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THE DETERMINATION OF THE COVERAGE  
OF CORRODABLE METALS WITH HYDROGEN  
DURING ELECTROLYTIC EVOLUTION

Technical Report No. 3  
to  
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Principal Investigator J. O'M. Bockris  
Research Associate R. Thacker

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University of Pennsylvania

Department of Chemistry

Electrochemistry Group

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## SUMMARY

Several original (except II, 2) methods have been established for the determination of the coverage with atomic hydrogen of a metal evolving hydrogen. These are:

I: Galvanostatic and potentiostatic transient methods.

II: Other methods which have now been evolved are:

(1): Direct measurement of the adsorbed hydrogen by transfer from a continuous rotating wire passing through two vessels.

(2): Measurements involving the addition of supplementary amounts of atomic hydrogen to the surface of an electrode (from the solution or through the metal).

(3): Direct measurement of pressure change in the gas phase over a solution in contact with a metal of high surface area.

(4): Measurement of the variation of the permeation rate with current density.

(5): Measurement of the diffusion coefficient of H in Fe and calculation of the surface concentration during hydrogen evolution from the equilibrium between the absorbed and adsorbed H and the concentration of hydrogen "just inside" the metal.

Methods involving measurement of the interfacial tension between a metal and solution (II,6); Raman and diffraction studies (II,7); and tracer studies with tritium (II,8) have been worked through in detail, and rejected.

The theory of the transient methods has been evaluated in detail, particularly with regard to the limitations in their application to the non-noble metals. The galvanostatic method is applicable to Ag, Cu, to noble metals in acid solutions, and to many metals in alkaline solutions; the potentiostatic method is applicable to the noble metals, and to Ni under certain limited conditions of potential in acid solutions.

Method II,1 gives the coverage directly and also provides indirectly information about the mechanism of the hydrogen evolution reaction on the metal, including those which corrode in acid solution. Method II,2 has been described in the Russian literature. It has proved inconclusive in the one report available. Method II,3 gives the equilibrium degree of coverage and heat of adsorption of hydrogen on a metal in the presence of an adsorbed water layer. It may be used for measurements with metals such as Ni in acid solutions. Method II,4 gives a clear distinction between the alternative proposed mechanisms for the desorption of H from a metal in solution (and thus indicates the order of magnitude of the coverage during evolution). Method II,5 depends upon the degree of accuracy which can be achieved in obtaining the heat of adsorption of H on a water covered surface, which is available from Method II,3. The methods II,3, II,4 and II,5 are the subjects of work at present in progress.

Data upon the variations of permeation rate (P) with current density is concordant in only two instances out of five investigations, three of which are recent and not concordant. These investigations are not applicable to the evaluation of surface coverage with hydrogen because: (i) They

were carried out before the significance of  $\frac{dP}{dI}$  with respect to surface coverage had been realized (cf. this Report), so that the range and accuracy aimed at in the former measurements is not suitable for significant evaluation of this coefficient; (ii) The results are entirely discrepant; (iii) No evidence that steady state conditions existed has been offered; (iv) The surfaces of the metals were certainly contaminated under the conditions used; it has been shown that such contamination may lead to a radical change in surface coverage.

Preliminary investigations of the variation of the rate of permeation of electrolytic hydrogen with current density, through Fe, Pd, Ni, Cu, Ti, Ta and U have been carried out using a technique which involves intentional contamination of the surface. In addition to iron and palladium, nickel has been found to be readily permeable to electrolytic hydrogen. Cu, Ti, Ta and U are slightly permeable. Measurements (Method II,4) made on Fe and Pd have given parameters for the kinetics of permeation of evolution of hydrogen which allow the evaluation of the desorption mechanism for hydrogen on these metals (and hence the order of magnitude of coverage). The diffusion coefficient of hydrogen in iron have been used in Method II,5 to obtain crude estimates of the coverage on Fe at medium current densities (using estimates of the heat of the hydrogen adsorption in the presence of water from gas phase data).

A technique has been evolved for measuring the variation with current density of the rate of permeation of electrolytic hydrogen through metals from uncontaminated surfaces.

THE DETERMINATION OF THE COVERAGE OF  
CORRODABLE METALS WITH HYDROGEN DURING  
ELECTROLYTIC EVOLUTION

(A): EVALUATION OF NEW METHODS.

I: Discussion of Range of Applicability of the Electrochemical Methods

(1): Galvanostatic Method:

In the method developed by Devanathan<sup>1,2</sup> the fractional monolayer of hydrogen on the surface of an electrode at a given current density is determined by means of an anodic galvanostatic impulse, introduced for a time of  $2 \cdot 10^{-6}$  sec., which causes anodic dissolution of the hydrogen present on the electrode, together with an (at first unknown) quantity of electricity for the formation of oxide, at the higher anodic potentials. From a study of the characteristic variation of potential with time, starting from, respectively the cathodic potential, at which  $H_2$  is being evolved, and an anodic potential such that no H is on the metal surface, it is possible to discriminate between the ionization of hydrogen and the other anodic processes (dissolution of metal or the formation of oxide, according to the pH employed).

Development of the theory of the method gives the following expression for the difference between the two Faradaic currents at any given potential:

$$i = i_H - i_{an} \quad (1)$$

where  $i_H$  is the current due to the dissolution of atomic hydrogen,  $i_{an}$  is the sum of the currents due to the anodic processes, and  $\theta$  is the coverage with H at the potential concerned, all at a given time, during the charging process. By plotting this difference as a function of time needed to attain each potential during the first type of charging curve, the quantity of electricity needed to dissolve the H present on the surface can be obtained from the area under the curve.

This area is:

$$\int_0^t i_H \left(1 - \frac{i_{an}\theta}{i_H}\right) dt \quad (2)$$

The condition for success of the measurements is that  $\frac{i_{an}\theta}{i_H}$  is small compared with unity. A rough estimation of the importance of this term in the integral can be made as follows.

It is known that

$$i_H = i_F - i_{an}(1-\theta) = i_F - i_{an} + i_{an}\theta \quad (3)$$

where  $i_F$  is the Faradaic current, and  $i_F - i_{an} = i_H - i_{an}\theta$ , thus,

$$\frac{i_{an}\theta}{i_H} = \frac{i_{an}\theta}{i_F - i_{an} + i_{an}\theta} = \frac{1}{\frac{i_F - i_{an}}{i_{an}\theta} + 1} \quad (4)$$

At low times,  $i_{an}$  is zero, i.e.,  $\frac{i_{an}\theta}{i_H}$  is zero. Only at highly anodic potentials is  $i_{an}$  comparable with  $i_H$  however, at the relevant anodic potential, ca 50 mv., the value of  $\theta$  decreases towards zero and hence  $i_{an}\theta$  remains negligible.

Equation (2) gives directly an approximate value for  $q_H$ , the coulombs of H adsorbed, whence the coverage is obtained. The sum of the errors involved is 7%.

The conditions necessary for the successful application of the galvanostatic method are:

(a): The reversible potential of the metal must occur at a potential more positive than 100 mv referred to the reversible hydrogen potential in the same solution in order to avoid the presence of H on the surface at potentials anodic to that of the reversible  $H_2$  electrode.

(b): The time of the sweep must be long enough so that the hydrogen has sufficient time to dissolve off. This is at least  $0.3 \frac{dt}{dV}$  sec.

(c): On the other hand, the sweep time must be less than  $10^{-5}/i_c$  sec., where  $i_c$  is the cathodic current density existing before the sweep, in order to avoid appreciable loss of H by combination during the sweep.

(d): The anodic c.d. must be sufficiently high so that the effect of the readsorption of hydrogen is negligible. Approximately the order of the lowest values is 100 ma. cm.<sup>-2</sup>

Consideration of these conditions in respect to the known kinetic and thermodynamic parameters for a range of metals indicates that the galvanostatic method may successfully be applied only to Ag, Cu, in acid and alkaline solutions, and to a wide range of transition metals in alkaline solutions; and the noble metals. (For these latter the oxide formation occurs at a potential much more positive than that of the reversible H<sub>2</sub> electrode and determinations can be made by a simple (non double pulse) coulometric method).

The main disadvantage of this method is, of course, its restricted applicability in acid solutions.

(2): Potentiostatic Method:

In the potentiostatic method,<sup>3</sup> the cathodic potential during the steady state evolution of hydrogen is changed in about one microsecond to an anodic potential which is sufficiently noble to correspond to the complete absence of H. The dissolution of adsorbed hydrogen will be complete in a time less than 1 millise., and will be uninfluenced by passivation of the metal, which would not commence, in most practical solutions, until after 1 sec. or more.

However, when the anodic pulse is passed, it causes not only the dissolution of the adsorbed hydrogen, but also the dissolution of the substrate, so that it is necessary to ascertain the conditions of  $i_H$ ,  $P_{H_2}$ ,

c.d., and order of concentration of atomic hydrogen on the surface, whereby a measurable anodic pulse of H, clearly separated from the pulse for the metal dissolution, would be expected.

After the switching in of the anodic potential  $V$ , let  $i$  be the total current at any instant,  $i_H$  the current for the dissolution of adsorbed H,  $i_{an}$  that for dissolution of the metal which takes place at a potential  $V$ ,  $C$  the capacity of the double layer, and  $t$  the time.

Then:

$$i = i_H + i_{an} + C \frac{dv}{dt} \quad (5)$$

After charging of the double layer is complete,

$$i = i_H + i_{an} \quad (6)$$

If  $(\theta_H)_t$  is the fraction of the surface covered with adsorbed hydrogen at time  $t$ ,

$$i_H = (l_0)_H \frac{(\theta_H)_t}{(\theta_{e,v})_H} e^{\frac{\alpha_H \eta F}{RT}} \quad (7)$$

and

$$i_{an} = (l_0)_{an} [1 - (\theta_H)_t] e^{\frac{\alpha_{an} \eta_{an} F}{RT}} \quad (8)$$

The potential terms are constant, whereupon:

$$i_H = I_H (\theta_H)_t \quad (9)$$

where

$$I_H = \frac{(l_0)_H}{(\theta_{e,v})_H} e^{\frac{\alpha_H \eta F}{RT}} \quad (10)$$

and

$$i_{an} = I_{an} [1 - (\theta_H)_t] \quad (11)$$

where:

$$I_{an} = (i_0)_{an} e^{\frac{\alpha_{an} \eta_{an} F}{RT}} \quad (12)$$

Also:

$$i_t = -FZ \frac{d(\theta_H)_t}{dt} = I_H (\theta_H)_t \quad (13)$$

(From 9)

$$\therefore (\theta_H)_t = -\frac{FZ}{I_H} \frac{d(\theta_H)_t}{dt} \quad (14)$$

Or:

$$\frac{d(\theta_H)_t}{(\theta_H)_t} = -\frac{I_H}{FZ} dt \quad (15)$$

Hence,

$$(\theta_H)_t = (\theta_H)_0 e^{-\frac{I_H t}{FZ}} \quad (16)$$

where  $(\theta_H)_{t=0}$  is the coverage during the cathodic polarization.

Thus,

$$i_t = I_H (\theta_H)_0 e^{-\frac{I_H t}{FZ}} + I_{an} \left[ 1 - (\theta_H)_0 e^{-\frac{I_H t}{FZ}} \right] \quad (17)$$

$$= \left[ I_H - I_{an} \right] (\theta_H)_0 e^{-\frac{I_H t}{FZ}} + I_{an} \quad (18)$$

$$\therefore \frac{i_t}{I_{an}} = \left( \frac{I_H}{I_{an}} - 1 \right) (\theta_H)_0 e^{-\frac{I_H t}{FZ}} + 1 \quad (19)$$

The quantity  $I_H$  contains  $\phi_{rev}$  (Cf. equation 10), and this can be expressed in terms of  $\phi_{t=0}$ , e.g., for a mechanism of hydrogen evolution  $H^+ + e_0 \xrightarrow{\text{slow}} H_{Ads}; 2H_{Ads} \xrightarrow{\text{fast}} H_2$  by means of the equation:

$$\frac{(\phi_H)_{t=0}}{\phi_{rev}} = e^{-\frac{\eta F}{4RT}} \quad (20)$$

If the cathodic overpotential during the cathodic polarization before the application of the anodic pulse is  $\eta_H$  then it can be shown<sup>1</sup> that:

$$\eta = |\eta_H| + 0.1 \quad (21)$$

where  $\eta$  is the minimum allowable for the anodic overpotential in the anodic pulse.

Further,

$$\eta_{an} = \eta - e_{rev} M \quad (22)$$

where  $e_{rev} M$  is the reversible potential of the metal in the given solution.

Making the relevant substitution in (19), one obtains:

$$\frac{i_t}{I_{an}} = \left[ \frac{(i_0)_H}{(i_0)_{an}} 10^{\frac{\eta}{0.059} \left\{ \alpha_H + \frac{1}{4} - \alpha_{an} (1 - e_{rev} M) \right\}} - (\phi_H)_0 \right] 10^{\frac{-(i_0)_H t}{2.303 F Z (\phi_H)_0}} 10^{\frac{\eta}{0.059} (\alpha_H + \frac{1}{4})} + 1 \quad (23)$$

The nature of the plot of  $i_t$  against time for the cases  $\frac{I_H}{I_{an}} > 1$ , and  $\frac{I_H}{I_{an}} < 1$  are shown in Figs. 1 and 2 respectively. The area bounded by the exponential curve and the abscissae  $i_t = I_{an}$  in both Figs. 1 and 2 is a measure of the dissolved atomic hydrogen (which is equivalent to the area under the curve).

To test whether the method would work for a particular metal, a useful criterion is that  $\frac{i_t}{I_{an}} > 10$  when  $\frac{I_H}{I_{an}} > 1$ , or  $\frac{i_t}{I_{an}} < \frac{1}{10}$ , when  $\frac{I_H}{I_{an}} < 1$ , at an arbitrary

time of  $10^{-5}$  sec. By fixing one of the variables  $(\theta_H)_0, \eta, t$  in equation (23) it is possible to express  $\frac{i_t}{I_{an}}$  in terms of the remaining two in a three dimensional drawing. For a particular metal the values of  $\frac{i_t}{I_{an}}$  for suitable combinations of  $\eta$  and  $(\theta_H)_0$  are evaluated and the results may be plotted. Such a plot for nickel is shown in Fig. 3. The surface ABCDEF represents values of  $\frac{i_t}{I_{an}}$  for any combination of  $\eta$  and  $(\theta_H)_0$ , when  $\eta$  ranges from 0.15 - 1.00 v. and  $(\theta_H)$  from  $10^{-3}$  - 1. The area ABF which lies below the surface  $(\frac{i_t}{I_{an}} = \frac{1}{10}, (\theta_H)_0, \eta)$  gives values of  $\eta$  and  $(\theta_H)_0$ , which fulfill the second criterion (i.e.,  $i_t/I_{an} < \frac{1}{10}$ ) and of course fixes the conditions under which the method would give results.

Construction of three dimensional diagrams such as that of Fig. 3 for a number of metals (that one shown is for Ni) showed that the following conditions exist for a satisfactory ratio of  $\frac{i_t}{I_{an}}$  for  $t < 10^{-5}$  sec. (Table I)

Table I  
EXAMINATION OF POTENTIOSTATIC METHOD  
FOR EVALUATION OF ADSORBED H

Ni	$\frac{i_t}{I_{an}} < 1/10$	when $(\theta_H)_0 = 0.89 - 1.0$ and $\eta = 0.15 - 0.26$ v.
Cu	No values of $(\theta_H)_0$ and $\eta$ in chosen ranges, give	
Fe		
Ag		$\frac{i_t}{I_{an}} < 1/10$ or $\frac{i_t}{I_{an}} > 10$
Pb	$\frac{i_t}{I_{an}} > 10$	when $(\theta_H)_0 = 0$ and $\eta = 0.15 - 0.48$
Au	$\frac{i_t}{I_{an}} > 10$	when $(\theta_H)_0 = 0-1.0$ and $\eta = 0.15 - 0.48$ v.

It can be seen from these theoretical results that even for metals which appear to be possible very restrictive assumptions have to be made for

a successful application. Similar results appear likely for other metals, and the chances of success with the potentiostatic method are therefore not good (principally because of the difficulty of obtaining suitable  $(O_{H_2O})^{-\eta}$  combinations in practical ranges). It was therefore decided not to experimentally investigate the method.

II: Examination of Other Possible Methods of Measuring Surface Coverage

(1) Direct measurement of the adsorbed hydrogen by transfer from a continuous rotating wire passing through two vessels.

Consider a continuous wire which passes through two vessels, as shown in Fig. 4. Vessel A contains a solution in which the wire is cathodically polarized. B is a vessel containing a solution of identical composition, initially free from  $H_2$ . The wire is moved continuously through A and B and through a "cleaning process" section, C. The speed of passage of the wire is such that there is (a) enough time for the wire to attain a steady state hydrogen evolution, and (b) insufficient time for significant evaporation to occur between the vessels A and B. The time to reach a steady state is given by the rise time of the circuit, i.e.,  $4 CR$ , where  $C$  is the double layer capacity and  $R$  the differential resistance of the electrode reaction, i.e.,  $\frac{\partial i}{\partial \eta}$ , where  $i = i_0 e^{\frac{-\alpha \eta F}{RT}}$  for  $\eta > 20$  mvs. The rise time at current densities of  $10^{-3}$  amp. cm.<sup>-2</sup> can thus be shown to be about  $1/\sim$  sec. If the gap between the vessels is 0.1 cms. the speed of passage of the wire has to be about 50 ft. sec.<sup>-1</sup>.

The orifices at D, D<sup>1</sup>, E and E<sup>1</sup> are prevented from spillage by enclosing the arrangement in a compartment with variable pressure. At D and E, the wire passes through a capillary (or is subjected to jets of  $N_2$ ) which limits the amount of electrolyte swept out to about one thousand layers (See below).

The originally  $H_2$  - free compartment B, contains a Ag cathode and sufficient Ag salt so that when the cathode is working Ag is deposited on

and no H is evolved. The wire receiving the anodic pulse due to this cathode desorbs the adsorbed  $H_2$  on it due to its cathodic polarization in compartment A. B thus receives at each rotation of the wire a quantity of  $H_2$  corresponding to the full amount on the surface.

For each sq. cm. of wire, and for a minimum 1% coverage, there would be delivered into the solution about  $10^{-11}$  moles of  $H_2$ . Upon passing a wire of length 3 ft.,  $10^5$  times through the system,  $5 \times 10^{-5}$  moles of  $H_2$  i.e., 2 ccs of  $H_2$  at N.T.P. will be introduced into compartment B. (Fig. 6) If this amount occupies a volume of 100 ccs, it is easily estimated, e.g., by means of chromatographic analysis.

This method appears to have simple applications to the determination of the variation of  $\theta$  with potential. Instrumentation would be cheap.

The major error lies in the amount  $H_2$  which is carried over in the solution accompanying the wire. A practical seal may be arranged which reduces this to 1000 layers of solution; it may be supposed that this solution is saturated with  $H_2$ . Then, the volume of solution per sq. cm. of electrode, is about  $10^{-5}$  ccs. Introducing the solubility of  $H_2$  at 1.8 ccs. per liter at  $20^\circ C$ , the amount of  $H_2$  is about  $2 \times 10^{-8}$  ccs., i.e.,  $0.5 \times 10^{-12}$  moles, a negligible quantity compared with that adsorbed on the wire, even at 1% coverage. Alternatively, the  $H_2$  in the solution in A swept through with the wire can be kept well below saturation with  $H_2$  by flowing the electrolyte in the first solution continuously so that saturation is avoided.

It may be pointed out that this method offers a general possibility of adsorption studies at solid solution interfaces under potential control. (It would thus avoid the difficulties of tracer studies in this field which arise when the metal is removed from the solution, washed, and exposed to a counter in the absence of a defined potential).

