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Kuo-Chin Chuang

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A STUDY OF THE DIFFERENCE EFFECTS ON ALPHA SOLID SOLUTIONS OF OXYGEN IN TITANIUM DISSOLVING IN HYDROFLUORIC ACID

BY

KUO-CHIN CHUANG

A

THESIS

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Approved by

M. E. Straumanis (Advisor) Wm. J. James

Harold Q. Fuller Andrew Larson

ABSTRACT

Alpha solid solutions of oxygen in titanium dissolving in hydrofluoric acid exhibited a positive difference effect with k values of 5.7, being independent of the concentration of HF, within the compositional range studied 0 to 5 w/o oxygen. This indicates that various TiO_x alloys are polarizable to the same extent by the same strength of anodic current in hydrofluoric acid.

The difference effect observed on TiO_x alloys dissolving in HF-HCl revealed that the effect is dependent on the oxygen content of the solid solution as well as on the concentration of HCl. The presence of HCl results in a higher k value for the difference effect and accordingly a higher polarizability of TiO_x. Measurements of dissolution potentials under different anodic current densities indicated the presence of a protective layer on the surface of the dissolving alloy. These measurements also give support to the explanation of higher polarizability in HF-HCl than in HF alone by the formation of protective layers, and by the effect of HCl on the nature of this layer.

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I INTRODUCTION

The dissolution mechanism of the alpha Ti-O solid solution in hydrofluoric acid was studied by measurements of the dissolution rate in various concentrations of hydrofluoric acid and by the calculation of the activation energy of the dissolution reaction. (1) Since this reaction is reported to involve both direct chemical and electrochemical reaction, the study of difference effects is essential for the understanding of the processes involved. The slope constant obtained from the plots of the difference effect versus current densities of TiO_x solid solutions (with composition ranging from 4.97 to 10.84 weight per cent oxygen) has been reported to be approximately 9.5 (1) and independent of the concentration of the hydrofluoric acid, which indicated that the TiO_x electrodes were strongly polarizable to an extent greater than expected. Since the slope constant of the same plot obtained for pure Ti dissolving in various concentrations of hydrofluoric acid was observed in this laboratory to be 5.7 (2), it was assumed that a transition region for this slope constant between 5.7 to 9.5 should exist at certain compositions of the alloy. This investigation was therefore taken in order to see whether this assumption was correct or not.

The main and more complete source of information (on the electrochemical behavior of metals) is, the experimental study of the electromotive behavior of the metal in the absence or presence of an anodic current. Therefore, the dissolution potentials of the specimens in acids were also measured both in an open vessel and while measuring the difference effects in a closed apparatus.

II LITERATURE REVIEW

The first article concerning the difference effect was published in 1927 by Thiel and Eckell. (3) The essence of the effect is as follows: When zinc was dissolved in sulfuric acid the rate of hydrogen evolution from zinc was found to be changed anodic polarization. The difference effect was then, and still is defined as:

$$\Delta = V_1 - V_2 \qquad (1)$$

where V_1 is the rate of hydrogen evolution of the metal in the acid ("self dissolution") and V_2, the rate of hydrogen evolution of the metal when it is under anodic current in the same acid under the same experimental conditions.

Streicher found on dissolving aluminum in NaOH that V_2 was less than V_1 as was found for zinc in sulfuric acid. (4) In this case Δ indicated the amount which has to be added to V_2 to restore the previous rate V_1, the effect was, therefore, positive. On the other hand, a negative difference effect was observed for Be and Mg in NaCl, Al in HCl. (5) (6) where V_2 was greater than V_1 and Δ was the amount to be subtracted from V_2 to get V_1.

Since it is assumed that the difference effect results from anodic polarization, it should be proportional to the anodic current density flowing through the dissolving electrode. In most cases a linear relation between the current density and the difference effect was found:

$$\Delta = k\ I \qquad (2)$$

The constant k can, therefore, be calculated from the measurement of the difference effect at different current densities. It was shown that the above equation for the positive effect can be derived on the basis of the theory of local elements (7). It was also shown that the presence of the positive difference effect during the dissolution of a metal must prove that the dissolution occurs because of the activity of local cells.

According to Faraday's law, one coulomb or 96,500 ampere seconds of current liberates one gram equivalent of hydrogen gas. The rate of hydrogen evolution due to the current flowing through the couple is therefore:

$$\frac{0.5\ (22,414)\ 60}{96,500\ (1,000)} \times (1000)(I) = 6.97\ I\ \text{mm}^3/\text{ma-min.} \qquad (3)$$

During the experiment, (at I ma./cm^2 anodic current density) however, one measures V_t, the total rate of hydrogen evolution from the system, instead of V_2, i.e.

$$V_t = V_2 + 6.97\ I$$

$$\text{thus,}\quad V_2 = V_t - 6.97\ I \qquad (4)$$

In the positive effect V_t is larger than V_1 so that k is always smaller than 6.97 because:

$$k \cdot \frac{\Delta}{I} = \frac{V_1 - V_2}{I} = k = 6.97 + \frac{V_1 - V_t}{I}$$

where V_1 is the rate of hydrogen evolution at 0 anodic current.

If $k = 6.97$, V_t is equal to V_1, which means that the increase in the evolution rate caused by the current is completely subdued by the difference effect, or 100% of the hydrogen volume produced by the current is annihilated by the reduction in the self dissolution rate. If k is 0, there is no difference effect at all, and accordingly no existence of polarization, because the increase in rate of evolution is exactly the volume developed by the current on the cathode. Therefore, k is a criterion for the expression of the polarizability of a metal. The polarizability is thus defined as:

$$\%P = \frac{100k}{6.97} = 14.35\ k\ \%$$

Assuming that no secondary processes, such as formation and breakdown of protective films, occurred during the anodic polarization, 100% should be the highest value for the polarizability.

For example the polarizability of Zn in H_2SO_4 was calculated to be 35.8% for a value of 2.5.

As previously mentioned, the k value of commercially pure titanium is 5.7, the % P is therefore $\frac{100 \times 5.7}{6.97} = 81.8$

(A) Titanium in hydrofluoric acid

During the dissolution of commercially pure titanium coupled with platinum in 0.1, 0.24, 0.5, 1.0 and 2 N hydrofluoric acid, a positive difference effect was observed (2). The difference effect was found to be directly proportional to the galvanic current up to 40 or 60 ma/cm^2, and to be independent of the concentration of the acid. At higher current densities the proportionality constant k decreased. Since k was determined to be 5.7, only 1.27 mm^3 hydrogen were developed by one ma/cm^2 on the cathode per minute according to the equation:

$$V_t - V_1 = (6.97 - 5.7)\ I \qquad (5)$$

The difference effect was explained under the assumptions that the dissolution of titanium in hydrofluoric acid was caused by the activity of local elements, the potential of titanium versus anodic current density increased linearly, and that the hydrogen overvoltage of the local cathodes was controlled by the local current in accordance with the logarithmic overvoltage function.

(B) Zinc in sulfuric acid

An average constant of 2.5 was obtained for current densities up to 73 ma/cm^2 on zinc dissolving in 2 N sulfuric acid (8). It was shown, using the above equation (eg. 5), that approximately one third of the current was utilized to offset the difference effect and two thirds contributed to the rate of dissolution of the zinc. The local elements on zinc are, therefore, less readily polarized by the anodic current in comparison with those on titanium.

(C) Aluminum

For aluminum coupled with platinum a positive difference effect was found in seven concentrations of hydrofluoric acid varied from 0.05 to 2.0 N. A slope constant of $k = 5.34$ was observed at current densities below 60 ma/cm^2 independent of the concentration of the acid (6). The corresponding polarizability was 71.7%. In hydrochloric acid, however, the positive difference effect was observed only at low current densities, and the negative at high current densities (up to 200 ma/cm^2). The effects were also independent of the concentration of the acid. The positive effect as in all other cases, was explained by the anodic polarization of aluminum by the additional polarizing current, and the negative one, which actually represented the overlapping of both effects, by the breakdown of the surface film because of the action of the same current and by a possible formation of metallic chunks according to Marsh and Schasehl, known as "Chunk Effect" (9).

(D) Zirconium in hydrofluoric acid

Extreme positive difference effects (k greater than 6.97) were observed on zirconium dissolving in hydrofluoric acid (10). The hydrogen volume developed by the internal polarization current was completely overbalanced by the positive difference effect. As in other cases, the effect was independent of the concentration of the acid and was accompanied by a strong shift in potential of the Zr toward noble values. The activity of Zr returned when the anodic current was cut off. As the effect of local currents, due to anodic polarization was reduced to a minimum, the high rate of dissolution of zirconium was explained by direct chemical action of zirconium with molecular HF. There were indications that the strong difference effect might be caused by the presence of oxygen in the metal and by the stability of this oxide in the acid. Because of this reason the experiments with TiO_x solid solutions were performed. (1)

(E) The Difference effect on TiO_x solid solutions dissolving in HF-HCl mixed acid.

The difference effect measurements were conducted on three specimens of alpha solid solutions. $TiO_{0.157}$, $TiO_{0.263}$, $TiO_{0.365}$, in a mixed acid HF-HCl. The concentration of HF was changed from 0.10N to 0.75N while that of HCl was kept constant at 1N with respect to the acid. The equations for the difference effect were $\Delta = 9.7I$, $\Delta = 9.6I$, $\Delta = 9.3I$ respectively. The large anodic polarization phenomenon observed were explained as due to concentration of Ti_2O_3 on the surface of the electrode as free titanium went into the solution and a possible secondary process of a dense film formation which slowed down the reaction.

III MEASUREMENT OF THE DIFFERENCE EFFECT

(A) Materials

Eight specimens of the alpha solid solution of oxygen in titanium were prepared. The composition of the specimens are tabulated in Table I. The Ti-O phase diagram shows that at room temperature, the alpha phase extends from 0 to 14.4 weight per cent oxygen. The region between 4.97 and 10.84 w/o oxygen was studied previously in this laboratory and the samples were available for this study. Therefore, only specimens of oxygen contents less than 4 w/o were prepared.

It was found that the preparation of Ti-O alloys of less than 4 w/o oxygen by sintering titanium powder with titanium dioxide at high temperatures was rather difficult. Therefore, instead of directly mixing titanium powder with titanium dioxide, three kinds of titanium powders of different purities (99.24 w/o, 98.27 w/o, 96.3 w/o titanium) were used. The powders were originally prepared by quantities of Ti + TiO_2 powders sintered at lower temperature. Since the oxygen content of the powders was higher than that of the first specimen desired, the purest titanium powder was mixed with the same amount of titanium hydride (Metal Hydrides Inc.) The amount of each powder required to prepare the alloy of desired composition was calculated on the assumption that the compact would pick up approximately 1 w/o of oxygen during the sintering process.

The calculated amounts of the powder were thoroughly mixed, and compacted in a cylindrical die of 2.54 cm diameter with a pressure of 30 tsi for the first four specimens. The other specimens were prepared in a die of 1.4 cm diameter under a pressure of 50 tsi.

The green compact was kept in an aluminum crucible, and the whole crucible was then placed in the porcelain tube of a vacuum furnace. The tube was evacuated to a pressure of less than 3 microns. The furnace was then heated up to 500° C. at a slow rate so that the pressure of the system could be maintained at less than 5 microns. At this temperature, the compact was presintered for one hour to remove the entrapped gases and moisture from the system. The titanium hydride for the first specimens also decomposed at this temperature. At the end of the preheating period the pressure in the reaction tube was decreased to 3 microns, the furnace was then heated up to 1350° C. and kept at this temperature for four hours. After the completion of the sintering process, the specimen was furnace cooled under the continuous evacuation of the reaction tube.

The surface layer of the specimen was removed to obtain homogeneous structures and the specimen was finished for accurate measurement of the surface area. For the first four specimens, the sintered alloy disks of about 2.5 cm in diameter were trimmed down to 1 x 1 cm square surfaces and the

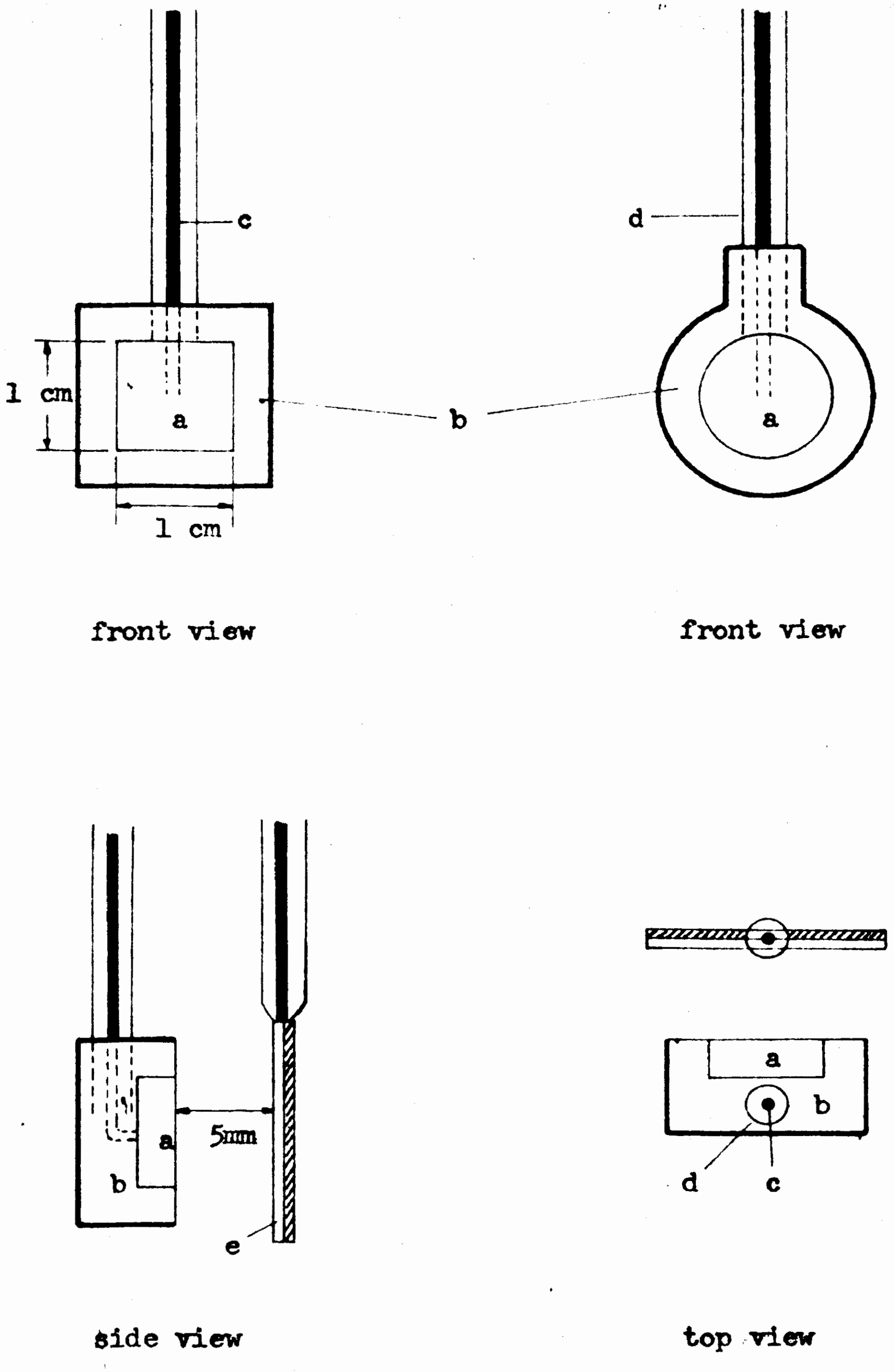


Figure 1

Sketch of the TiO electrode

a) TiO$_x$

b) plastic

c) glass tube

d) copper wire

edges measured with a micrometer. The trimmings were saved for analyses. For the other specimens used in their disk shapes, the average diameter of each specimen for the calculation of the surface area was obtained from four readings. The porosity and homogeneity of the samples were checked with a microscope. Three specimens (No. 2, No. 5, No. 8) were checked with x-ray diffraction analysis to be sure that no second phase was present. Each specimen was then mounted in bakelite (or lucite) so that the surface of a known extent was exposed to the acid. A copper wire was connected to the back of the specimen to make it an electrode. Figure 1 shows the schematic diagram of the electrodes used in this investigation. The platinum electrode of 2 x 2 cm coupled with the specimen was prepared from a platinum sheet. The platinum electrode was platinized before use to reduce the hydrogen overpotential.

The analysis of each specimen was performed by the hydrogen evolution method (11), assuming the alloy contained only titanium and oxygen. The reaction was given as:

$$TiO_x + 3HF \longrightarrow TiF_3 + xH_2O + (1.5 - 2x)\ H_2.$$

The results are tabulated in Table 1.

TABLE I

The Compositions of the Specimens

Number	w/o O	a/o O	Formula
1	0.785	2.31	$TiO_{0.024}$
2	1.22	3.56	$TiO_{0.037}$

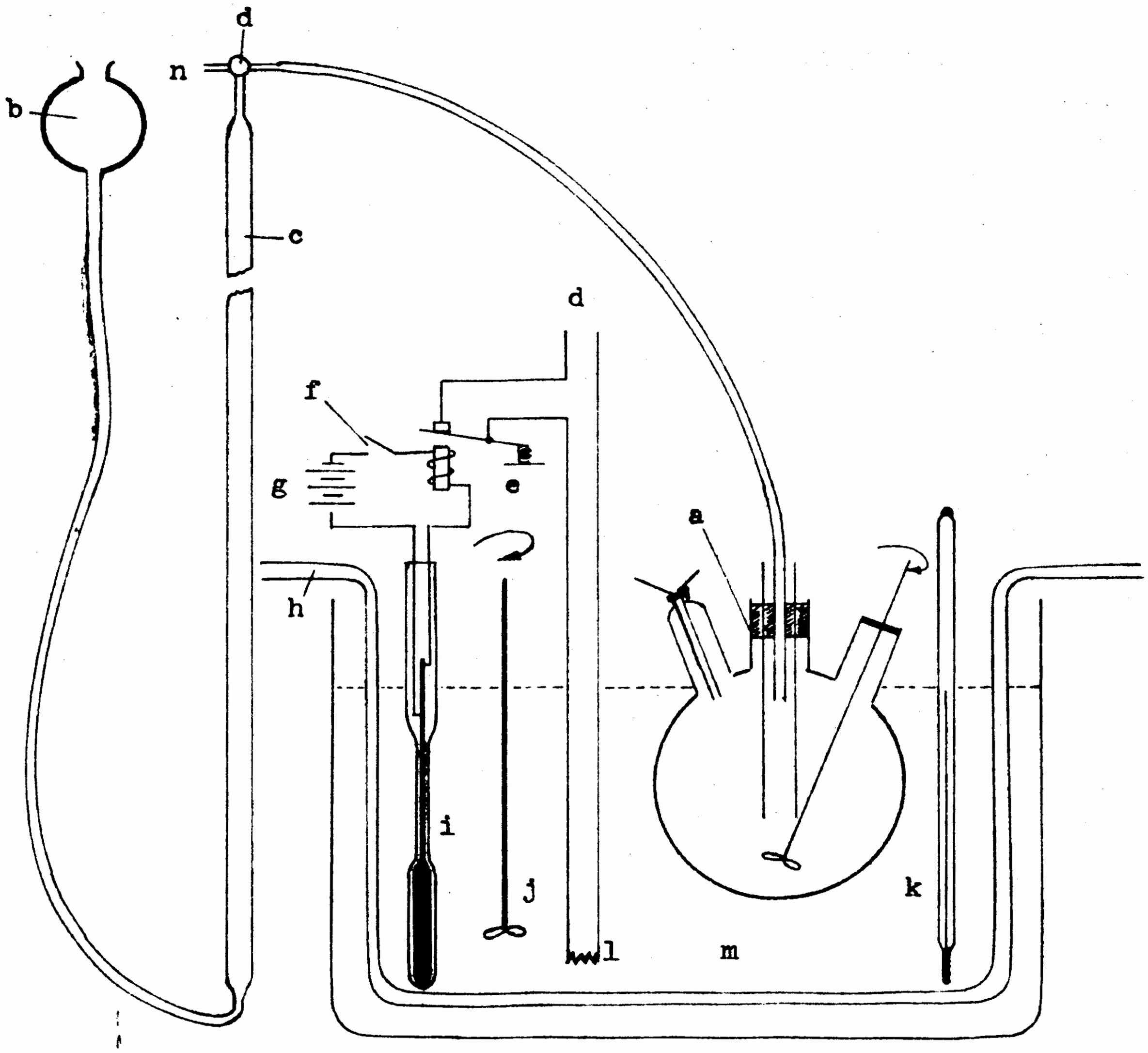
3	1.82	5.26	$TiO_{0.0555}$
4	2.62	7.46	$TiO_{0.0806}$
5	3.30	9.26	$TiO_{0.102}$
6	4.113	11.38	$TiO_{0.128}$
7	4.633	12.70	$TiO_{0.145}$
8	5.01	13.63	$TiO_{0.158}$

Fisher's reagent grade hydrofluoric acid (48%) was used for all experiments in this investigation. The concentrated acid was diluted to approximately 2N, then titrated with standard NaOH solution to find its exact concentration.

(B) Apparatus

For the measurement of the difference effect the rate of dissolution of the specimen in the acid with and without anodic current has to be determined in terms of hydrogen gas evolved in a certain time interval. The anodic current was supplied by the TiO_x -Pt couple itself, instead of using current from an external source to avoid the evolution of oxygen at the anode.

The assembled apparatus is shown schematically in Figure 2. Figure 3 is a photograph of the whole system. A wax lined three neck reactor flask was assembled so that one of the side openings contained a glass fitting equipped with a three way stopcock "e" and funnel "f", for the purpose of introducing into the system hydrogen and acid



a) reactor flask	h) cooling coil
b) leveling bulb	i) mercury thermal regulator
c) gas burette	j) stirrer
d) valve for outlet of gas	k) thermometer
e) relay normally closed	l) heating element
f) switch	m) water bath
g) battery, 6 V	n) outlet of gas

Figure 2

Schematic diagram showing the arrangement of apparatus for measurements of the difference effect.

