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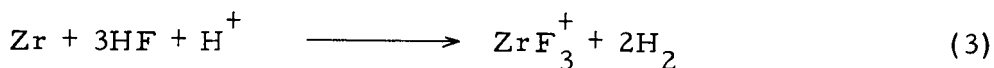
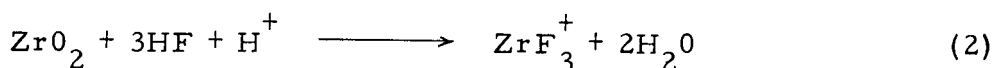
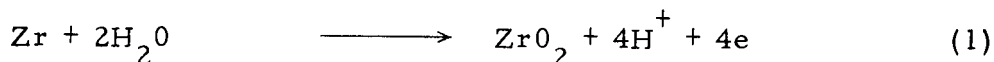
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Title THE OSCILLATING ZIRCONIUM ELECTRODE

Abstract approved _____

Chittick and Scott found some conditions under which an anodic zirconium electrode exhibited oscillations in potential and current. An attempt to account for the mechanism of current oscillation has been given in this paper. The system studied consisted of graphite as a cathode positioned 10 cm from zirconium as an anode which had an exposed area of 4 cm² on a single side in an electrolyte. The four variables, external resistance, concentration of sodium fluoride, concentration of sulfuric acid, and temperature were varied in the experiment. From the experiment, factors interpreting current oscillation were deduced. They are the rates of three reactions and diffusion of one reactant species, as follows:



and rate of diffusion of HF species to the zirconium electrode. The

rate of reaction (1) is controlled by the external resistance, and the rates of reaction (2) and (3) depend mainly on the concentration of HF at the zirconium electrode surface. The diffusion of HF species apparently depends also on the HF concentration in the bulk and temperature. Adjustment of four variables resulted in a regular current oscillation which had fixed maximum and minimum currents and period. Failure of adjustment resulted in irregular oscillation and in extreme cases in the disappearance of oscillation. As could be considered from the complexity of the oscillation mechanism, the reproducibility was not high. The main causes of poor reproducibility may be reaction (3) and variations in the surface condition of the zirconium electrode; therefore, the previous history of the zirconium electrode strongly affects the results.

THE OSCILLATING ZIRCONIUM ELECTRODE

by

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
Statement of the Problem	1
Purpose of Study	1
Terminology	3
EXPERIMENTAL	4
System	4
Results	4
DISCUSSION	14
Observations on Anodic Zirconium	14
Factors Influencing Current Oscillations	16
Regular Oscillations	23
Irregular Oscillations and Disappearance of Oscillation	26
Effect of Acidity	27
CONCLUSION	28
BIBLIOGRAPHY	29

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Schematic diagram of the system and circuit.	5
2	Current-time plot at zero external resistance.	9
3	Current-time plot of regular oscillation.	10
4	Current-time plot of regular and irregular oscillations.	11
5	Oscillation when the circuit was opened for a moment.	12
6	Plot of limiting current vs. $[\text{NaF}]$ in $2\text{NH}_2\text{SO}_4$.	19
7	Plot of maximum current vs. $[\text{NaF}]$ in $2\text{NH}_2\text{SO}_4$.	22
8	Minimum current vs. $[\text{NaF}]$ plot in $2\text{NH}_2\text{SO}_4$.	24

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Conditions for Regular Oscillation	6
2	The Effect of Addition of NaF on Maximum and Minimum Currents at Fixed External Resistance (20.5°C, 6N H ₂ SO ₄ , 90 ohms).	8
3	Current at 30 Seconds After Maximum, and Limiting Current at Zero External Resistance	8
4	Effect of addition of ZrF ₆ ⁼ to an Oscillating Cell	15
5	Calculated Diffusion Coefficients of HF (D x 10 ⁵ cm ² - sec ⁻¹)	20
6	Diffusion Coefficient at 25°C for Aqueous Solutions	21
7	Calculated (nFA/δ) x 10 ⁷ coulomb-cm.	26