(2): Measurements involving the addition of supplementary amount of atomic hydrogen to the surface of an electrode (from the solution or through the metal).

These are analagous to those of an experiment due to Frumkin<sup>4</sup> C (Fig. 5) is a cathode, A and B are independent anodes. H<sub>2</sub> is evolved to steady state on the side C. When the overpotential,  $\eta$  of this evolution has been measured for a current density  $i_1$ , electrolysis is commenced on the side C'' and H permeates to C' and thereby introduces an increased surface coverage on C' above that corresponding to the steady state on C' at  $i_1$ .

If the proton discharge reaction  $H^+ + e_0 \rightarrow H_{ad}$  is rate determining, the velocity of the overall reaction is:

$$v = k_1 (1-\theta)$$

where  $k_1$  is constant at  $\eta$ , and  $i_1$ . If  $\theta$  is increased, therefore, and  $i_1$  remains constant,  $\eta$  increases. Conversely, if the electrochemical adsorption step  $H^+ + H_{ad} + e_0 \rightarrow H_2$  is rate determining, the overall reaction rate is

$$v = k_2 \theta$$

where  $k_2$  is a constant at  $\eta$ , and  $i_1$ . Hence, increase of H at constant  $i_1$ , causes  $\eta$  to decrease.

Thus, observation of the change of  $\eta$  upon permeation of H from C' to C' gives a diagnostic criterion concerning the rate determining step.

However, the proton discharge rate determining step is associated with a low coverage ( $\theta < 0.1$ ) and the electrochemical desorption is associated with a high coverage ( $\theta > 1$ ). Hence, the coverage can qualitatively be obtained.

This method has been applied by Frumkin<sup>4</sup> to Ni but with somewhat contradictory results. It yields only qualitative results. The experiments would be fairly easy.

(3): Direct measurement of pressure change in the gas phase over a solution in contact with a metal of high surface area.

The normal method of measurement of surface coverage from the gas phase is to observe the pressure change in the gas phase when gas at a known pressure is brought into contact with the metal. The initial and final pressures involved are usually of the order of  $10^{-5}$  -  $10^{-4}$  mms. Hg. In systems containing water, the pressure will clearly be that of the saturation vapour pressure of water and hence pressure changes of this order would not be practicably measurable. The direct method has, thus, not hitherto been considered.

However, the following considerations show that, if sufficiently large areas of metal are used, a practical measurement may become possible. Suppose that the metal area is 10000 sq. cm. and that the coverage with H is of the order of 0.1. Then, the moles of H adsorbed =  $10^4 \times 10^{-9} \times 10^{-1} = 10^{-6}$  moles.

Let the initial partial pressure of  $H_2$  be of the order 30 mms., i.e. substantially greater than the water vapour pressure at room temperature. Let the 10,000 sq. cm. of metal powder be in contact with a gas space of 10 ccs. and suppose that the initial state of the system is one in which the metal powder is kept out of contact with the aqueous phase and  $H_2$  (e.g., the powder is maintained in an ampoule), and the solution is saturated with  $H_2$ . The number of moles of  $H_2$  in the gas phase is given by:

$$\frac{30}{760} \times \frac{10}{1000} = n(0.08 \times 298)$$

i.e.,  $n = 2 \times 10^{-5}$  moles  $H_2$ .

The metal is then brought into contact with the water-hydrogen system which is closed, the pressure in the gas phase being measured. In the conditions chosen, the adsorption of  $10^{-6}$  moles  $H_2$ , causes a pressure change 1/20th of the total  $H_2$  pressure, i.e., 1.5 mm. in a total pressure of some

30+15 mms, a pressure change of some 2%. The pressure change available for measurement may clearly be increased by change of metal area or decrease of gas volume. Thus, direct measurement of  $H_2$  adsorption thus appears possible.

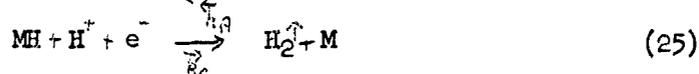
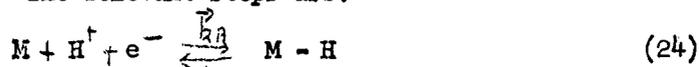
This method has the considerable advantage that variation of the adsorption of H on a metal in the presence of water can be carried out and hence the integral heat of adsorption of H on a water covered surface can be obtained. This quantity is of great interest to the evaluation of the surface coverage of a metal with H under conditions of  $H_2$  evolution. It will be shown below (Section A II 5) that if this quantity is known, the degree of coverage can be calculated from experiments on permeation rates.

This method in itself does not provide a complete solution to the problems of the present project, because the aim of this is the study of the coverage of a metal with H, during evolution and in corroding media (where the direct method clearly cannot be applied). Changes with potential and current density are also not measurable. It may be possible, however, to make measurements of the equilibrium adsorption of H from solutions of pH 2-3 on electrodes of materials closely similar to Fe (e.g., Ni) and to determine the decrease in the heat of adsorption of H on Ni compared with that from the gas phase caused by the adsorption of water. With this quantity (together with the reported data), a reasonably accurate value of  $\Delta H_{Ads}$  for H on Fe in the presence of water can be obtained (and applied to the permeation studies). The above method would give rise to heats of adsorption from changes observed at various temperatures if the adsorption is reversible. If this proves not to be the case, analogous experiments may be carried out by measuring the resistance change on a wire already covered with a film of water when hydrogen adsorbs upon it.

(4): Variation of the permeation rate with current density.

The variation of the electrolytic permeation rate of H through a metal with current density can lead to a knowledge of the mechanism of the H<sub>2</sub> evolution reaction, and hence qualitatively the coverage. The corresponding experimental data can also be used to obtain a quantitative estimate of the coverage.

Consider electrochemical desorption to be the slow step in the H<sub>2</sub> evolution reaction. The relevant steps are:<sup>5</sup>



where the k's are the appropriate rate constants. Let V<sub>1</sub>, V<sub>2</sub>, V<sub>3</sub> be the rates of (24) in the forward direction, (24) in the backward direction, and (25) in the forward direction respectively. Then:

$$V_1 = \overset{\rightarrow}{k_A} a_{H^+} (1 - \theta) e^{-\frac{\eta F}{2RT}} = a_1 (1 - \theta) \quad (26)$$

$$V_2 = \overset{\leftarrow}{k_B} \theta e^{\frac{\eta F}{2RT}} = a_2 \theta \quad (27)$$

$$V_3 = \overset{\rightarrow}{k_C} a_{H^+} \theta e^{-\frac{\eta F}{2RT}} = a_3 \theta \quad (28)$$

a<sub>H<sup>+</sup></sub> is the activity of H<sup>+</sup> in solution in the double layer.

Assuming that the back reaction rate of (25) is negligible,

$$V_1 = V_2 + V_3 \quad (29)$$

i.e.,

$$a_1 (1 - \theta) = a_2 \theta + a_3 \theta \quad (30)$$

and

$$\theta = \frac{a_1}{a_1 + a_2 + a_3} \quad (31)$$

If (25) is the rate determining step then:

$$a_3 < a_1 + a_2 \quad \text{and} \quad a_2 > 10a_1$$

Hence,

$$\theta = a_1/a_2$$

i.e.,

$$\theta = a_{H^+} \frac{k_A}{k_B} \frac{e^{-\eta/2.303}}{e^{\eta F/2RT}} \tag{33}$$

For the conditions corresponding to (32),

$$\eta = \frac{2RT}{3F} \ln i_0 - \frac{2RT}{3F} \ln i \tag{35}$$

$$\theta = K a_{H^+} e^{-2/3 (\ln i_0 - \ln i)} \tag{36}$$

$$\ln \theta = C + 2/3 \ln i \tag{37}$$

$$\therefore \frac{\partial \ln \theta}{\partial \ln i} = \frac{2}{3} \tag{38}$$

We make the assumption that the permeation rate is proportional to the surface coverage. This basic assumption was proved explicitly by Ward<sup>6</sup> for H diffusion through Cu from the gas phase. It appears to be a reasonable assumption that either the surface reaction or the bulk diffusion is the rate determining step in the permeation process.

The, from these assumptions and (38),

$$P \propto i^{2/3} \tag{39}$$

The Tafel slope which would be associated with (39) is:

$$\begin{aligned} \frac{\partial \eta}{\partial \ln i} &= \frac{-2RT}{3F} = - \frac{b}{2.303} \\ &= - 0.04 \text{ at } 25^\circ\text{C} \end{aligned}$$

In a similar way, the current dependence of permeation rate for other possible mechanisms can be worked out. The results are summarized in the Table II below.

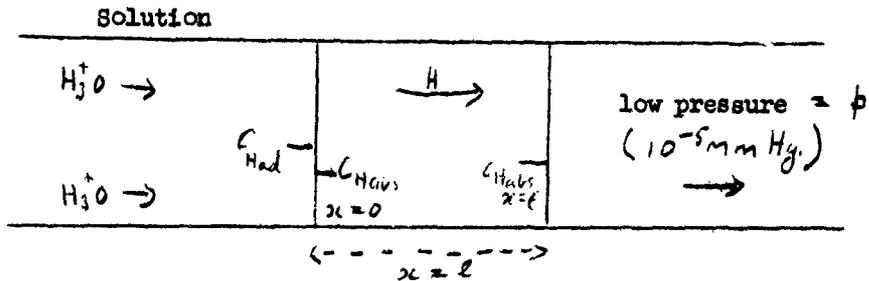
Table II

PERMEATION OF ELECTROLYTIC H AS A FUNCTION OF CURRENT DENSITYDEPENDENCE ON MECHANISM:

Slow Step	Tafel Slope at 25°C	Permeation - Current Relation	Qualitative Coverage
A Slow discharge followed by rapid combination	0.12	$P \propto i^{1/2}$	$< 0.1$
B Slow discharge followed by rapid electrochemical desorption	0.12	P independent of i	$< 0.1$
C Rapid discharge followed by slow combination desorption	0.03	$P \propto i^{1/2}$	$< 0.1$
D Fast discharge followed by slow electrochemical desorption (low potentials)	0.04	$P \propto i^{2/3}$	$< 0.1$
E Fast discharge followed by slow electrochemical desorption (high potential)	0.12	P independent of i	$\approx 1$

It can be seen from Table II that the dependence of P on i, together with the Tafel slope, distinguishes among mechanisms except B and E. As the mechanism is associated with characteristic coverages, information on  $\theta$  can thus be obtained.

- (5): Measurement of the diffusion coefficient of H in Fe and calculation of the surface concentration during hydrogen evolution from the equilibrium between the adsorbed and absorbed H and the concentration of H just inside the metal.



The rate of passage of adsorbed atomic hydrogen from the surface into the metal is given by:

$$R_{diff.} = k_{ads} 10^{-9} \theta, \quad (40)$$

where  $k_{diff}$  is the rate constant (gram at cm.<sup>-2</sup> sec.<sup>-1</sup>) for the process,  $\theta$  is the coverage, and  $10^{-9}$  is a factor equal to the number of moles per sq. cm. on a fully covered surface. The rate of transfer of absorbed H to the surface from the layer just inside the metal is:

$$k_{abs} C_{abs} (1 - \theta) 10^{-8} \quad (41)$$

where  $C_{abs}$  is the concentration of absorbed hydrogen in gm. at/cc. just inside the metal. At equilibrium the rate of the forward and back reactions are equal, i.e.,

$$k_{ad} \theta 10^{-9} = k_{abr} C_{abs} (1 - \theta) 10^{-8} \quad (45)$$

Therefore,

$$\theta = \frac{10 \frac{k_{abs}}{k_{ads}} C_{abs}}{1 + 10 \frac{k_{abs}}{k_{ads}} C_{abs}} \quad (43)$$

Thus, a knowledge of  $\frac{k_{ads}}{k_{des}}$  (i.e., K, the equilibrium constant between the surface adsorbed and the surface adsorbed H) and  $c_{abs}$  permits the calculation of the coverage.

The term  $c_{abs}$  can be calculated as follows:

According to Fick's first law:

$$P = -D \frac{\partial c}{\partial x}$$

Where P is the permeation rate, D the diffusion constant, and  $\frac{\partial c_{abs}}{\partial x}$  is the concentration gradient. (For the permeation rate does not change with time during an experiment and therefore there is no decrease of  $\frac{\partial c}{\partial x}$  with time, i.e.,  $c_{abs}$  does not increase with time, and the initial value of  $c_{abs}$  is known to be negligible.

To a first approximation, assuming a low pressure on the low pressure side of the metal,

$$P = \frac{D}{l} c_{abs} \quad (45)$$

where l is the thickness of the metal. D can be calculated from the time,  $t_{crit}$ , taken for the steady state permeation rate to be attained.

For this condition, Barrer<sup>7</sup> showed that:

$$D = \frac{l^2}{6 t_{crit}} \quad (46)$$

The equilibrium constant K between  $H_{abs}$  and  $H_{ads}$  may be calculated as follows:

$$\Delta F^\circ = -RT \ln K \quad (47)$$

where  $\Delta F^\circ$  is the standard free energy change for the reaction H just inside the metal to H adsorbed on the surface.

$$\Delta F^\circ = \Delta H^\circ - T \Delta S^\circ \quad (48)$$

where  $\Delta H^\circ$  and  $\Delta S^\circ$  are the standard heat content, and standard entropy change of this reaction respectively. The H atoms on the surface of a metal covered with water (i.e., in contact with solution), are assumed to be

immobile. Their entropy therefore arises only from the vibrational term. Upon transfer to the interior of the metal, no change in translational degrees of freedom occur and the vibrational entropy remains constant. Hence,

$$\Delta S^\circ = 0 \quad (49)$$

Thus the standard free energy change for the reaction is

$$\Delta F^\circ = -1/2 [H_{\text{solution}} - H_{\text{adsorption}}] \quad (50)$$

The heat of solution of hydrogen in metal from the gas phase is well known, but only the heat of adsorption from the gas phase onto water free surfaces are known. The effect of the solvent on the heat of adsorption is not easy to calculate accurately, but it can be seen that the effect of the presence of water molecules on the metal surface will be to change the heat of adsorption of H in a way corresponding to that caused by increase of coverage of H on a surface, and the best approximation to the desired value would be expected to be that for  $\theta = 1$  in the gas phase adsorption.

Suppose that one makes (at identical ambient conditions, including current density) two determinations of permeation rates,  $P_1$  and  $P_2$ , respectively on two metals, one of which ('1') is a noble metal, say Pt, and the other of which ('2') is a metal, say Fe, which cannot be examined by the transient methods discussed under section AI above.

$$\frac{P_1}{P_2} = \frac{D_1 C_{\text{ads}1}}{D_2 C_{\text{ads}2}} \quad (51)$$

Hence,

$$\frac{P_1}{P_2} = \frac{D_1}{D_2} \frac{C_{\text{ads}1}}{C_{\text{ads}2}} \frac{K_2}{K_1} \quad (52)$$

where the quantities  $K$  and  $c_{\text{ads}}$  are those already defined.  $P_1/P_2$  and  $D_1/D_2$  are directly measurable. Also  $c_{\text{ads}1}$  is known from the electrolytic methods, e.g., '1' is Pt, values for which are known from the work of Breithe.<sup>8</sup> Thus,

if  $K_2/K_1$  is known  $c_{ads_2}$  can be obtained. Now  $K_2/K_1 = e^{-\frac{(\Delta F_2^\circ - \Delta F_1^\circ)}{RT}}$ , where the standard free energies are those of the reaction between bulk and surface for metals '1' and '2', respectively. Both  $\Delta F_1^\circ$  and  $\Delta F_2^\circ$  contain terms due to the effect of the adsorption of water upon the heat of adsorption of H. It seems reasonable to assume that the effect of water adsorption on the heats is to reduce them from the zero coverage value to the same degree for both metals. Thus, the correction for the effect of water on the heat of adsorption of H on the metal disappears from the expression for  $K_2/K_1$  which is thus knowable from heats of solution of  $H_2$  in the noble metal and Fe at low coverage.

(6): Measurement of the solid-liquid interfacial tension.

It is well known that by application of electrocapillary thermodynamics to Hg solution interfaces information can be obtained concerning specific adsorption at the interface.

At the present time, no methods are known whereby an absolute measurement of the interfacial tension solid-liquid can be made as a function of potential. However, the change of the solid-liquid interfacial tension can be obtained from the measurement of the contact angle between a gas bubble formed in the solution, and the metal.

In the method used by Wark and Cox<sup>9</sup>, and later by Wolstenholme and Schulman<sup>10</sup>, a gas bubble is formed at the end of a tube in the solution, and is lowered until it touches the surface of the metal. By slightly increasing or decreasing the gas pressure the bubbles can be made to advance or recede giving values of  $\theta_A$  and  $\theta_R$  for the contact angle.

When the surface of the metal is absolutely smooth a value  $\theta_E$  intermediate between  $\theta_A$  and  $\theta_R$  can be obtained by gently vibrating the apparatus after bringing the bubble into the advancing position. This is an equilibrium value, which with smooth surfaces is the same whether from an advancing or

receding position.

The contact angle  $\theta$  is related to the tension of the interfaces,  $g\gamma_l$ , (gas/liquid),  $g\gamma_s$ , (gas/solid),  $l\gamma_s$ , (liquid/solid), by the equation<sup>10a</sup>

$$\cos \theta = \frac{g\gamma_s - l\gamma_s}{g\gamma_l} \quad (53)$$

can be determined by means of the capillary rise method, and  $l\gamma_s$  by means of the bubble (contact angle) method.

Frumkin and others<sup>11</sup> applied this method to a study of the Hg- solution interface (to which results were already known by normal electrocapillary method) and obtained excellent agreement with electrocapillary measurements. However, when they applied the method to the solid-solution interface, the surface tension became independent of potential. It was suggested that this was due to a film of liquid which prevented gas-solid contact.

Uddin, Schäfer and Wulff<sup>12</sup> measured the solid-gas surface tensions at Cu and Ag wires in various ambient atmospheres. Their method depends upon measuring the extension of a wire upon addition of a series of weights, the extension being a function of the solid-gas interfacial tension. Exploratory calculations were made for this method and show that the expected extension would be in the micronrange at ordinary temperatures. Further, it was found that the temperature constancy required to obtain significant results for a wire of some 10 ft. in length is greater than 0.001°C. The extensions expected for weights for which the metal would remain in the elastic range would be less than those caused by the temperature fluctuations.

Rehbinder and Wenstrom<sup>13</sup> showed that the plot of the logarithmic decrement of a pendulum, the point of suspension of which is in contact with a metal through an electrolytic solution, is dependent upon potential in a way which is similar to that of an electrocapillary curve. Bockris and Parry Jones<sup>14</sup> showed that this relation did not depend on surface hardness,

(as claimed by Reh binder and Wenstrom<sup>13</sup>), but upon the variation of friction with potential. Staicopoulos<sup>15</sup> examined the method in the presence of organic substances, and attempted to deduce their adsorption from the variation of the logarithmic decrement with potential and concentration. However, this method does not present a sound method for adsorption determinations because there is no firm thermodynamic relation between the logarithmic decrement and potential, so that the electrocapillary thermodynamics cannot be applied.

A further possibility might exist from the observation of the deformation of a thin membrane sealed to the end of a glass tube in contact with the solution. If the membrane were sufficiently thin it would distort due to the electrostatic force caused by the surface charge density induced upon the interface. This distortion would be analogous to the change of position of the liquid in an electrocapillarometer. It would be balanced by the change in solid-liquid surface tensions, which would be a function of the difference in free surface energy between water covered and H- covered surfaces.

For a "membrane bubble" of radius 0.1 cm., the excess pressure is  $= 2000 \text{ dynes cm.}^{-2}$ , if the  $\gamma$  value is  $100 \text{ dynes cm.}^{-1}$ , an appropriate order of magnitude. This pressure is thus equivalent to about 2 grams. wt. on 1 sq. cm. Calculation showed that such a magnitude would cause a displacement of a membrane of thickness  $10^{-2}$  cms. by about  $10^{-4}$  cms. An optical lever would be applicable.