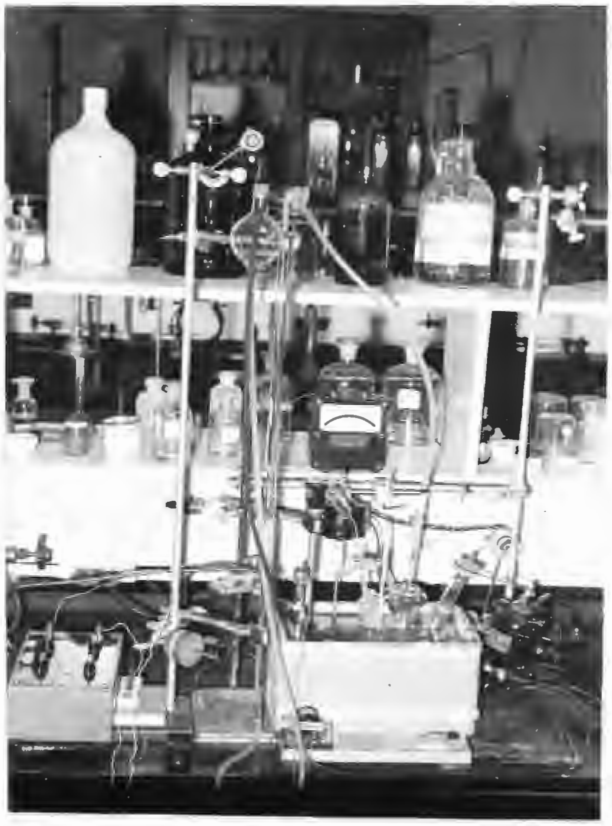
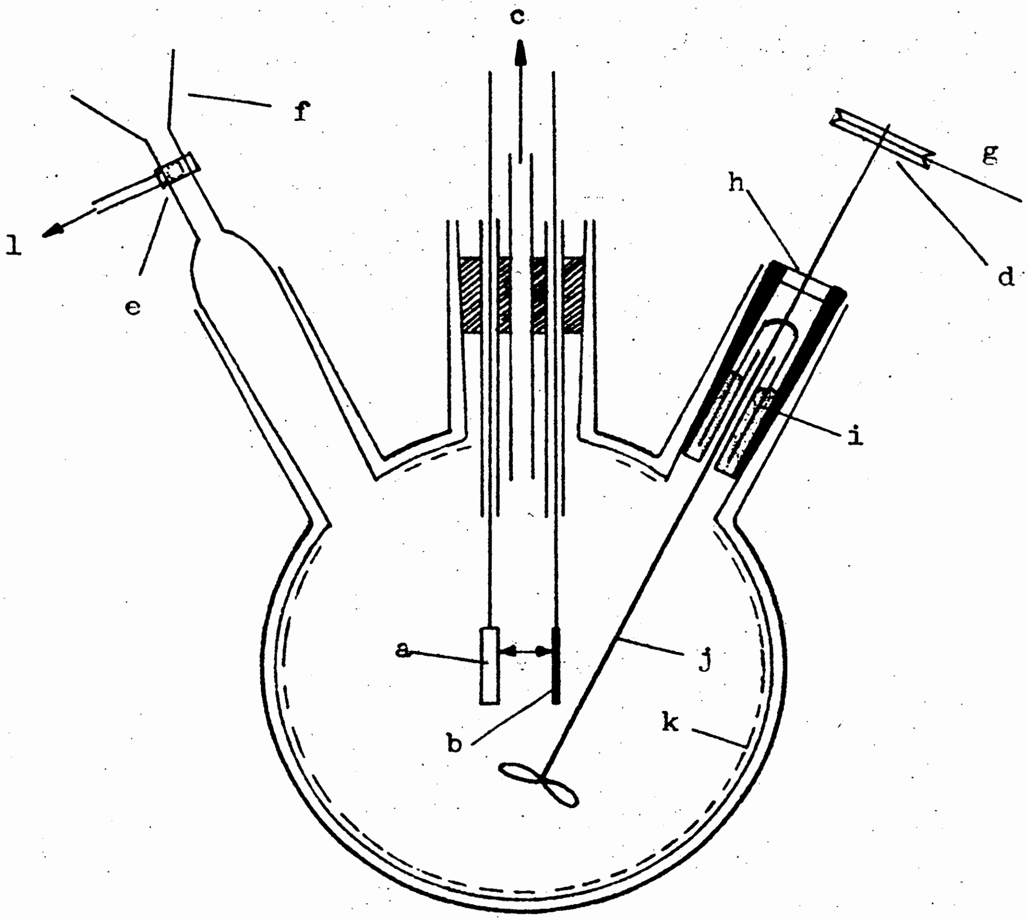


Figure 3

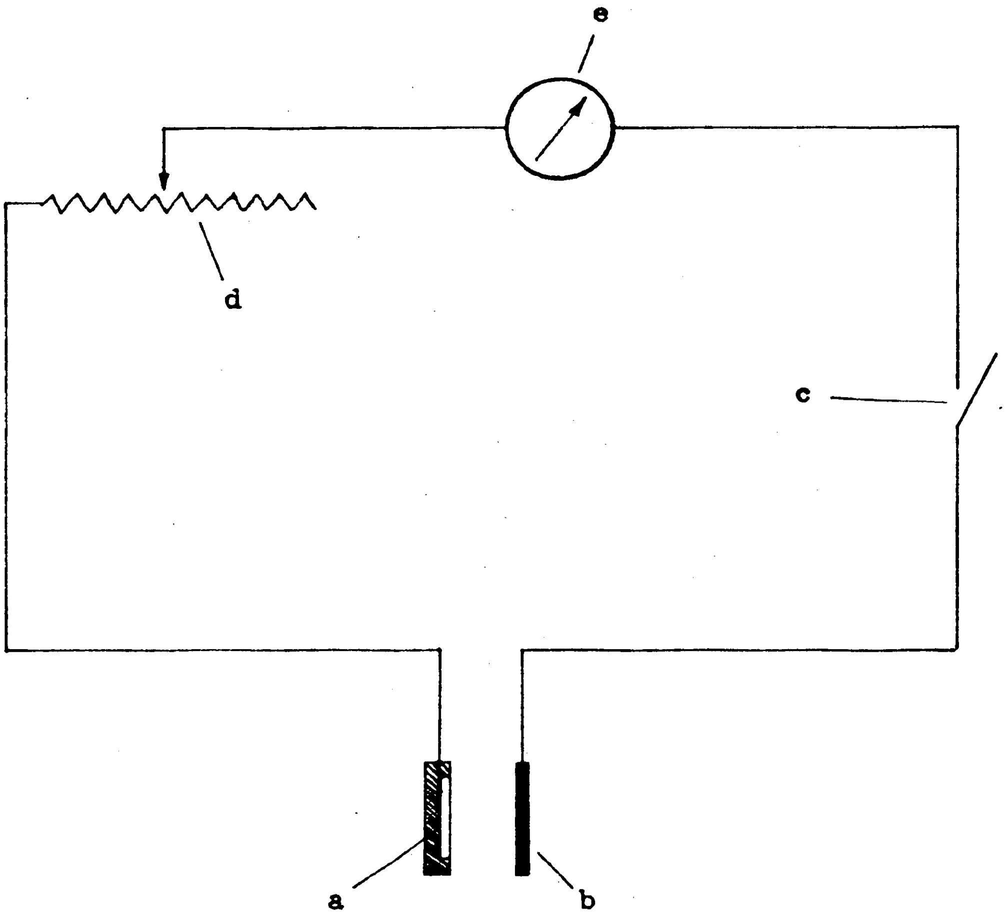
Photograph of the apparatus for determining the difference effects



a- TiO_x electrode	g - driving belt
b- Pt electrode	h - ball bearing
c- outlet to gas burette	i - mercury seal
d- pulley	j - plastic stirring rod
e- three way stopcock	k - beeswax coating
f- funnel for addition of acid	l - inlet of hydrogen

Figure 4

Apparatus for determining the difference effect



a) TiO_x electrode

b) Pt electrode

c) switch

d) resistance box

e) milliammeter

Figure 5

Circuit diagram for the measurement of the difference effect respectively. The other side opening held the mercury seal "i", through which a stirring mechanism was inserted. The center opening was fitted with a taper joint which held the electrodes and the outlet tube leading to the gas burette. A schematic diagram of the reactor flask is shown in Figure 4. The position of the electrodes was so adjusted that they were always immersed in a volume of 150 ml. A gas burette "c", was connected with the reactor flask to collect and to measure the volume of hydrogen evolved. A leveling bulb was used in connection with the gas burette to adjust the water column in the burette so that the pressure of the system could be approximated to that of the atmosphere. The reactor flask was immersed in a water bath in which a thermoregulator was used to maintain a constant temperature of 25±0.1° C. throughout the experiment. The current was measured by a d.c. milliampere meter in the circuit. Figure 5 shows the electrical circuit for the measurement of the current flowing through the electrodes. A resistance box was used to adjust the strength of the current in the circuit.

(C) Procedure for the measurement of the difference effect

The calculated amount of distilled water required to prepare the desired concentration of the acid was placed in the reactor flask and then the electrodes were inserted into the flask. Ten minutes were allowed to level out the temperature difference between the added water and the system.

The water leveling bulb, connected to the gas burette, was raised to a position to fill the water in the burette up to the narrow neck, so that only a neglegible amount of air remained in the burette during the following flushing operation. For the latter purpose a steady stream of hydrogen was introduced from "l", through the three way stopcock "e" into the system. The gas (hydrogen and air) was allowed to flow through the system and to exit under the water surface of the constant temperature bath. The flushing operation was continued for about ten minutes. At the end of this period the displacement of air by hydrogen was estimated to be quite complete. The main purpose for flushing the system was to expel the oxygen in order to preserve the trivalent state of titanium. At the end of the above flushing operation, the calculated amount of 2 N HF was poured into the funnel "f", and then the valve to the gas tank was closed. Some hydrogen displaced by the acid was allowed to exit in the same way as already mentioned. By turning the valve of the gas burette, the connection of the burette with the reactor flask was established. Another ten minutes were provided for the whole system to approach temperature equilibrium. Meanwhile, the barometric pressure and the room temperature were recorded. The preparation for measurement was completed at this point, the stirring motor was started, and the initial burette reading was taken.

The hydrogen evolved from the reaction between the metal and the acid displaced the water column in the burette. By continuous lowering of the leveling bulb, the pressure of the system could be adjusted to that of the outside atmosphere. The reduction of the volume of the evolved hydrogen to standard conditions was thus possible.

The reading of the burette was taken at regular time intervals, which were chosen to be 10 minutes for 0.25 N HF, and 5 minutes for 0.50 and 0.75 N HF. Readings were taken as long as an approximately constant rate of dissolution was recorded, at which time the circuit was closed to allow the flow of current through the cell. The circuit was opened again after one or two readings were made. The rate with the circuit open was determined again. The same operations were repeated with every change in current density. The anodic current was controlled by the resistance box "r", in Figure 5. Usually the measurement was started from 0 ohm resistance to allow the highest current density, then gradually increased to higher resistance for lower current density.

In case the entire volume of water in the burette was displaced with hydrogen before a sufficient amount of data were obtained, the three way stopcock above the gas burette "d", was turned so as to allow the exhaustion of hydrogen while raised. The volume measurement could thus be continued without repeating the flushing operation. Five minutes were provided for the system to approach equilibrium before the next reading. Barometric pressure and room temperature readings were taken again before finishing the measurements, then, the stirring motor was stopped, the electrodes removed from the reactor flask and kept in distilled water so that any poisoning of the platinum electrode could be prevented. The acid was sucked out through a siphon. The average readings of both barometric pressure and room temperature were taken for the calculation.

(D) Calculation

Since the volume was measured above water, the vapor pressure of water in addition to the correction for brass scale of the barometer at that temperature was taken into account. In order to simplify the calculation, the conversion factor was obtained by the equation:

$$\frac{1}{A} \times \frac{P}{T} \times \frac{273.1}{760} = \frac{P}{AT} \times 0.3594 \times 1000$$

where P is the corrected pressure in mm Hg; T, the average temperature in °K; A, the average surface area of the specimen in cm^2. The rate during a time interval was obtained by subtracting the initial from the subsequent burette reading. This value was multiplied by the correction factor to obtain the rate of hydrogen evolution expressed in mm^3/cm^2-min, at STP. The values for could thus be calculated from the Equation:

$$\Delta = V_1 - V_t + 6.97\ I$$

where V_1 is the rate obtained during open circuit, and V_t, that during closed circuit with a current density of I ma./cm^2 flowing through the cell. The current density I was obtained by dividing the current reading in ma. by the surface area of the dissolving specimen in cm^2. The average V_1 was found from the values before and after application of the anodic current.

The value of Δ as well as the proportionality constant k was calculated for each current density. The average value of k at each concentration of acid was also calculated.

An example of the calculation of Δ and k for the first specimen $TiO_{0.024}$ (0.785 w/o O) dissolved in 0.25 N HF, taken from Table I of the Appendix, is given below:

Average self-dissolution rate $V_1 = \frac{296.8 + 278.2}{2} = 274.0$ mm^3/cm^2-min.

Average total rate $V_t = \frac{295.1 + 306.0}{2} = 300.6$ mm^3/cm^2-min.

The rate provided by current density I = 6.97 I = 6.97 (19) = 132.4 mm/cm-min. $\Delta = V_1 - V_t + 6.97\ I = 274.0 - 300.6 + 132.4 = 105.8$ mm/cm-min.

$k = \Delta / I = 105.8 / 19 = 5.57$ mm^3/ma-min.

(E) Results

The difference effect on specimens dissolving in HF were determined in three concentrations; 0.25, 0.50 and 0.75 N. Some measurements were taken in mixed acids of HF and HCl. Specimen No. 3 ($TiO_{0.0555}$) was excluded because it had a smaller surface area than 1 cm, consequently, the result was less accurate. The results are tabulated in Appendix, Table I to Table XXI.

A summary of k values for each specimen obtained in different concentrations of HF is given in Table II:

TABLE II

Summary of Average k Values of 7 Specimens in HF

Specimen	Formula	k values			Average slope k
		0.25N	0.50N	0.75N	
1	$TiO_{0.024}$	5.38	5.56	5.19	5.40
2	$TiO_{0.037}$	5.82	5.71	5.72	5.78
4	$TiO_{0.0806}$	6.59	6.11	5.97	6.00
5	$TiO_{0.102}$	5.77	5.59	5.48	5.86
6	$TiO_{0.128}$	5.17	5.29	5.50	5.35
7	$TiO_{0.145}$	5.42	5.78	6.51	6.00
8	$TiO_{0.158}$	5.12	5.50	5.20	5.35

The difference effects are plotted versus current density in Figures 6, 7, 8, 9, 10, 11, and 12 for specimens 1, 2, 4, 5, 6, 7, and 8 respectively. It can be seen that the values of k remain approximately constant within the experi-

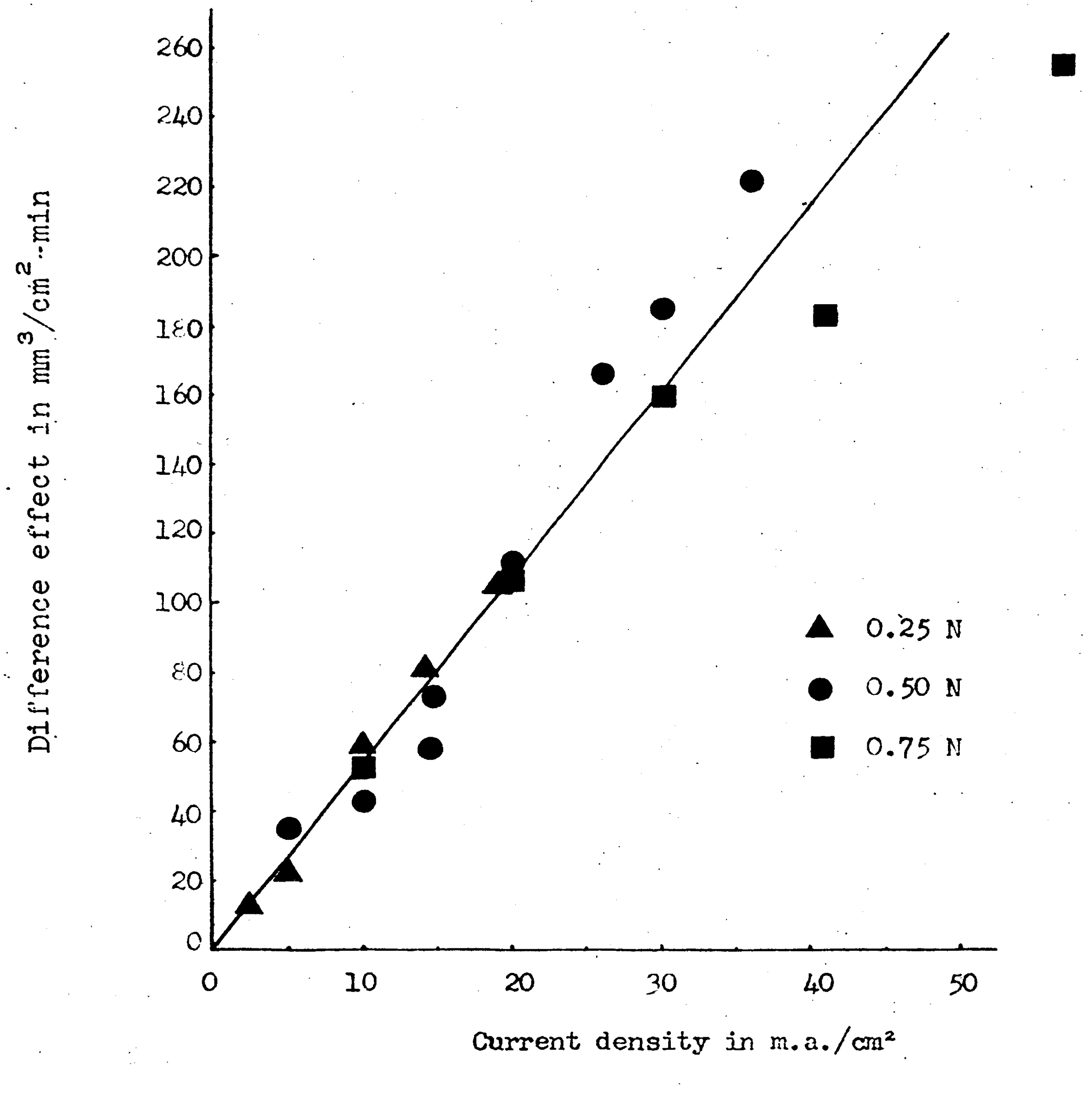


Figure 6

Difference effect on specimen # 1 $TiC_{0.824}$(0.785 w/o O)

versus current density in three concentrations of HF

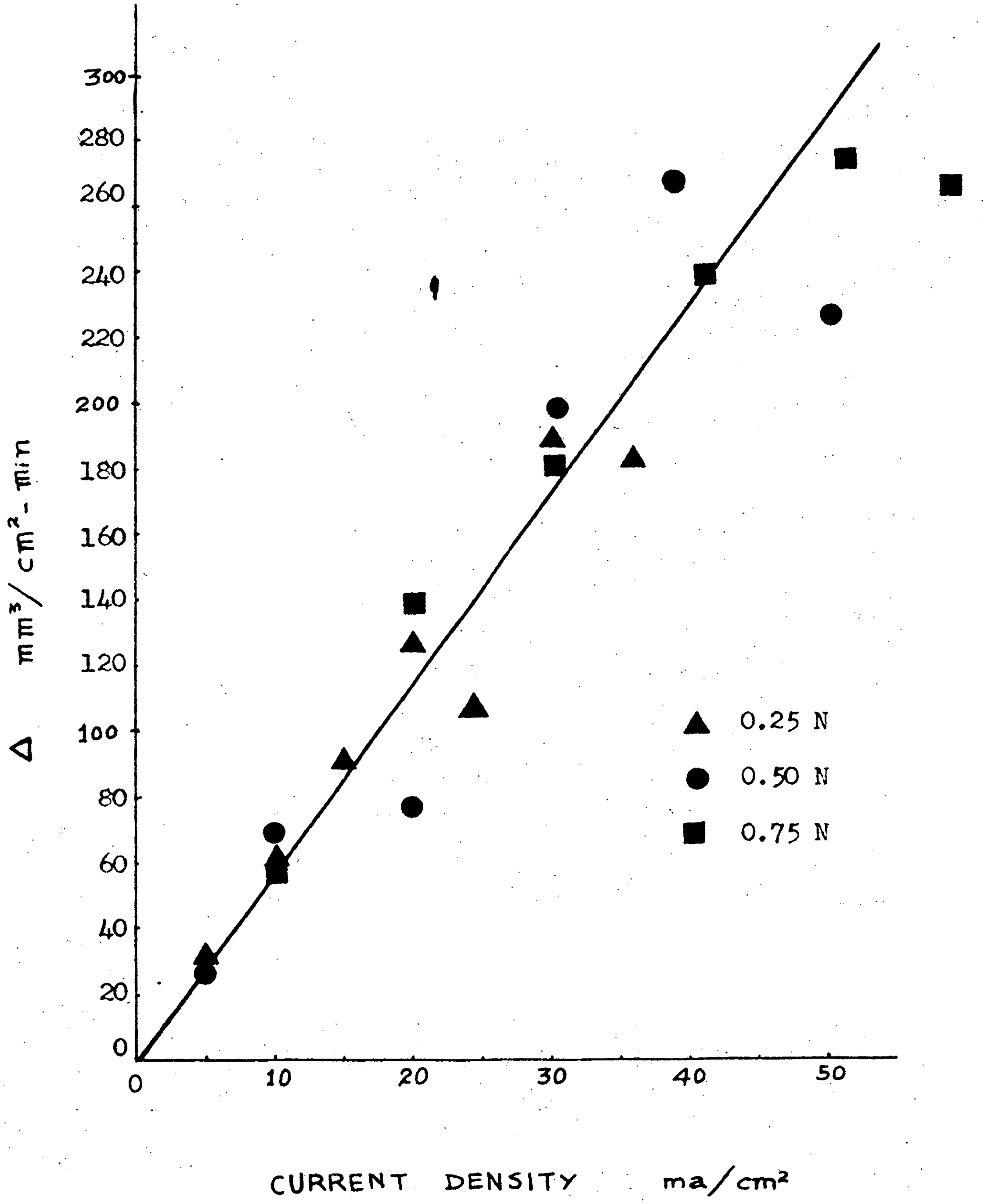


Figure 7

Difference effect on specimen # 2 (1.22 w/o oxygen) versus current density in hydrofluoric acid.

