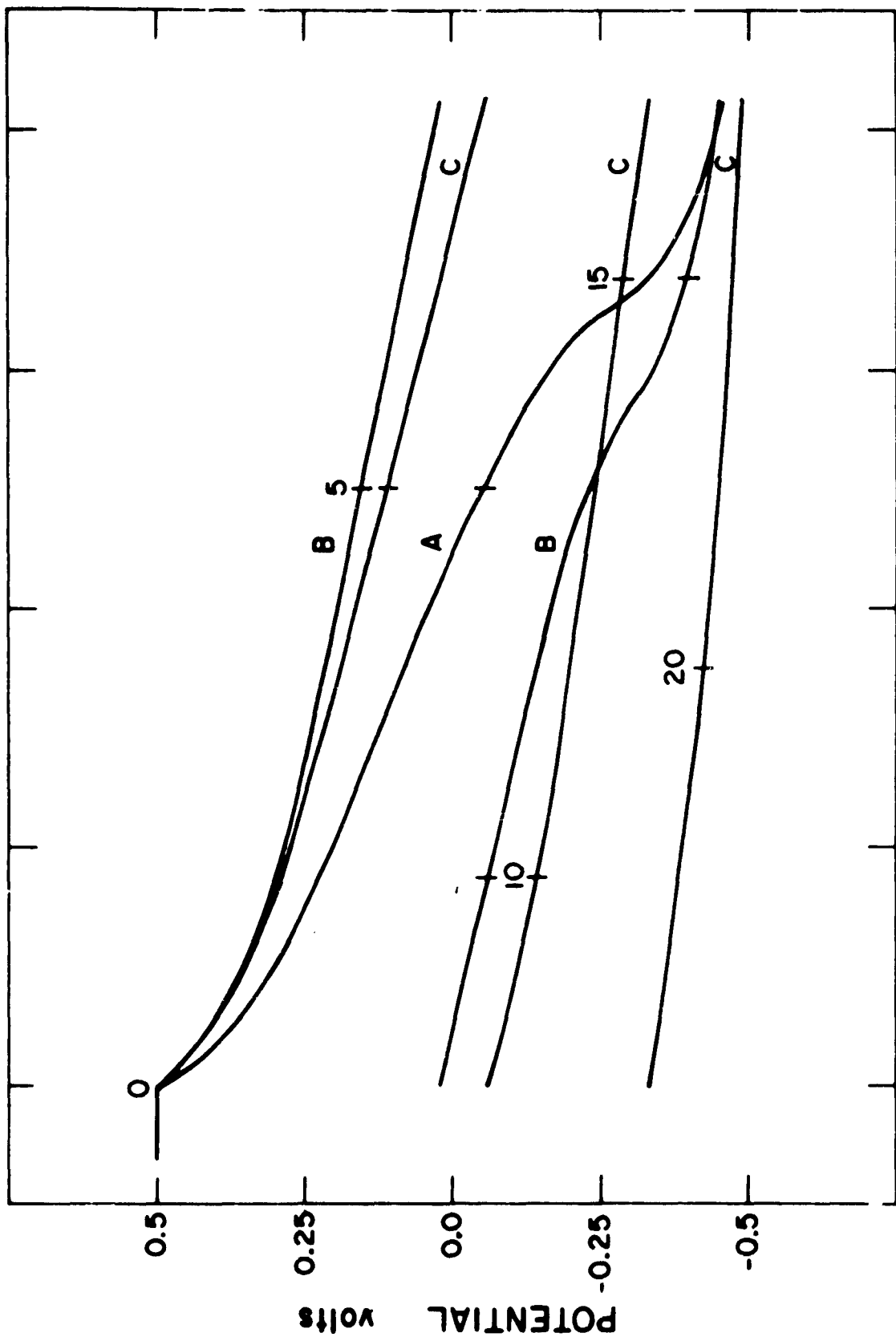


Fig. 9