In order to apply electrocapillary thermodynamics, to such a system, and thus to obtain the Gibbs surface excess of adsorbed H, it is necessary to observe the variation of the surface tension of the metal-solution interface with potential. The electric tension is  $2\pi\sigma\zeta^2$  and if  $\sigma = 10^{-6}$  coulombs per sq. cm., and  $\zeta = 4$ ,  $P = 6 \times (10^{-6})^2 \cdot 4.3 \times 10^9 \text{ dynes cm.}^{-2} \approx 1 \text{ dyne sq. cm.}$  This electric tension is thus several orders of magnitude less than

that of the excess pressure due to a membrane of reasonable radius and therefore the  $\gamma$  - potential relation could not in practice be observed and the electrocapillary thermodynamics would thus not be applicable.

This method is to be considered further, because measurement of the Gibbs surface excess can be achieved in electrocapillary thermodynamics if the surface tension-solution concentration relation is observable at a given potential. (Although the detailed information available from full electrocapillary thermodynamics is not thus available).

(7): Optical methods.

Electron diffraction was used many years ago to measure the degree of coverage of Ni catalysts with atomic hydrogen by Davisson and Germer<sup>16</sup>. The work is discussed by Trappnell.<sup>17</sup> Literature search shows no further references. The method will not be considered further because of the difficulty of distinction between adsorbed hydrogen and adsorbed water.

Similar difficulties apply to all other optical methods, including that of the reflection of polarized light.<sup>18</sup>

(8): Use of tracers.

Tracer measurements with tritium were considered in the context of a program in this department for measuring adsorption at the solid-solution interface of ions from solution. Exchange with the water would, however, make the adsorbed water and tritium indistinguishable.

(B): EXPERIMENTAL INVESTIGATIONS

I. Introduction

The evaluation of five new methods which may be used for the determination of the fraction of a monolayer of hydrogen present on a metal during electrolytic evolution indicates that methods II, 1, 4 and 5 have direct application to the determination of this quantity on transition metals which dissolve in

acid solutions (method II, 1, may not be applied to the metal during net current flow). Of these, method II 4 and II.5 were chosen as being experimentally more accessible than method II, 1, which requires extensive preliminary investigations concerning the appropriate time of passage of the moving wire in the solution.

It is known<sup>19</sup> that the mechanism of hydrogen evolution is considerably effected by the presence of capillary active trace impurities in the solution; and that these may bring about a change in mechanism<sup>20</sup> from combinative desorption to an electrochemical desorption, thus causing changes in the order of magnitude of  $\theta$ . Further experiments carried out on contaminated metal surfaces in solution are clearly not comparable with those of other experimenters. The technique involved in attaining satisfactory conditions of lack of contamination are, however, involved and laborious. They require extensive equipment. Consequently, it was decided to evaluate experimentally the method II, 4 and II, 5 with the more simple set ups possible if contamination is not to be avoided. Such experiments also give information concerning permeation and diffusion under typical conditions met in practice. The present report concerns this phase of the work and the evaluation and construction of the method for use under fully controlled conditions at the metal-solution interface.

The systems chosen are a series of metals in 0.1 aqueous N HCl. The latter solution represents a suitable compromise between the desirable tendency to reduce the corrosion rates of e.g., Fe, and thus allows investigation down to c.d.'s of the order of milliamps; and the desirable tendency to have solutions of relatively high conductance, and thus reduce disturbing heating effects at the interface.

Iron was chosen for three reasons: (i): The permeation rate is particularly large; (ii): The metal is of special practical interest because of

its embrittlement properties and the practical consequence thereof; (iii): Fe is a transition metal roughly "in the middle" of a series of metals to which particular attention has recently been devoted in respect of the mechanism of the hydrogen evolution reaction,<sup>21</sup> and for which it is generally agreed that the mechanism is common.

Pd, Ni, Cu, Ta, Ti, U were chosen because it is well known that these metals absorb hydrogen well<sup>22</sup> and their swelling and embrittlement during the evolution of hydrogen has been qualitatively observed.

II: Previous work on permeation of electrolytic hydrogen through metals.

The permeation of electrolytic hydrogen as a function of current density through iron was first investigated by Bodenstein<sup>23</sup> who found the relation  $P = k I^{1/2}$  where P is the permeation rate, and I is the current density. Borelius and Lindblom,<sup>24</sup> however, showed that over a wide range of current densities the relationship is  $P = k (I^{1/2} - I_t^{1/2})$  where  $I_t$  is a threshold current density below which there is no permeation of electrolytic hydrogen. Aten and Zieren,<sup>25</sup> Korber and Ploum,<sup>26</sup> Baukloh and Zimmermann<sup>27</sup>, and Smithells and Ransley,<sup>28</sup> carried out measurements of P, but not as a function of I.

The rate of permeation, more recently, of electrolytic hydrogen through mild steel, palladium, nickel, cobalt, copper, zinc, silver, platinum and lead was investigated by Heath<sup>29</sup> who found that only iron and palladium were permeable to electrolytic hydrogen and that the permeation rate is proportional to the square root of the current density and inversely proportional to the thickness. Wahlin and Haumann<sup>31</sup> investigated the permeation rates of H<sub>2</sub> through iron, palladium, aluminum, copper, molybdenum, cobalt, gold, silver, nickel, platinum, tantalum, and niobium, but no relationship between permeation rate and current density was found. Similarly, Ewing and Ubbelohde<sup>32</sup> measured the permeation rate of electrolytic hydrogen through iron (current density range 0.2 - 2.5 amp cm.<sup>-2</sup>), at temperature between 90 - 170°C. They found

that their results could be represented by the relationship  $P = KI^n \exp(-E/RT)$  where K and n are constants. Over the temperature range studied  $E = 7.9 \text{ KCal mole}^{-1}$  and at  $90^\circ\text{C}$ ,  $n = 0.18$ .

In recent years, several examinations have been made of the "transfer of overpotential." (Refs. 33, 34, 35, 36). A general result of such measurements is an extreme sensitivity to capillary active substances on the solution side of the electrode and apparently different in dependence on the effect of the substances on the diffusion through the metal and on the rate of the h.e.r.

In Summary, investigation of passed work in this field shows that: (i) Of the several investigations of the dependence of P on I for Fe, only two are concordant (Bodenstein,<sup>23</sup> 1922 and Heath,<sup>29</sup> 1952), whilst in other, and more recent investigations,  $dP/dI = 0 - 0.7$ , and is widely discrepant. (ii): No attempt has been recorded of investigation of the significance of these discrepancies, in particular, the dependence on surface contamination and the composition of the iron alloy used. (iii): Values of  $dP/dI$  for other metals (except the value of Heath for Pd<sup>29</sup>) are not known. That for Pd is discrepant with investigations of the mechanism of hydrogen evolution on that metal.<sup>37</sup>

It has been shown in this report that the value of  $dP/dI$  is characteristic of the surface coverage, a relation not previously stated. The evaluation of this coefficient under properly controlled conditions is consequently regarded as offering data of significance to the order of magnitude determination of surface coverage of a metal with H and under conditions for which the metal corrodes in the absence of cathodic current under an applied e.m.f.).

### III: Experimental Techniques.

#### (1): Requirements for sensitive permeation measurements

An aim of the present work is to utilize the information regarding coverage with H which can be obtained from permeation measurements for a wide

variety of metals. It was hence considered necessary to evolve equipment sensitive enough to cover the range of expected permeation rates through a representative series of metals, particularly in the transition group, where the surface coverage has probably the same order but is at present ambiguous.

The problem arises as to how order estimates of the likely permeation rate can be made, in order that the required sensitivity limits can be ascertained. Extensive data is available from gas phase diffusion at high temperatures. In the following method of estimation, it is assumed that the relative values of the electrolytic permeation rates at room temperature will be in the same ratio as that of the P values from the gas phase work, recalculated to room temperature. It is clear that the same law may not be followed over this extrapolation. In cases for which a comparison is possible, the method proved to be correct to one order of magnitude.\*

Then, from the data of Smithells and Ransley,<sup>28</sup> Ham<sup>38</sup> and Barrer,<sup>39</sup> one has (for the relation  $P = P_0 e^{-E/RT}$ ):

Metal	$P_0$ cc. mm. sec <sup>-1</sup> cm <sup>-2</sup>	E Kcal/g.at.
Pd	$3 \times 10^{-2}$	10.5
Fe	$1.63 \times 10^{-3}$	9.6
Ni	$1.44 \times 10^{-2}$	13.3
Cu	$2.3 \times 10^{-2}$	16.6
Mo	$0.93 \times 10^{-2}$	20.2
Pt	$1.18 \times 10^{-2}$	18

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\* The experimental results presented below verified this assumption and show that, roughly,  $\frac{P_{i,sol}^n}{P_{i,gas}} = 10^5$

At 298° K the P values calculated from this data are:

Metal	$P_{298^{\circ}\text{C}}$ cc. mm. sec <sup>-1</sup> cm <sup>-2</sup>
Pd	$1.4 \times 10^{-9}$
Fe	$3 \times 10^{-11}$
Ni	$3 \times 10^{-13}$
Cu	$2 \times 10^{-15}$
Mo	$2.8 \times 10^{-17}$
Pt	$4 \times 10^{-17}$

A rough value of the permeation coefficient of H<sub>2</sub> in Fe at 25°C was calculated from the values of Heath,<sup>29</sup> expressed in ccs. mm. cm<sup>-2</sup> sec<sup>-1</sup>, as  $2.32 \times 10^{-6}$ . Thus, the estimated value for P<sub>H</sub> for Pt in aqueous acid solution is, therefore given by:

$$\begin{aligned} (P_{\text{H,pT}})_{\text{sol}^n} &= (P_{\text{H,Fe}})_{\text{sol}^n} \frac{(P_{\text{H,Pt}})_{\text{gas}, 25^{\circ}}}{(P_{\text{H,Fe}})_{\text{gas}, 25^{\circ}}} \\ &= 2.3 \times 10^{-6} \frac{0.4 \times 10^{-16}}{0.3 \times 10^{-10}} \\ &= 3 \times 10^{-12} \text{ ccs. mm. sec}^{-1} \text{ cm}^{-2} \end{aligned}$$

Calculations of this type, carried out for a representative series of metals, showed that the range which might be required would be from about  $10^{-6}$  to  $10^{-12}$  ccs. mm. cm<sup>-2</sup> sec<sup>-1</sup>. Thus the throughput in molecules sec<sup>-1</sup> cm<sup>-2</sup> is:

$$\frac{3 \times 10^{-12} \times 6 \times 10^{23}}{2 \times 10^4} = 9 \times 10^7 \text{ molecules sec}^{-1} \\ 5 \times 10^9 \text{ molecules min}^{-1} \text{ cm}^{-2}$$

It is desirable to make readings at minute intervals. The sensitivities of various methods of measuring low pressure is given in Table III.

Table III

SENSITIVITY OF METHODS OF MEASURING SMALL AMOUNTS OF GAS\*

	<u>Smallest amount of H measurable</u>
Ionization Gauge:	$3.10^9$ molecules/cc
Dynacon Electrometer ( $H^3$ ):	$3.10^8$ molecules/cc
Mass Spectrometer:	$3.10^6$ molecules/cc

The problem is just on the limit of measurement with an ionization gauge, but the fact that the figures chosen in the estimation have referred to the most stringent requirements indicates that this method may be suitable for all the metals to be examined.

However, the use of an ionization gauge to give measurements in the region of  $10^{-7}$  -  $10^{-8}$  mm. of Hg predicates the existance of vacuum systems which can be brought to pressures of about 1/10th of the pressure to be measured, i.e.  $10^{-8}$  -  $10^{-9}$  mm Hg. To this end a "Vac Ion" pump (VA 1402) with a pumping capacity of 10 l/sec. at  $10^{-7}$  mm Hg and capable of evacuating volumes of the order of 1 liter to  $10^{-10}$  mm Hg was obtained and tested to find out under what conditions such low pressures could be attained.

(2): Testing of low pressure system.

The essential components of a Vac-Ion pump are shown in Fig. (6). An anode grid of large surface area is surrounded on both sides by two cold cathode plates of titanium. The electrode assembly is contained inside a stainless steel compartment with vacuum welded joints. A voltage of up to 3 KV can be applied between the anode and cathode plates which are contained in a magnetic field provided by a strong permanent magnet on the outside of the containing envelope. In operation of the pump an initial pressure of 15 - 20  $\mu$ Hg is produced by a rotary oil pump which is isolated when the power has been applied to the anode.

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\* Under conditions in which the minimum pressure is  $10^{-8}$  mm Hg.

The working limits of the pump were established on two types of systems. In the first (Fig. 7) a test volume (capacity 700 cc) of glass was connected to the Vac-Ion pump by a Kovar seal and a stainless steel flange in which the vacuum seal was an annealed copper washer. The test volume was also connected to a rotary oil pump through a greased vacuum stopcock (Apiezon L grease, vap. pressure  $10^{-11}$  mm Hg). Before assembly all the metal parts were polished, and the glass pickled in chromic-sulphuric acid mixture, washed in conductance water, and carefully dried. The whole volume was initially evacuated to 3  $\mu$  Hg by the rotary pump which was isolated after applying power to the "Vac Ion" pump. The pressure in the test volume was measured by a DPM 36 ionization gauge (VGIA tube) connected in series with a Kintel microammeter on which pressures down to  $10^{-8}$  mm Hg could be read. The pressure in the pump itself was assessed from a calibration curve supplied by the manufacturers, and from a knowledge of the ion current read off a gauge on the power supply. The pressure readings with time are shown in Table IV.

Table IV

RESULTS OF TEST OF VAC ION AND DPM GAUGE IN VACUA TO  $10^{-8}$  mm. Hg

<u>Time interval from switching on Vac Ion</u>	<u>Pressure DPM 36 Gauge</u>	<u>Pressure Vac Ion</u>
<u>hrs.</u>	<u>mm. Hg</u>	<u>mm. Hg</u>
1/2	$2.2 \times 10^{-6}$	$5 \times 10^{-7}$
10	$1.4 \times 10^{-7}$	$8 \times 10^{-8}$
13 1/2	$1.4 \times 10^{-7}$	$8 \times 10^{-8}$
22	$1.3 \times 10^{-7}$	$6 \times 10^{-8}$
44 1/2	$1.2 \times 10^{-7}$	$4 \times 10^{-8}$
57	$8 \times 10^{-8}$	$3 \times 10^{-8}$

The second system examined was identical with the first except that the vacuum stopcock was eliminated. Connection between the system and the rotary pump was made through a constricted tube which could be closed by fusion under vacuum. During the initial evacuation by the rotary pump the test volume and flange were heated 350°C by heating tapes for 17 1/2 hours. The "Vac Ion" pump was started up, and the constriction sealed off in the manner described. Heating of the glass parts was continued for a further period of 49 hours. Pressure readings with time are given in Table V.

The results in Table IV indicate that the "Vac Ion" pump is capable of producing pressures as low as  $10^{-8}$  mm Hg in a system containing a low vapour pressure grease. The results in Table V show that if grease is eliminated,

Table V

RESULTS OF TEST OF VAC ION AND DPM GAUGE IN VACUA TO  $10^{-10}$  mms. Hg

Time interval from switching on Vac Ion	Temperature	Pressure DPM 36 Gauge	Pressure Vac Ion
1/2 hour	350°C	$3.6 \times 10^{-6}$ mm Hg	$10^{-6}$ mm Hg
1		$10^{-6}$	$3 \times 10^{-7}$
6		$2.6 \times 10^{-7}$	$10^{-7}$
15 1/2		$3 \times 10^{-7}$	$10^{-7}$
24 1/2		$1.4 \times 10^{-7}$	$8 \times 10^{-8}$
29		$10^{-7}$	$7 \times 10^{-8}$
49	Started to cool	$3.3 \times 10^{-8}$	$1.5 \times 10^{-8}$
57 1/2	80°C	$10^{-8}$	$10^{-9}$ mm Hg
76	Room temperature	$10^{-8}$	$10^{-10}$ mm Hg

and gassing of the tubes is facilitated by baking at 300°C for periods of 75 hours the systems set up makes it possible to attain pressures of  $10^{-10}$  mm Hg.

(3): Initial systems used in permeation experiments.

The successful development of the low pressure vacuum systems and pressure measurement to  $10^{-10}$  mms. Hg was followed by development of techniques for the permeation measurements. During this work, higher pressure ( $10^{-7}$  mms. Hg) were used, and the metal was SAE 1010 steel. In the course of this development, it was found possible to make crude exploratory measurements with U, Ta, Ti, Cu, Ni.

(4): Technique of exploratory permeation measurements.

(i) Vacuum system

The vacuum system consisted of a manifold 3 cm. diameter tube, 1.5 meter long, which could be evacuated to  $10^{-7}$  mm Hg. by a two stage mercury diffusion pump, backed by a rotary oil pump. The high pressure side of the diffusion pump is connected to a 5 l. bulb which could be used as a fore pump instead of the rotary oil pump. Such a system works well for long periods so long as the pressure on the 5 l. bulb remains at least a power of ten less than the minimum pressure (0.1 mm Hg) required to back the diffusion pump. (This eliminates pump wear ). Pressures down to  $10^{-7}$  mm Hg on the manifold were measured on a PHG 09 ionization gauge. Continuous evacuation of the manifold during the period of this work was found to be necessary to avoid the possibility of readsorption of gases by the walls of the system, and by the grease.

(ii) Electrodes

The material under consideration was fabricated in the form of a disc 1.3 cm diameter, 0.5 mm thickness which was silver soldered to a Kovar tube of the same diameter. The tube was joined to a Kovar glass tube by a house-keeper seal, which was in turn joined to a pyrex glass tube by a graded seal. The cathode assembly was tested for vacuum tightness by incorporating it in a system of approximately 100 cc capacity (A in Fig.(8)) which could be

evacuated through a greased vacuum stopcock. The pressure in the volume A was measured by a Stokes TP5 vacuum gauge. After several hours of evacuation, A was isolated from the line, and the pressure was measured at five minute intervals. The nature of the plot of  $p$  against  $t$  clearly indicates whether the pressure increase with time is due to a leak or to outgassing of the walls of the system. (A linear plot of  $p$  against  $t$  indicates a leak). This can be confirmed by enclosing the suspected area of the leak in an atmosphere of  $H_2$  gas, which results in a sudden increased rate of change of  $p$  with  $t$ . An exponential change of  $p$  with  $t$  indicates outgassing of the walls. The two types of behaviour are shown in Fig. (9).

Electrical contact with the disc is made with Pt wire wrapped round the Kovar tube. The Kovar tube and Pt wire are coated with Apiezon wax such that only the metal disc is available for contact with the solution.

Metals such as Ti, Ta, and U, which are difficult to silver-solder to kovar metal, can be waxed directly to a glass tube. It was found that the seal was able to withstand satisfactorily a vacuum of  $10^{-7}$  mm. Hg with practice. Before final connection of the electrodes to the volume A, the internal surfaces were cleaned mechanically by the use of an abrasive, and finally pickled in concentrated HCl, washed with water, and then carefully dried. The external surface of the metal disc was polished with fine emery paper just before use.

#### (11) Cell

The cell Fig. (8) consisted of 1 l. beaker to which has been attached an anode compartment, and a cooling coil. The anode compartment was connected to the rest of the cell through two holes at the lower end. The anode consisted of a piece of Pt foil 1 Cm. square, which was connected to a electrical circuit by a Pt lead. The electrolyte was stirred by a glass propeller. The  $H_2$  overpotential at the cathode was measured against a

saturated calomel electrode.