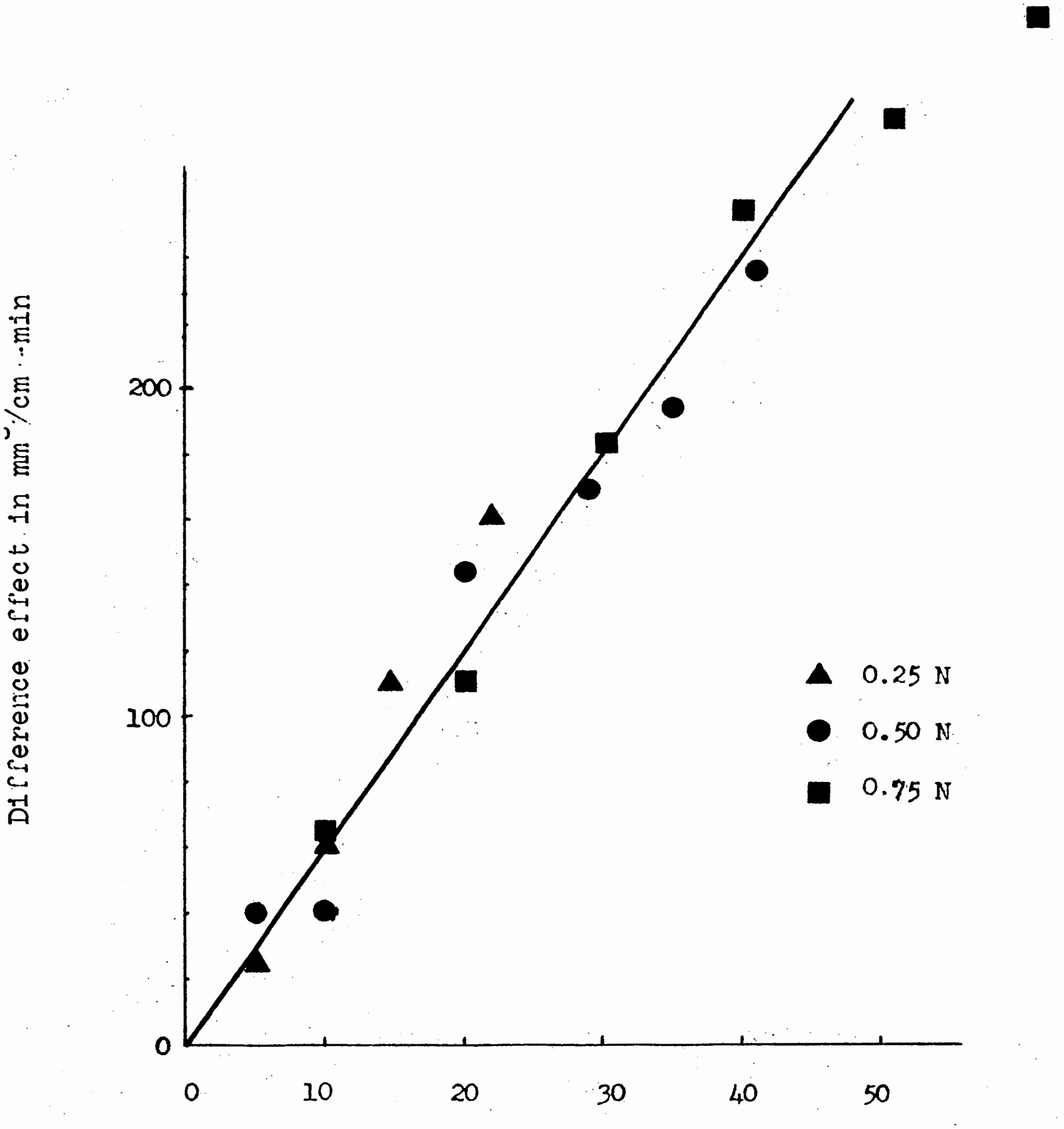


Figure 8

Difference effect on specimen # 4 (2.62 w/o oxygen) versus current density in hydrofluoric acid

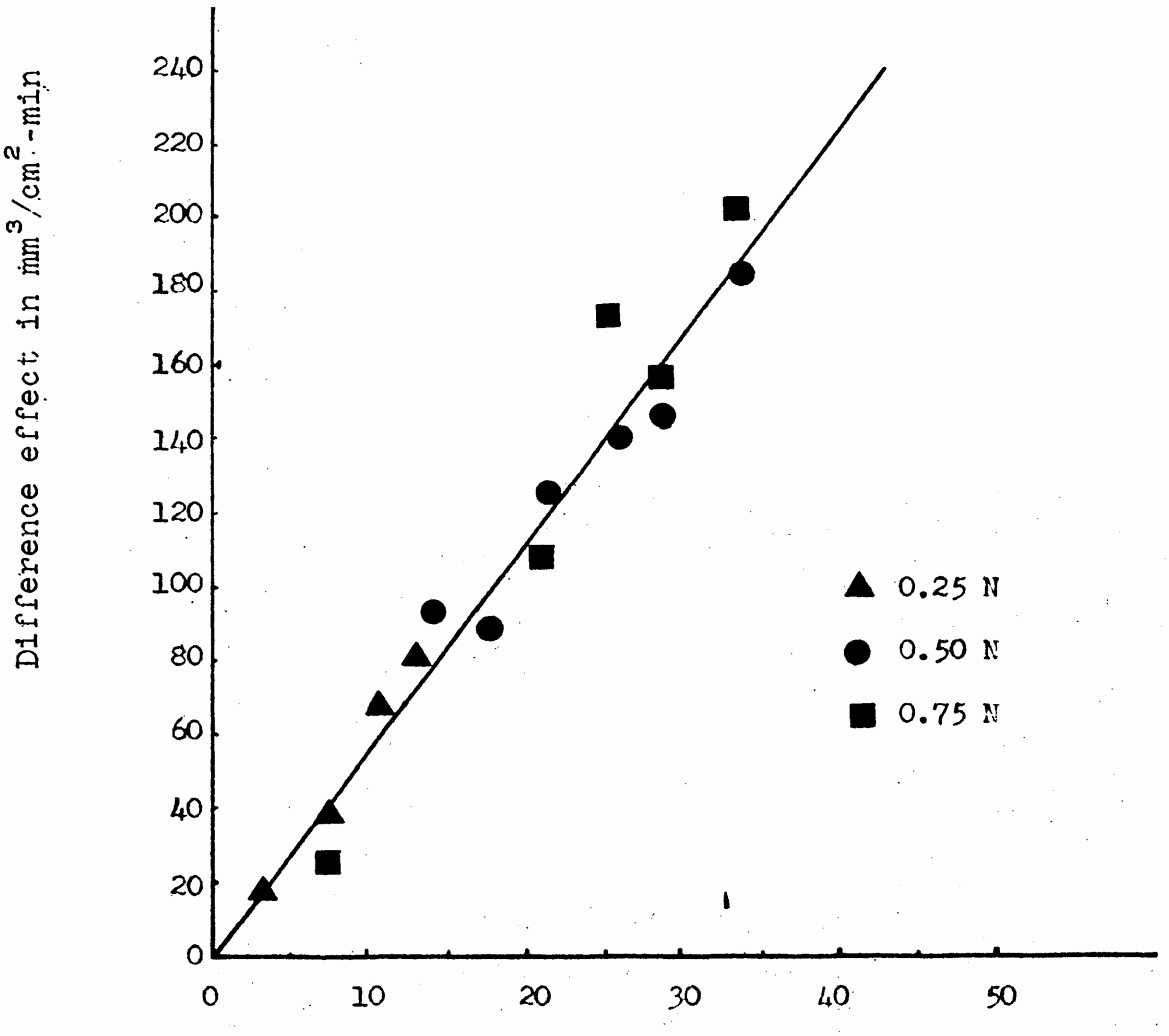


Figure 9

Difference effect on specimen # 5 TiO (3.30 w/o O) versus current density in three concentrations of HF.

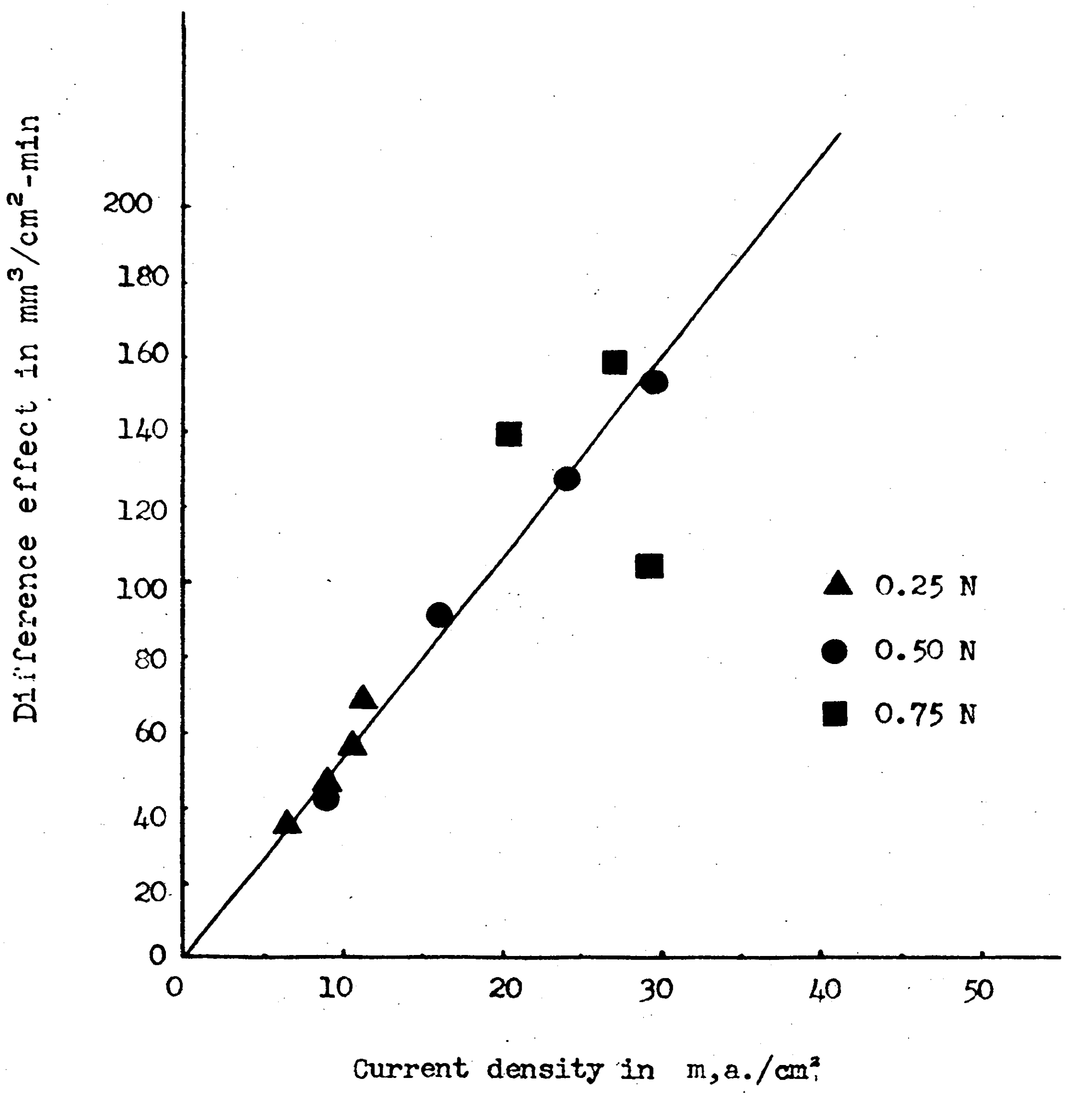


Figure 10

Difference effect on specimen # 6 (4.113 w/o oxygen) versus current density in hydrofluoric acid.

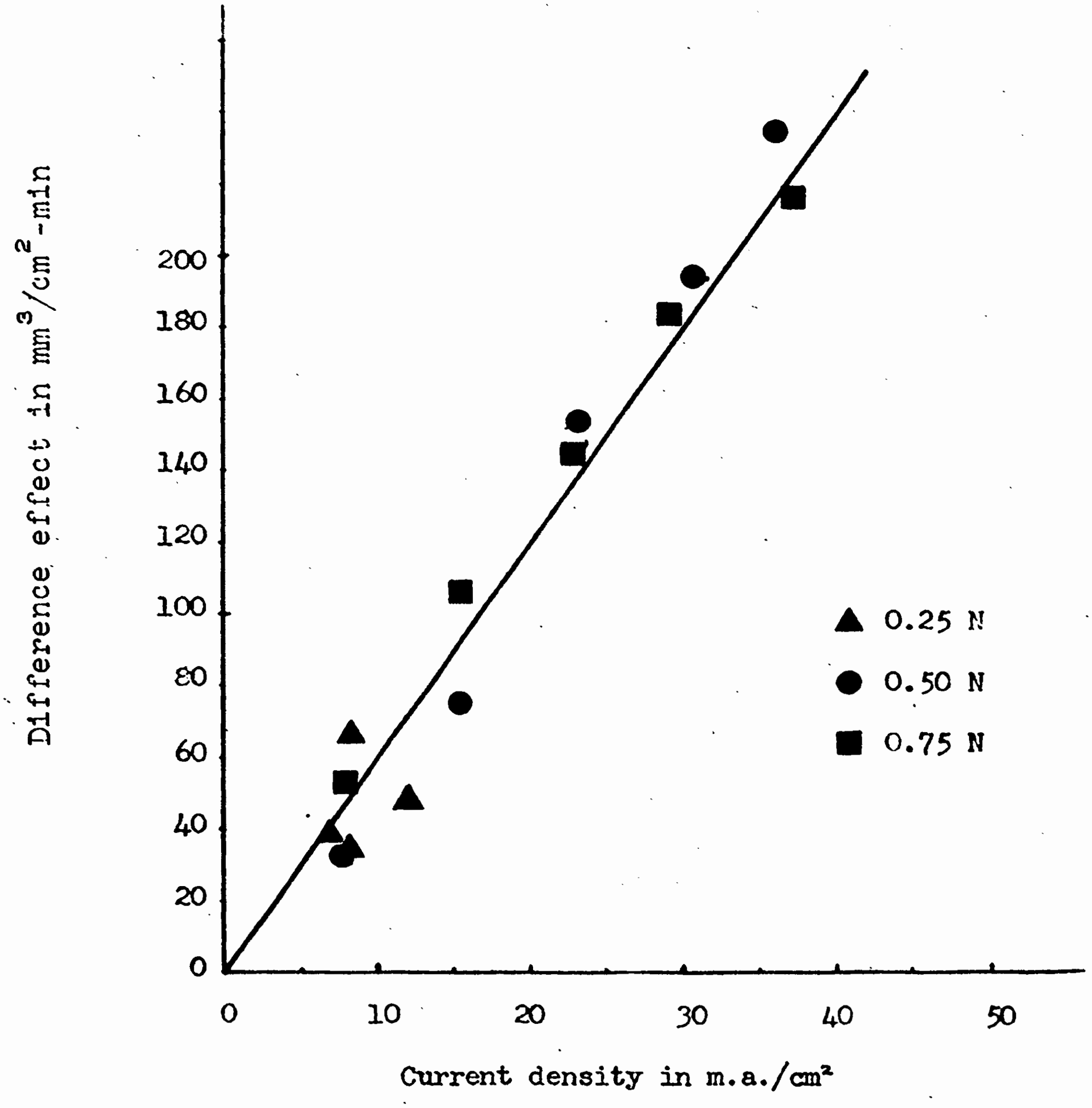


Figure 11

Difference effect on specimen # 7 (4.63 w/o oxygen) versus current density in hydrofluoric acid.

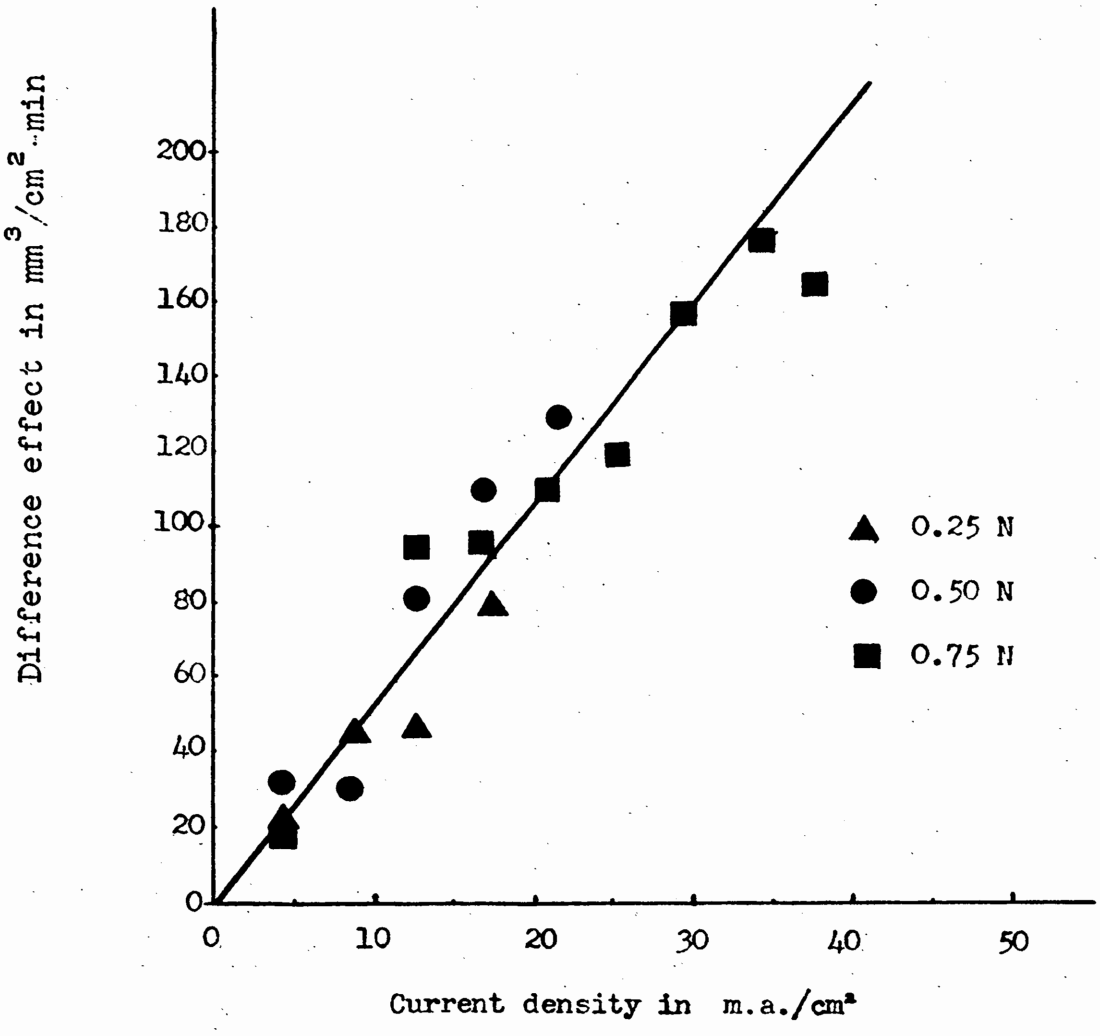


Figure 12

Difference effect on specimen # 8 (5.01 w/o oxygen) versus current density in three concentrations of hydrofluoric acid.

mental error. If the k's are considered constant, the average deviation from the average k is about ±0.4 which is less than the experimental error. These results would appear to be contrary to those obtained by a previous investigator (1) who found that the k values were higher for TiO_x (above 5 % O) than for Ti. However, his studies were carried out in the presence of HCl additions. Although the hydrochloric acid does not appear to alter the reaction kinetics, it is quite possible that the acid does influence the nature of film formation on the metal surface thus altering the k values. Because of this, some measurements in mixed acids HF-HCl were made. The results are summarized in Table III:

TABLE III

The difference effect on TiO solid solution in a mixture of HF and HCl

Specimen		Concentration		k
No.	Formula	HF	HCl	
5	$TiO_{0.102}$	0.50	-	5.74 ± 1.1
5	-	0.50	0.10	5.56 ± 0.3
5	-	0.50	1.0	7.47 ± 0.3
5	-	0.50	2.0	8.98 ± 1.2
6	$TiO_{0.128}$	0.25	1.0	6.35
7	$TiO_{0.145}$	0.25	1.0	6.51
8	$TiO_{0.158}$	0.50	-	5.50
8	-	0.50	0.50	7.63
8	-	0.50	1.0	8.28

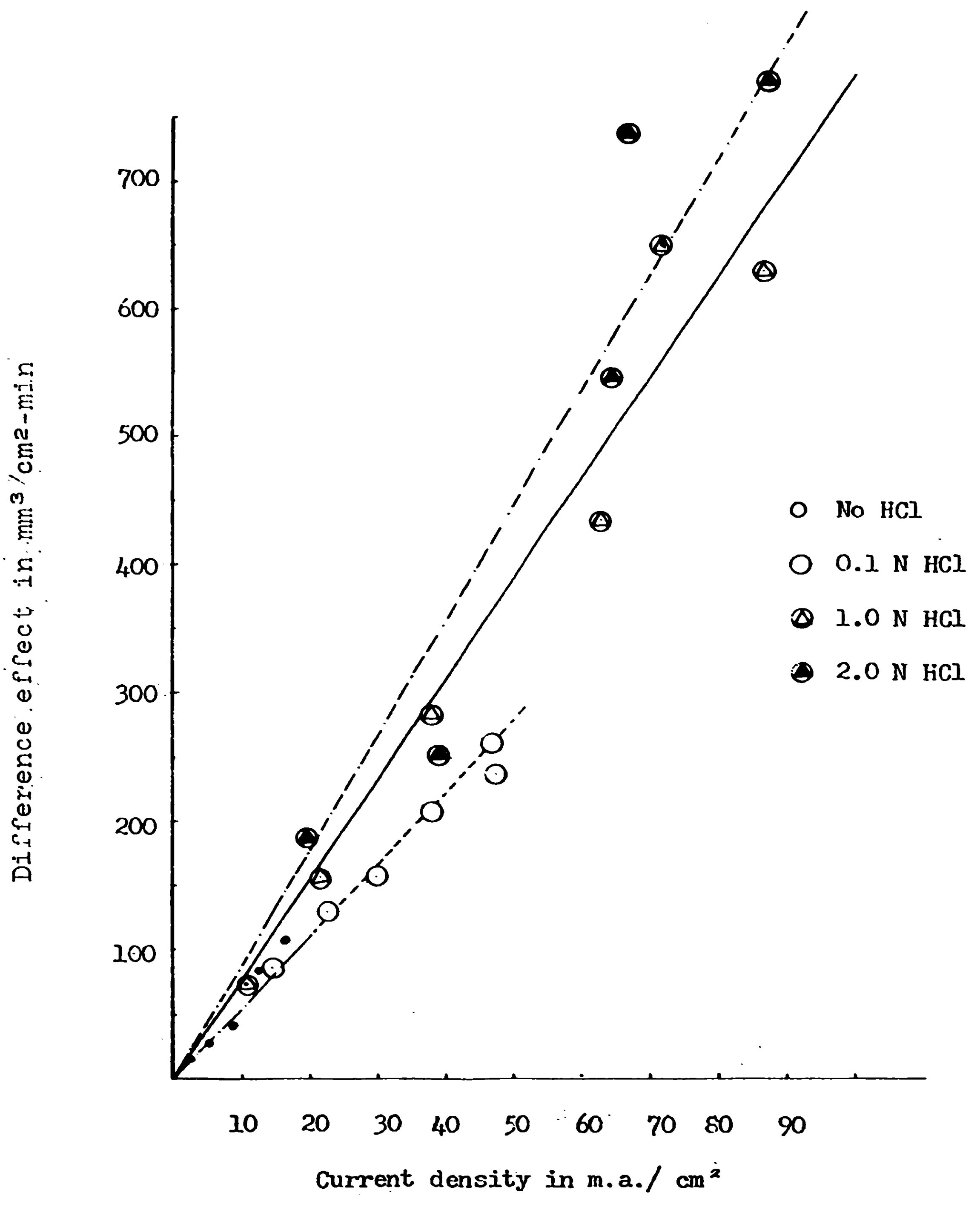


Figure 13

Difference effect on specimen # 5 (3.30 w/o oxygen) versus current density in the mixture of 0.5 N hydrofluoric acid and various concentrations of hydrochloric acids.

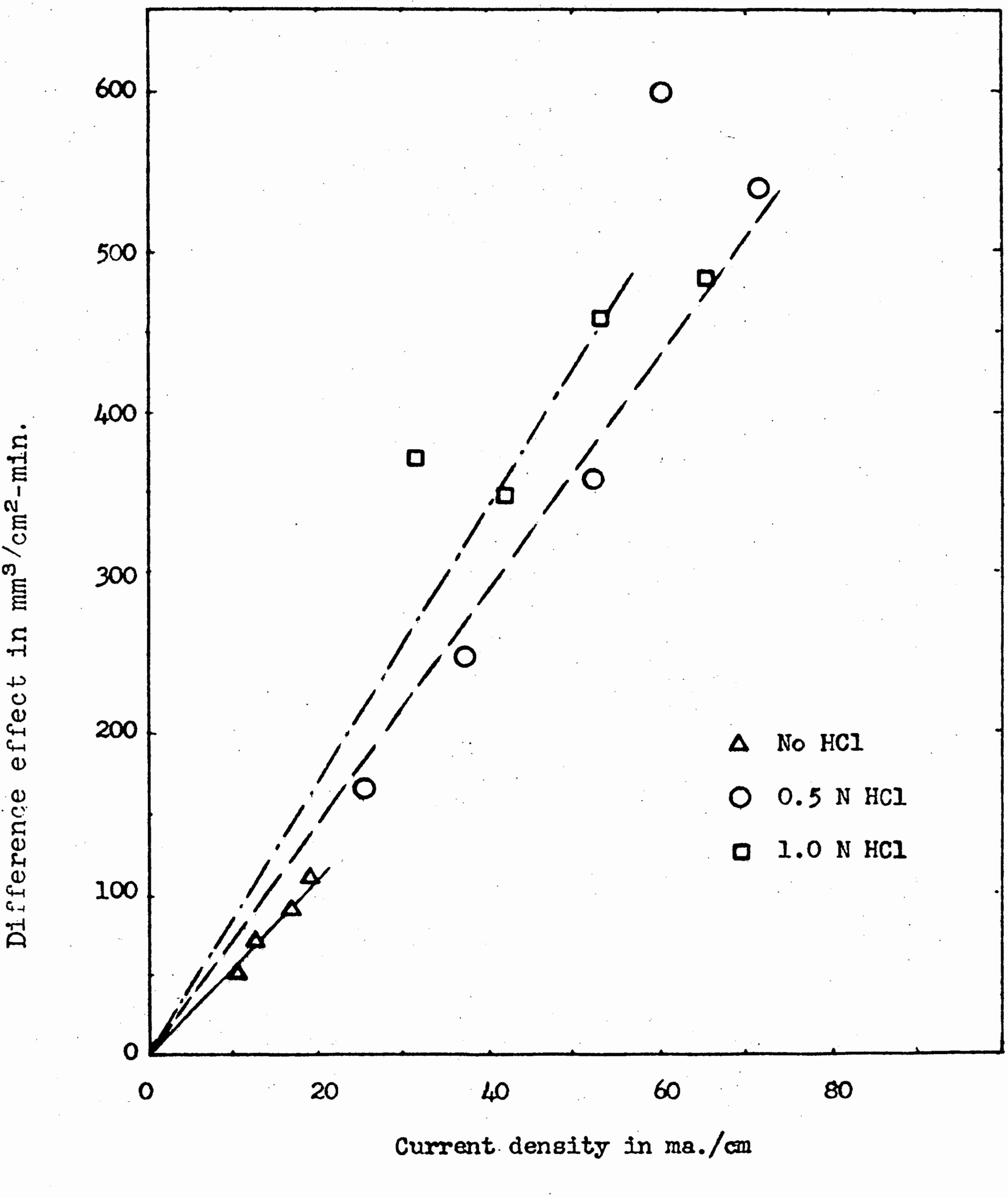


Figure 14

Difference effects on $TiO_{0.158}$ (8, 5.01 w/o O) versus current density in the mixture of 0.5 N hydrofluoric acid and various concentrations of hydrochloric acids.