THE OSCILLATING ZIRCONIUM ELECTRODE

INTRODUCTION

Statement of the Problem

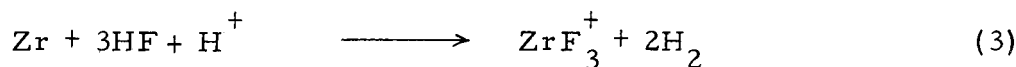
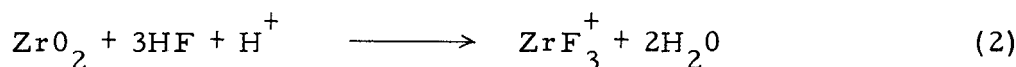
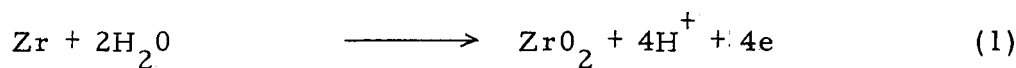
Iron, cobalt and chromium electrodes have been found to exhibit periodic fluctuations in potential under special conditions of current density and electrolyte composition (5; 6; 7; 10). Maraghini, Adams and Van Rysselberghe (9) observed occasional periodic fluctuations in potential when zirconium was anodized in 0.2M NaF solution. Umezono and Morioka studied the potential fluctuations of anodized zirconium electrode in acid solutions (H_2SO_4 , HNO_3 , HCl) containing halide salts (KF, KCl, KBr, KI)(13). Chittick and Scott found some conditions under which anodic zirconium exhibited oscillations in potential and current. They reported the oscillation in current was observed when zirconium was used as an anode in galvanic cell with a cathode of graphite, lead dioxide or manganese dioxide and with a variety of acid electrolytes (4). Chittick and Clifton also worked on the same system (3). Observations by those workers are summarized in the discussion section.

Purpose of Study

The theory successfully interpreting the mechanism of current

oscillations in a system which consists of zirconium and graphite as electrodes in sodium fluoride-sulfuric acid solutions has not previously been proposed. The mechanism seems to be very complicated. The theory proposed in this paper can account for the observations on this system but it is not to be implied that the theory is the only one which can explain the phenomena.

Three reactions which might possibly occur at anodic zirconium surface and diffusion of one reactant are considered. They are:



and diffusion of HF species to the zirconium electrode.

Only reaction (1) is an electrochemical reaction; it results in a current. Reaction (2) and (3) are not electrochemical; however, these two and the diffusion of HF species can affect the rate of reaction (1). The current oscillation could be reasonably understood only when their rates are taken into consideration.

From the observations described later, it is concluded that reaction (1) is initially very rapid. After the surface has been largely covered with ZrO_2 , reaction (2) is presumed to determine the current, by dissolving away the ZrO_2 . This implies that the current is then

related to the HF concentration at the electrode surface.

Terminology

Now it is necessary to define terms used in this paper.

1. "Maximum current" or "peak current" is the current at the peak of the oscillation.
2. "Minimum current" is the current at the bottom of the oscillation.
3. "Period" is the period of time from one peak to the next peak or from one bottom to the next bottom of current oscillation.
4. "Regular oscillation" is the oscillation that has the same maximum and minimum current and period for each fluctuation, and oscillation does not decay.
5. "Limiting current" is the final leveled current when oscillation has decayed.

EXPERIMENTAL

System

The system consisted of a rectangular graphite electrode as cathode positioned 10 cm from a zirconium electrode as anode which had an exposed area of 4 cm^2 on a single side (remainder of the surface was covered with paraffin) in sodium fluoride-sulfuric acid solution. A standard calomel electrode was positioned close to the zirconium electrode in order to measure the potential difference between them. The zirconium electrode was shaved with a blade or immersed in hydrofluoric acid solution to clean its surface before it was used. In the experiment the solution was 1,000 ml of 2.0 N, 4.0 N or 6.0 N sulfuric acid to which sodium fluoride was added. Current was drawn through the circuit (Figure 1). External resistance was so adjusted as to give a regular current oscillation under the conditions of fixed other variables such as concentrations of NaF and H_2SO_4 , and temperature. Current-time plots of oscillations were recorded with a recording potentiometer. Potential oscillations were observed on a vacuum tube voltmeter.