(iv) Procedure

The electrode compartment A was assembled as described in section (ii), and evacuated to  $10^{-7}$  mm Hg for 24 hours. Tap T was closed to isolate A from the line, and the pressure change at 5 min. intervals recorded. If the rate of outgassing was negligibly small, the cathode surface was polished, and the cell raised into position. The cell was then filled with N/10 HCl solution and the current is switched on. Pressure readings are recorded at 2 min. intervals, until the steady state permeation conditions have been attained. Experiments were carried out over the current density range  $10^{-4}$  - amp. sq. cm<sup>-1</sup>. At the lower current densities, where there is little evolution of hydrogen, vigorous agitation of the electrolyte was necessary to facilitate the removal of gas bubbles from the metal surface. At current densities between 0.5 and 1 amp. cm<sup>-2</sup>, there was a marked heating of the electrolyte. The temperature was kept down by circulating ice water through the cooling coil. The simple anode compartment used in the cell described here was effective in removing cathode depolarization.

IV: (1) Results

In fig. 10 is shown a typical plot of increasing H<sub>2</sub> pressure as recorded on the vacuum gauge on the electrode assembly A in Fig. (8). Such plots were preceded by a test of pressure constancy over a time of 2-3 hours.

Fig. 11 gives a summary of the permeation data for H<sub>2</sub> on SAE 1010 steel, in 0.1 N HCl (without decontamination) as a function of current density. The data comprise the results from some thirty five independent runs. The least square analysis shows:

$$\frac{\log P}{\log I} = 0.52 \pm 0.07$$

In Fig. 12, similar data is summarized for Pd in 0.1 N HCl. The least squares analysis shows:

$$\frac{\log P}{\log I} = 0.6 \pm 0.04$$

Measurements of hydrogen overpotential on Fe (fig. 13) show an exchange c.d. of  $6.10^{-6}$  is in excellent agreement with the recent measurements of D. F. A Koch.<sup>40</sup>

Figs. 14 and 15 give the  $p - t$  data for Ni and Cu; and fig. 16 gives the change of pressure with time on the diffusion side after charging  $T_a, T_i$  &  $t$  for some 4 hours. (Parameters, and derived diffusion coefficients are given in Table VII).

A sample calculation of  $p$  is given: the plot of  $p$  with time shown in Fig. 10 was obtained for a cylindrical cathode (6.35 length, 1.3 cm diameter and 0.38 mm wall thickness) of 1010 steel immersed in the electrolyte to a depth of 1 cm. Thus, the change in the number of moles of  $H_2$  in the electrode assembly A with time is given by

$$\frac{dn}{dt} = \frac{V}{RT} \frac{dp}{dt}$$

where  $T$  is the absolute temperature,  $R$  the gas constant and  $V$  the volume of electrode assembly A (Fig. 8).  $\frac{dp}{dt}$  is the change of pressure in the volume A with time in the steady state.

The permeation rate  $P$  is given by

$$P = \frac{dn}{dt} \times \frac{l}{a} \quad (52)$$

where  $l$  is the thickness, and  $a$  is the area of the electrode immersed in the electrolyte.

Volume of section A in Fig. 8 = 109.7 cc

Area of immersion = 6.14 sq. cm.

Slope = 3  $\mu$  /min.

$$T = 300^{\circ}\text{C}$$

$$R = 82.05 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\text{Thickness} = 0.38 \text{ mm.}$$

Permeation rate

$$P = \frac{108.7 \times 3 \times 10^{-3} \times 0.38}{82.05 \times 300 \times 760 \times 60 \times 4.76}$$

$$= 0.18 \times 10^{-10} \text{ mole mm sec}^{-1} \text{ cm}^{-2}$$

#### IV: (2) Discussion

In the contaminated solutions used, fig. (11) indicates that  $P = KI^{1/2}$  for SAE 1010 steel. Reference to table (II) shows that this result is consistent only with a mechanism for the hydrogen evolution reaction on Fe for 0.1 n HCl of slow proton transfer followed by rapid combinative desorption. This conclusion indicates qualitatively that the coverage of adsorbed H on the metal is low (i.e., about one tenth).

A quantitative attempt to calculate this coverage may be made by the method described in section (A II (5)).

In a typical experiment with SAE 1010 steel,  $P = 4 \times 10^{-10} \text{ gm at sec.}^{-1} \text{ cm}^{-2}$  at a current density of 1 amp  $\text{cm}^{-2}$ .  $l = 0.055 \text{ cm}$ .  $t_{\text{rit}} = 2.3 \text{ min}$ . From (46),  $D = 4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ . (For comparison with other values see table VII.) Hence from (45),  $c_{\text{obs}} = 5.5 \times 10^{-6} \text{ gm at cc}^{-1}$ . The heat of solution of  $\text{H}_2$  in iron is 7.0 KCal. mole.<sup>41</sup>

The heat of adsorption of hydrogen on Cu, Ni, W, and Fe for different surface coverage are given in table (VI). As discussed in section A II 5, the uncertainty due to the water correction will be least on a fully covered surface in the gas phase adsorption.

For iron three values are recorded for a fully covered surface. The values of Morozov<sup>49</sup> and Kwan<sup>46</sup> are in fair agreement but differ considerably from that of Beeck.<sup>47</sup> The value of Morozov<sup>49</sup> has been chosen for the calculation presented here.

The heat of adsorption of H<sub>2</sub> in Fe on a fully covered surface is -6 KCal/mole<sup>-1</sup> (Morozov).<sup>48</sup>

$$\begin{aligned}\Delta H^\circ &= -1/2 (7 - (-6)) \\ &= -6.5 \text{ KCal gm at}^{-1}\end{aligned}$$

The standard entropy change for the transfer surface to metal interior calculated in section A II, 5 is zero.

$$\Delta F^\circ = -6.5$$

and

$$\therefore \frac{k}{k} = 10^{\frac{6.5}{1.78 \times 2.303} \times \frac{1000}{300}} = 10^{4.4}$$

$$\theta = \frac{10 \times 10^{4.4} \times 5.5 \times 10^{-6}}{1 + 10 \times 10^{4.4} \times 5.5 \times 10^{-6}} = 0.6$$

This order of magnitude of  $\theta$  is not inconsistent with the indications of the  $\frac{dP}{dI}$  method, which would have led to the expectation  $\theta < 0.2$ . The value calculated on the above method in the region  $0.9 > \theta > 0.1$  is highly sensitive to the value of the parameters used (e.g. heat of solution of H<sub>2</sub> in Fe).

For Pd, the result of  $\frac{dP}{dI} = 0.6$  is a reasonable approximation to the value of  $n = 0.67$  required by the electrochemical desorption mechanism under conditions of low coverage.

The results on Ti, Ta and U illustrate for the first time electrolytic permeation through these metals. The results are as yet insufficient for discussion.

Table VI

HEATS OF ADSORPTION OF HYDROGEN AS A FUNCTION OF METAL AND COVERAGE

<u>Author</u>	<u>Metal</u>	<u>Condition</u>	<u>-H<sub>ads</sub>* KCal/mole</u>
Ward <sup>6</sup>	Cooper	-	9
Iijima <sup>42</sup>	Nickel	-	16
		on surface contaminated with oxygen	6
Roberts <sup>43</sup>	Tungsten	Coverage 0	45
		" 1	18
Rideal and Trapnell <sup>44</sup>		" 70%	14
		" 75%	11
		" 80%	7
		" 85%	3
		" 90%	2
Kwan <sup>46</sup>	Iron	low pressure	17
		high pressure	5
Beeck <sup>45</sup>	Iron	low coverage	45
		full coverage	15
Kwan <sup>48</sup>	Iron	Coverage 0.01	17
		" 0.1	5
Morozov <sup>49</sup>	Iron	low coverage	9
		high coverage	6

\* H<sub>ads</sub> is the heat content charge accompanying adsorption of gas from the gas phase onto the metal surface.

It is possible to calculate  $D$ , the diffusion coefficient from the value of  $t = t_{crit.}$  corresponding to the extrapolated linear section of the  $p-t$  relation. Results are shown in table VII.

Table VII

VALUE OF DIFFUSION COEFFICIENTS

Metal	$D(\text{cm}^2 \text{ sec}^{-1})$	Lit. values
Fe	$1.5 \times 10^{-6}$	$2 \times 10^{-6}$ <sup>36</sup>
Pd	$7.3 \times 10^{-7}$	$2 \times 10^{-6}$ <sup>50</sup>
Ni	$7.6 \times 10^{-9}$	
Cu	$1 \times 10^{-8}$	

V: Investigation of Permeation Under High Purity Conditions

(1): Introduction

It has been shown that the rate of permeation of electrolytic H through metals is highly sensitive to small traces of surface contaminants.<sup>51</sup> It is therefore necessary to obtain a state in which the electrodes surface is "clean." This necessity arises not only because of the need to make investigations in a standard state but also to find a "zero position" in the investigation of the effect of capillary active substances on the permeation rate.

It is known from work on the hydrogen evolution kinetics that such work is difficult to carry out and to obtain satisfactory conditions two preliminary investigations were necessary.

(2): Investigation of the effect of cleaning of an Fe surface in H<sub>2</sub> on a subsequent diffusion process.

The technique for the preparation of the Fe electrode surfaces has already been evaluated by D. F. A. Koch<sup>40</sup> and involved reduction of the surface in H<sub>2</sub>. It was desired to utilize essentially this technique in the

permeation work so that results would be comparable with those obtained in a parallel study of the hydrogen evolution on Fe. However, the technique could not be taken over without investigation because of the necessity of establishing that  $H_2$  diffused in from the gas phase during the cleaning process can be essentially removed by subsequent evacuation.

The direct object of the experiment described here is to establish that when cooling an Fe cylinder from some  $800^\circ C$  in contact on one side with  $H_2$  gas at 1 At. and evacuated on the other at a certain rate, the equilibrium  $H_2$  solubility (or less) for the given temperatures is maintained. If it can be proved that a given procedure of evacuation reduces the quantity of  $H_2$  present to a value less than that observed during permeation, the process of degassing is satisfactory.

To do this, steel cylinders were heated to  $800^\circ C$  with the outside surface in contact with  $H_2$ , the inside being evacuated. The cylinder was cooled over a time of about 3 hrs. to  $340^\circ C$  and the gas in contact with the outer surface changed to Ar. The temperature of the cylinder was then raised to  $800^\circ C$  and the evolved gases collected in an evacuated bulb, in which the pressure was followed as a function of time. A typical result of such a plot is shown in fig. 17, and the amount of  $H_2$  removed calculated per cc of Fe ( $5 \times 10^{-7}$  mole/cc) and compared with the equilibrium solubility of  $H_2$  in Fe at  $340^\circ C$  ( $5 \times 10^{-6}$  mole/cc). The amount is: (i) Some ten times less than that corresponding to the equilibrium solubility at this temperature (as is expected from the mode of contact with  $H_2$  at  $340^\circ C$ , i.e., evacuation of the inside of the cylinder); (ii) It was (hence) about  $10^2$  times less than the  $H_2$  content expected during electrolytic permeation ( $3.5 \times 10^{-5}$  mole/cc).

This process was repeated at  $120^\circ C$  with similar results and it was therefore concluded that sufficient  $H_2$  could be removed from the cylinders to avoid interference with the electrolytically permeated  $H_2$ .

A verification of this result can be obtained from the permeation rate at 340°C. This can be measured before changing the gas on the outside of the steel cylinders to Ar by collecting the evolved H<sub>2</sub> in the previously evacuated bulb where the pressure is recorded as a function of time. The results from such an experiment are shown in fig. 18. By utilizing Fick's first law and making the assumptions that the concentration just inside the metal on the vacuum side of the metal is zero, and that for small metal thicknesses the concentration gradient is linear, it is possible to calculate an approximate value of the amount of hydrogen in the bulk metal. The value found in this way accords well with the value found from the degassing experiment.

(3): Establishment of metal solution boundary

It is not possible to utilize cements, waxes, etc., to delineate the area of the electrode in contact with the solution on account of the "poisoning" effects of these agents on the electrode surface thus produced. It would be satisfactory from this point of view simply to immerse a chosen length of the electrode in the solution and assume that creep effects did not introduce a systematic lack of definition of surface area.

For this investigation three cylindrical cathodes (dimensions: length 6.33 cm., diameter 1.36 cm. OD, and 0.38 mm wall thickness) were applied in electrolysis experiments using the apparatus depicted in fig. 8. The respective depths of immersion of the cylindrical cathodes in the electrolyte were 1, 3 and 5 cm, and the current density in each case was maintained at 10<sup>-2</sup> amp cm<sup>-2</sup>. The permeation rates were measured in the manner described.

(Section B III)

In each case it was observed that the creep of electrolyte up the cathode amounted to about 1 mm above the level of the liquid level. This was probably due to a combination of the meniscus effect and turbulence on the surface of

the electrolyte caused by the motion of the stirrer. In addition to this, there was a more erratic type of creep in each case which extended 5-6 mm. above the level of the liquid and resulted in corrosion of the iron surface as evidenced by a marked discoloration.

Table VIII shows the permeation rates evaluated on the basis of the apparent and real area of immersion (real area = apparent area + area due to 1 mm. of creep). There is a strong effect of creep up the electrodes, which must therefore be allowed for in evaluation of results for any given depth of immersion.

Table VIII

EFFECT OF CREEP OF ELECTROLYTE ON THE PERMEATION RATE FOR A CYLINDRICAL

No.	Depth of immersion	Amount of visible creep	Area cm <sup>2</sup>	CATHODE		Permeation rate per sq. cm. based on immersed area (10+10)	Permeation rate per sq. cm. based on total Area	Diff. Coefficient (cm <sup>2</sup> sec <sup>-1</sup> )
				Total Area cm <sup>2</sup>	Total Current (Amp)			
1	1 cm.	1 mm.	5.71	6.14	0.043	0.26	0.23	$3 \times 10^{-6}$
2	3	1 mm.	14.23	14.66	0.14	0.19	0.18	$2 \times 10^{-6}$
3	5 cm.	1 mm.	22.75	23.18	0.23	0.10	0.10	$2 \times 10^{-6}$

(4): Technique of permeation experiments carried out under conditions of high purity.

(1): Vacuum system

The vacuum system is substantially the same as that described in section B III 4 (1).

(11): H<sub>2</sub> Purification

Cylinder hydrogen is purified from moisture, carbon monoxide, oxygen, and carbon dioxide by passing the gas over silica gel, activated hopcalite,

platinized asbestos heated to 600°C, and drierite. Volatile carbonaceous and sulfurous compounds are removed by adsorption on activated charcoal kept at liquid nitrogen temperature. Before use, moisture is removed from these materials by heating in a current of argon.

(iii): Electrodes

The two essential requirements (a) that the surface of the metal must be cleaned in H<sub>2</sub> at 800° and (b) only the metal under investigation should come into contact with the highly purified solution, precludes the use of the type of electrodes (see B III (4) (ii)) used in the preliminary investigations. An ideal type of electrode which would meet both of these requirements consists of a disc or thimble of this metal which is satisfactorily (i.e. leak proof) sealed directly to a glass tube. Several attempts were made to produce such an electrode from sheet iron, but satisfactory vacuum seals could not be produced.

Pending satisfactory development of this type of electrode, investigation were commenced on an electrode fabricated in the form of a closed cylinder of the material (length 6 to 10 cm. diameter 0.7 cm. and wall thickness 0.038 cm.). Connection of this electrode tube to the evacuable volume B, fig. (19), is made by a kovar seal, the vacuum joint being made with silver solder. Possible contamination of the electrolyte with Ni, Co, Ag and Cu from the kovar and the silver solder is minimized by immersion of the lower end of the cylinder in the electrolyte. In this case it is only necessary to subject the end of the electrode tube to high temperature H<sub>2</sub> treatment, thus reducing the possibility of breakdown of the silver soldered joint. Vacuum testing of the electrode assembly B (fig. 19) is carried out in a similar manner to that described in B II (4) (i). Electrical contact to the electrode tube is made with a nickel wire inside the tube at the silver soldered joint. The nickel wire passes up the glass slide and is welded to a W wire which is vacuumatically

sealed through the glass bulb (fig. 19).

(iv): The cell

The consideration which resulted in the cell design described below are:

- (a) For purposes of determining the diagnostic criteria it is necessary to have the permeation rates at a minimum of five values of the current density.
- (b) For each measurement of the permeation rate at a particular current density the electrode tube must be in the same initial standard state.
- (c) The electrode surface must be cleaned by reduction in hydrogen at 800°C.
- (d) The electrode assemblies must be thoroughly outgassed by continuous evacuation for several hours.
- (e) Electrolysis must be carried out in highly purified solutions.
- (f) Final purification of the electrolyte by pre-electrolysis must be carried out in the cathode compartment.
- (g) The volume of electrolyte must be kept down to a minimum to facilitate speedy purification.

It emerges from these considerations that the cell must be provided with at least five electrode assemblies. An arrangement, similar to the standard type of electrolytic cell for studying the mechanism of the hydrogen evolution reaction on metal wires was found to be impractical because of the difficulty of producing a small enough cathode compartment to house all the electrodes. As a result of this it was concluded in order to fulfill condition (g) each electrode assembly should have a separate cathode compartment. The possibility of seven such compartments having a common anode compartment was considered, but was ruled out because of overheating which would take place during simultaneous pre-electrolysis in all of the seven cathode compartments. (Total current  $\approx 10$  amps) to avoid the difficulty each cathode compartment was fitted with a separate anode compartment.

A typical unit cell is depicted in fig. (19). The electrode assembly B is essentially the same as A in fig. 8 (B III (4) (1)). In the upper position the electrode tube is contained in a furnace, where the high

temperature hydrogen pretreatment can be carried out, and the bulb B can be connected to a vacuum line. The height of the electrode assembly can be adjusted by a ground glass slide, and on disconnection from the vacuum line can be moved to a lower position such that the tip of the electrode tube reaches almost to the base of the cathode compartment. The cathode compartment is provided with a pre-electrolysis electrode attached to a ground glass slide so that it can be moved clear of the electrolyte. The anode compartment is connected through a glass sintered disc and a ground glass stopcock to the cathode compartment. Seven such unit cells are banked together side by side as depicted in fig. (20). The two outer cells are used for potential measurements against a saturated calomel electrode which has a salt bridge of purified electrolyte terminating in a Luggin capillary. The height of the electrolyte in the outer compartment is adjusted so the tip of the Luggin capillary is 1 mm. below the level of the electrolyte. For the potential measurements the electrode tube is lowered so that only the lower surface touches the surface of the electrolyte thus keeping the ohmic drop to a minimum. The initial preparation of HCl solution is carried out in a separate vessel which is connected to the cells by a manifold.

The entire ensemble is shown in photographs 1 and 2.

(5): Procedure in the high purity measurements.

(1): Cleaning of components

At the termination of each experiment, the entire cell sections, in their seven parts, were subject to emptying and washing with tap water, with particular reference to the removal of the previous solution from the sintered discs. The cells were then immersed in the Beckmann solution and allowed to remain therein for two hours. A fresh Beckmann solution was made up about every five runs.

After removing the Beckmann solution, the cells were washed with a number of (about six) rinses of equilibrium water and then allowed to stand in equilibrium water (filling the whole cell) overnight. Thereafter, the cells were once more rinsed with six changes of conductance water (conductivity  $10^{-7}$  mhos  $\text{cm}^{-1}$ ) and preserved out of contact with air, filled with conductance water.

(iii): Water

Water was obtained from the normal departmental supply of distilled water by distillation of this in a standard commercial still and then redistillation from alkaline  $\text{KMnO}_4$  with two condensations and a final distillation in a  $\text{N}_2$  atmosphere. The water thus obtained has a specific conductance of about  $5 \times 10^{-7}$  mhos  $\text{cm}^{-1}$ . It was transferred from the final vessel to a distillation vessel supplying the cells and once more distilled in  $\text{H}_2$ , the product being led to a cell in which its conductance was measured. If it is less than  $3 \times 10^{-7}$  mhos  $\text{cm}^{-1}$ , the water is accepted (in most cases, it is less than  $1 \times 10^{-7}$  mhos  $\text{cm}^{-1}$ ).