The plots of the difference effect versus current density for specimens No. 5 and No. 8 are shown in Figures 13 and 14 respectively. A substantial increase in k values in comparison with those obtained in HF alone can be seen from Table IV, especially with Specimens No. 5 and No. 8. The following phenomena were observed during these experiments:

(1) The lower the circuit resistance was, the greater were the fluctuations of the current. Very severe fluctuations (± 15 ma.) were observed at 0 ohm resistance of the box.

(2) The current readings at 0 resistance were even less than those at 1 ohm, and sometimes less than 2 ohms box resistance.

(3) The greater these fluctuations, the higher the k value calculated; the highest k values were found in most cases from the measurement at 0 ohm resistance of the box.

One measurement was also performed in a mixture of HF and NaCl in order to see whether the Cl ion was important in the reaction or not. Almost the same phenomena and the same results were obtained as in the case of HF-HCl.

Measurements at higher stirring speed (increasing it from 286 to 1800 rpm.) were made to study the relation between the speed, the current density, its fluctuations and the k constants. The results are summarized as follows:

Specimen No. 8	k	
$TiO_{0.158}$	at 286 rpm	at 1800 rpm
in 0.5 N HF	5.50	5.56 ± 0.4
in 0.5 N HF-0.5 N HCl	7.63	6.67 ± 0.3

The fluctuations of currents were greatly reduced with increasing stirring speed. As a consequence, more constant k values were obtained.

IV MEASUREMENTS OF DISSOLUTION POTENTIALS OF THE DISSOLVING ALLOYS

(A) Dissolution Potentials without anodic current

The dissolution potentials of four specimens in two concentrations of HF and in two mixed acids (0.105 N HF-1.0 N HCl and 0.25 N HF-1.0 N HCl) were made, since it is reported that potential measurements are the most useful tool in helping to understand corrosion processes (13). For the measurements a 1 N calomel electrode was used as the reference electrode. The E. M. F. of the TiO_x/HF, 1N KCl, Hg_2Cl_2/Hg cell was determined with a precision potentiometer. The Calomel half cell was prepared according to the specifications of Daniels (14). The accuracy of the measurements was checked with a pure zinc electrode in equilibrium with 1 M zinc sulfate solution. The average of three emf readings of the cell (Zn/ 1 M ZnSO, 1 N KCl, Hg_2Cl_2/Hg) was 1.0686 at 28° C. According to the equation given for the potential of the 1 N calomel electrode,

$$E_{cal} = 0.2800 - 0.00024\ (t - 25)$$

$$E_{cal} = 0.27928 \text{ at } 28°\ C.$$

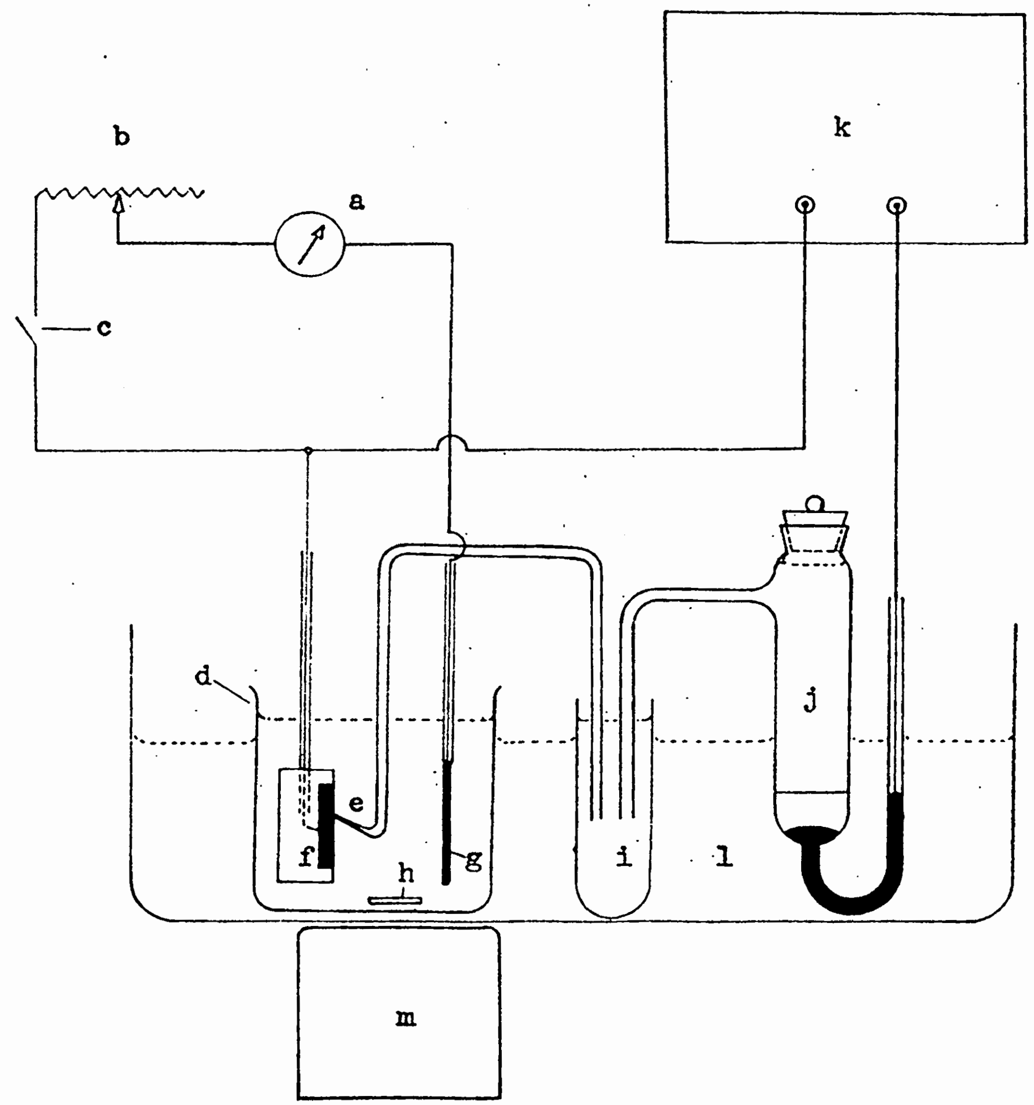
Thus, $E_{Zn} = 0.27928 - 1.0686 = -0.7893$ volts on the hydrogen scale.

The calculated E at 28° C. using the equation,

$$E'_{Zn} = E'_{Zn} + \frac{RT}{nF} \ln (rm)$$

when E = -0.7628, r = .043 (15)

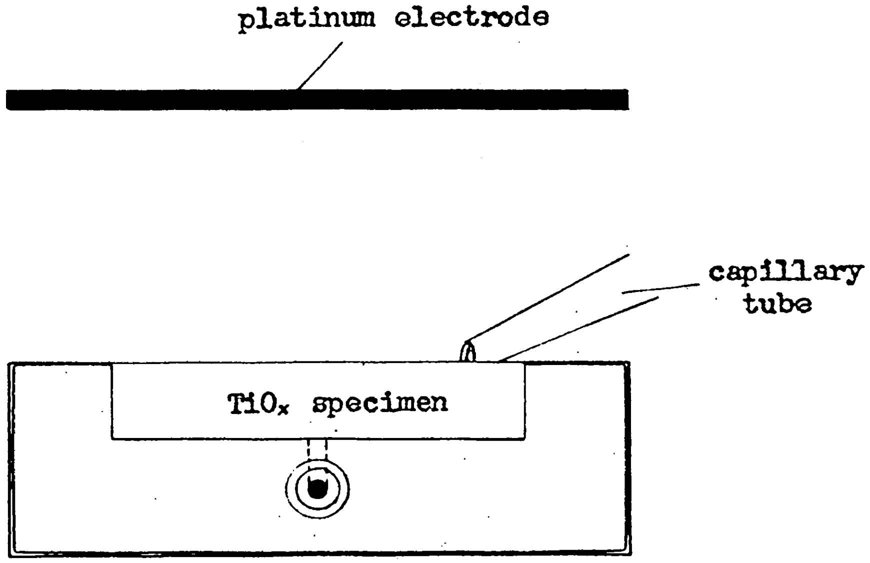
is -0.8036 volts.



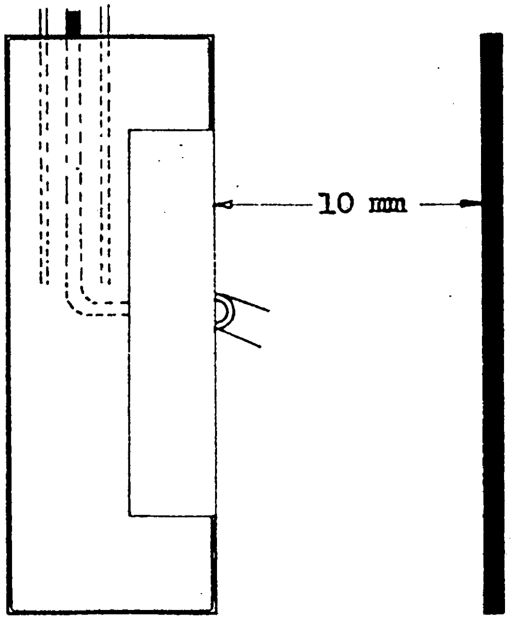
a) milliammeter	h) stirring rod
b) resistance box	i) salt bridge
c) switch	j) calomel electrode
d) plastic beaker	k) precision potentiometer
e) capillary tube	l) water bath
f) TiO_x electrode	m) magnetic stirrer
g) Pt electrode	

Figure 15

Apparatus for measurements of the dissolution potential



top view



side view

Figure 16

Sketch showing the end of capillary tube

As the difference between the two values is only 0.0143 volts, the method works satisfactorily. The electrode of titanium was prepared from a commercial grade sheet ordered from Titanium Corporation of America, containing 0.1 Fe, 0.02 N w/o, and a trace of O.

(1) Apparatus and Procedure

The measurements of the dissolution potentials were made by the apparatus as shown schematically in Figure 15. The beaker "b", containing the acid and the stirring rod of the magnetic stirrer was immersed into the water bath "c", to maintain the system at an approximately constant temperature. The magnetic stirrer "s", was placed below the water bath. Since no temperature regulator was used, the measurements were made at room temperature. A stirring speed of roughly 300 rpm. was maintained by setting 50 on the dial of the ohmic controller. A salt bridge of saturated KCl solution was used for the connection between the reference electrode and a thin capillary tube extended to the surface of the specimen to exclude the junction potential. The end of the thin capillary tube making contact with the surface of the specimen was cut in a shape as shown in Figure 16 to provide a close contact between the tube and the dissolving specimen. The reading for the potential difference of the chain was taken as soon

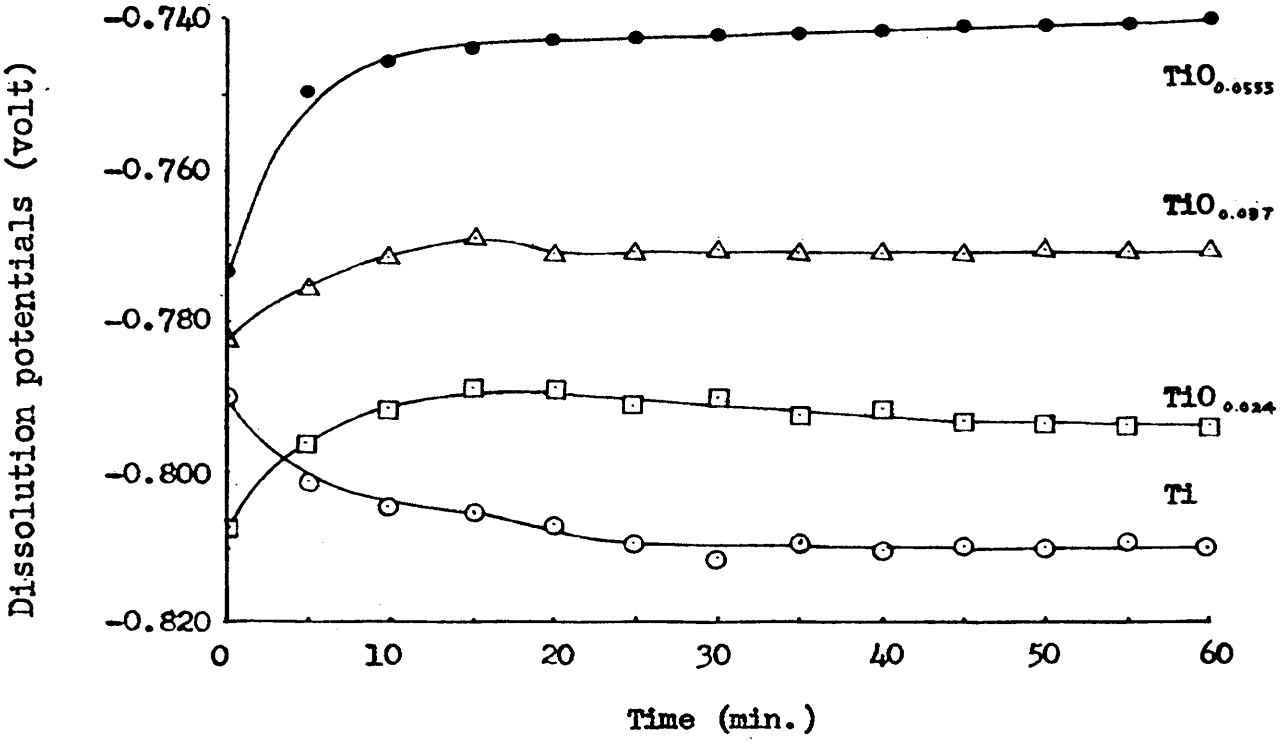


Figure 17

Dissolution Potentials of TiO_x in 0.25 N HF versus time.

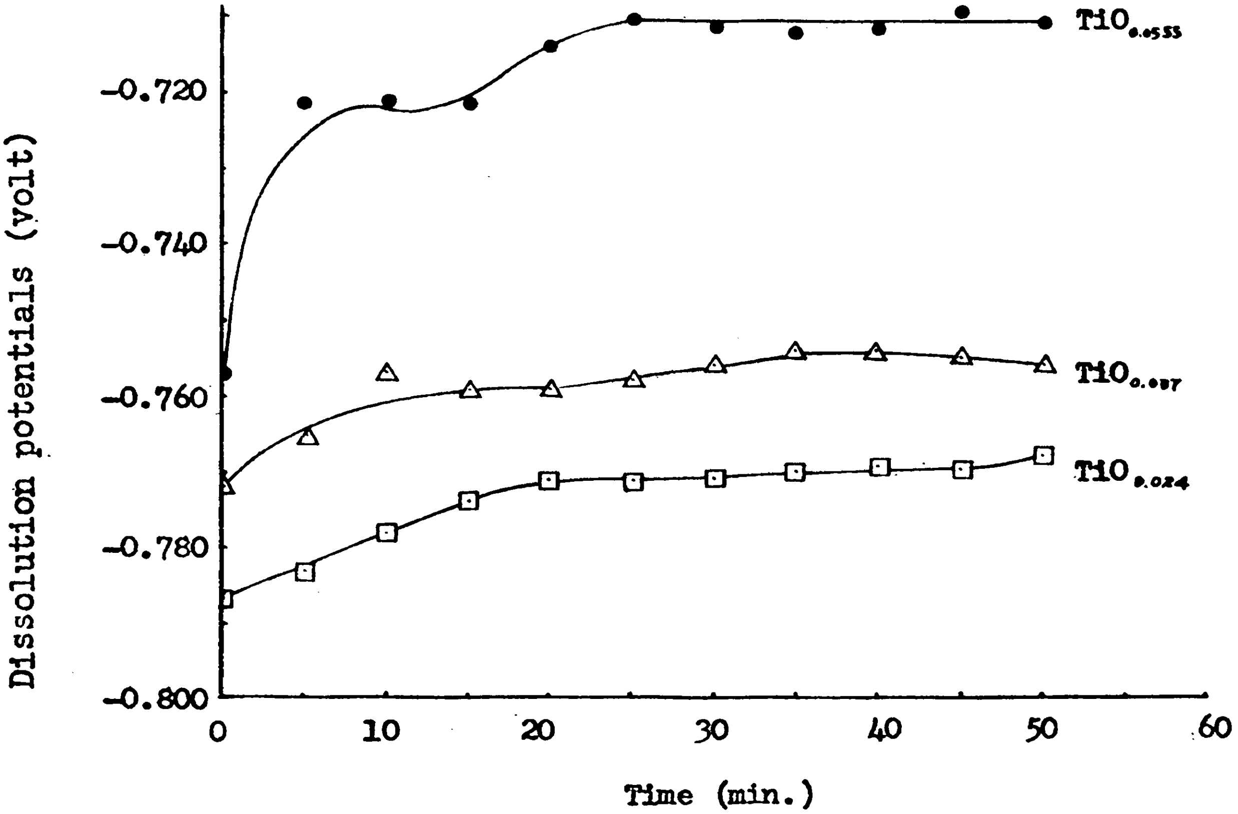


Figure 18

Dissolution Potentials of TiO_x in 0.50 N HF versus Time.

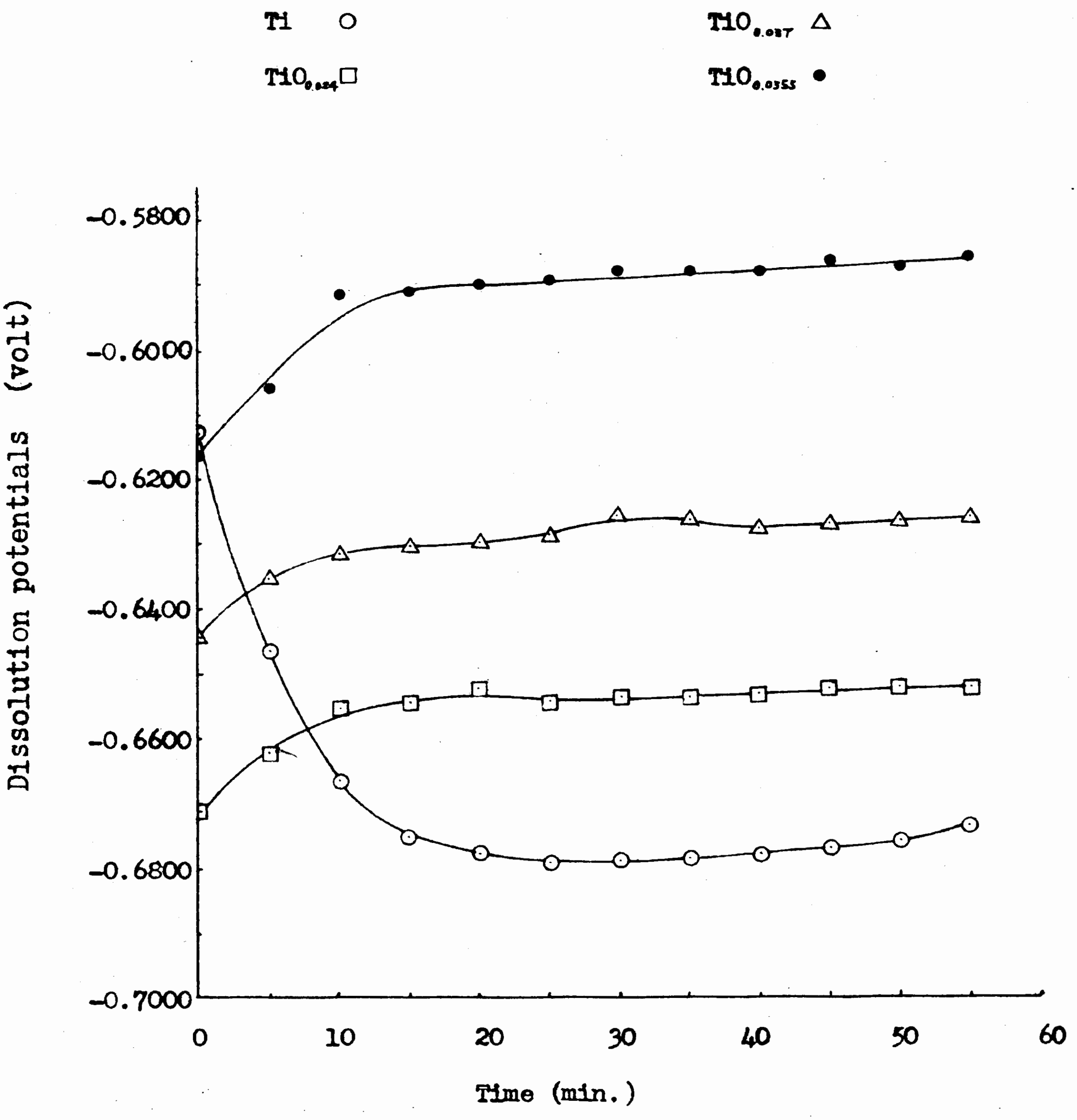


Figure 19

Dissolution Potentials of TiO$_x$ in 0.105N HF-1.0N HCl versus Time

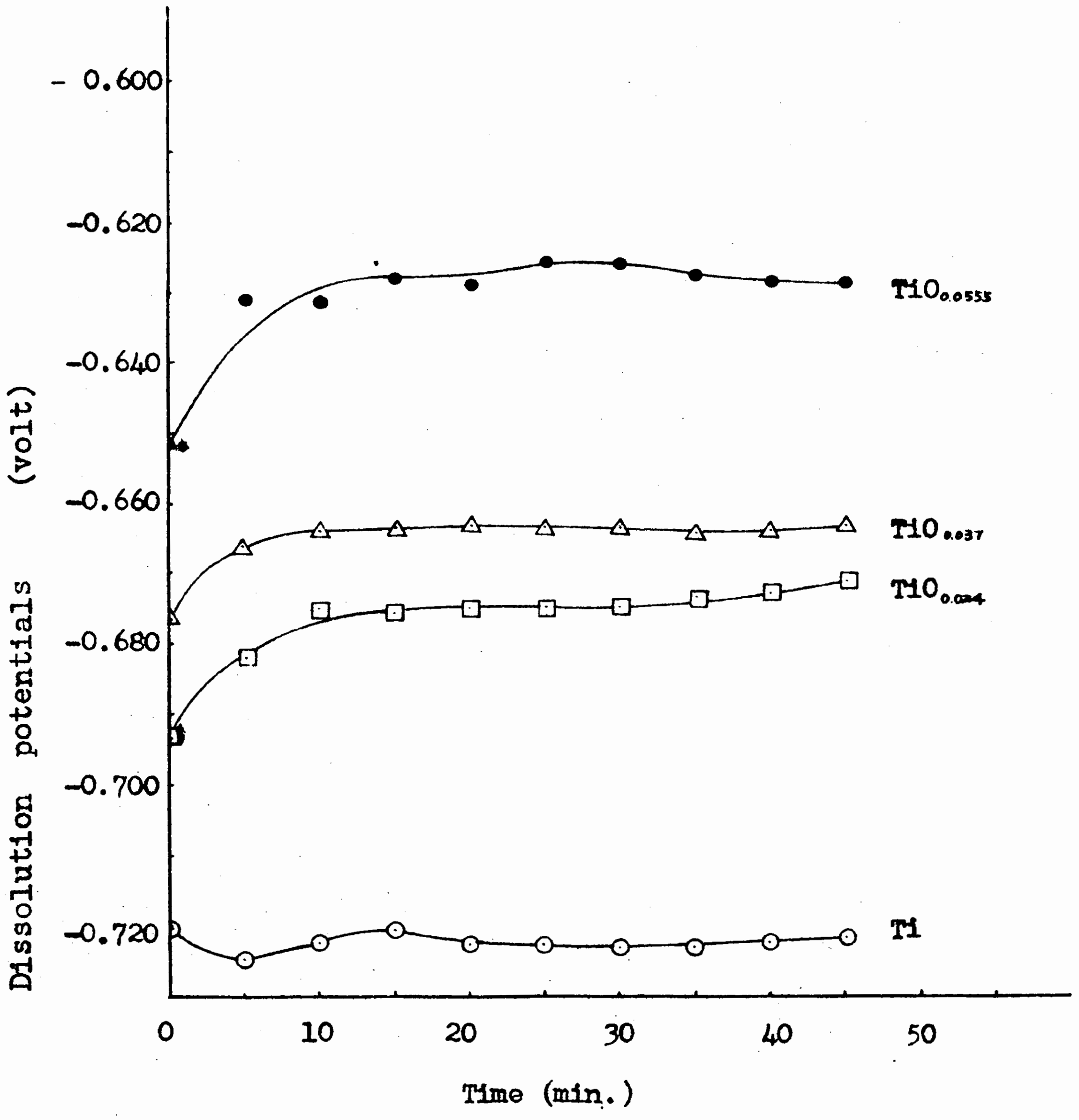


Figure 20

Dissolution Potentials of TiO_x in 0.25 N HF-1.0 N HCl versus Time.

as possible after the electrode was immersed into the acid, and later at 5 minute intervals.