Results

The conditions which give the regular current oscillation and

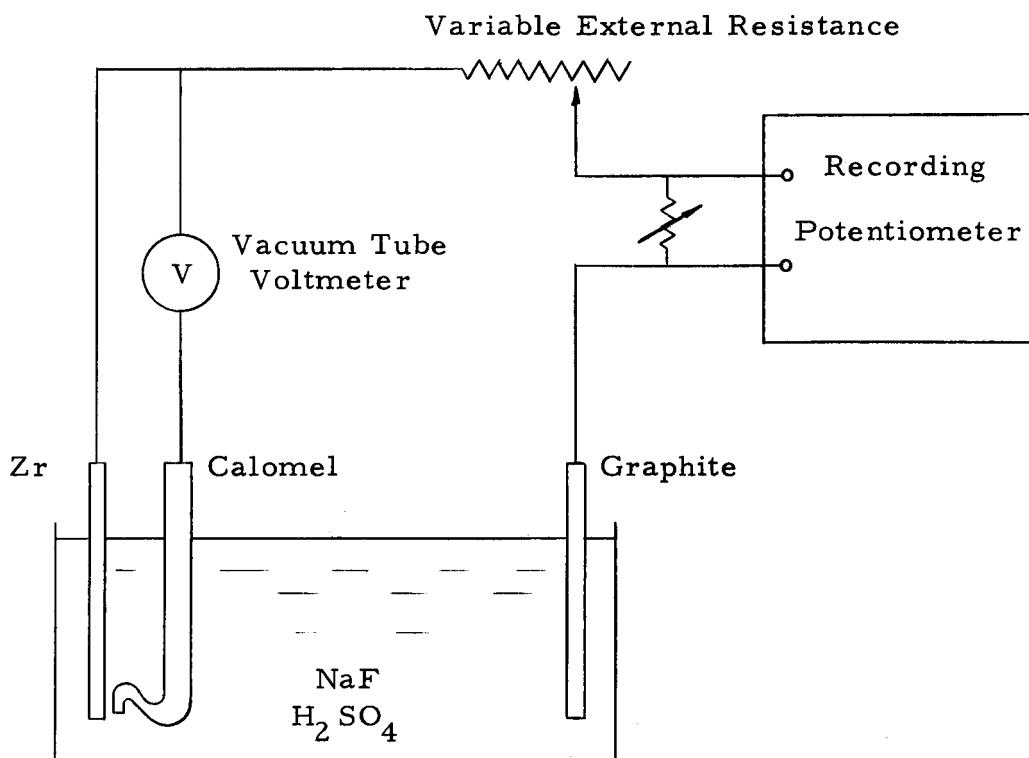


Figure 1. Schematic diagram of the system and circuit.

its maximum and minimum currents and period are listed in Table 1.

Table 1. Conditions for Regular Oscillation

[NaF] x 10 ² (mole/l)	External Resistance, ohm	Current, ma		Period, sec.
		Max.	Min.	
<u>6N H₂SO₄, 15°C</u>				
1.19	300	3.0	0.65	31.5
2.38	90	8.6	1.7	18.5
3.57	55	12.8	3.0	12.5
4.76	--	--	--	--
5.95	--	--	--	--
<u>6N H₂SO₄, 20°C</u>				
1.19	200	4.6	0.6	42
2.39	90	9.5	1.5	24
3.57	60	13.5	2.5	16
4.76	55	14.0	3.0	10.5
5.95	55	15.0	5.0	9.7
<u>6N H₂SO₄, 25°C</u>				
1.19	150	5.7	0.75	31
2.38	10	9.7	5.0	5.0
3.57	--	--	--	--
4.76	--	--	--	--
5.95	--	--	--	--
<u>4N H₂SO₄, 15°C</u>				
1.19	250	4.4	0.7	39
2.38	90	8.2	2.0	22
3.57	50	13.2	2.9	11
4.76	40	10.0	6.5	8.3
5.95	10	13.0	9.5	9.0