(These lower conductance values were only obtained after a few weeks of use of the vessels concerned).

(iv): Preparation of HCl

The HCl gas was produced in a pure state by utilizing Analar KCl, which is first heated to  $400^\circ\text{C}$  to remove organic traces, and then brought into contact with a controlled stream of Analar  $\text{H}_2\text{SO}_4$ . The gas is passed through two traps at  $-80^\circ\text{C}$  to remove water and other condensable materials and led into the water in the cell.

The concentration is determined conductimetrically, using a standard a.c. bridge.

(v): Preparation of the electrodes

Electrodes were mechanically polished, electropolished, and then introduced

into the  $H_2$  atmosphere at  $800^\circ C$ , and maintained in this for 20 minutes when they became bright.

(vi): Purification of solution

It has been found that the solution in measurements on the hydrogen evolution kinetics is a frequent source of contamination unless rigorously purified. (The effect is particularly strong in hydrogen permeation work). The procedure used was as follows:

The conductance water filling the cells at the end of the cell washing was displaced by  $H_2$  pressure and the highly purified water is distilled into the cell in  $H_2$ . Small quantities of water were distilled in and used for washing purposes, whereafter they were emptied from the cell through the taps  $T_d$  in fig. 19. After some 3-4 rinsings, the water is distilled into the cells in the required quantities; the HCl being subsequently introduced as described above.

The pre-electrolysis electrodes were then lowered into the solutions and electrolysis upon them commenced at about 1 amps.  $cm^{-2}$ . It can be shown that if  $c_t$  is the amount of impurity remaining after time  $t$ , and  $c_0$  the amount at  $t = 0$ ,

$$c_t = c_0 e^{-DA t / \delta v}$$

where  $D$  is the diffusion coefficient of typical capillary active substances,  $A$  the electrode area,  $\delta$  the thickness of the diffusion layer,  $v$  the volume to be purified, and  $t$  the time of passage of current. For a given system, as  $D$  is roughly the same for the likely surface contaminants,

$$c_t = c_0 e^{-K A t}$$

where  $K$  is constant, so that the area of the pre-electrolysis electrode can compensate for time of electrolysis. This was set conveniently at about 12 hours and the  $A$  value at about 2.5 sq. cms.

During passage of the current on this scavenger electrolysis, the connecting tube between cathodes and anode had to be cooled, to avoid evaporation of solution at the tops and interruption of current overnight.

At the end of pre-electrolysis, the scavenger cathode was removed whilst the current is passing and retracted into its compartment L, fig. 19. H<sub>2</sub> is passed into the cell during the whole course of the purification.

(vii): Hydrogen

This was described in IV, (ii).

(viii): Procedure

At the commencement of the run, the hydrogen overpotential was measured on two independent Fe electrodes in the compartments M and N (Fig. 20) in order to establish the overpotential c.d. relation for the given condition of solution, etc.

Thereafter, the purified electrodes, after H<sub>2</sub> treatment, were lowered in the H<sub>2</sub> atmosphere, into the electrolyte, and electrolysis commenced at a series of c.d.'s. The lower limit of c.d. is set by the rate of corrosion of Fe, the higher limit by the heating effects in the solution. The pressure increase with time was measured on the Stokes TP 3 gauges. Measurements were carried out in parallel on five electrodes.

(ix): Contaminants

The effect of capillary active agents in effecting both the rate of permeation and the hydrogen electrode kinetics will be studied by introducing controlled quantities into the closed system.

(6): Present position and immediate future work.

Measurements of P with the high purity technique are at present in their early stages.

The immediate future program consists of an evaluation of  $\frac{dP}{dI}$  under controlled conditions on five metals; the evaluation of the effect of a series

of capillary active materials upon the value of  $P$ ,  $\frac{dP}{dI}$  and surface coverage by the method of A II 5; and the measurement of the heat of adsorption of  $H_2$  in solution.

These measurements are thus aimed at quantitative H-coverage measurements on corrodable metals in acid solutions by three independent methods with variation of current density, pH and additive variables.

Text for the Figures

Fig. 1 Plot of  $i_t$  against  $t$  for the case of  $\frac{I_H}{I_{an}} > 1$ .

Fig. 2 Plot of  $i_t$  against  $t$  for the case of  $\frac{I_H}{I_{an}} < 1$ .

Fig. 3 Plot of  $\frac{i_t}{I_{an}}$  against  $(a_H)_0$ , and  $\eta$  for nickel.

Fig. 4 Apparatus for measuring directly the adsorbed hydrogen by transfer from a continuous rotating wire passing through two vessels.

Fig. 5 Apparatus for making measurements involving the addition of supplementary amounts of atomic hydrogen to the surface of an electrode.

A and B anodes  
C cathode  
D and E separate solutions

Fig. 6 Diagram of "Vac Ion" pump. A. cold cathodes; B. anode grid; C. rotary oil pump; D. power supply; E. connection to system.

Fig. 7 Apparatus for testing "Vac Ion" pump. A. "Vac Ion" pump; B. test volume; C. rotary pump; D. ionization gauge.

Fig. 8 Cell used in preliminary permeation experiments. A. electrode assembly; B. anode compartment; C. water cooling coil; D. saturated calomel reference electrode; E. vacuum gauge lead.

Fig. 9 Pressure changes in evacuated systems.

Curve (1)  $p - t$  behaviour exhibited during outgassing  
Curve (2)  $p - t$  behaviour exhibited by a leak  
AB - pressure change - air leak  
BC - pressure change -  $H_2$  leak

Fig. 10 Typical plot of pressure with time for permeation of electrolytic hydrogen through SAE 1010 steel.

Fig. 11 Plot of  $\log_{10}P$  against  $\log_{10}I$  for SAE 1010 steel. Solid line - obtained by the method of least squares.

Fig. 12 Plot of  $\log_{10}P$  against  $\log_{10}I$  for palladium. Solid line - obtained by the method of least squares.

Fig. 13 Overpotential measured against sat. calomel reference electrode against  $\log_{10}I$  for SAE 1010 steel.

Fig. 14 Plot of pressure change with time for the permeation of electrolytic  $H_2$  through nickel.

Fig. 15 Plot of pressure change with time for the permeation of electrolytic  $H_2$  through copper.

Fig. 16 Degassing of electrolytic hydrogen from titanium, tantalum and uranium.

Fig. 17 Pressure change resulting from degassing of steel cylinder surrounded by argon, and evacuated on the inside into evacuated bulb as a function of time.

AB - At  $340^{\circ}\text{C}$  CD - At  $800^{\circ}\text{C}$

Fig. 18 Pressure change with time resulting from permeation of hydrogen from gas phase through steel at  $340^{\circ}\text{C}$  into evacuated bulb as a function of time.

Fig. 19 Unit cell. L' anode compartment; M. cathode compartment; L. pre-electrolysis electrode; B. electrode assembly.

Fig. 20 Layout of cell used in permeation experiments under conditions of high purity. L' anode compartment; M. cathode compartment; S. solution preparation vessel.

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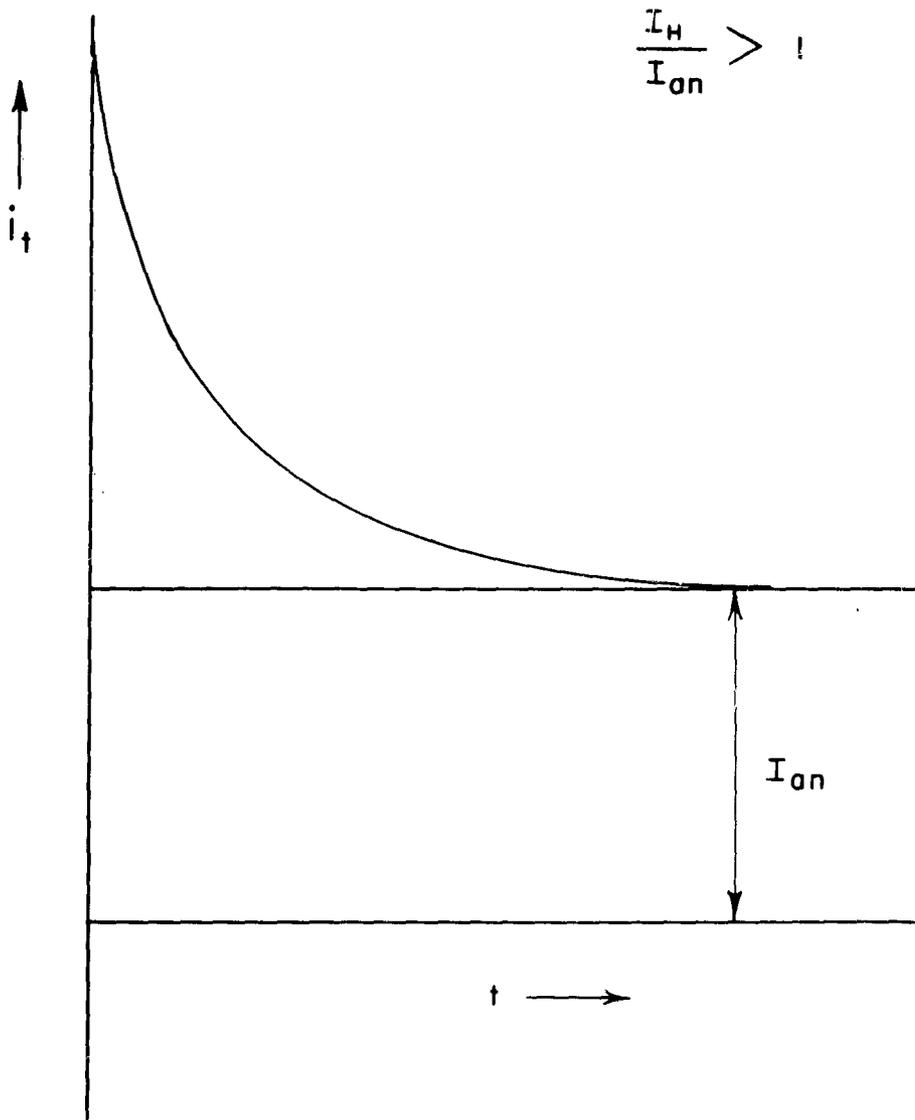