(2) Results

The dissolution potential E' was expressed on the hydrogen scale by adding E'_{cal} (calculated value for that particular temperature) to the potential as measured against the calomel electrode. The results are tabulated in the Appendix, Table XXIX to Table XXXII. Plots of the dissolution potential versus time in varying HF concentrations are shown in Figures 17, 18, 19, and 20. It was found that

(1) The higher the oxygen content of the alloy, the more noble its E' in the same concentration of acid.

(2) For the same alloy, E' was more noble in the lower concentration of the acid.

(3) Keeping the concentration of HF constant, the addition of HCl shifted the E' of the alloy to more noble potentials.

(4) Pure titanium was the only electrode which became less noble in the course of time.

(5) A steady potential was obtained after 20 minutes in most cases.

(B) The Effect of Current Density on the Dissolution Potential E'

As the difference effect is directly proportional to the anodic current density, the measurement of E' under different current densities is most interesting. The potential measurements were carried out as previously described. However, a platinized platinum electrode as used in difference effect measurements was coupled with the TiO_x electrode. The same circuit as that shown in Figure 15 was used to control and to measure the current flowing through the chain. In order to introduce the capillary tube, the distance between the electrodes was increased to 10 mm. The capillary tube was designed to approach the TiO_x surface from one side so as to reduce its shielding effect, the iR drop and to minimize the disturbance of the equipotential surface.

Starting with the highest current density delivered by the cell, each measurement was taken 5 minutes after the change in current density. Three readings were recorded for each current density following each other in 1 minute intervals.

The specimens $TiO_{0.037}$, $TiO_{0.158}$, $TiO_{0.128}$ and $TiO_{0.145}$ were measured in three concentrations of HF; namely, 0.25, 0.50, and 0.75 N. The E' of the pure Ti electrode was determined in 0.1, 0.25, 0.50 and 1.0 N HF.

The average value of three readings is tabulated in the Appendix, Table XXXIII to Table XXXVII. The same calculation as previously described is applied. The plots of the

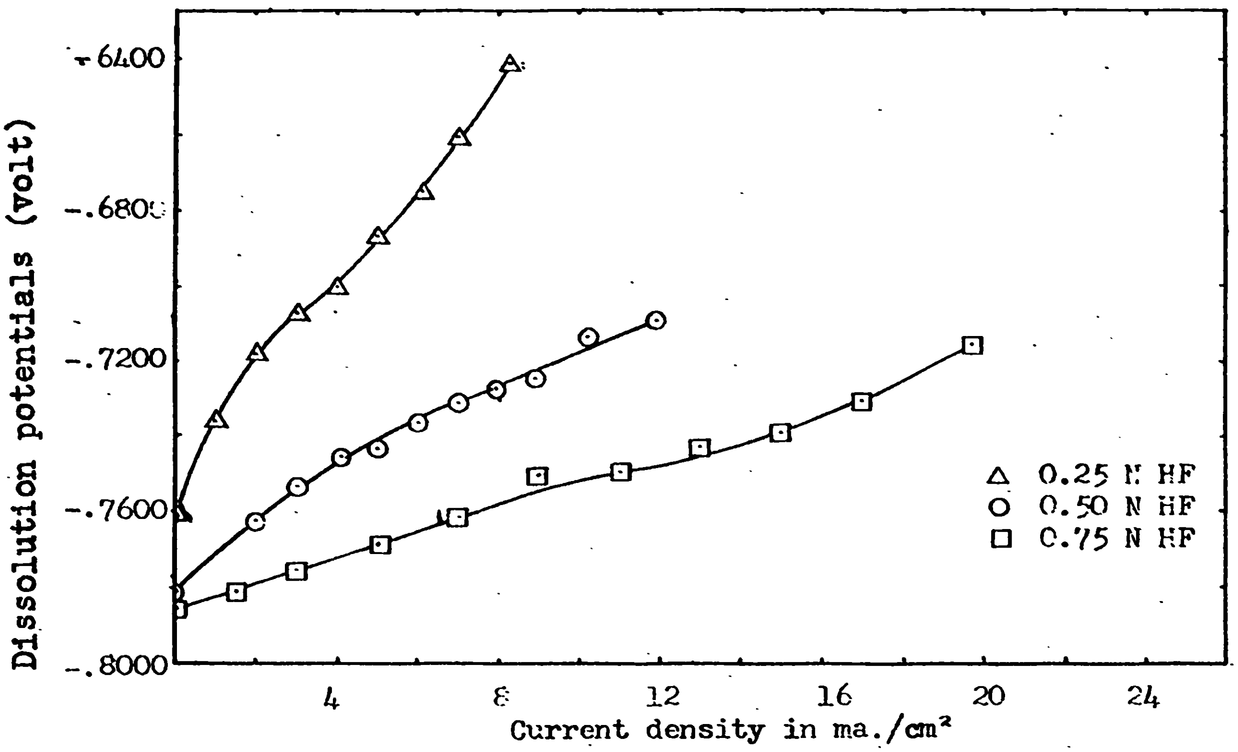


Figure 21
The effect of current density on the dissolution potential of $TiO_{0.037}$

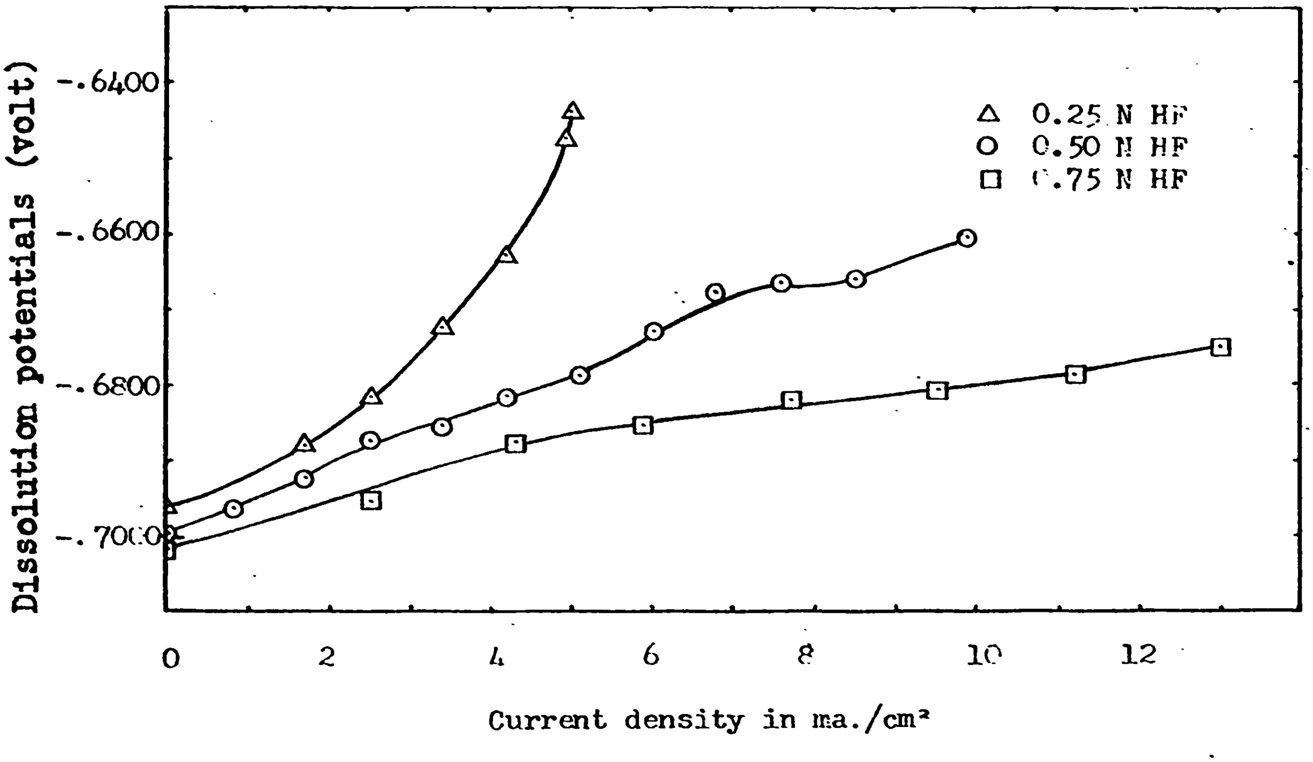


Figure 22
The effect of current density on the dissolution potential of $TiO_{0.158}$

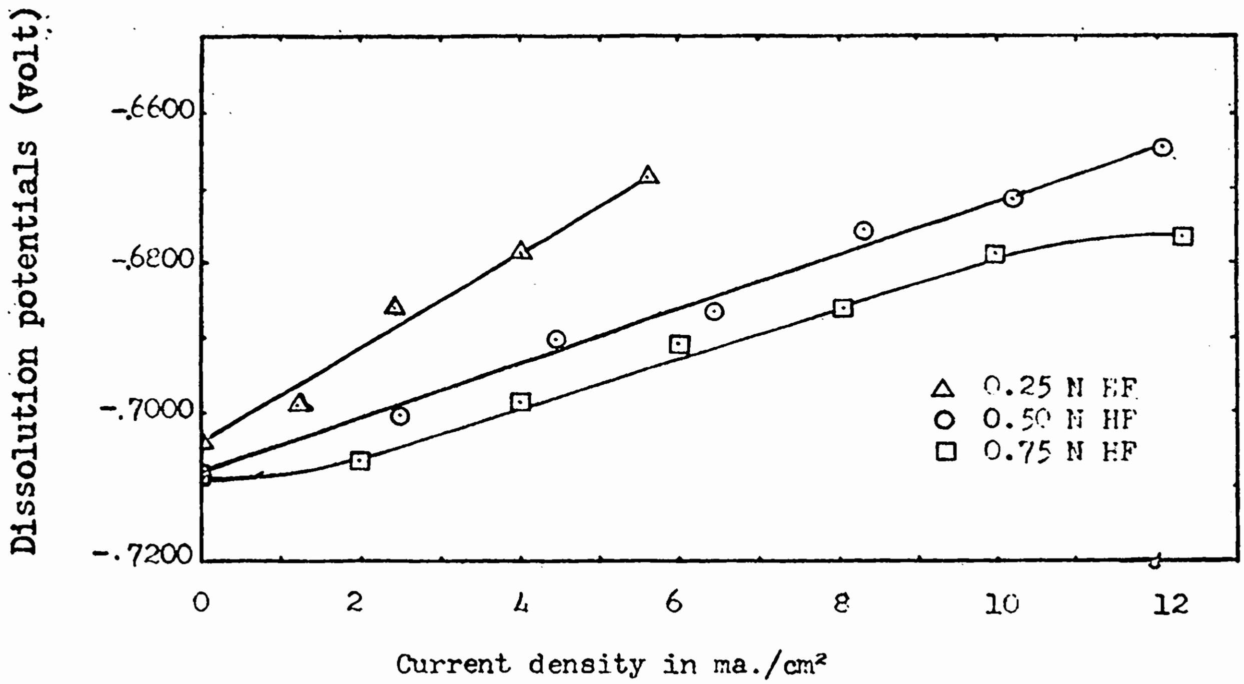


Figure 23

The effect of current density on the dissolution potential of Specimen # 7 $TiO_{0.145}$ in HF

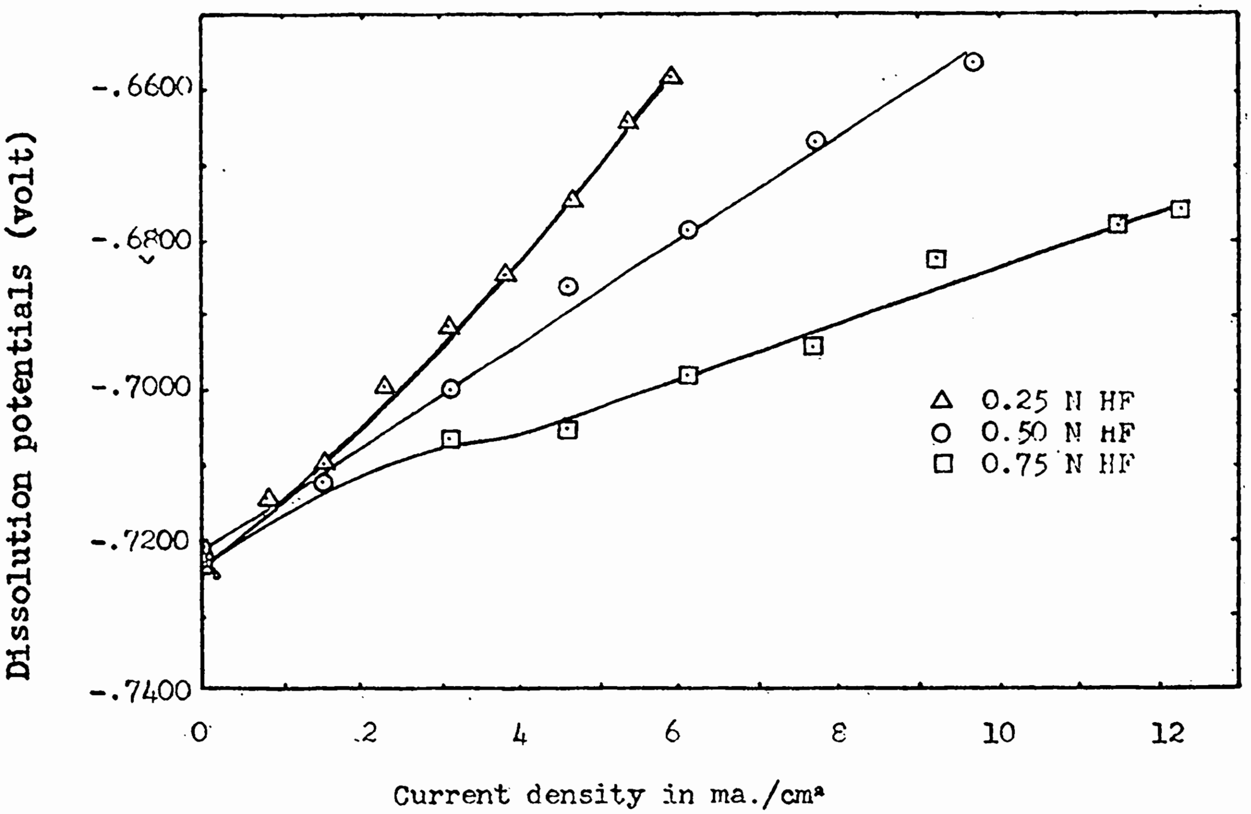


Figure 24
The effect of current density on the dissolution potential of specimen # 6 in HF

dissolution potentials E' versus current density are shown in Figures 21, 22, 23, 24, 25, for $TiO_{0.037}$, $TiO_{0.158}$, $TiO_{0.145}$ and $TiO_{0.128}$ respectively.

It can be seen, from these curves, that in each case the increase in current density is associated with the shifting of E' toward more positive (noble) values. The increase in potential is greater the lower the concentration of the acid. This effect is similar to that observed on Al (6) and Zr (10).

(C) Potential Measurements During the Measurement of Difference Effect

The measurement of the dissolution potential under different current densities described above gave evidence of an approximately linear relationship between the potential and the current density. However, the measurements were carried out in an open vessel. Under such conditions, some other factors might be involved. It might be that the dissolution potential varies linearly with the total current density (the sum of I and the dissolution rate converted into the current), therefore, a simultaneous measurement of both dissolution potentials and of the difference effects was made.

The apparatus used for potential measurements, consisting of the 1 N calomel half cell, salt bridge, capillary

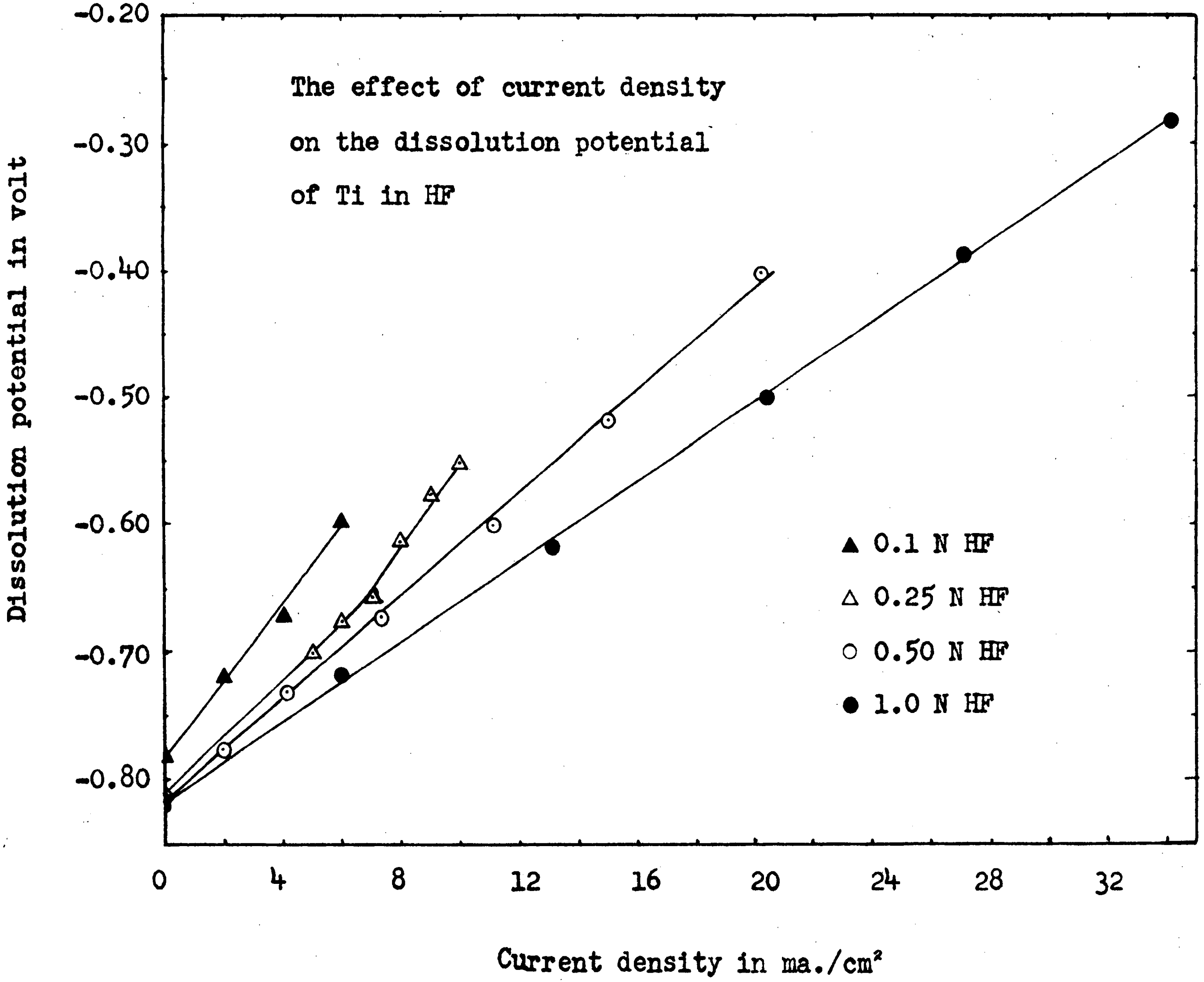

The effect of current density
on the dissolution potential
of Ti in HF
Dissolution potential in volt
-0.20
-0.30
-0.40
-0.50
-0.60
-0.70
-0.80
0
4
8
12
16
20
24
28
32
Current density in ma./cm²
▲ 0.1 N HF
△ 0.25 N HF
○ 0.50 N HF
● 1.0 N HF

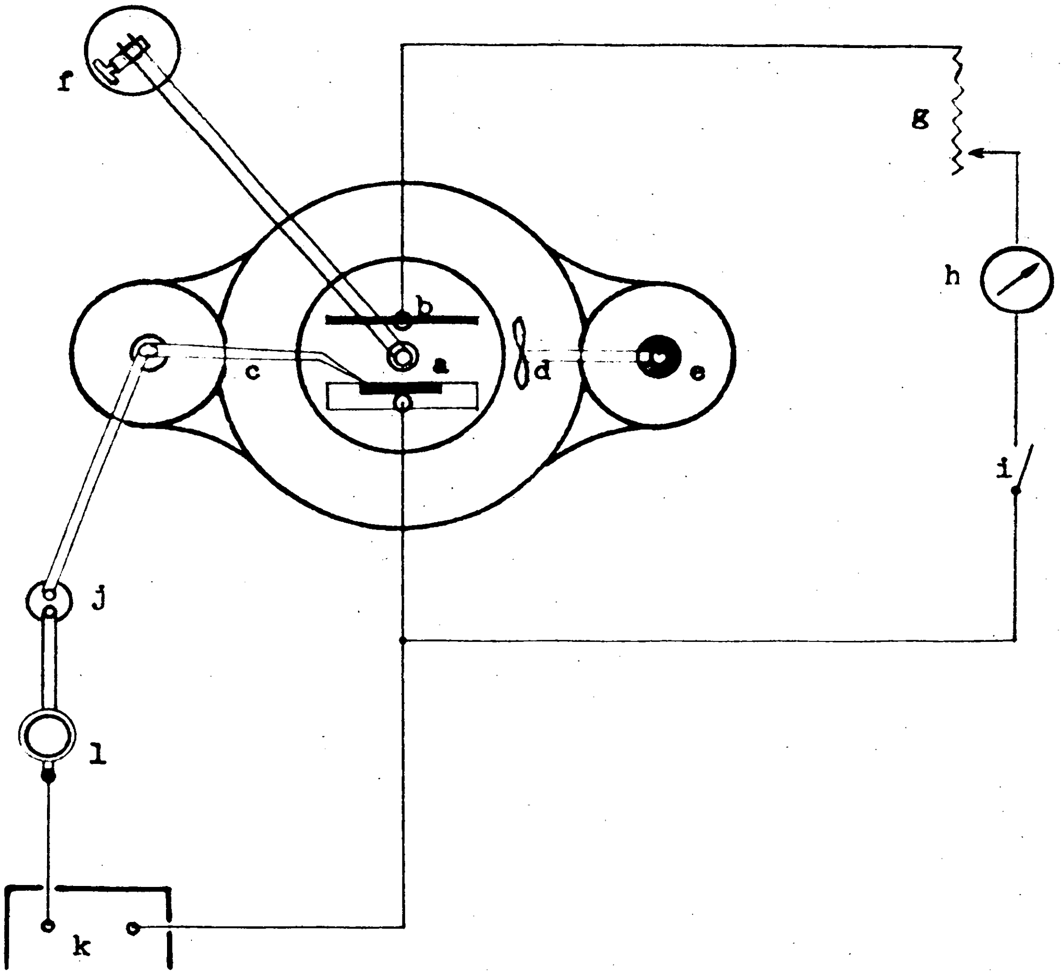
Figure 25

tube and potentiometer, were assembled in combination with those for difference effect measurements. The glass fitting in one of the side openings of the reactor flask was replaced by a taper joint sealed around the capillary tube extended to the surface of the dissolving electrode. The other parts of the apparatus were exactly the same as previously described in the measurement of difference effect. The salt bridge and the calomel half cell were also placed in the constant temperature water bath, which was kept at 25 ± 0.1 ° C. A schematic diagram of the arrangement is shown in Figure 26. The capillary tube was designed following the specifications already mentioned (see Figure 16). The vertical adjustment was achieved by moving the TiO_x electrode, while the horizontal adjustment was achieved by rotating the capillary.