Table 1. Continued

[NaF] x 10 ² (mole/l)	External Resistance, ohm	Current, ma		Period, sec.
		Max.	Min.	
<u>4N H₂SO₄, 20° C</u>				
1. 19	250	4. 1	0. 8	37
2. 38	100	8. 7	2. 4	16
3. 57	60	13. 6	3. 1	12
4. 76	47	17. 0	5. 0	8. 3
5. 95	40	20. 0	6. 5	6. 5
<u>4N H₂SO₄, 25° C</u>				
1. 19	100	5. 6	1. 5	22. 5
2. 38	15	8. 8	5. 6	9. 0
3. 57	0. 1	9. 8	8. 8	8. 0
4. 76	--	--	--	--
5. 95	--	--	--	--
<u>2N H₂SO₄, 15° C</u>				
1. 19	250	3. 8	0. 8	41
2. 38	90	8. 3	1. 9	17
3. 57	50	12. 3	3. 0	12
4. 76	25	15. 5	5. 5	7. 5
5. 95	20	16. 0	7. 5	6. 5
<u>2N H₂SO₄, 20° C</u>				
1. 19	250	4. 2	0. 8	36
2. 38	100	9. 0	2. 3	14. 3
3. 57	57	14. 5	3. 4	10. 5
4. 76	47	17. 2	5. 2	6. 7
5. 95	40	21. 0	7. 0	5. 2
<u>2N H₂SO₄, 25° C</u>				
1. 19	200	4. 4	0. 85	28. 5
2. 38	90	5. 2	3. 8	10. 5
3. 57	20	13. 0	8. 0	6. 0
4. 76	10	15. 5	9. 5	5. 5
5. 95	0. 1	18. 3	12. 5	4. 5

Table 2. The Effect of Addition of NaF on Maximum and Minimum Currents at Fixed External Resistance (20, 5°C, 6N H₂SO₄, 90 ohms).

[NaF] x 10 ² (mole/l)	Current, ma	
	Maximum	Minimum
1.19	12.0	1.6
1.78	11.9	1.8
2.38	11.8	2.0

Table 3. Current at 30 Seconds After Maximum, and Limiting Current at Zero External Resistance

[NaF] x 10 ² (mole/l)	15°C ma		20°C ma		25°C ma	
	i ₃₀	i _l	i ₃₀	i _l	i ₃₀	i _l
	<u>6N H₂SO₄</u>					
1.19	1.6	--	2.3	--	2.4	--
2.38	3.7	4.8	4.0	5.5	6.6	--
3.57	6.0	7.4	5.7	8.4	9.8	11.7
4.76	8.6	11.0	9.0	11.5	--	--
5.95	--	--	10.5	13.0	--	--
7.14	--	--	--	--	--	--
	<u>4N H₂SO₄</u>					
1.19	1.9	2.3	2.0	2.4	3.2	3.1
2.38	4.1	5.5	4.7	6.1	6.8	7.7
3.57	6.2	8.0	6.8	8.7	10.0	12.1
4.76	9.0	10.8	9.8	11.0	11.0	11.3
5.95	11.5	14.0	11.8	14.2	--	--
7.14	--	--	--	--	--	--
	<u>2N H₂SO₄</u>					
1.19	2.0	2.2	2.0	2.4	2.4	2.8
2.38	3.9	4.8	4.7	5.8	5.7	7.1
3.57	6.5	7.4	7.2	8.4	10.0	10.7
4.76	10.2	10.8	10.0	11.8	13.0	14.6
5.95	11.8	13.8	14.0	13.6	16.5	17.5
7.14	15.5	16.7	15.0	15.7	10.0	10.7