FIG. 1

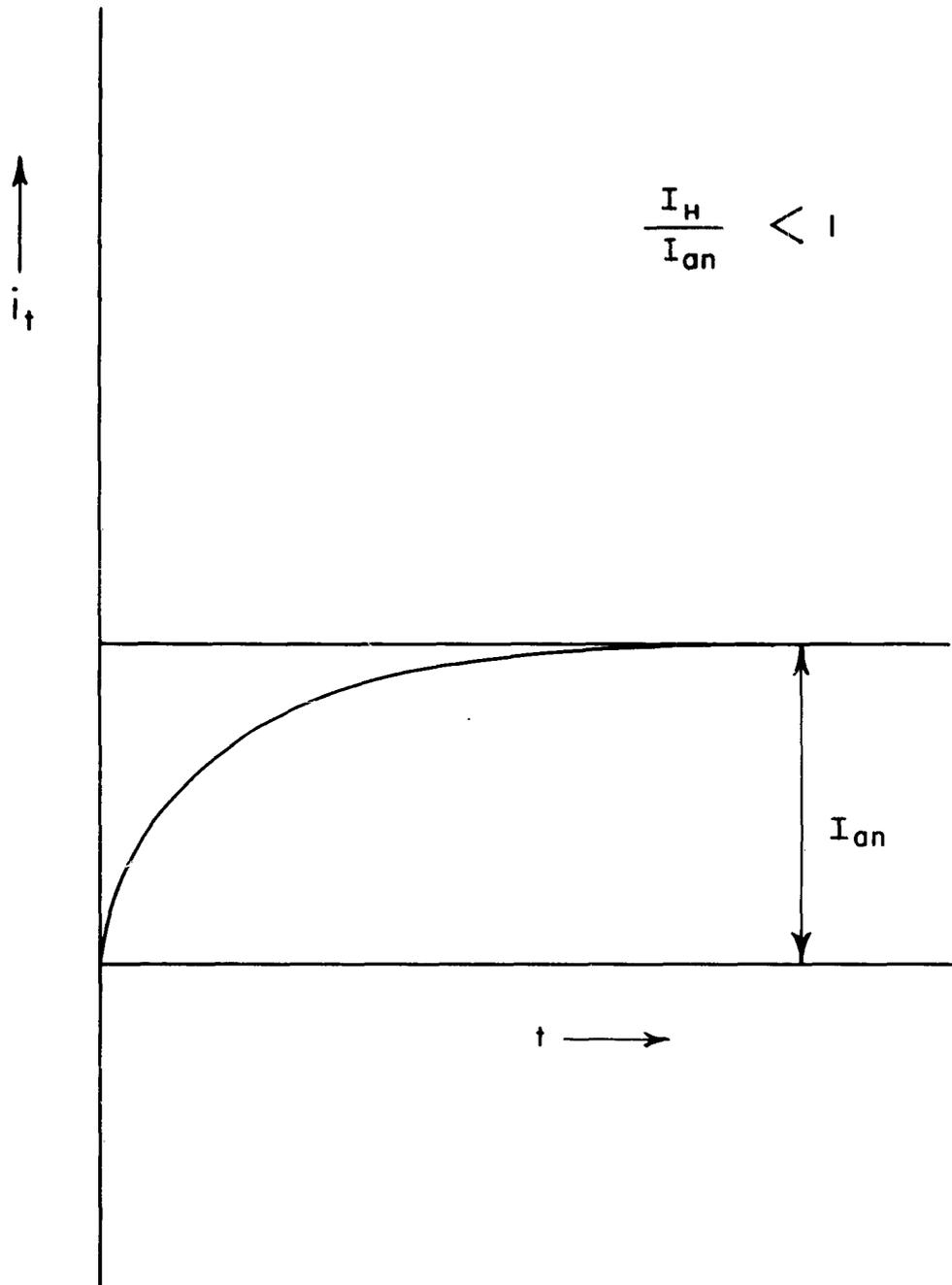


FIG. 2

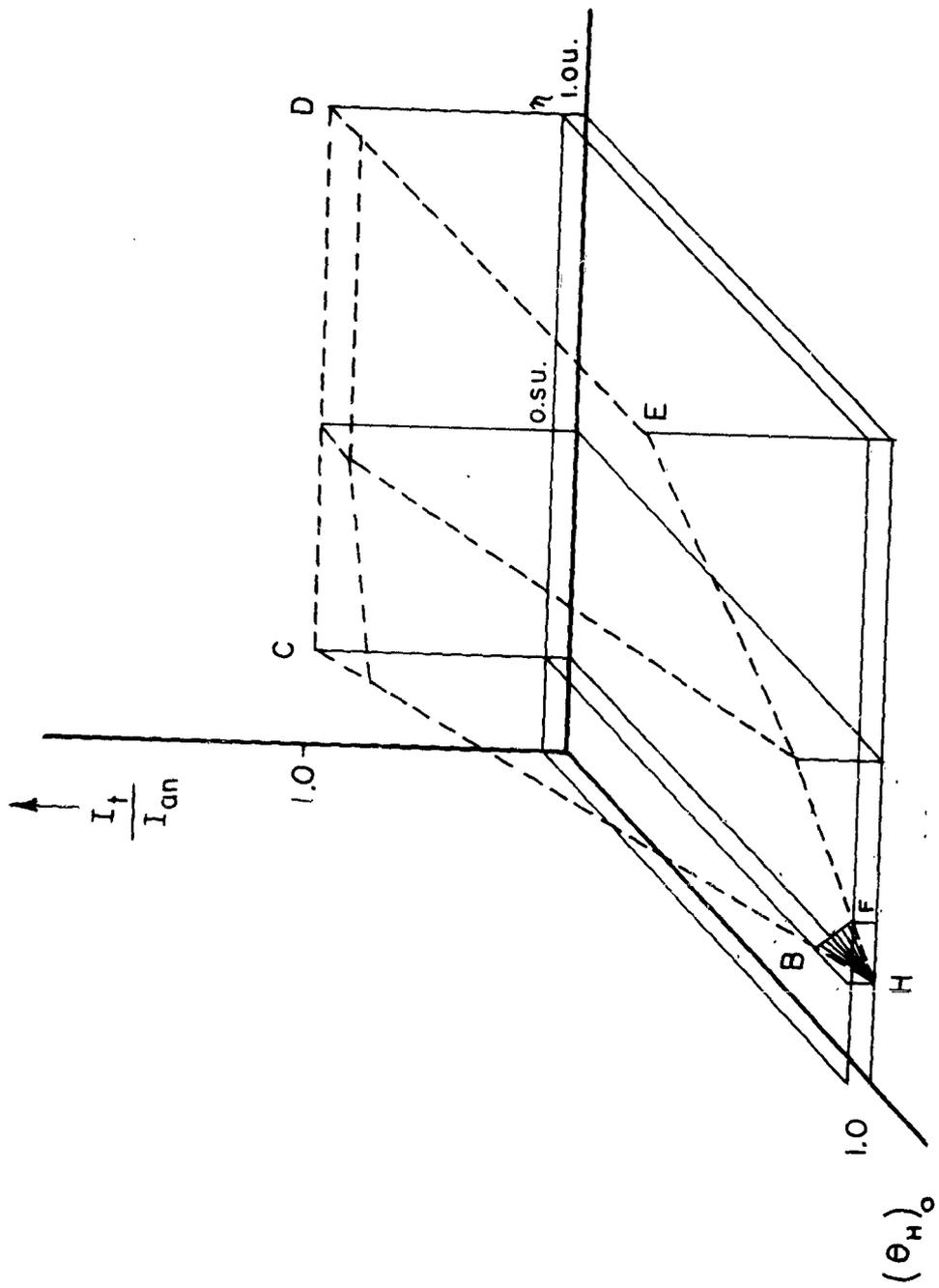


FIG. 3

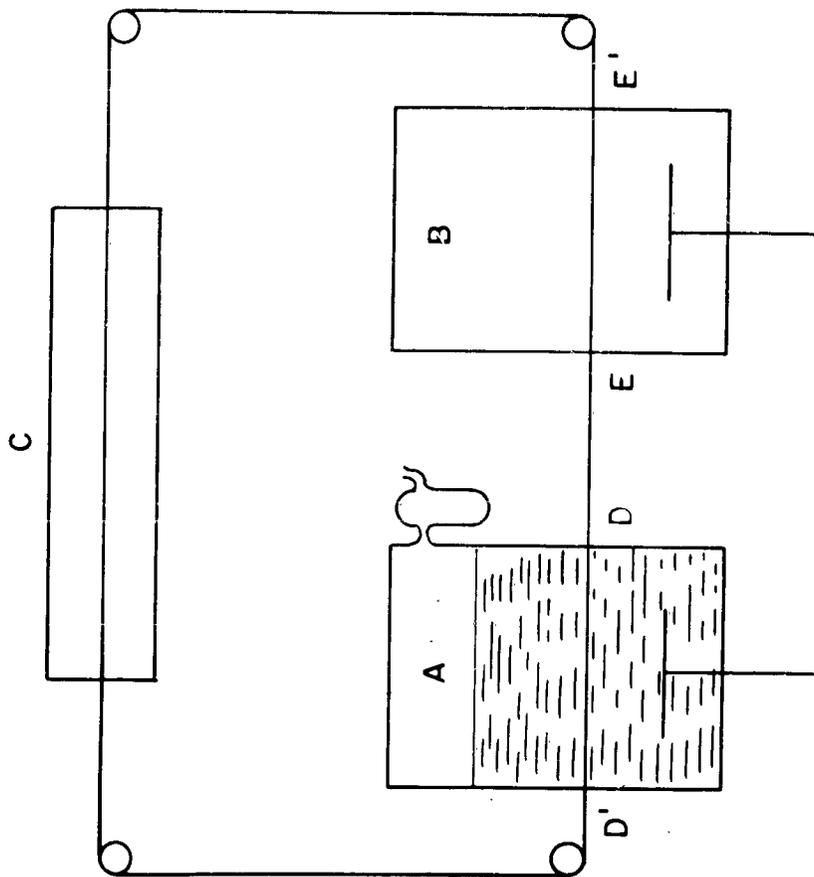


FIG. 4

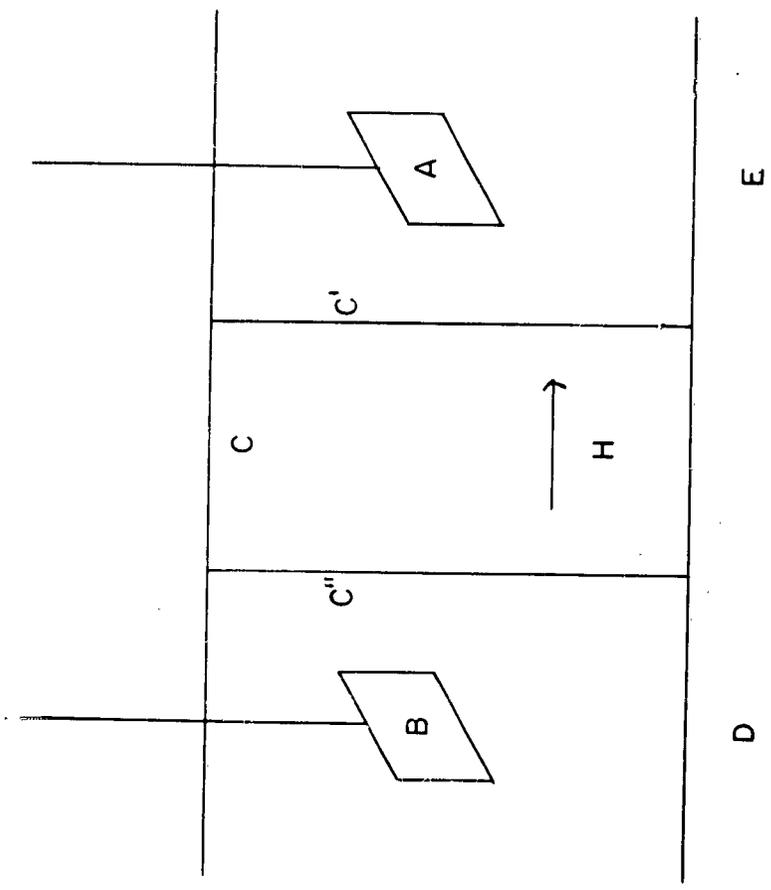


FIG. 5

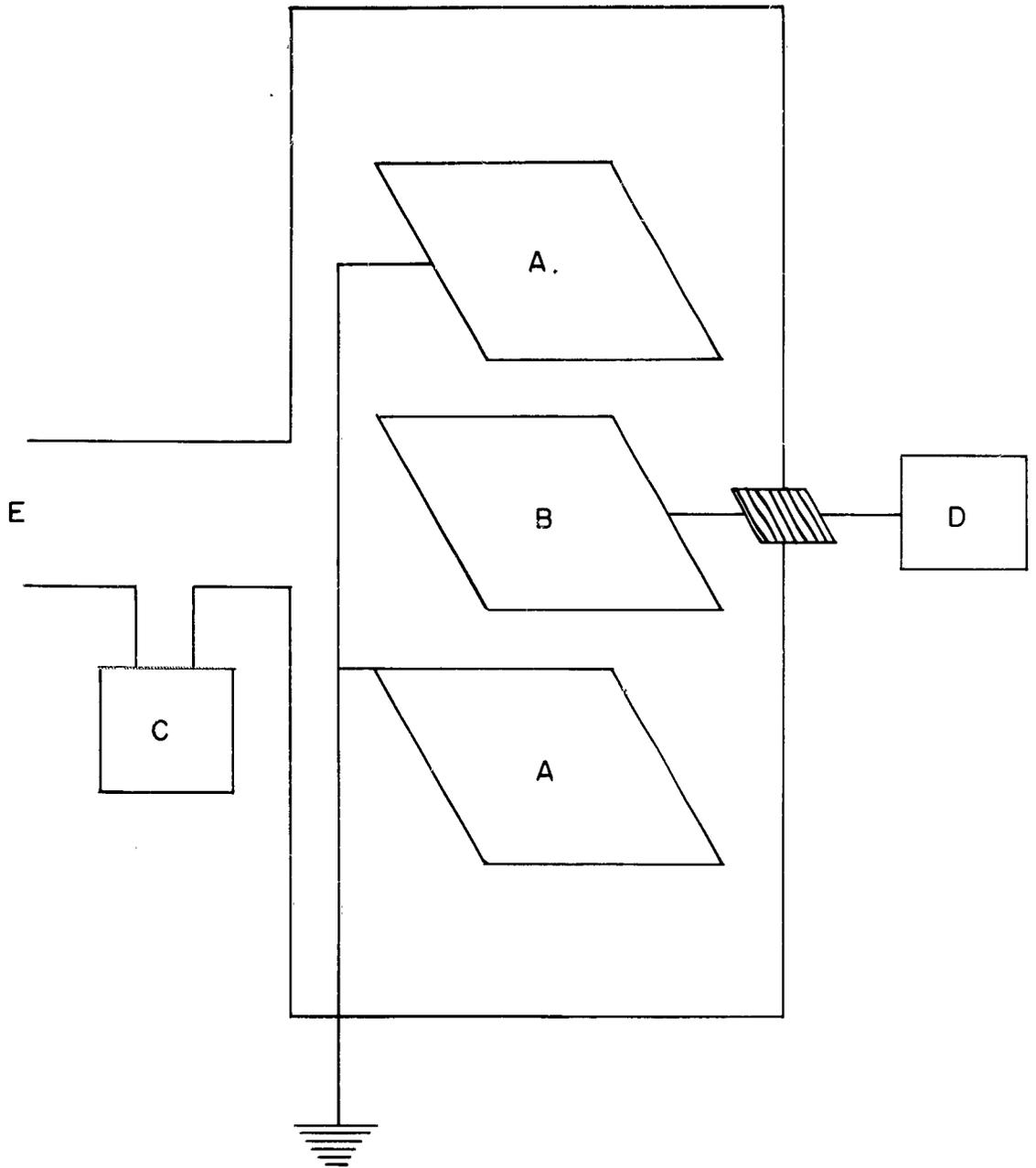


FIG. 6

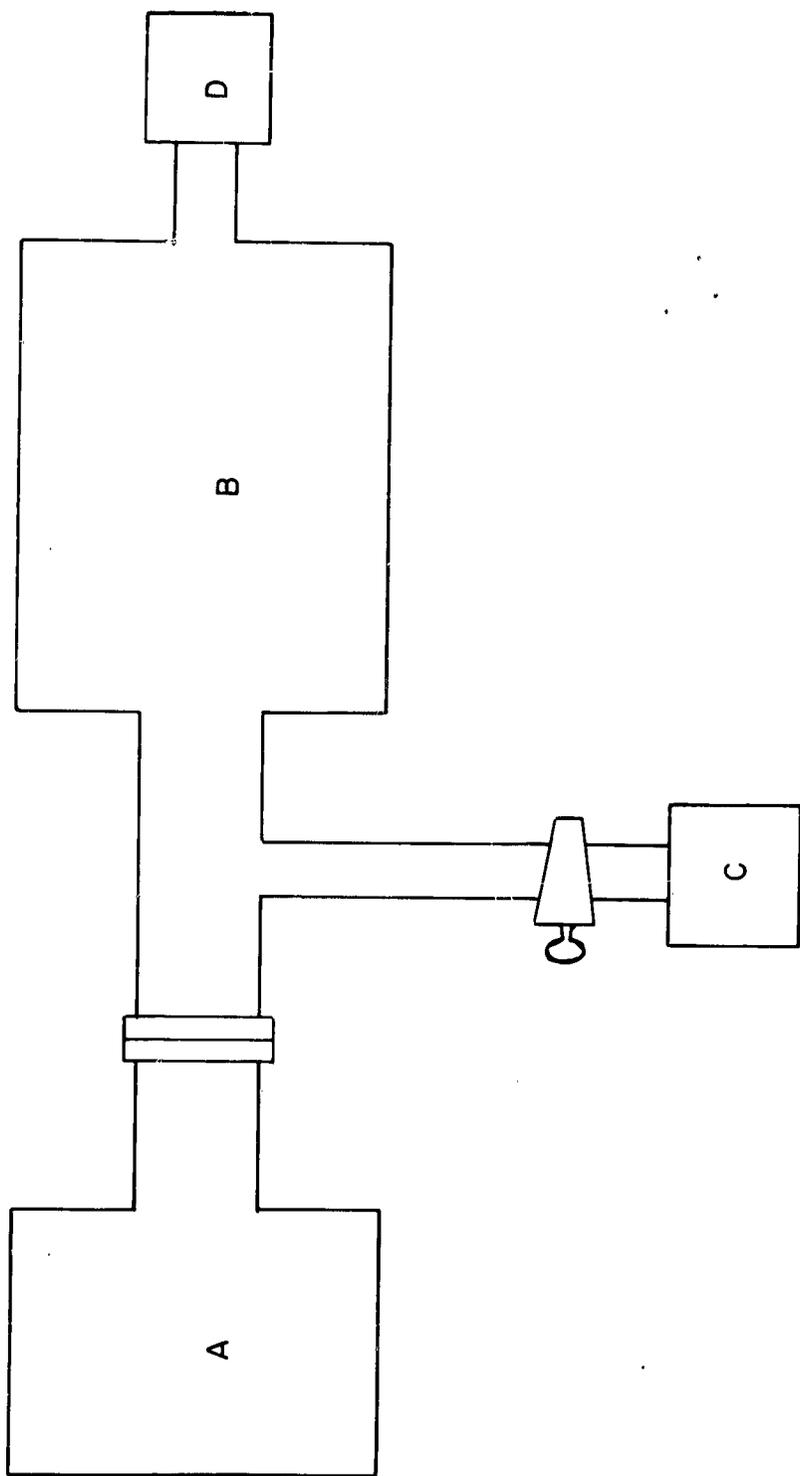


FIG. 7

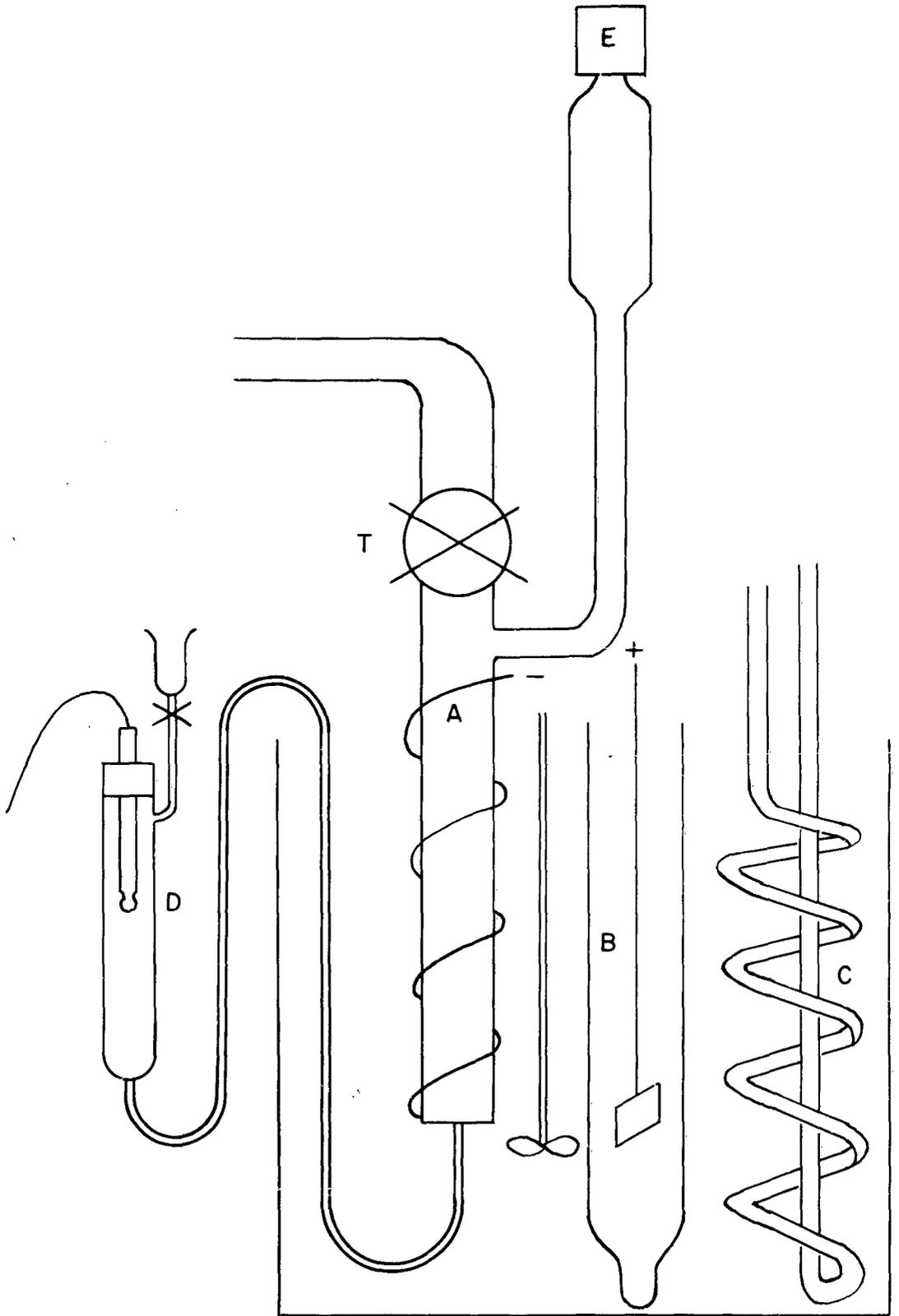
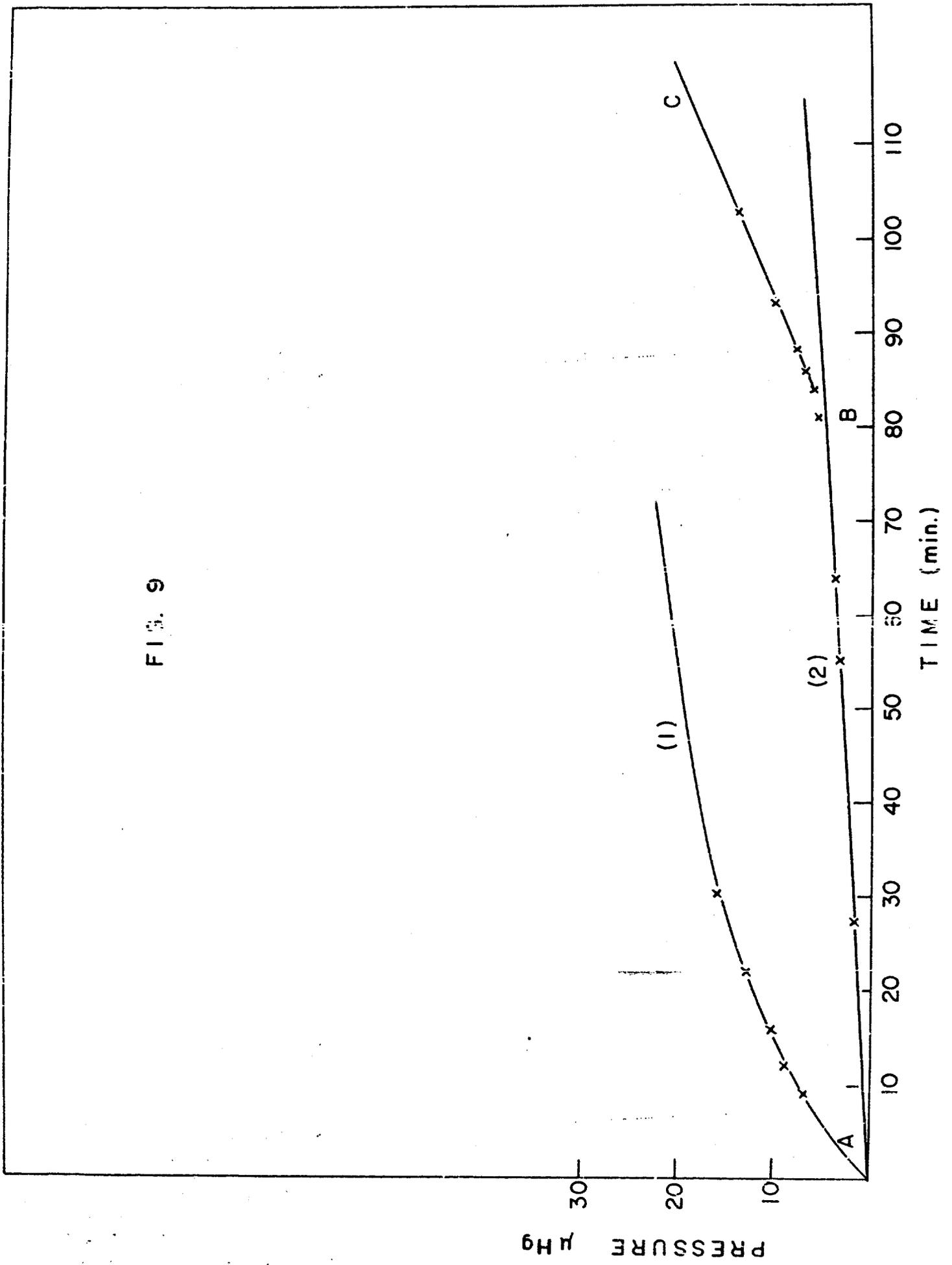
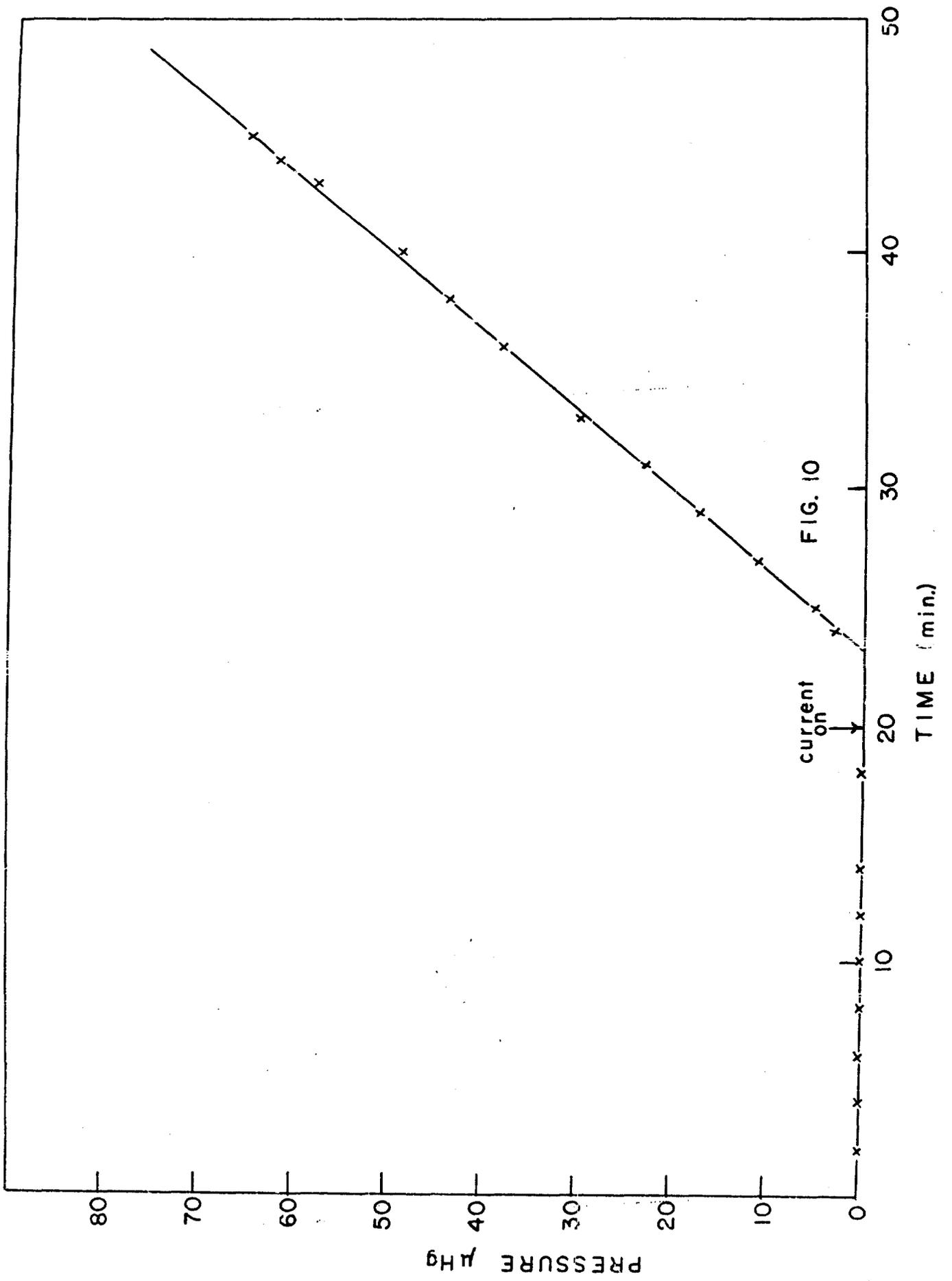