The measurements were carried out as given in the description of the difference effect. However, particular attention was required in keeping the end of the capillary tube in contact with the surface of the dissolving specimen. Two emf readings were taken at each time interval. The potentiometer current was adjusted for every other emf reading. Two specimens $TiO_{0.128}$ and $TiO_{0.158}$ were measured in 0.25, 0.50, and 0.75 N HF; and the third $TiO_{0.102}$ in 0.50 N HF, 0.50 N HF-0.10 N HCl and 0.5 N HF-1.0 N HCl. The dissolution potentials were expressed on the hydrogen scale.

The results are tabulated in Table XXXVIII to Table XLVI of the Appendix. The plots of dissolution potential versus measured current density I for $TiO_{0.128}$, $TiO_{0.145}$ and $TiO_{0.158}$ in different acids are shown in Figures 27, 28, and 29, respectively. The measured current density, I, instead of the total current density (I plus current density converted from V) was chosen for the abscissa, because V_t's were nearly equal to V_1's at all current densities in the same acid. If the potential was plotted against the total current density, it would simply shift the curves to the right of the abscissa with additional difficulty in the choice of scale in abscissa due to large value of current density.

It can be seen that the results are similar to those obtained in the open vessel. Each increase in current density is accompanied by increase in potential toward more noble value. The greater slope of the curve for the plot in a more diluted acid is similar to that measured in the open vessel.



a) TiO_x electrode	g) resistance box
b) Pt electrode	h) milliammeter
c) capillary tube	i) switch
d) stirrer	j) salt bridge
e) mercury seal	k) potentiometer
f) gas burette	l) calomel electrode

Figure 26

Schematic diagram showing the arrangement of apparatus for measurements of dissolution potentials during measurements of the difference effects, top view.

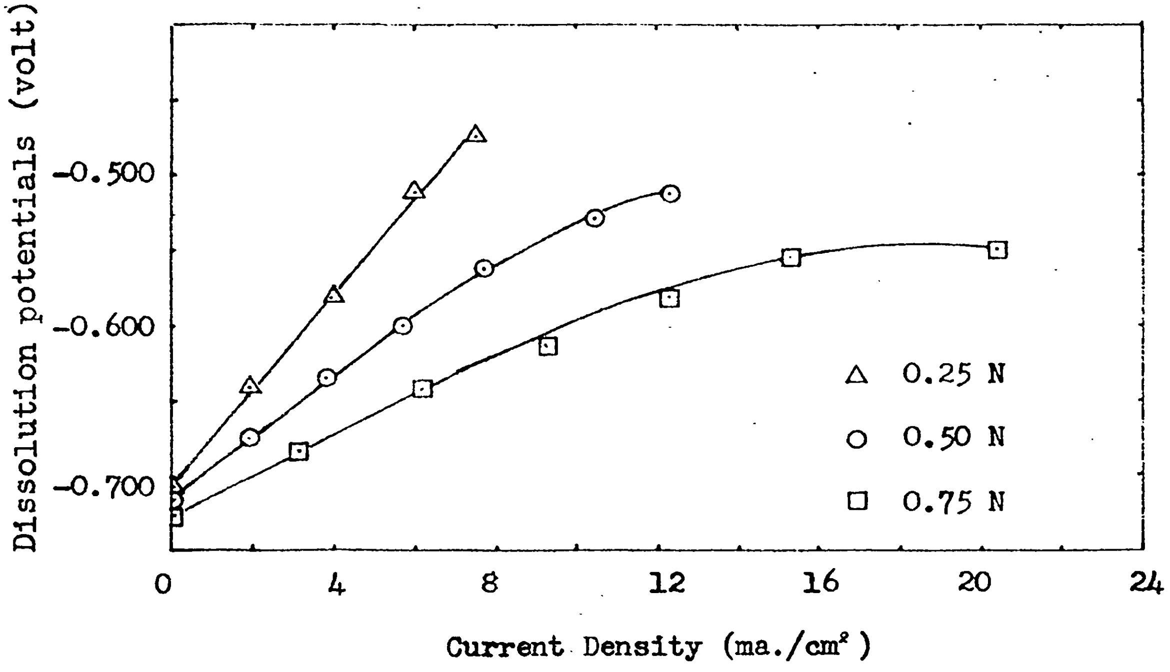


Figure 27

The effect of current density on the dissolution potential of $TiO_{.48}$ in HF

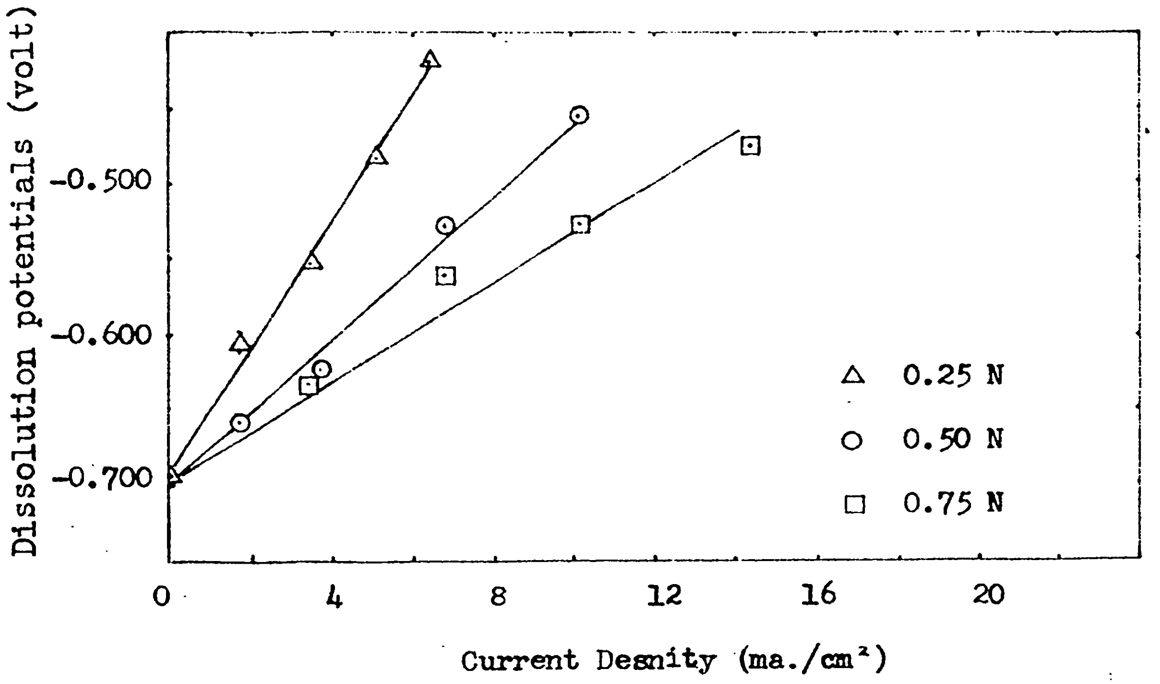
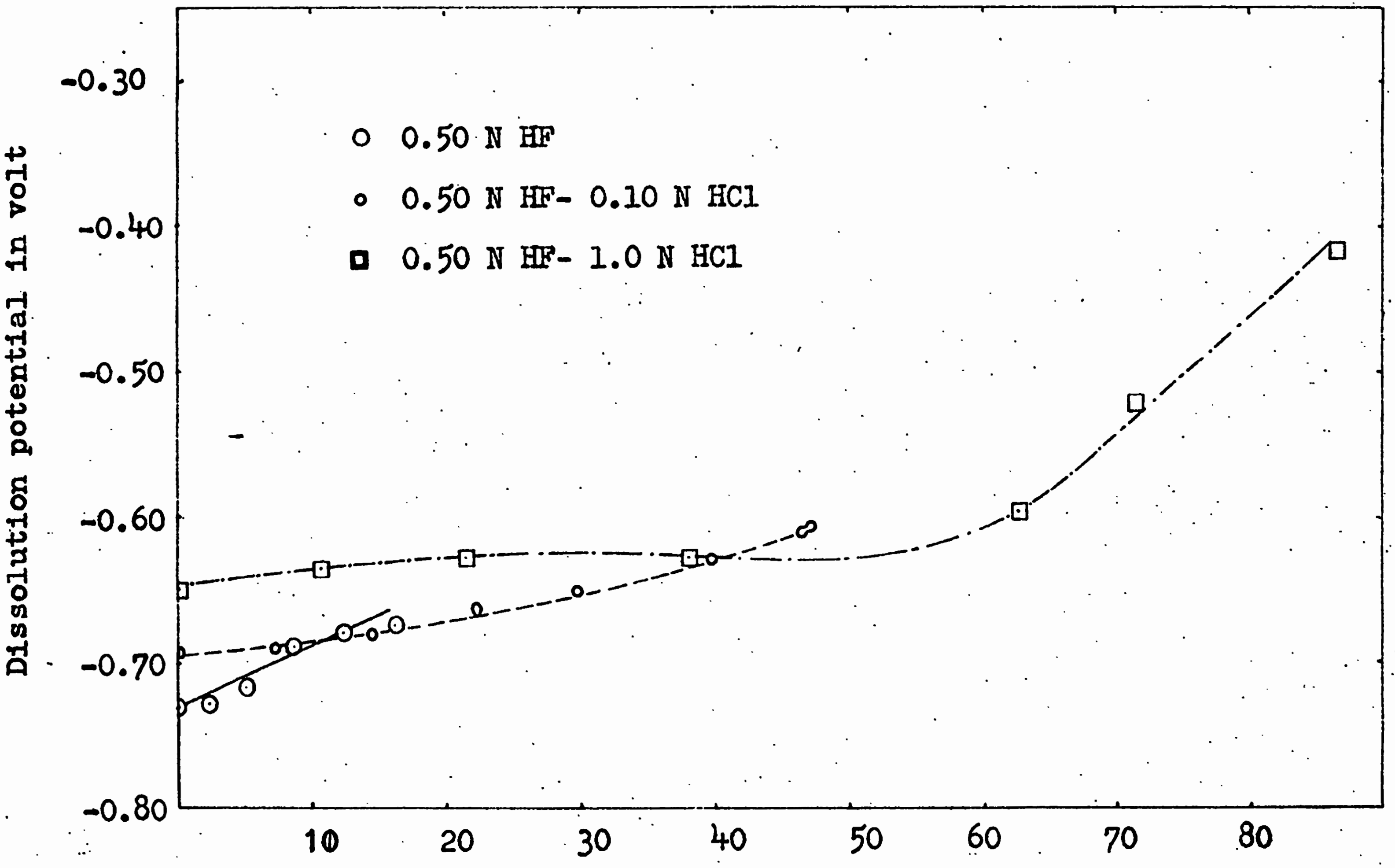


Figure 28

The effect of current density on the dissolution potential of $TiO_{.50}$ in HF



Current density in ma./cm²

Figure 29

The effect of current density on the dissolution potential of $TiO_{0.102}$ in HF-HCl

V DISCUSSIONS AND CONCLUSION

The principal factors that determine the dissolution rate of metal in aqueous solutions are: (1) the local cell action, (2) the physical and chemical properties of the dissolving surface, (3) its composition and (4) the physical and chemical properties of the solvent. In the local cell mechanism, the surface of the metal is said to consist of both cathodic and anodic areas. These two areas being short circuited by the electrolyte thus act as an irreversible cell, that is, the ions of metal in the anodic area go into the solution while an equivalent amount of hydrogen is evolved from the cathodic area of the surface. The rate of dissolution is thus derived as follows: (16)

$$V = \frac{V}{A \Delta t} = K Z' \frac{(\eta - E')}{r}$$

where k is a conversion constant; Z', the number of active cathodes; η, the hydrogen overvoltage of the local cathode; E', the dissolution potential of the anodic area; r, the average resistance of one local cell. The second factor results in whether or not a protective film is formed. If the film formed adheres to the surface and covers a fraction or all of the local cathodes, the dissolution rate will be retarded. Some evidences of film formation have been found for instance in the form of an oxide film on iron passivated in nitric acid. and on aluminum if anodically treated in dilute sulfuric acid, currently used for anodizing Al for better corrosion protection. In the hydrogen evolution type of dissolution, it was postulated by Müller that the protective film is porous in nature (17). This approach was later developed further in assuming that both anodic and cathodic reaction occurs in the pores of the film (8).

Evans postulated that the most probable factor governing the rate of destruction of an oxide film by an acid is based on lattice defects of the coating (film). The following is quoted from Evan's "The Corrosion and Oxidation of Metal" (18).

> Zinc oxide contains metal in excess of the formula ZnO. If the excess metal is interstitial, it might easily enter the liquid, and the process having started and the structure being thereby loosened, dissolution would probably continue. Nickel oxide, which has a similar formula, contains less metal than corresponds to NiO, and is (more) resistant to acids.

The dissolution rate is therefore dependent upon the structural nature of the film formed.

Based upon above theories, the discussion is presented in two parts; namely, (1) the difference effect on alpha solid solutions of oxygen in titanium dissolving in hydrofluoric acid, and (2) the dissolution potentials of these solid solutions in hydrofluoric acid.

(A) <u>The difference effect on alpha solid solution of oxygen in</u>

titanium dissolving in hydrofluoric acid.

As previously mentioned, the slope constant k does not change appreciably with the composition within the region studied. This suggests that the alloys are polarizable to the same degree in hydrofluoric acid regardless of oxygen contents in the alloys. From the equation of Thiel, the equation

$$\Delta = \frac{k_1 \; k_2 \; Z' \; I}{r} = k \; I$$

has been derived (8). This suggests that the resistance in the local cells is nearly constant. Since the value of k is constant and independent of the acid concentration, the resistance of hydrofluoric acid in the interface must change very slowly with its concentration, otherwise a well balanced relation must exist between the resistance of the acid and the contact resistance of the local cathodes. Although the contact resistance between the local cathodes and the base metal is usually considered to be negligible, it probably is not. On the other hand, the data concerning electric conductivity of hydrofluoric acid at different concentrations is, unfortunately, not available.

The alpha solid solution has a close packed hexagonal structure of titanium with interstitial oxygen ion chemically bonded to a limited number of titanium atoms (11). Titanium loses its electrons while oxygen gains electrons. Depending upon the relative position and the interatomic distance, titanium may lose 1 to 3 electrons in its 3d and 4s levels. Of course, it may also stay atomic ($3d^2\ 4s^2$). The dissolution experiments revealed that 2 Ti were associated with 3 O. Accordingly, it can be said that the alpha solid solution is a solution of Ti_2O_3 in Ti.

Thus, in hydrofluoric acid, the dissolution reactions are:

$$Ti + 3\ HF \longrightarrow TiF_3 + 1.5\ H_2 \qquad (I)$$

$$Ti_2O_3 + 6\ HF \longrightarrow 2TiF_3 + 3\ H_2O \qquad (II)$$

A third equation expressing the dissolution of TiO_x as a whole was combined from the above equations.

$$TiO_x + 3\ HF \longrightarrow TiF_3 + xH_2O + 0.5\ (3-2x)\ H_2 \qquad (III)$$

A further reaction is probably due to the action of the local elements;

$$Ti + 3\ H^+ \longrightarrow Ti^{3+} + 1.5\ H_2 \qquad (IV)$$

which concerns only the metallic titanium in the solid solution.

Following the above postulated dissolution mechanisms of alpha Ti-O solid solution in hydrofluoric acid, the positive difference effect observed in HF can be explained properly as follows:

During the self dissolution period, both reactions (I and IV) and the direct chemical reactions (I and II) contribute to the dissolution of the alloy. However, when the anodic current is applied, the extraction of electrons (IV) stimulates the accumulation of Ti_2O_3 on the surface of the electrode as Ti atoms go into the solution. This accumulated oxide layer slows down the reaction between molecular HF and TiO_x by increasing the diffusion barrier, it may also cover parts of the local elements. Thus, the dissolution is inhibited and anodic passivation caused. The latter depends on the rate of dissolution of these oxides, as a slowest process, in HF. The constancy of k values in various TiO_x alloys can be explained by the assumption that variation in oxygen content of the specimens is not great enough to change the rate of dissolution of the oxide layer in HF. In fact it was found that the rate of H_2 evolution from TiO_x alloys is nearly independent of the oxygen content of the alloys. (1)

On the other hand, the difference effect on TiO_x in HF-HCl mixture has a k value much higher than that obtained in HF alone. Apparently the addition of HCl greatly increases the electric conductivity of the acid in addition to the increase in the molecular HF concentration. As a consequence, the reaction of acids with metallic titanium (Ti°) in the alloy becomes more rapid, and higher self dissolution rates are obtained. Therefore, upon the application of anodic current, the Ti_2O_3 layer is formed much faster than in the case of HF alone; on the other hand, the addition of HCl does not change practically the dissolution rate of Ti_2O_3 alone. The dissolution of the metallic Ti is retarded by formation of this layer on the surface mainly because of the covering of the anodic areas and of a hindering of the molecular HF to diffuse to the surface of TiO_x. At high current densities (above 60 ma./cm^2), the rate of Ti_2O_3 accumulation overtakes that of its dissolution in HF. As the oxide layer becomes thicker than an optimum thickness, its breakdown starts and results in the fluctuations of current. The fact that the current measured at 0 resistance of the box was less than that measured at 1 ohm resistance, lends support to the existance of a thick protective film on the surface of the electrode. There is also a possibility that this oxide layer contains less metal than corresponds to Ti_2O_3 as in the case of NiO.

If the film is Ti_2O_3, then its dissolution depends largely on the chemical reaction II as well as on its lattice defects. An increase in the stirring speed may be able to accelerate its dissolution in HF-HCl. The experimental results, however, are not conclusive. In the same mixed acid HF-HCl, as the stirring speed was increased from 286 to 1800 rpm. the current became much more stable, and more constant k values were obtained. Additional evidence comes from the induction period observed with each change of current density. With the circuit closed, the recorded rate in the first time interval (5 min.) was greater than in the following one. Whereas with the circuit open, the reverse was observed. The evidence can be seen in Table XXVI, XXVIII, XLVI, and XLVII of the Appendix.

Although the difference effect is independent of the concentration of HF whether the acid is a mixture or not, it may be dependent to some extent on the concentration of HCl in the mixture of HF-HCl as found in this investigation, (see Table III Figures 13.4). At low concentrations of HCl (0.1 N), the k value is not affected; but at relatively high concentrations (1.0 N, 2.0 N), a greater k values are obtained. It is reported that HCl can hardly attack metallic titanium at room temperature because the oxide film covering the surface of the metal is almost insoluble in HCl at this temperature. However, in the presence of HF, it may affect the thickness, porosity or adherability of the protective film formed when metallic titanium goes into solution. In other words V_1, the self dissolution rate during open circuit is increased, yet, V_2, the rate while the circuit is closed, is reduced by the accumulation of the protective film covering the anodic surface.

The main source of error in these experiments comes from the fact that V_t is nearly equal to $V_1, k = 6.97$, which means a small error in the measurement of dissolution rate would cause a greater error in k value especially at small current densities. The fluctuation of current at high current densities is another possible source of error. In the presence of HCl, the dissolution mechanism is somewhat complicated, for instance the dissolution potential becomes more noble yet the dissolution rate increases; more factors could thus be involved, and accordingly, greater difficulty is encountered in tracing the source of error.

The k value of the difference effect for some TiO_x alloys (4.9 to 10 w/o O) dissolving in HF-1.0 N HCl is reported to be about 9.5, while those obtained in this investigation using the same mixed acids are 7.5 and 8.3 for $TiO_{0.102}$ (3.3% O) and $TiO_{0.158}$ (5.01%) respectively. Since only one run was made for each above k value, it is not appropriate to compare the accuracy of these two results with those obtained by the previous investigator. Nevertheless, a constant k value of about 9 at compositions of 5 or more per cent oxygen in weight in the alpha solid solution appears reasonable. Since the k value for pure titanium dissolving in HF-1.0 N HCl has been checked several times to be 5.7, (the same as obtained in HF alone) it would seem to indicate that in the mixed acid HF-1.0 N HCl, the transition region assumed (k $5.7 \rightarrow 9$) is the region studied in this investigation (0 to 5 w/o oxygen), although further investigation is necessary in order to pinpoint the exact relation between the k value and the oxygen content of the solid solution.

(B) The Dissolution Potentials of Alpha Ti-O Solid Solution Dissolving in Hydrofluoric Acid.

Measurements of the dissolution potentials of TiO_x alloys and of pure Ti were made in various concentrations of acid, and at different current densities. The results obtained in the first part of the experiments (in Fig. 17, 18, 19 and 20) show that in the same acid, the dissolution potentials of all but the pure titanium electrode become more noble in the course of time, and that the more oxygen the alloy contained, the more noble was the measured stable potential. It is reported that pure titanium is always thoroughly covered by a thin oxide film, (1) (18) the initial potential is therefore more noble. As the oxide film is dissolved in HF, the surface of Ti becomes less noble. Similar phenomena were observed by previous investigators on Al dissolving in HF and on Zr dissolving in HF (6) (10). In the case of TiO_x, the oxide layer accumulates as the dissolution proceeds and the E's therefore become more noble. A stable potential was achieved after 20 minutes when probably the rates of formation and dissolution of the oxide layer came to equilibrium. The fact that the alloys became more noble in more dilute acids is in agreement with those observed on most metals dissolving in HF. The direct potential measurements under anodic polarization give evidence of the strong influence of the anodic current on the dissolution potential of TiO_x. The increase in potential is the greater the lower the concentration of the acid. This effect is similar to that reported in the cases of Al and Zr, and is in agreement with the postulated accumulation of oxide layer on the surface of the electrode when Ti atoms are removed. The observation of the less pronounced influence of the anodic current on the dissolution potential of TiO_x in mixed HF-HCl acid (Figure 29) and of the sudden increase of the potential due to high current density cannot be explained without further study. However, in the latter case, since the severe current fluctuations also occur at this current density, it would seem to indicate that the protective layer must be affected by the presence of HCl, especially at high current densities. The accumulation of thick oxide layers is favored because Ti atoms are removed at a fast rate at high current densities. A difficulty is encountered in the explanation of the fact that for all electrodes, even for pure titanium the measured stable potentials are much more noble than that of active metal given in the reference. The shifting of dissolution potential to a more noble value due to the addition of HCl can be explained by the influence of either H^+ or Cl^- on the hydride film (20). However, as a matter of fact, the accumulation of oxide layers is also affected by the presence of HCl.