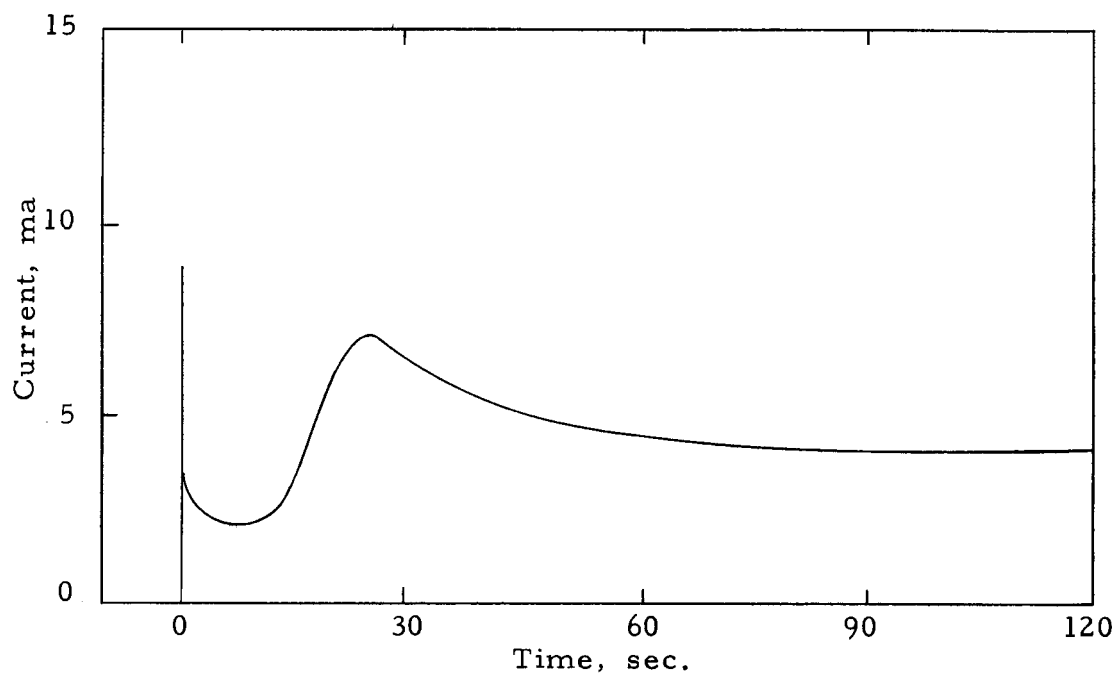


Figure 2. Current-time plot at zero external resistance.
(Temperature, 15° C. Conc. of NaF, 2.38×10^{-2}
moles/l. Conc. of H₂SO₄, 6N)

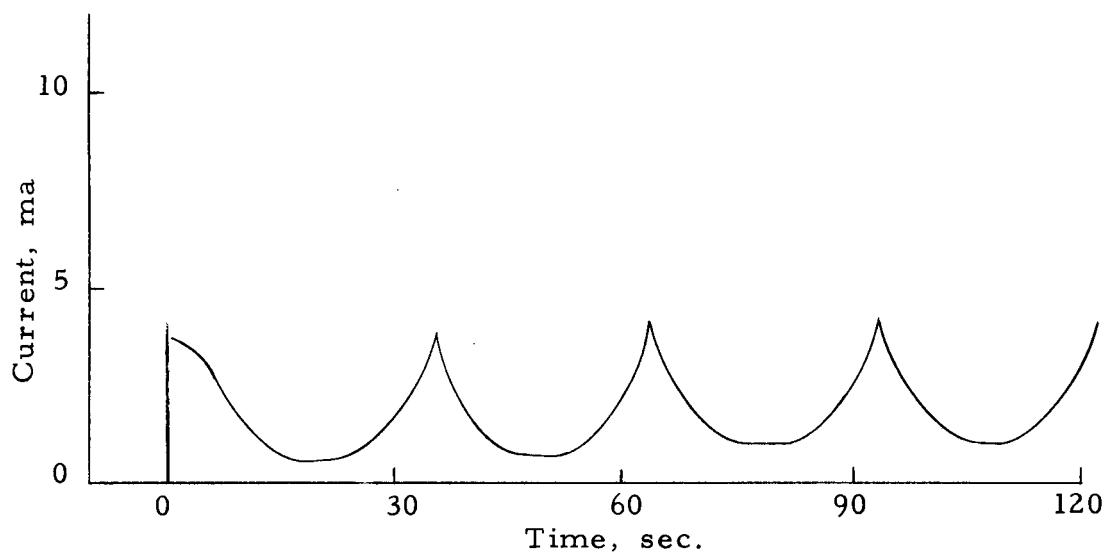


Figure 3. Current-time plot of regular oscillation. (Temperature, 20° C. Conc. of NaF, 1.19×10^{-2} moles/l. Conc. of H_2SO_4 , 4N. External resistance, 200 ohms.)