FIG. 8

FIG. 9





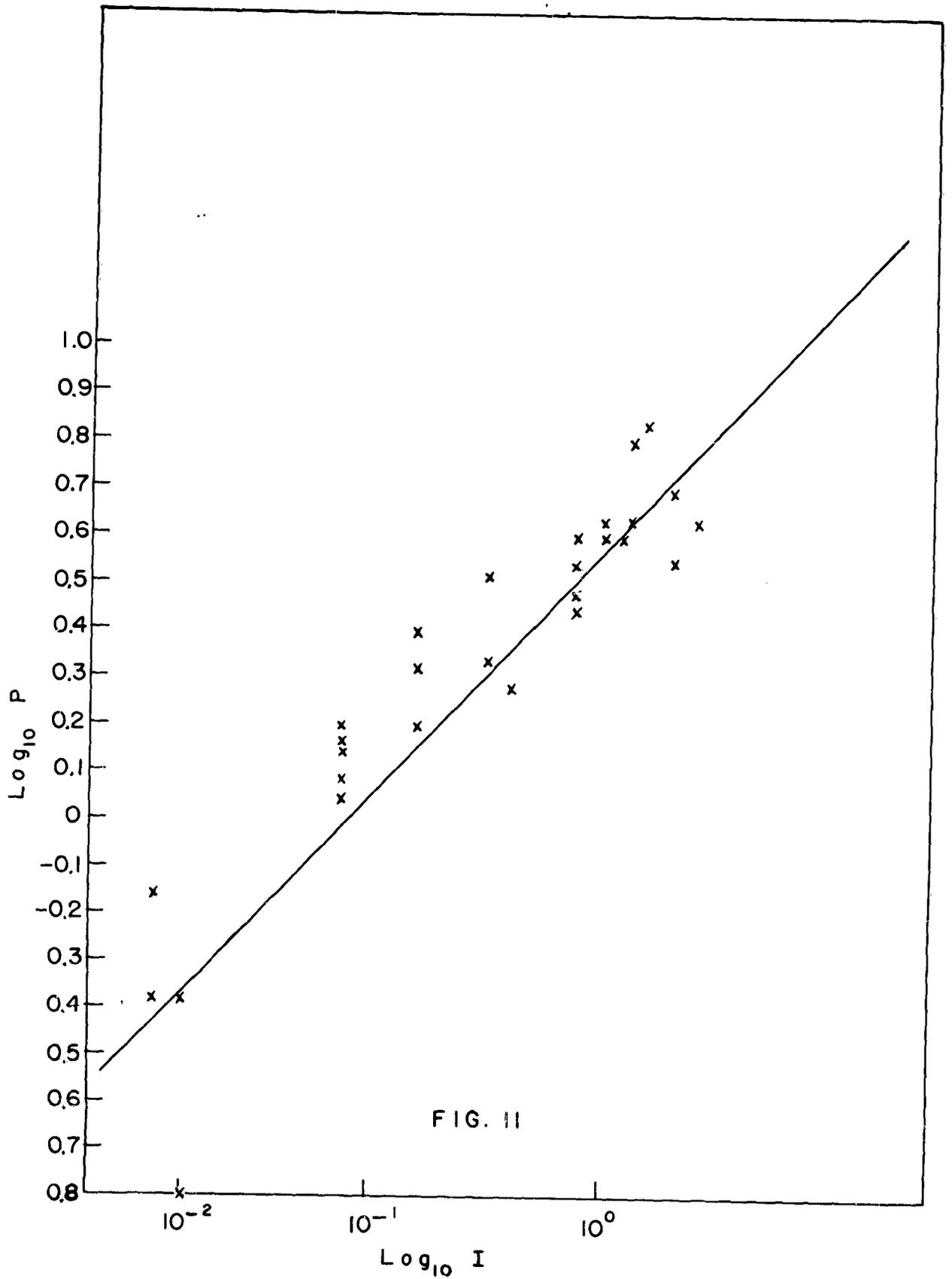
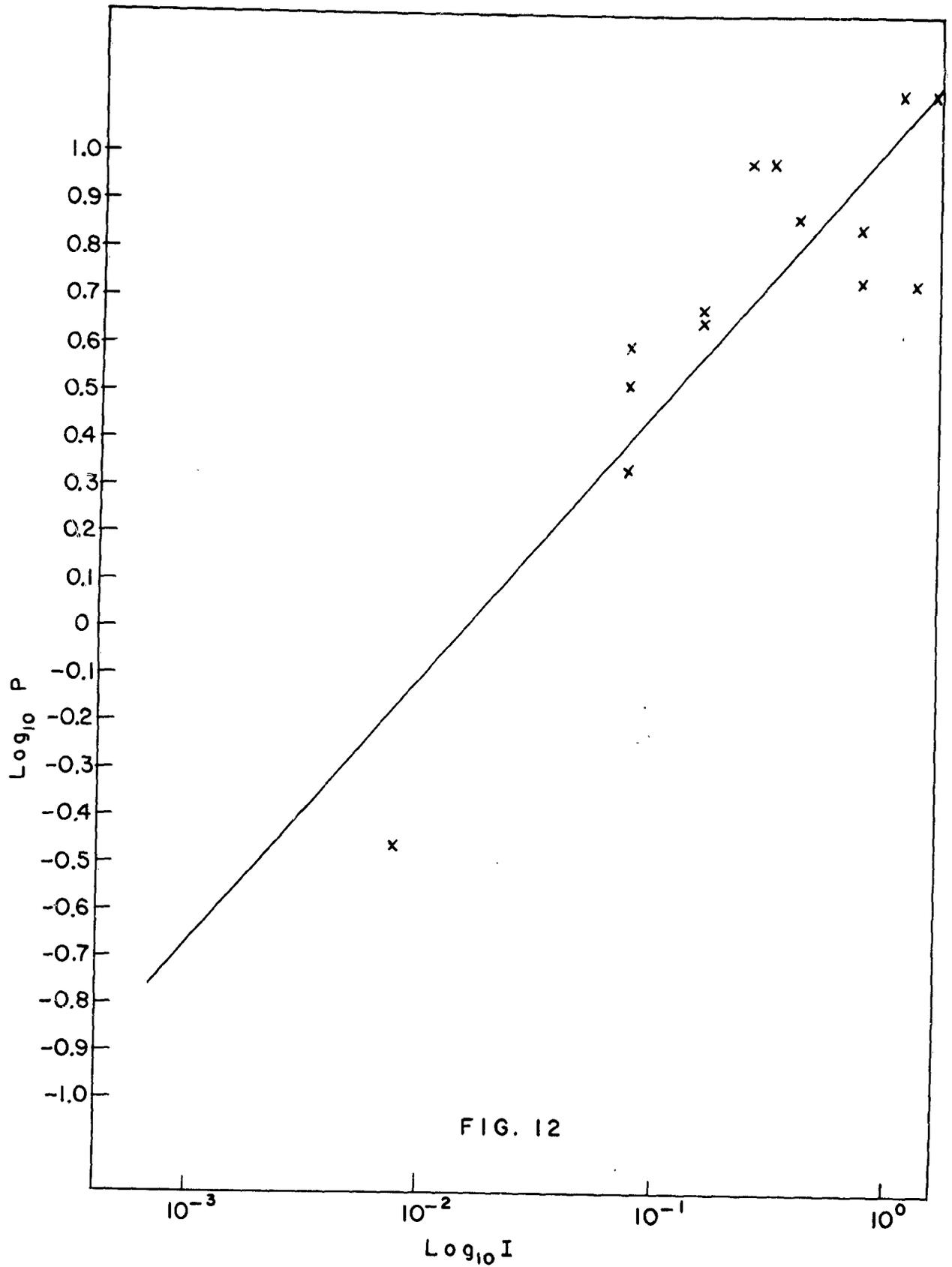
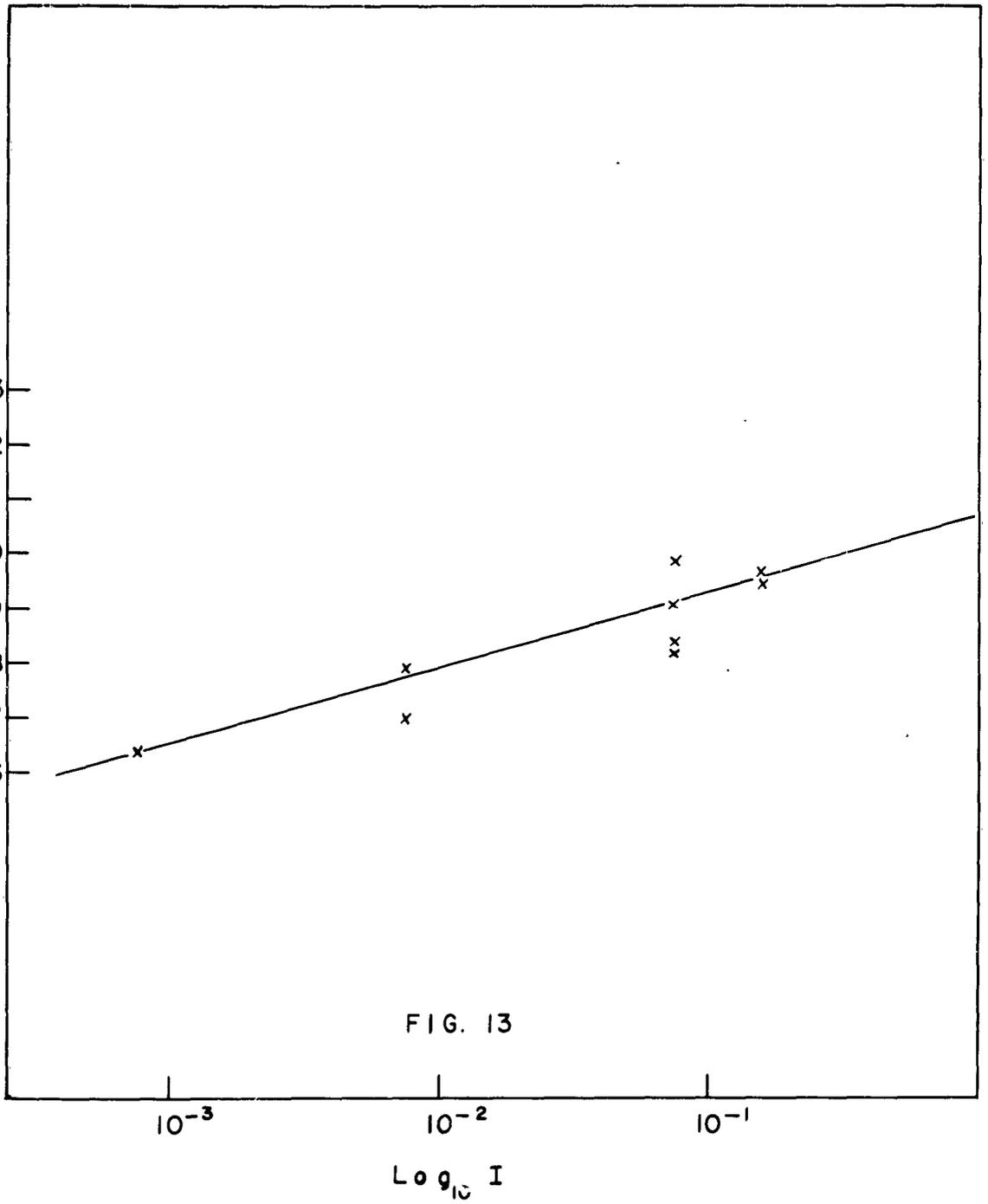