A quantitative interpretation of the curves obtained in plotting the dissolution potentials versus current densities is unfortunately unattainable without the knowledge of all the factors involved. Nevertheless, the experiments furnish enough evidence in favor of the formation of protective layers. Based upon the experimental results and discussions given above, the summarizing conclusion is as follows:

(1) For the difference effect on TiO_x dissolving in pure HF, k is practically constant within the composition range studied, however, when it is dissolved in HF-HCl, k values increase from 5.7 for pure Ti to about 9 for TiO_x with 5. w/o oxygen. According to a previous investigator, k values stay constant between 5 to 10 w/o oxygen in the solid solutions, therefore, they will not be changed with further increase in oxygen content up to 10 w/o oxygen in the solid solution.

(2) The constancy of k in pure HF is due to the fact that the

variation in oxygen content of the specimens is not great enough to change the rate of dissolution of the oxide layer accumulated on the surface of the electrode when Ti atoms go into solution under anodic current. Since k is nearly equal to that obtained for pure Ti, it is reasonable to consider that the dissolution of Ti not bonded to oxygen in TiO_x alloys in HF has the same mechanism as that of pure Ti.

(3) The addition of HCl improves the ionic conductivity of the electrolyte, causes higher current densities and higher dissolution rate. During anodic polarization, the presence of HCl affects the thickness, porosity or adherability of the protective layer and results in higher k values than in HF alone.

(4) The surface of dissolving TiO_x alloy is passivated by an anodic current; in pure hydrofluoric acid, the polarizability is approximately constant, (% P = 81.5) regardless of the oxygen content of the solid solution (0 to 5 w/o O). When dissolved in HF-HCl, TiO_x is polarizable to a greater extent than in HF alone, depending upon the oxygen content of the solid solution as well as on the concentration of HCl. A greater polarizability than expected (128%) is calculated for $TiO_{0.158}$ in HF-1N HCl.

(5) The severe anodic polarization is caused by the formation of a protective layer possibly oxide which remains during dissolution of atomic titanium under anodic current. A particularly thick layer may form during anodic polarization at high current density in the presence of HCl.

VI APPENDIX

This appendix includes tables containing all of the data for the difference effect and potential measurements.

Table I through XXI gives data for:

The Difference Effects on TiO_x Dissolving in Hydrofluoric Acid.

Table XXII through XXVIII gives data for:

The Difference Effects on TiO_x Dissolving in HF-HCl

Table XXIX through XXXII gives data for:

The Dissolution Potentials of TiO_x without anodic current

Table XXXIII through XLVII gives data for:

The Effect of Current Density on the Dissolution Potentials of TiO_x

Table I
Difference Effect on $TiO_{0.024}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 1, 0.785 w/o O)

Time	V_1	I	6.971	V_t	Δ	
min.	$mm^3/cm^2 \cdot min.$	ma/cm^2		$mm^3/cm^2 \cdot min.$		$mm^3/ma \cdot min.$
10	269.8	-	-	-		
20	-	19	-	295.1		
30	-	19	132.4	306.0	105.8	5.57
40	278.2	-	-	-		
50	-	14	-	295.1		
60	-	14	97.6	286.6	80.8	5.77
70	269.8	-	-	-		
80	-	10	-	286.6		
90	-	10	69.7	269.8	59.7	5.91
100	265.5	-	-	-		
110	-	5	-	274.0		
120	-	5	34.85	278.2	22.15	4.43
130	261.3	-	-	-		
140	-	2.5	-	261.3		
150	-	2.5	17.43	278.2	13.23	5.29
160	269.8	-	-	-		

Average k=5.38±0.43

Table II
Difference Effect on $TiO_{0.024}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 1, 0.785 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	$mm^3/cm^2 \cdot min.$	ma/cm^2	$mm^3/cm^2 \cdot min.$			$mm^3/ma \cdot min.$
10	502	-	-	-		
20	-	36.25	-	536		
30	-	36.25	252.7	536	222.7	6.14
40	511	-	-	-		
50	-	30.2	-	553		
60	-	30.2	210.5	538	185	6.12
70	529	-	-	-		
80	-	25.8	-	540		
90	-	25.8	179.8	510	166.3	6.44
100	494	-	-	-		
110	-	20.0	-	511		
120	-	19.5	138.1	511	112.6	5.70
130	477	-	-	-		
140	-	14.7	102.6	519	57.6	3.92
150	451	-	-	-		
160	-	14.78	103.0	485	73	4.94
170	459	-	-	-		
180	-	10.0	-	474		
190	-	9.8	69.0	481	42.5	4.29
200	443	-	-	-		
210	-	5.0	-	464		
220	-	5.0	34.85	459	34.85	6.97
230	485	-	-	-		

Average k=5.56±0.89

Table III

Difference Effect on $TiO_{0.024}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 1, 0.785 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm³/cm²-min.	ma/cm²	mm³/cm²-min.			mm³/ma-min.
10	719.8	-	-	-		
20	-	56.8	-	867.1		
30	-	56.8	395.9	850.7	256.8	4.52
40	719.8	-	-	-		
50	-	41	-	834.3		
60	-	41	285.8	818.0	183.5	4.48
70	728.0	-	-	-		
80	719.8	-	-	-		
90	-	30	-	793.5		
100	-	30	209.1	777.1	160	5.33
110	752.6	-	-	-		
120	-	20	-	777.1		
130	-	20	139.4	768.9	106.7	5.34
140	736.2	-	-	-		
150	-	10	-	752.6		
160	-	10	69.7	760.7	53.3	5.33
170	728	-	-	-		
180	-	5	-	728.0		
190	-	5	34.9	736.2	30.8	6.16
200	728	-	-	-		

Average k=5.19±0.47

Table IV

Difference Effect on $TiO_{0.037}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 2, 1.22 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2		mm^3/cm^2·min.		mm^3/ma·min.
10	470	-	-	-		
20	-	35.1	244.7	554	183	5.21
30	445	-	-	-		
40	-	35.1	244.7	487	183	5.21
50	470	-	-	-		
60	-	30.3	211.2	496	189.7	6.26
70	-	30.3	211.2	461		
80	444	-	-	-		
90	-	24.5	170.8	444	106.8	4.36
100	-	24.5	170.8	394		
110	268	-	-	-		
120	-	20.0	139.4	277	126.4	6.32
130	-	20.0	-	310		
140	293	-	-	-		
150	-	15.0	-	310		
160	-	15.0	104.6	293	91.6	6.11
170	284	-	-	-		
180	-	-	-	301		
190	-	10.0	69.7	277	61.2	6.12
200	277	-	-	-		
210	-	5.0	-	277		
220	-	5.0	34.85	284	31.9	6.38
230	277	-	-	-		

Average k=5.82±0.58

Difference Effect on $TiO_{0.037}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 2, 1.22 w/o O)

Time min.	V_1 mm^3/cm^2,min.	I ma/cm^2	6.971	V_t	Δ	K mm^3/ma-min.
			mm^3/cm^2-min.			
10	839.7	-	-	-		
20	-	50.5	-	932.1		
30	-	50.5	352.0	864.9	226	4.47
40	705.3	-	-	-		
50	-	39.1	-	705.3		
60	-	39.1	272.5	764.1	268.3	6.86
70	755.7	-	-	-		
80	-	30.7	214	772.5	198	6.83
90	780.9	-	-	-		
100	-	20.0	-	806.1		
110	-	20.0	139.4	806.1	76.4	3.82
120	705.3	-	-	-		
130	-	10.0	-	713.7		
140	-	10.0	69.7	738.9	69.7	6.97
150	747.3	-	-	-		
160	-	5.0	-	764.1		
170	-	5.0	34.85	747.3	26.45	5.29
180	747.3	-	-	-		

Average k=5.71±1.18

Table VI

Difference Effect on $TiO_{0.037}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 2, 1.22 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm³/cm²-min.	ma/cm²	mm³/cm²-min.			mm³/ma-min.
10	1436	-	-	-		
20	-	59.0	411.2	1311	267.6	4.54
30	898.8	-	-	-		
40	-	51.5	359.5	1024.8	275.5	5.35
50	982.8	-	-	-		
60	-	41.0	285.8	957.6	239.6	5.84
70	957.6	-	-	-		
80	-	30.5	213.6	999.6	180.6	5.92
90	974.4	-	-	-		
100	-	20.0	139.4	974.4	139.4	6.97
110	974.4	-	-	-		
120	-	10.0	69.7	991.2	57.1	5.71
130	982.8	-	-	-		

Average k=5.72±0.52

Table VII
Difference Effect on $TiO_{0.0806}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 4, 2.62 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
10	254.4	-	-	-		
20	-	22	153.3	229.0	161.7	7.35
30	-	22	153.3	271.4		
40	262.9	-	-	-		
50	-	14.8	103.2	212		
60	-	14.8	103.2	262.9	111.7	7.55
70	229	-	-	-		
80	-	10.1	70.2	220		
90	-	10.1	70.2	229	61.7	6.13
100	203.5	-	-	-		
110	-	5.04	35.1	203.5		
120	-	5.04	35.1	221	25.6	5.32
130	203.5	-	-	-		

Average k=6.59±0.86

Table VIII
Difference Effect on $TiO_{0.0806}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 4, 2.62 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
10	1126.7	-	-	-		
20	-	41.0	285.8	1152.6		
30	-	41.0	285.8	1070.3	236.4	5.77
40	897.4	-	-	-		
50	-	35.0	243.95	913.9		
60	-	35.0	243.95	905.6	194.6	5.56
70	823.3	-	-	-		
80	-	29.2	202.8	856.2		
90	-	29.0	202.8	856.2	169.9	5.84
100	856.2	-	-	-		
110	1193.4	-	-	-		
120	-	20.1	140.1	1127.9		
130	-	20.1	140.1	1037.3	144.25	7.18
140	979.7	-	-	-		
150	-	10.0	-	971.5		
160	-	9.98	69.63	955	40.83	4.09
170	889.2	-	-	-		
180	880.9	5.0	34.82	880.9	40.3	8.20
190	-	5.0	34.82	856.2	40.3	
200	860.3	-	-	-		

Average k=6.11±1.09

Table IX
Difference Effect on $TiO_{0.0806}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 4, 2.62 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
10	1559.4	-	-	-		
20	-	70.0	-	-		
30	-	69.8	473.7	1207.3	473.7	6.49
40	956.8	-	-	-		
50	-	61.5	-	1048.0		
60	-	61.1	427.3	982.7	314	5.12
70	848.3	-	-	-		
80	-	50.8	-	914.9		
90	-	51.0	354.8	865.1	283.7	5.68
100	789.5	-	-	-		
110	-	40.0	-	79.79		
120	-	40.4	280.1	831.5	255.6	6.36
130	-	-	-	-		
140	790.5	-	-	-		
150	-	30.2	-	807.4		
160	-	30.2	210.5	799.0	184.0	6.13
170	765.3	-	-	-		
180	-	20.1	-	782.1		
190	-	20.2	140.4	799.0	110.9	5.50
200	756.9	-	-	-		
210	-	10.0	-	748.5		
220	-	10.0	69.7	773.7	65.2	6.52
230	756.9	-	-	-		

Average k=5.97±0.46

Table X
Difference Effect on $TiO_{0.102}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 5, 3.30 w/o O)

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	6.971	V_t	Δ	K mm^3/ma-min.
			mm^3/cm^2-min.			
5	248.5	-	-	-		
10	248.5	-	-	-		
15	225.6	-	-	-		
20	230.7	-	-	-		
25	-	13.04	-	248.5		
30	-	13.04	91.1	237.0	80.6	6.15
35	225.6	-	-	-		
40	-	10.64	-	237.0		
45	-	10.64	74.2	225.6	67.9	6.37
50	225.6	-	-	-		
70	319.9	-	-	-		
75	-	3.6	-	308.4		
80	-	3.6	24.9	319.9	18.8	5.26
85	296.3	-	-	-		
90	-	7.14	-	308.4		
95	-	7.14	49.8	308.4	37.7	5.28
100	284.2	-	-	-		

Average k=5.77±0.49

Table XI

Difference Effect on $TiO_{0.102}$ in 0.50N HF at 25°C.

H_2 volumes reduced to S.T.P. (Specimen No. 5, 3.30 w/o O)

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	6.971	V_t	Δ	K mm^3/ma-min.
			mm^3/cm^2-min.			
5	355.6	-	-	-		
10	378.4	-	-	-		
15	355.6	-	-	-		
20	-	33.56	234	438.4		
25	-	-	-	461.2	184.7	5.50
30	378.4	-	-	-		
35	-	28.7	200	449.8		
40	-	-	-	438.4	146.4	5.10
45	402.7	-	-	-		
50	-	25.1	174.9	449.8		
55	-	-	-	425.5	140	5.58
60	402.7	-	-	-		
65	-	21.3	148.5	438.4		
70	-	-	-	414.1	124.9	5.86
75	402.7	-	-	-		
80	-	17.7	123.4	449.8		
85	-	-	-	438.4	87.7	4.95
90	414.1	-	-	-		
95	-	14.04	98.1	425.5		
100	-	-	-	444.1	92.4	6.57
105	444.1	-	-	-		
110	-	10.5	73.2	438.4		
115	-	-	-	438.4	81.7	7.78
120	449.8	-	-	-		

Average $k=5.59\pm0.41$

Table XII

Difference Effect on $TiO_{0.102}$ in 0.75N HF at 25° C.
H_2 volumes reduced to S.T.P. (Specimen No. 5, 3.30 w/o O)

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	6.971	V_t	Δ	K mm^3/ma-min.
			mm^3/cm^2-min.			
5	920.9	-	-	-		
10	932.9	-	-	-		
15	-	33.4	232.8	897.0		
20	-	-	-	968.8	202.9	6.07
25	873.1	-	-	-		
30	-	28.6	199.3	873.1		
35	-	-	-	920.9	157.5	5.51
40	837.2	-	-	-		
45	-	25	142.3	765		
50	-	-	-	861.1	174	6.97
55	789.4	-	-	-		
60	-	-	-	-		
65	777.4	-	-	-		
70	-	20.7	144.3	825.2		
75	-	-	-	789.4	108.2	5.23
80	765.4	-	-	-		
85	-	17.4	121.3	789.4		
90	-	-	-	813.3	61.5	3.53
95	717.6	-	-	-		
100	-	14.3	99.7	801.3		
105	-	-	-	765	46.1	3.24
110	741.5	-	-	-		
115	-	7.14	49.8	789.4		
120	-	-	-	801.3	25.9	3.63
125	801.3	-	-	-		
130	-	-	-	-		

Average k=5.48±0.83

Table XIII
Difference Effect on $TiO_{0.128}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 6, 4.633 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
10	334.7	-	-	-		
20	-	11.04	76.9	320.4		
30	-	11.04	76.9	313	69.3	6.28
40	284	-	-	-		
50	-	10.52	73.3	316		
60	-	10.52	73.3	324	36.7	3.49
70	284	-	-	-		
80	-	8.99	61.9	306		
90	-	8.99	61.9	313	47.2	5.31
100	306	-	-	-		
110	306	-	-	-		
120	-	6.4	44.6	320		
130	-	6.4	44.6	299	35.9	5.60
140	299	-	-	-		

Average k=5.17±0.83

Table XIV

Difference Effect on $TiO_{0.128}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 6, 4.633 w/o O)

Time min.	V_1 mm³/cm²-min.	I ma/cm²	6.971 mm³/cm²-min.	V_t mm³/cm²-min.	Δ mm³/cm²-min.	K mm³/ma-min.
10	908.6	-	-	-		
15	1116	29.5	-	-		
20	961.2	29.5	-	-		
25	-	29.5	205.5	1014		
30	-	29.5	205.5	961.2	152.9	5.19
35	908.6	-	-	-		
40	-	23.9	166.7	961.2		
45	-	23.9	166.7	987.5	127.2	5.32
50	961.2	-	-	-		
55	-	15.9	111.1	934.9		
60	-	15.9	111.1	987.5	91.2	5.72
65	929.3	-	-	-		
70	921.3	-	-	-		
75	-	7.97	55.55	934.9		
80	-	7.97	55.55	947.6	42.4	5.32
85	934.9	-	-	-		

Average $k = 5.39 \pm 0.14$

Table XV
Difference Effect on $TiO_{0.128}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 6, 4.633 w/o O)

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	6.971 I mm^3/cm^2-min.	V_t mm^3/cm^2-min.	Δ mm^3/cm^2-min.	K mm^3/ma-min.
5	851	-	-	-		
10	866	-	-	-		
15	-	29.2	203.3	975.5		
20	-	29.2	203.3	959.6	104.5	3.58
25	887.8	-	-	-		
30	908.6	-	-	-		
35	-	27.1	188.9	953		
40	-	27.1	188.9	975	152	5.61
45	945	-	-	-		
50	-	20.1	140	945		
55	-	20.1	140	931	140	6.97
60	931	-	-	-		
65	902	-	-	-		
70	-	16.1	-	931		
75	-	16.1	112.2	857.6	90.7	5.63
80	-	16.1	-	916.5		
85	843	-	-	-		

Average k=5.50±0.98

Table XVI
Difference Effect on $TiO_{0.145}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 7, 4.113 w/o O)

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	6.971	V_t	Δ	K mm^3/ma-min.
			mm^3/cm^2-min.			
10	267	-	-	-		
20	-	11.8	82.2	297	48.9	4.14
30	260.4	-	-	-		
40	345.1	-	-	-		
50	-	8.61	60	325.6		
60	-	8.61	60	306	66.5	7.72
70	299.5	-	-	-		
80	-	8.27	57.6	345.1		
90	-	8.27	57.6	358.1	34.8	4.21
100	358.1	-	-	-		
110	-	7.08	49.3	358.1		
120	-	7.08	49.3	364.4	39.7	5.61
130	345.1	-	-	-		

Average k=5.42±1.24

Table XVII
Difference Effect on $TiO_{0.145}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 7, 4.113 w/o O)

Time	V_1	I	6.97I	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
5	546.7	-	-	-		
10	559.7	-	-	-		
15	-	36.4	253.4	559.7		
20	-	36.4	253.4	585	234.3	6.44
25	546.7	-	-	-		
30	-	30.6	213.5	585		
35	-	30.6	213.5	534.4	194.3	6.34
40	534.4	-	-	-		
45	-	23.0	160.1	483.1		
50	-	23.0	160.1	585	154	6.70
55	521.4	-	-	-		
60	-	15.3	106.7	546.7		
65	-	15.3	106.7	598	75	4.89
70	559.7	-	-	-		
75	-	7.67	53.4	546.7		
80	-	7.67	53.4	559.7	34.6	4.52
85	509.2	-	-	-		

Average k=5.78±0.86

Table XVIII
Difference Effect on $TiO_{0.145}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 7, 4.113 w/o O)

Time	V_1	I	6.97I	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2		mm^3/cm^2-min.		mm^3/ma-min.
5	329.0	-	-	-		
10	-	37.1	258.8	373.7		
15	-	37.1	258.8	373.7	217.7	5.86
20	333.8	-	-	-		
25	-	29	202.8	347.6		
30	-	29	202.8	385.9	184.4	6.33
35	361.4	-	-	-		
40	-	22.6	157.4	361.4		
45	-	22.6	157.4	385.9	145.2	6.42
50	361.4	-	-	-		
55	-	15.3	106.7	373.7		
60	-	15.3	106.7	373.7	106.7	6.97
65	385.9	-	-	-		
70	-	7.66	53.4	373.7		
75	-	7.66	53.4	399.7	53.4	6.97
80	385.9	-	-	-		
85	399.7	-	-	-		

Average $k = 6.51 \pm 0.37$

Table XIX

Difference Effect on $TiO_{0.158}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	6.971	V_t	Δ	K mm^3/ma-min.
			mm^3/cm^2-min.			
5	230.4	-	-	-		
10	-	17.4	-	258.3		
15	-	17.4	121	272.7	78.7	4.52
20	258.3	-	-	-		
25	-	12.7	-	279.5		
30	-	12.7	88.6	265.1	46.2	3.64
35	243.9	-	-	-		
40	-	8.47	-	237.2		
45	-	8.47	59.3	237.2	45.6	5.38
50	216.8	-	-	-		
55	195.7	-	-	-		
60	-	4.24	-	230.4		
65	-	4.24	29.56	230.4	21.9	6.97
70	237.2	-	-	-		

Average k=5.12±1.05

Table XX

Difference Effect on $TiO_{0.158}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
5	830	-	-	-		
10	-	27.6	192.4	900		
15	-	27.6	192.4	872	80.1	2.90 *
20	717.4	-	-	-		
25	-	21.6	150.6	731.8		
30	-	21.6	150.6	745.3	129.4	5.99
35	717.4	-	-	-		
40	-	16.9	117.8	759.8		
45	-	16.9	117.8	759.8	110.6	6.54
50	703	-	-	-		
55	689.5	-	-	-		
60	-	12.6	87.8	675		
65	-	12.6	87.8	703	81.1	6.44
70	675	-	-	-		
75	-	8.41	58.6	689.5		
80	-	8.41	58.6	717.4	30.2	3.59
85	675	-	-	-		
90	-	4.24	29.6	576.8		
95	-	4.24	29.6	717.4	32.1	7.57
100	624.2	-	-	-		

Average k=5.50±1.51

k'=5.64±1.02

Table XXI

Difference Effect on $TiO_{0.158}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time	V_1	I	6.971	Vt	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
5	913.1	-	-	-		
10	-	37.7	262.8	1011.3		
15	-	37.7	262.8	997.8	164.5	4.36
20	899.5	-	-	-		
25	-	34.3	239.1	969.8		
30	-	34.3	239.1	997.8	176	5.13
35	941.9	-	-	-		
40	-	29.5	205.6	997.8		
45	-	29.5	205.6	1011.3	156.9	5.32
50	969.8	-	-	-		
55	941.9	-	-	-		
60	-	25.2	175.6	1025.7		
65	-	25.2	175.6	1011.3	119.8	4.75
70	983.4	-	-	-		
75	-	20.8	145	1025.7		
80	-	20.8	145	1011.3	110	5.29
85	983.4	-	-	-		
90	-	16.8	117.1	1025.7		
95	-	16.8	117.1	1011.3	96	5.71
100	1011.3	-	-	-		
105	1077.4	-	-	-		
110	-	17.4	121.3	1008.8		
115	853.8	17.4	121.3	-	78.1	4.49
120	-	12.6	87.8	867.3		
125	-	12.6	87.8	909.7	94.6	7.51
130	936.8	-	-	-		
135	-	8.51	59.3	1021.5		
140	-	8.51	59.3	1063	17	
145	1063	-	-	-		
150	867.3	-	-	-		
155	-	4.2	29.3	909.7		
160	-	4.2	29.3	895.3	17.9	4.26
165	914.8	-	-	-		

Average k=5.20$\pm$0.67

Table XXII
Difference Effect on $TiO_{0.128}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 6, 4.113 w/o O)
Concentration: HF 0.25N; HCl 1.0N

Time	V_1	I	6.97I	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
5	267.8	-	-	-		
10	-	31.9	222.2	361.8		
15	-	31.9	222.2	322	195.1	6.12
20	361.8	-	-	-		
25	-	23.9	166.6	280.5		
30	-	23.9	166.6	307.6	193.8	8.10
35	280.5	16.3	-	-		
40	-	16.3	113.3	294.9		
45	-	16.3	113.3	334.7	86.2	5.30
50	294.9	-	-	-		
55	-	7.95	55.4	294.9		
60	-	7.95	55.4	334.7	41.8	5.25
65	307.6	-	-	-		
70	-	28.5	198.3	322		
75	-	28.5	198.3	307.6	195.1	6.97
80	322	-	-	-		

Average k=6.35±0.95

Table XXIII
Difference Effect on $TiO_{0.145}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 7, 4.633 w/o O)
Concentration: HF <u>0.25N</u>; HCl <u>1.0N</u>