TIME seconds Fig. 10

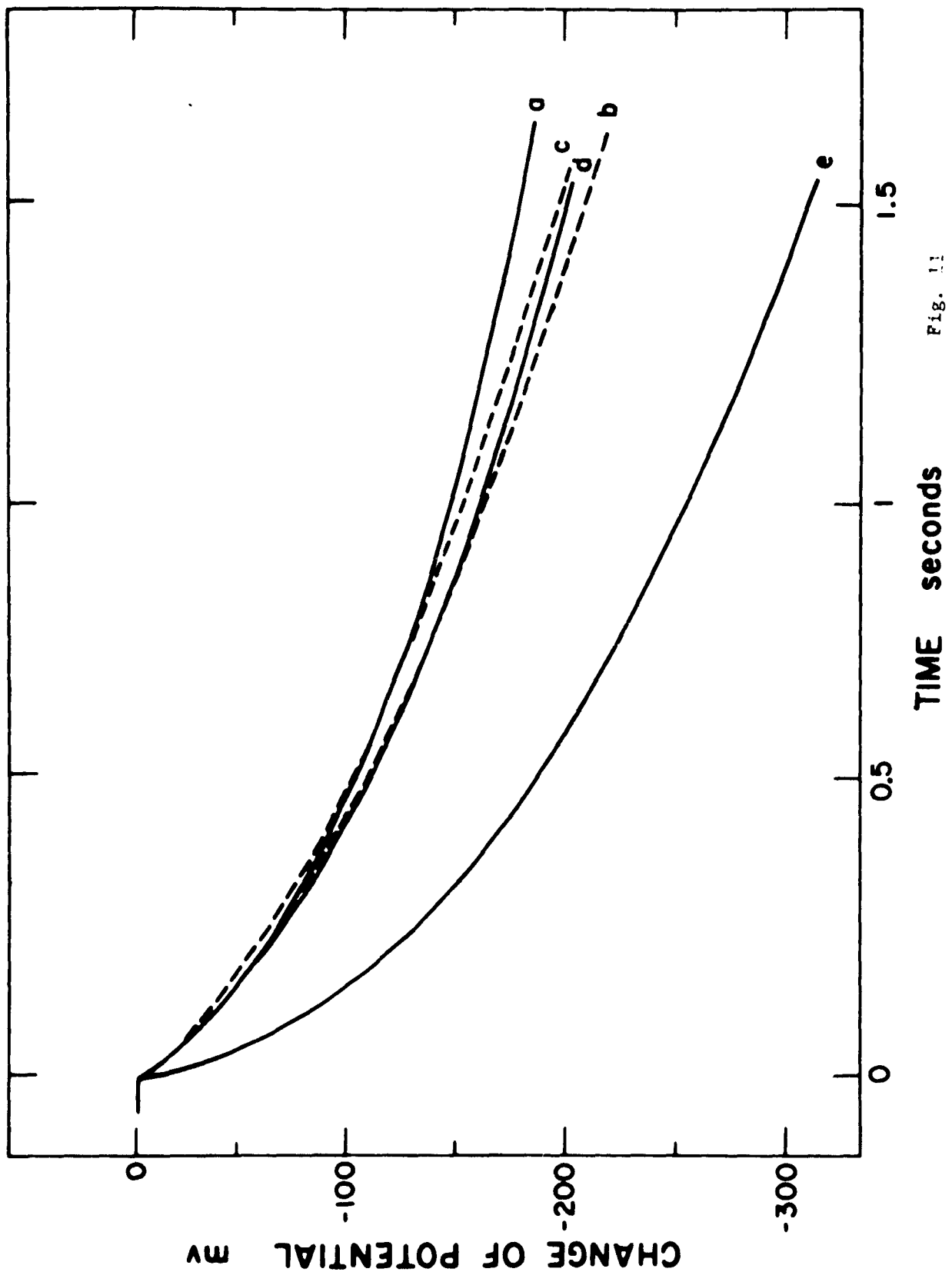