FIG. II



Potential against Sat. Calomel Electrode

1.3  
1.2  
1.1  
1.0  
0.9  
0.8  
0.7  
0.6



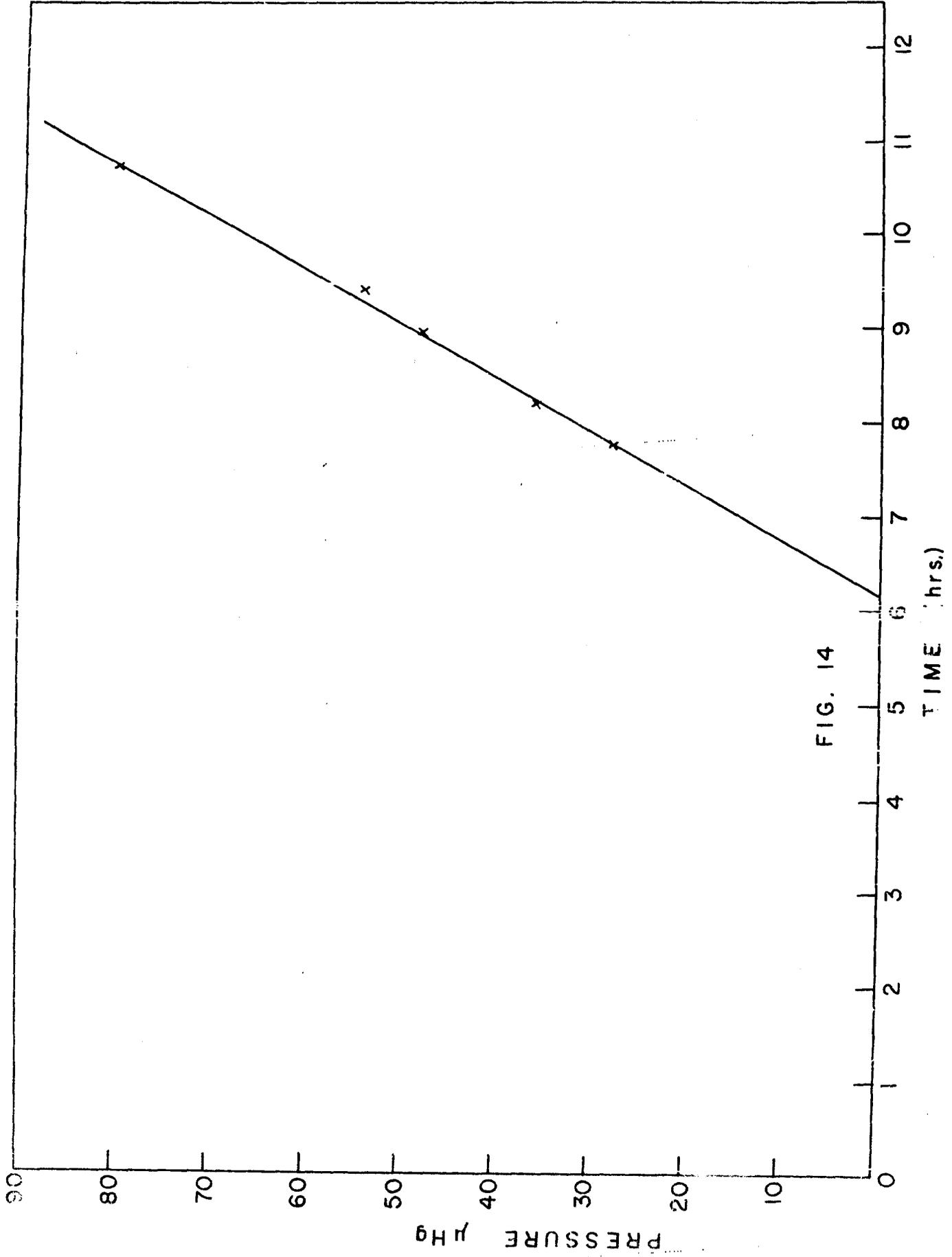


FIG. 14

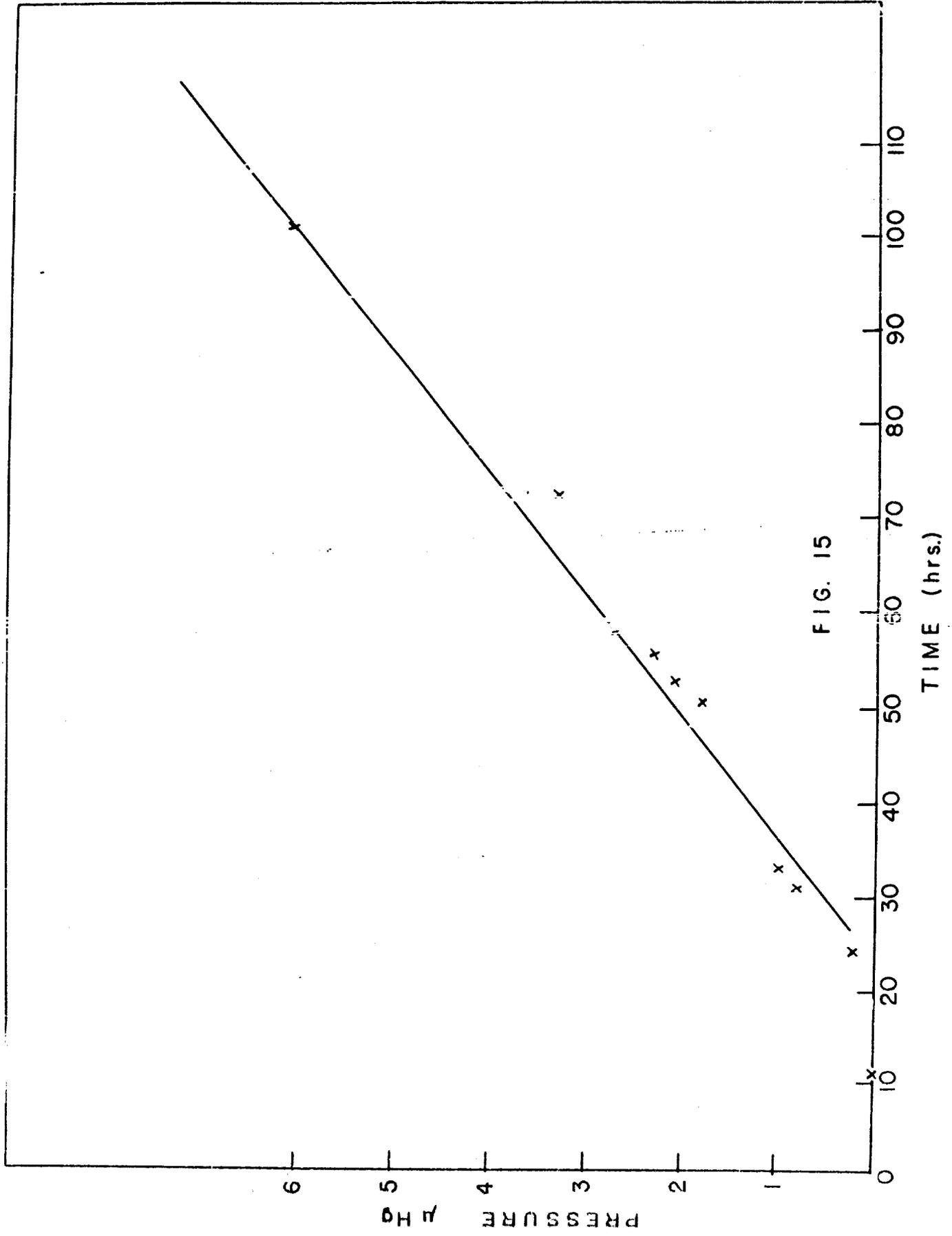


FIG. 15

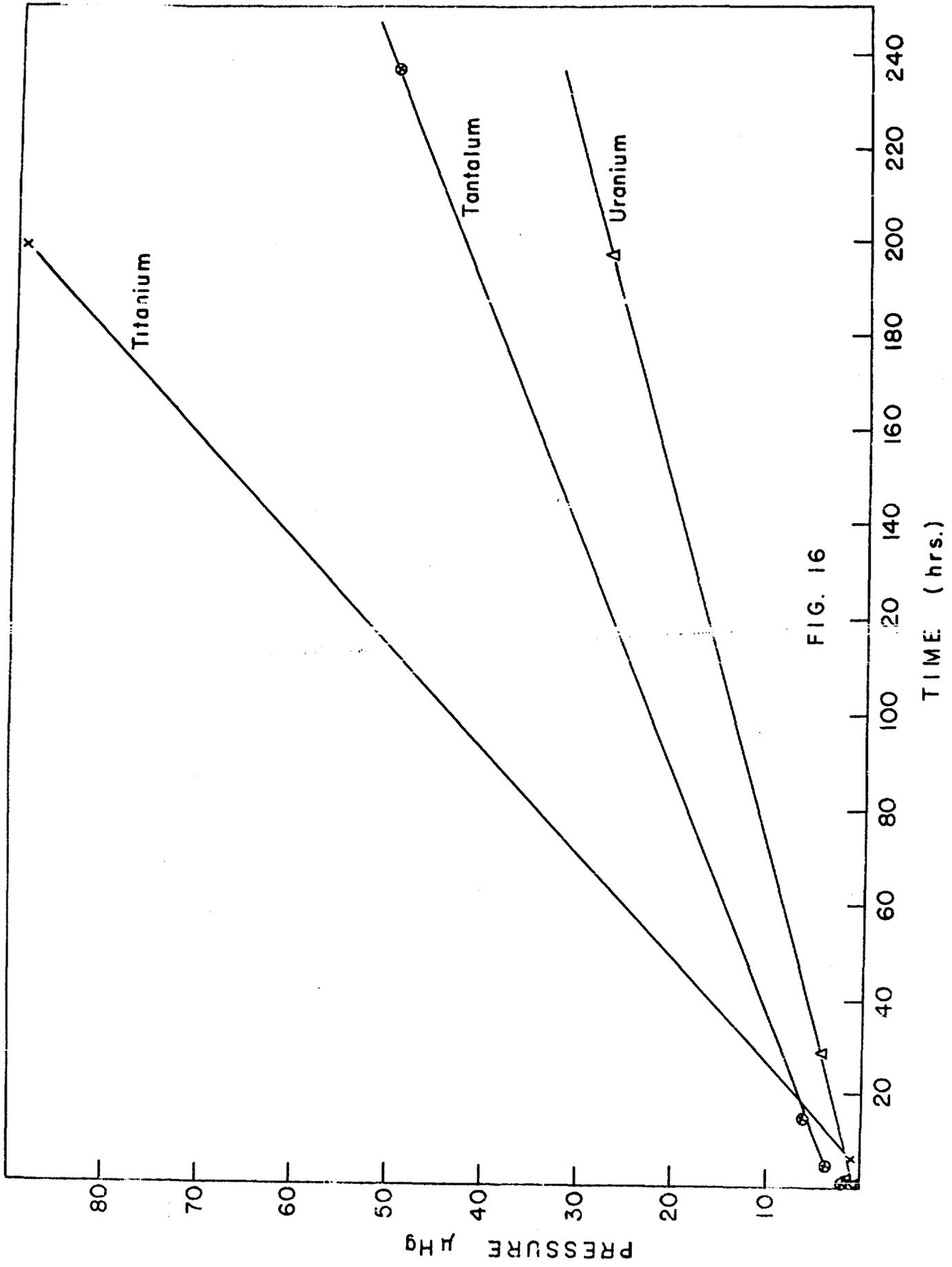
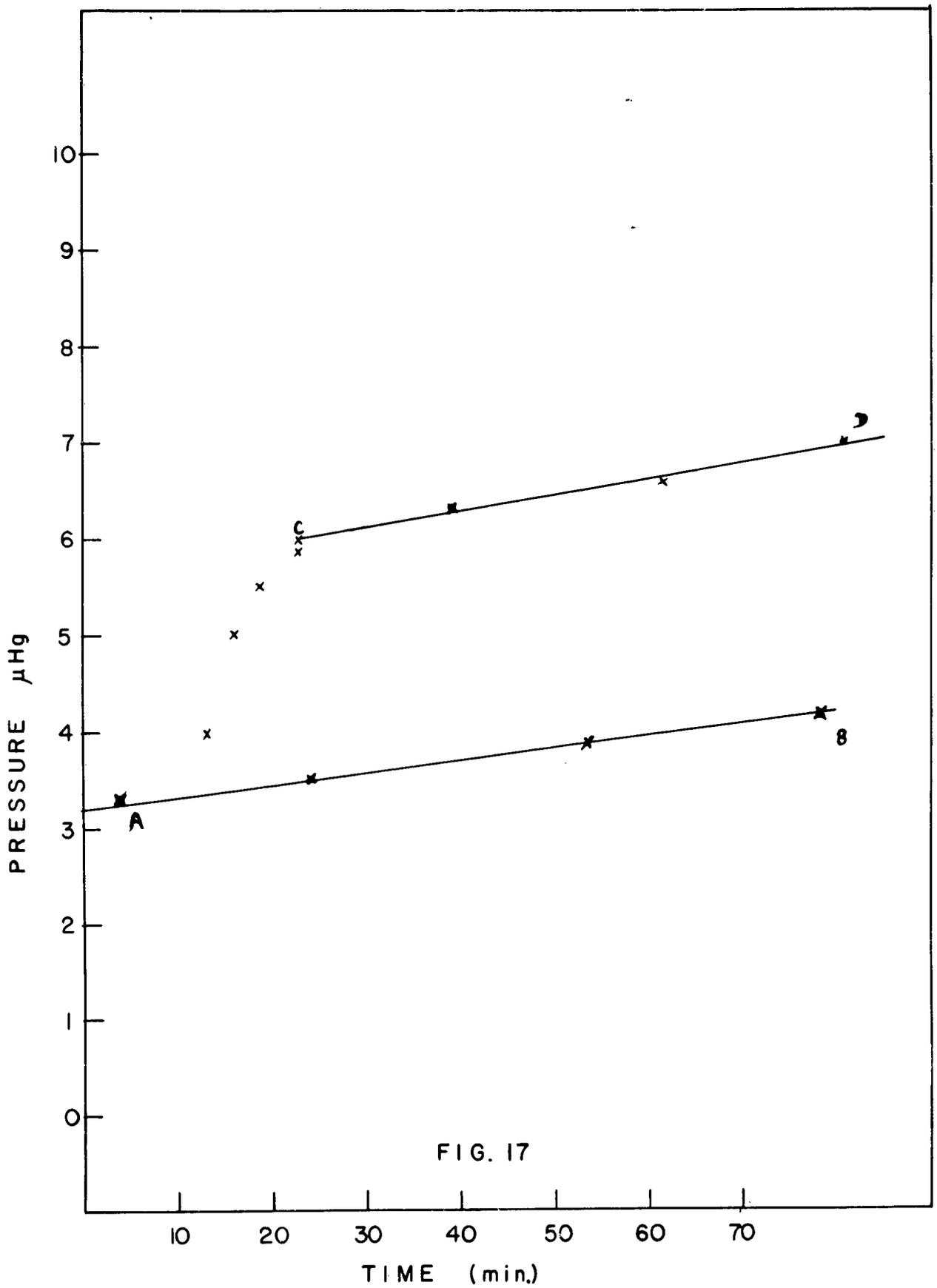
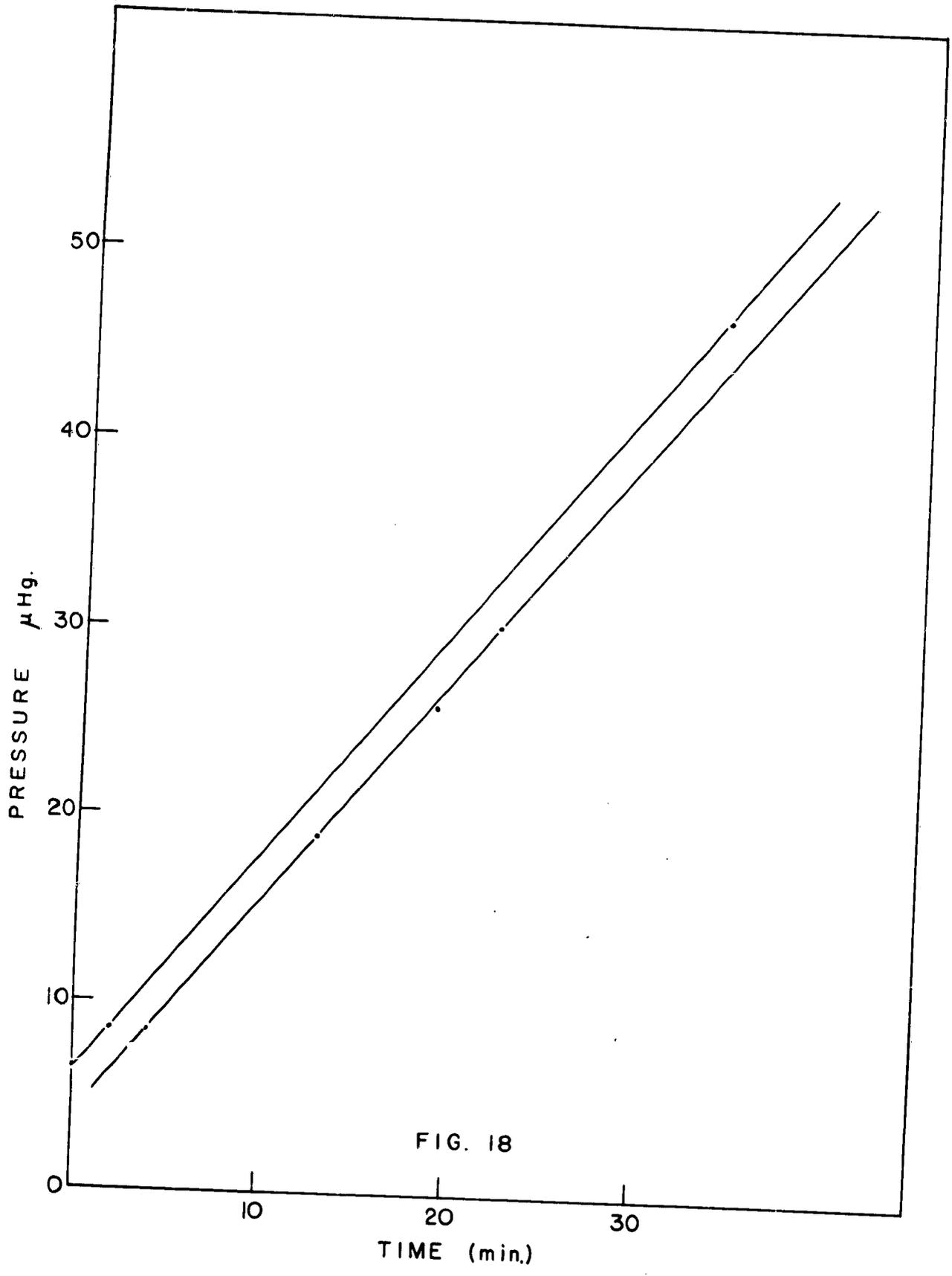


FIG. 16





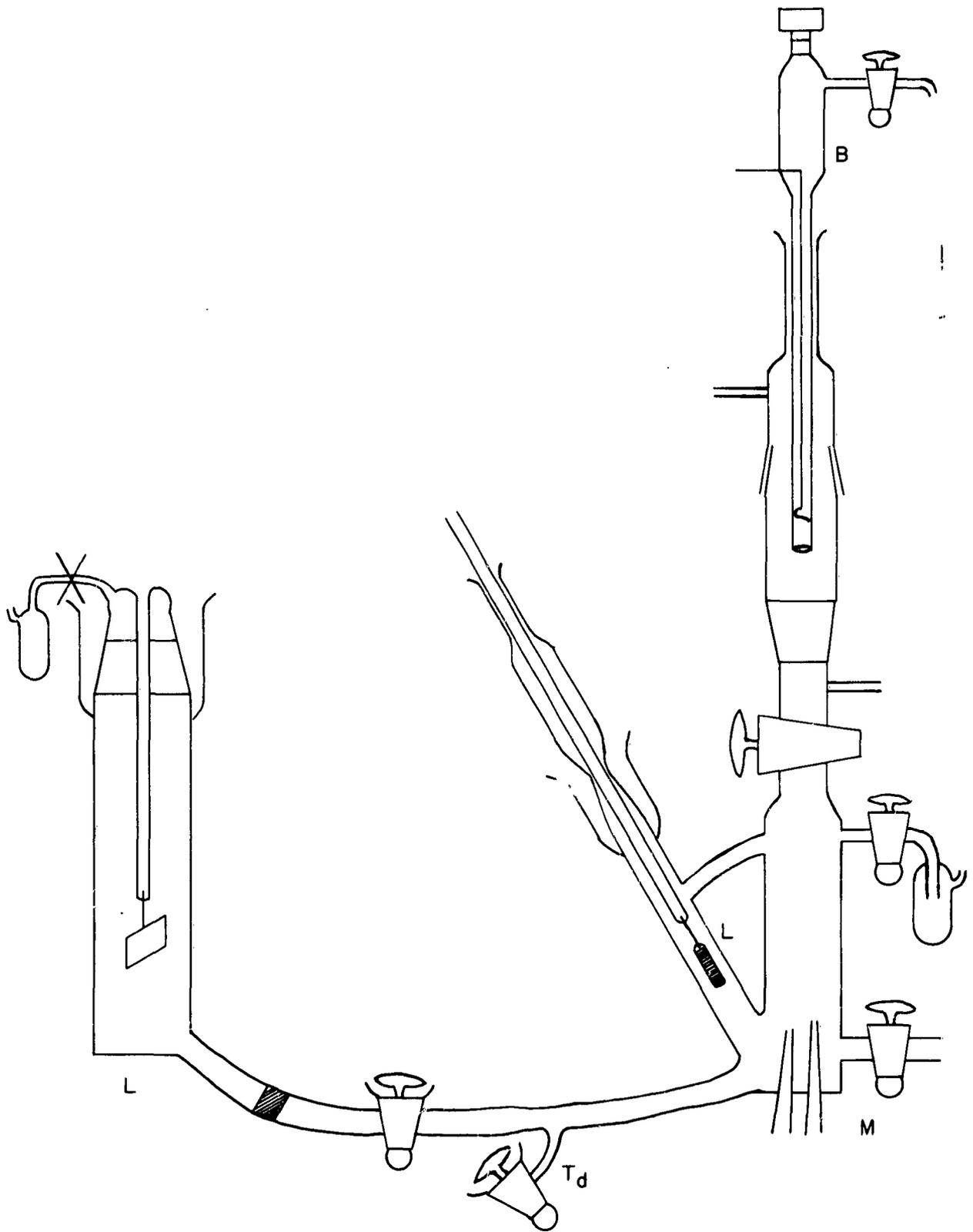


FIG. 19

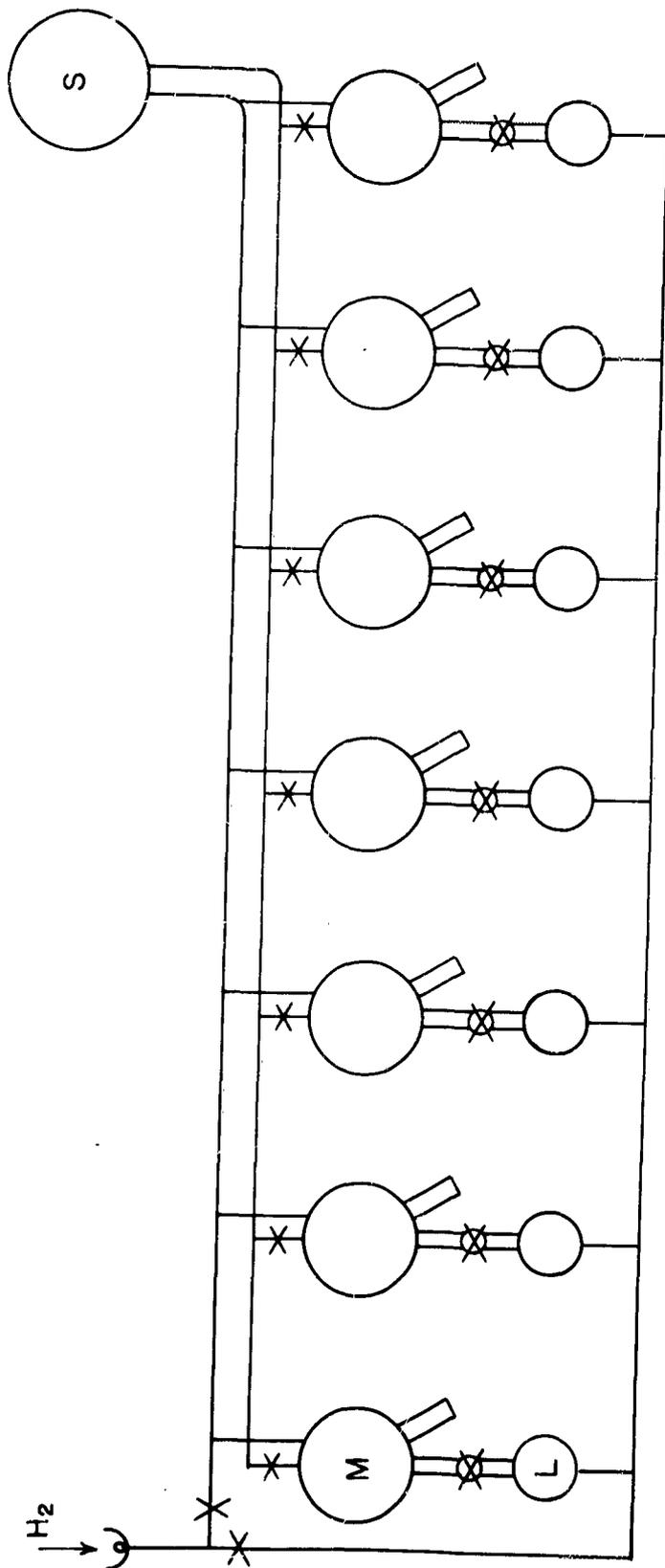


FIG 20