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
5	329	37.1	-	-		
10	-	37.1	258.8	373.7		
15	-	37.1	258.8	373.7	217.4	5.86
20	333.8	-	-	-		
25	-	29	202.8	347.6		
30	-	29	202.8	385.9	184.4	6.33
35	361.4	-	-	-		
40	-	22.6	157.4	361.4		
45	-	22.6	157.4	385.9	145.2	6.42
50	361.4	-	-	-		
55	-	15.3	106.7	373.7		
60	-	15.3	106.7	373.7	106.7	6.97
65	385.9	-	-	-		
70	-	7.66	53.4	373.7		
75	-	7.66	53.4	399.7	53.4	6.97
80	385.9	-	-	-		
85	399.7	-	-	-		

Average k=6.51±0.37

Table XXIV

Difference Effect on $TiO_{0.158}$ in 0.5N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm³/cm²-min.	ma/cm²	mm³/cm²-min.			mm³/ma-min.
5	662	-	-	-		
10	-	24.7	172.2	634		
15	-	24.7	172.2	606	163.2	6.61
20	584	-	-	-		
25	550	-	-	-		
30	-	20.7	144.4	606		
35	-	20.7	144.4	578	95.4	4.61
40	536	-	-	-		
45	522	-	-	-		
50	-	16.6	115.5	536		
55	-	16.6	115.5	522	66.5	4.01
60	466	-	-	-		
65	486	-	-	-		
70	-	12.4	86.7	515		
75	-	12.4	86.7	508	71.7	5.78
80	480	-	-	-		
85	494	-	-	-		
90	-	8.29	57.8	480		
95	-	8.29	57.8	452	53.8	6.49
100	430	-	-	-		

Average k=5.50±0.95

Table XXV

Difference Effect on TiO$_{0.158}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)
Concentration: HF 0.50N; HCl 0.5N

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
5	912	-	-	-		
10	-	59.7	415.9	612		
15	-	59.7	415.9	570	600.9	10.07
20	640	-	-	-		
25	740	-	-	-		
30	-	70.4	491	656		
35	-	70.4	491	570	540	7.67
40	640	-	-	-		
45	740	-	-	-		
50	-	51.4	358.2	740		
55	-	51.4	358.2	656	358.2	6.97
60	656	-	-	-		
65	640	-	-	-		
70	-	36.7	255.9	640		
75	-	36.7	255.9	626	248.8	6.78
80	612	-	-	-		
85	612	-	-	-		
90	-	24.9	173.3	626		
95	-	24.9	173.3	612	166.3	6.68
100	612	-	-	-		

Average k=7.63±0.99

Table XXVI
Difference Effect on $TiO_{0.158}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)
Concentration: HF <u>0.5N</u>; HCl <u>1.0N</u>

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	<u>6.971</u> mm^3/cm^2-min.	<u>V_t</u>	<u>Δ</u>	K mm^3/ma-min.
5	624	-	-	-		
10	-	30.6	213.7	402		
15	-	30.6	213.7	402	373.7	12.2
20	500	-	-	-		
25	582	-	-	-		
30	-	52.2	363.9	472		
35	-	52.2	363.9	394	460.9	8.83
40	458	-	-	-		
45	596	-	-	-		
50	-	64.6	450.6	540		
55	-	64.4	450.6	472	485.6	7.52
60	486	-	-	-		
65	582	-	-	-		
70	-	41.4	288.9	444		
75	-	41.4	288.9	596	350.9	8.48
80	582	-	-	-		
85	596	-	-	-		

Average k=9.28±1.48

k=8.28±0.50

Table XXVII

Difference Effect on $TiO_{0.158}$ in 0.5N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			mm^3/ma-min.
5	832	-	-	-		
10	-	18.1	126.2	790		
15	-	18.1	126.2	720	111.2	6.14
20	648	-	-	-		
25	664	-	-	-		
30	-	16.2	112.9	678		
35	-	16.2	112.9	634	91.9	5.67
40	606	-	-	-		
45	578	-	-	-		
50	-	12.3	85.7	592		
55	-	12.3	85.7	578	71.7	5.83
60	564	-	-	-		
65	-	10.1	70.4	564		
70	-	10.1	70.4	564	51.4	5.09
75	522	-	-	-		

Average k=5.55±0.36

Table XXVIII
Difference Effect on $TiO_{0.158}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)
Concentration: HF 0.5N; HCl 0.5N

Time min.	V_1 mm³/cm²-min.	I ma/cm²	6.971	V_t	Δ	K mm³/ma-min.
			mm³/cm²-min.			
5	603.4	-	-	-		
10	-	76.9	536	626.6		
15	-	76.9	531.1	566.9	518.2	6.74
20	554.5	-	-	-		
25	711.1	-	-	-		
30	-	76.2	531.1	626.6		
35	-	76.2	531.1	651.4	536.9	7.04
40	578.5	-	-	-		
45	651.4	-	-	-		
50	-	67	467	651.4		
55	-	67	467	615	448.8	6.69
60	578.5	-	-	-		
65	633.2	-	-	-		
70	-	38.8	270.4	681.3		
75	-	38.8	270.4	638.2	240.6	6.20
80	626.6	-	-	-		

Average k=6.67±0.23

Table XXIX
Dissolution Potentials of electrodes in 0.25N HF

	Dissolution Potentials E' in volts			
Time	Ti	$TiO_{0.024}$	$TiO_{0.037}$	$TiO_{0.0555}$
0	-0.7881	-0.8074	-0.7823	-0.7733
5	-0.8010	-0.7960	-0.7753	-0.7497
10	-0.8046	-0.7916	-0.7713	-0.7453
15	-0.8051	-0.7888	-0.7689	-0.7439
20	-0.8067	-0.7883	-0.7710	-0.7423
25	-0.8093	-0.7911	-0.7704	-0.7423
30	-0.8103	-0.7899	-0.7704	-0.7417
35	-0.8091	-0.7921	-0.7706	-0.7417
40	-0.8101	-0.7918	-0.7708	-0.7415
45	-0.8097	-0.7930	-0.7708	-0.7407
50	-0.8097	-0.7932	-0.7704	-0.7407
55	-0.8093	-0.7934	-0.7704	-0.7402
60	-0.8095	-0.7934	-0.7704	-0.7396
65	-0.8097	-0.7934	-0.7704	-0.7400

Table XXX
Dissolution Potentials of electrodes in 0.50N HF

	Dissolution Potentials E' in volts		
Time	$TiO_{0.024}$	$TiO_{0.037}$	$TiO_{0.0555}$
0	-0.8074	-0.7926	-0. 770
5	-0.8034	-0.7854	-0.7414
10	-0.7984	-0.7774	-0.7414
15	-0.7942	-0.7798	-0.7414
20	-0.7918	-0.7796	-0.7342
25	-0.7918	-0.7782	-0.7304
30	-0.7914	-0.7762	-0.7314
35	-0.7906	-0.7744	-0.7324
40	-0.7898	-0.7744	-0.7320
45	-0.7898	-0.7754	-0.7294
50	-0.7882	-0.7762	-0.7310
55	-0.7866	-0.7762	-0.7310

Table XXXI
Dissolution Potentials of electrodes in 0.105N HF 1.00 N HCl

Time	Ti	$TiO_{0.024}$	$TiO_{0.037}$	$TiO_{0.0555}$
	Dissolution Potentials E' in volts			
0	-0.6128	-0.6710	-0.6447	-0.6162
5	-0.6464	-0.6622	-0.6351	-0.6060
10	-0.6666	-	-0.6313	-0.5916
15	-0.6750	-0.6554	-0.6301	-0.5908
20	-0.6778	-0.6542	-0.6297	-0.5894
25	-0.6790	-0.6522	-0.6287	-0.5888
30	-0.6786	-0.6542	-0.6253	-0.5876
35	-0.6784	-0.6536	-0.6261	-0.5876
40	-0.6776	-0.6536	-0.6271	-0.5876
45	-0.6770	-0.6530	-0.6267	-0.5864
50	-0.6758	-0.6520	-0.6265	-0.5866
55	-0.6732	-0.6484	-0.6257	-0.5854

Table XXXII
Dissolution Potentials in 0.25N HF 1.00 N HCl

	Dissolution Potentials E' in volts			
Time	Ti	$TiO_{0.024}$	$TiO_{0.037}$	$TiO_{0.0555}$
0	-0.7208	-0.6931	-0.6768	-0.6515
5	-0.7248	-0.6813	-0.6660	-0.6305
10	-0.7222	-0.6749	-0.6640	-0.6307
15	-0.7204	-0.6753	-0.6636	-0.6277
20	-0.7224	-0.6743	-0.6630	-0.6287
25	-0.7228	-0.6747	-0.6634	-0.6255
30	-0.7230	-0.6743	-0.6633	-0.6253
35	-0.7230	-0.6731	-0.6641	-0.6275
40	-0.7222	-0.6729	-0.6639	-0.6281
45	-0.7216	-0.6711	-0.6630	-0.6283

Table XXXIII

The effect of current density on the dissolution potential of $TiO_{0.037}$ in HF

0.25N		0.50N		0.75N	
I (ma./cm²)	E' (volts)	I	E'	I	E'
8.3	-0.6404	11.9	-0.7086	19.7	-
7.0	-0.6600	10.2	-0.7136	17.0	-0.7300
6.1	-0.6742	8.9	-0.7244	15.0	-0.7388
5.0	-0.6865	7.9	-0.7270	13.0	-0.7422
4.0	-0.7000	7.0	-0.7304	11.0	-0.7492
3.0	-0.7070	6.0	-0.7364	9.0	-0.7500
2.0	-0.7178	5.0	-0.7428	7.0	-0.7610
1.0	-0.7258	4.1	-0.7450	5.0	-0.7682
0	-0.7602	3.0	-0.7528	3.0	-0.7752
		2.0	-0.7620	1.5	-0.7806
		1.0	-0.7700	0	-0.7858
		0	-0.7804		

Table XXXIV
The effect of current density on the dissolution potential of $TiO_{0.158}$ in HF

0.25N		0.50N		0.75N	
I (ma./cm^2)	E' (volts)	I	E'	I	E'
		9.9	-0.6610		
		8.5	-0.6662	12.5	-0.6752
5.0	-0.6600	7.6	-0.6668	11.2	-0.6792
4.9	-0.6440	6.8	-0.6686	9.5	-0.6810
4.9	-0.6468	6.0	-0.6730	7.7	-0.6826
4.2	-0.6635	5.1	-0.6788	5.9	-0.6854
3.4	-0.6722	4.2	-0.6818	4.3	-0.6878
2.5	-0.6816	3.4	-0.6854	2.5	-0.6952
1.7	-0.6884	2.5	-0.6876	0	-0.7010
0	-0.6962	1.7	-0.6928		
		0.8	-0.6962		
		0	-0.7002		

Table XXXV
The effect of current density on the dissolution potential of Specimen No. 6 in HF

0.25N		0.50N		0.75N	
I (ma./cm^2)	E' (volts)	I	E'	I	E'
		9.7	-0.6566	12.3	-0.6760
5.9	-0.6582	7.7	-0.6672	11.5	-0.6784
5.4	-0.6640	6.1	-0.6786	9.2	-0.6826
4.6	-0.6746	5.7	-0.6672	7.7	-0.6948
3.8	-0.6848	4.6	-0.6860	6.1	-0.6980
3.1	-0.6918	3.1	-0.7000	4.6	-0.7055
2.3	-0.6992	1.5	-0.7122	3.1	-0.7069
1.5	-0.7100	0	-0.7218	1.5	-0.7126
0.8	-0.7142			0	-0.7220
0	-0.7250				

Table XXXVI
The effect of current density on the dissolution potential of Specimen No. 7 in HF

0.25N		0.50N		0.75N	
I (ma./cm^2)	E' (volts)	I	E'	I	E'
		12.07	-0.6642	12.35	-0.6764
5.6	-0.6684	10.2	-0.6716	9.96	-0.6788
4.0	-0.6784	8.3	-0.6756	8.05	-0.6860
2.4	-0.6860	6.42	-0.6866	5.98	-0.6910
1.2	-0.6990	4.46	-0.6907	3.99	-0.6986
0	-0.7036	2.55	-0.7022	1.99	-0.7064
		0	-0.7088	0	-0.7080

Table XXXVII
The effect of current density on the dissolution potential of pure Ti in HF

0.1N

I (ma./cm)	E' (volts)
6.0	-0.5971
4.0	-0.6710
2.0	-0.7190
0	-0.7820

0.25N

I (ma./cm)	E' (volts)
10	-0.5502
9.0	-0.5770
8.0	-0.6144
7.0	-0.6528
6.0	-0.6726
5.0	-0.7006
0	-0.8190

0.50N

I (ma./cm)	E' (volts)
20.2	-0.4008
15.0	-0.5188
11.04	-0.6012
7.25	-0.6720
4.1	-0.7316
2.0	-0.7756
0	-0.8120

1.0N

I (ma./cm)	E' (volts)
34.15	-0.2840
27.15	-0.3890
20.4	-0.5024
13.1	-0.6200
6.0	-0.7198
0	-0.8120

Table XXXVIII

Difference Effect on $TiO_{0.128}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 6, 4.633 w/o O)

Time min.	V_E mm³/cm²-min.	I ma/cm²	V_t	Δ	K	E' (volts)
			mm³/cm²-min.			
10	180	-	-	-	-	-0.7150
20	-	7.5	189.9	47.4	6.32	-0.4754
30	189.9	-	-	-	-	-0.7072
40	-	6.0	186.6	34.9	5.82	-0.5120
50	176.8	-	-	-	-	-0.7074
60	-	3.9	189.9	16.5	4.23	-0.5870
70	183.5	-	-	-	-	-0.7060
80	-	1.9	199.9	4.8	2.4	-0.6428
90	199.9	-	-	-	-	-0.7080

Average k= 5.46

Table XXXIX

Difference Effect on $TiO_{0.128}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 6, 4.633 w/o O)

Time min.	V_1 mm³/cm²-min.	I ma/cm²	V_t mm³/cm²-min.	Δ mm³/cm²-min.	K mm³/cm²-min.	E' (volts)
5	419.4	-	-	-	-	-
10	419.4	-	-	-	-	-0.7180
15	-	12.3	432.6	79.1	6.43	-0.5136
20	419.4	-	-	-	-	-0.7160
25	-	10.4	439.2	56.0	5.38	-0.5292
30	426.0	-	-	-	-	-0.7190
35	-	7.7	419.4	63.7	8.25	-0.5680
40	432.6	-	-	-	-	-0.7160
45	-	5.7	458.8	20	3.51	-0.6000
50	445.6	-	-	-	-	-0.7156
55	-	3.8	458.8	19.9	5.24	-0.6360
60	445.6	-	-	-	-	-0.7204
65	-	1.9	458.8	6.6	3.48	-0.6772
70	445.6	-	-	-	-	-0.7180

Average k= 5.4

Table XL
Difference Effect on $TiO_{0.128}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 6, 4.633 w/o O)

Time min.	V_1 mm³/cm²-min.	I ma/cm²	V_t	Δ	K	E' (volts)
			mm³/cm²-min.			
5	571.6	-	-	-	-	-0.7330
10	-	18.4	571.6	121.5	6.60	-0.5500
15	558.4	-	-	-	-	-0.7360
20	-	15.3	571.6	100.1	6.54	-0.5556
25	558.4	-	-	-	-	-0.7300
30	-	12.3	571.6	79.1	6.43	-0.5812
35	571.6	-	-	-	-	-0.7300
40	-	9.2	598.2	55.7	6.05	-0.6136
45	598.2	-	-	-	-	-0.7284
50	-	6.1	598.2	35.8	5.78	-0.6436
55	584.8	-	-	-	-	-0.7240
60	-	3.1	611.4	21.6	6.97	-0.6840
65	638	-	-	-	-	-0.7204

Average k= 6.41

Table XLI

Difference Effect on $TiO_{0.158}$ in 0.25N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time	V_1	I	V_t	Δ	K	E' (volts)
min.	mm^3/cm^2-min.	ma/cm^2		mm^3/cm^2-min.		
10	132.9	-	-	-	-	-0.6948
20	-	1.7	139.7	-	-	-0.5986
30	-	1.7	147.3	8.4	4.94	-0.6100
40	147.3	-	-	-	-	-0.6886
50	-	3.4	139.7	-	-	-0.5527
60	-	3.4	154.9	23.7	6.97	-0.5570
70	147.3	-	-	-	-	-0.6900
80	-	5.1	147.3	-	-	-0.4860
90	-	5.1	154.9	35.5	6.97	-0.4810
100	154.9	-	-	-	-	-0.6884
110	-	6.4	169.3	-	-	-0.4200
120	-	6.4	169.3	30.2	4.72	-0.4200
130	154.9	-	-	-	-	-0.6920

Average k=5.9

Table XLII
Difference Effect on $TiO_{0.158}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time	V_1	I	V_t	Δ	K	
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			E' (volts)
5	291.2	-	-	-	-	-0.7000
10	-	1.7	304.8	5.0	-	-0.6620
15	-	1.7	291.2	5	2.94	-0.6572
20	291.2	-	-	-	-	-0.7000
25	291.2	-	-	-	-	-0.7000
30	-	3.4	304.8	-	-	-0.6230
35	-	3.4	320	16.9	4.97	-0.6230
40	320	-	-	-	-	-0.6930
45	0	6.8	348.8	-	-	-0.5360
50	-	6.8	392.8	45.4	6.68	-0.5200
55	436.8	-	-	-	-	-0.6900
60	-	10.1	443.6	-	-	-0.4512
65	-	10.1	458.8	56	5.54	-0.4592
70	436.8	-	-	-	-	-0.6880

Average k=5.7

Table XLIII

Difference Effect on $TiO_{0.158}$ in 0.75N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 8, 5.01 w/o O)

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	V_t	Δ	K	E' (volts)
			mm^3/cm^2-min.			
5	981.3	-	-	-	-	-0.6930
10	-	3.4	996.6	-	-	-0.6340
15	-	3.4	951.7	8.5	2.5	-0.6230
20	936.5	-	-	-	-	-0.6940
25	-	6.8	981.3	-	-	-0.5682
30	-	6.8	936.5	17.8	2.6	-0.5644
35	922.1	-	-	-	-	-0.6970
40	-	10.2	922.1	63.4	6.22	-0.5288
45	906.8	-	-	-	-	-0.6964
50	-	14.4	936.5	85.5	5.93	-0.4754
55	906.8	-	-	-	-	-0.6960
60	-	-	-	-	-	-0.

Table XLIV
Difference Effect on $TiO_{0.102}$ in 0.50N HF at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 5, 3.30 w/o O)

Time min.	V_1 mm³/cm²-min.	I ma/cm²	V_t	Δ	K	E' (volts)
			mm³/cm²-min.			
5	477.1	-	-	-	-	-0.7064
10	-	16.04	477.1	-	-	-0.7010
15	-	16.32	470.9	106.7	6.59	-0.6772
20	483.3	-	-	-	-	-0.7000
25	-	12.2	458.5	-	-	-0.6820
30	-	12.2	458.5	85	6.97	-0.6816
35	458.5	-	-	-	-	-0.7000
40	-	8.6	446.1	28.9	3.36	-0.6900
45	408.9	-	-	-	-	-0.7010
50	-	8.7	408.9	41.9	4.82	-0.6900
55	371.8	-	-	-	-	-0.7202
60	-	5.1	371.8	-	-	-0.7170
65	-	5.1	359.4	29.2	5.73	-0.7170
70	346.9	-	-	-	-	-0.7304
75	-	2.3	334.6	-	-	-0.7282
80	-	2.3	346.9	16	6.97	-0.7282
85	346.9	-	-	-	-	-0.7282

Average k=5.74±1.12

Table XLV

Difference Effect on $TiO_{0.102}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 5, 3.3 w/o O)
Concentration: HF <u>0.50N</u>; HCl <u>0.10N</u>

Time min.	V_1 mm^3/cm^2-min.	I ma/cm^2	V_t	Δ mm^3/cm^2-min.	K	E' (volts)
5	483.4	-	-	-	-	-0.6940
10	-	47.1	557.8	237.7	5.05	-0.6098
15	471.0	-	-	-	-	-0.6970
20	-	46.5	533	262.1	5.64	-0.6116
25	471.0	-	-	-	-	-0.6916
30	-	37.9	508	-	-	-0.6288
35	-	37.9	508	208.7	5.51	-0.6330
40	433.9	-	-	-	-	-0.6964
45	-	29.7	446.3	-	-	-0.6524
50	-	29.7	508	157.6	5.31	-0.6524
55	421.5	-	-	-	-	-0.6960
60	-	22.2	458.6	-	-	-0.6650
65	-	22.2	458.6	130	5.91	-0.6650
70	446.3	-	-	-	-	-0.7036
75	-	14.3	446.3	-	-	-0.6820
80	-	14.3	446.3	87.3	6.10	-0.6820
85	446.3	-	-	-	-	-0.6970
90	-	7.2	458.6	-	-	-0.6910
100	-	7.2	464.9	-	-	-0.6900
105	454.2	-	-	-	-	-0.6970

Average k=5.56±0.26

Table XLVI

Difference Effect on $TiO_{0.102}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 5, 3.30 w/o O)
Concentration: HF <u>0.50N</u>; HCl <u>1.0N</u>

Time	V_1	I	V_t	Δ	K	E' (volts)
min.	mm^3/cm^2-min.	ma/cm^2	mm^3/cm^2-min.			
5	729.4	-	-	-	-	-0.6480
10	-	71.6	592.2	-	-	-0.5244
15	-	71.6	511.2	649.7	9.07	-0.5220
20	673.3	-	-	-	-	-0.6500
25	-	86.6	648.3	-	-	-0.4248
30	-	86.6	610.9	631.7	7.29	-0.4108
35	642.1	-	-	-	-	-0.6522
40	685.7	-	-	-	-	-0.6520
45	-	62.7	710.7	-	-	-0.6070
50	-	62.7	710.7	437.0	6.97	-0.5870
55	735.6	-	-	-	-	-0.6420
60	-	37.9	748.1	-	-	-0.6300
65	-	37.9	710.7	286.6	7.56	-0.6272
70	748.1	-	-	-	-	-0.6420
75	748.1	-	-	-	-	-0.6420
80	-	21.5	748.1	-	-	-0.6260
90	-	21.5	760.5	157.6	7.33	-0.6324
95	773.0	-	-	-	-	-0.6420
100	-	10.7	760.5	-	-	-0.6376
105	-	10.7	773.0	87.6	8.18	-0.6340
110	786.5	-	-	-	-	-0.6420

Average k=7.47 ± 0.32

Table XLVII
Difference Effect on $TiO_{0.102}$ in HF-HCl at 25°C.
H_2 volumes reduced to S.T.P. (Specimen No. 5, 3.30 w/o O)
Concentration: HF <u>0.50N</u>; HCl <u>2.0N</u>

Time	V_1	I	6.971	V_t	Δ	K
min.	mm^3/cm^2-min.	ma/cm^2		mm^3/cm^2-min.		mm^3/ma-min.
5	624.5	-	-	-		
10	-	65.9	-	339.5		
15	-	65.9	459.3	334.7	737.6	11.2
20	606.3	-	-	-		
25	709.4	-	-	-		
30	-	87.4	-	442.6		
35	-	87.4	609.2	424.4	779.0	8.91
40	497.2	-	-	-		
45	745.7	-	-	-		
50	-	64.4	-	636.6		
55	-	64.4	448.9	569.9	545.9	8.48
60	654.8	-	-	-		
65	-	38.8	-	654.8		
70	-	38.8	270.4	606.3	252.2	6.5
75	569.9	-	-	-		
80	-	19.3	-	485.0		
85	-	19.3	134.5	497.2	189	9.79
90	521.4	-	-	-		

Average k=8.98±1.22

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VITA

The author was born on October 13, 1935, in Chia-yi, Taiwan. He received the Bachelor of Science Degree in Mining and Metallurgical Engineering from Cheng Kung University, Taiwan, in 1957. After his military service in Chinese Armed Forces, he came to the United States of America and entered the Graduate School of the University of Missouri, School of Mines and Metallurgy for the continuation of his study in Metallurgical Engineering. The author has been granted a position of Research Assistant for the Contract A.E.C. AT(11-1) 73, Project 5, "Corrosion of Nuclear Metals", during his course of study.