Fig. 11

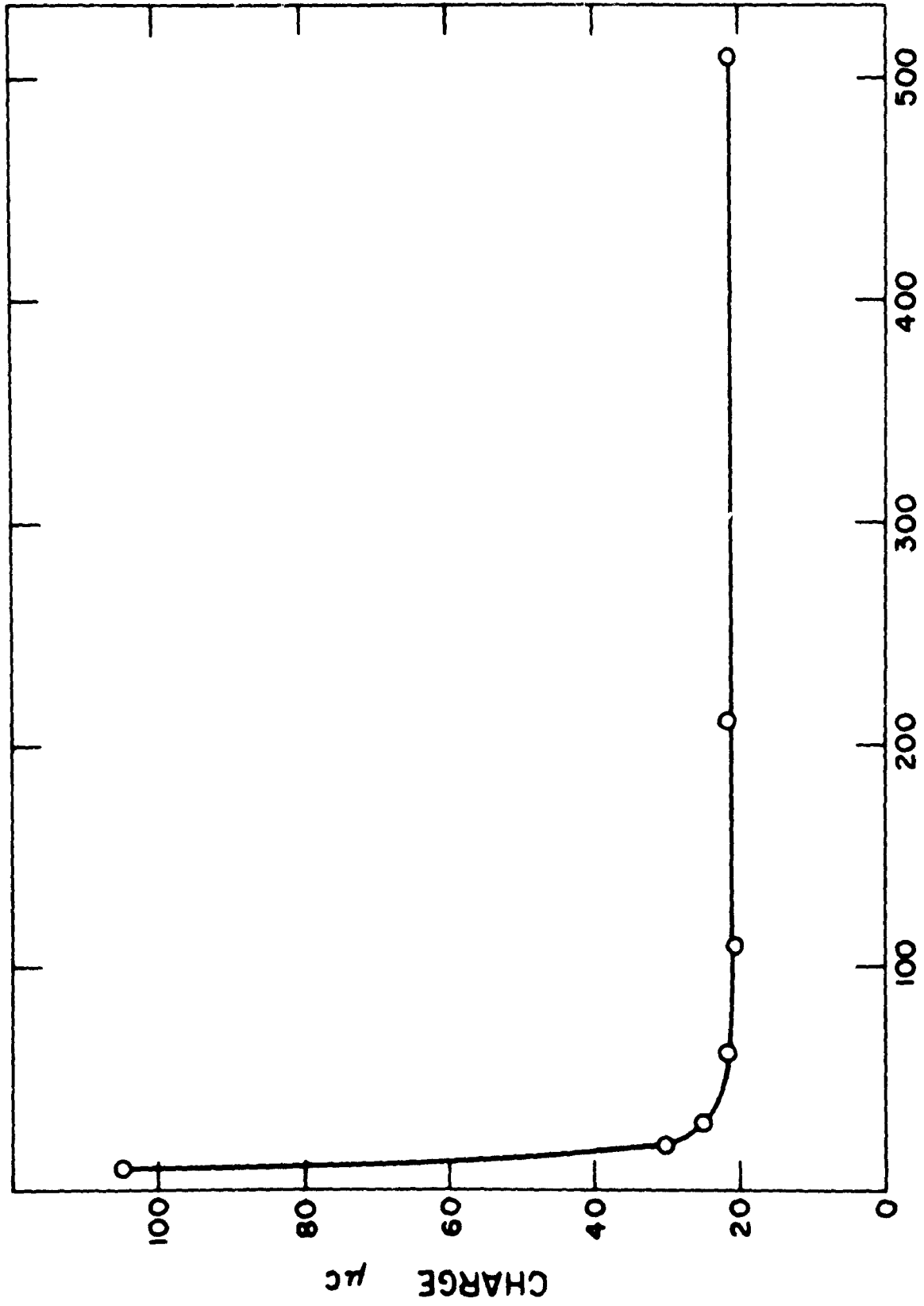


Fig. 12