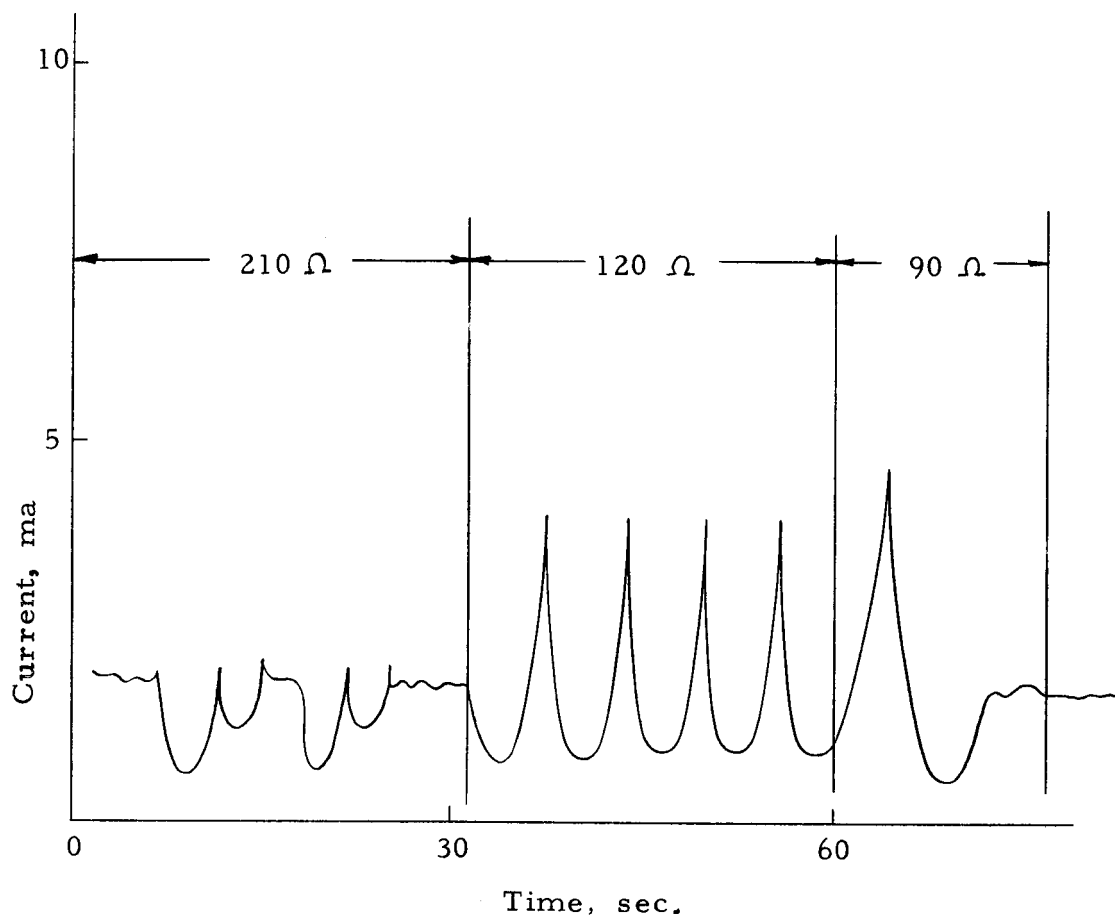


Figure 4. Current-time plot of regular and irregular oscillations.
(Temperature, 20°C . Conc. of NaF, 1.78×10^{-2}
moles/l. Conc. of H_2SO_4 , 6N)

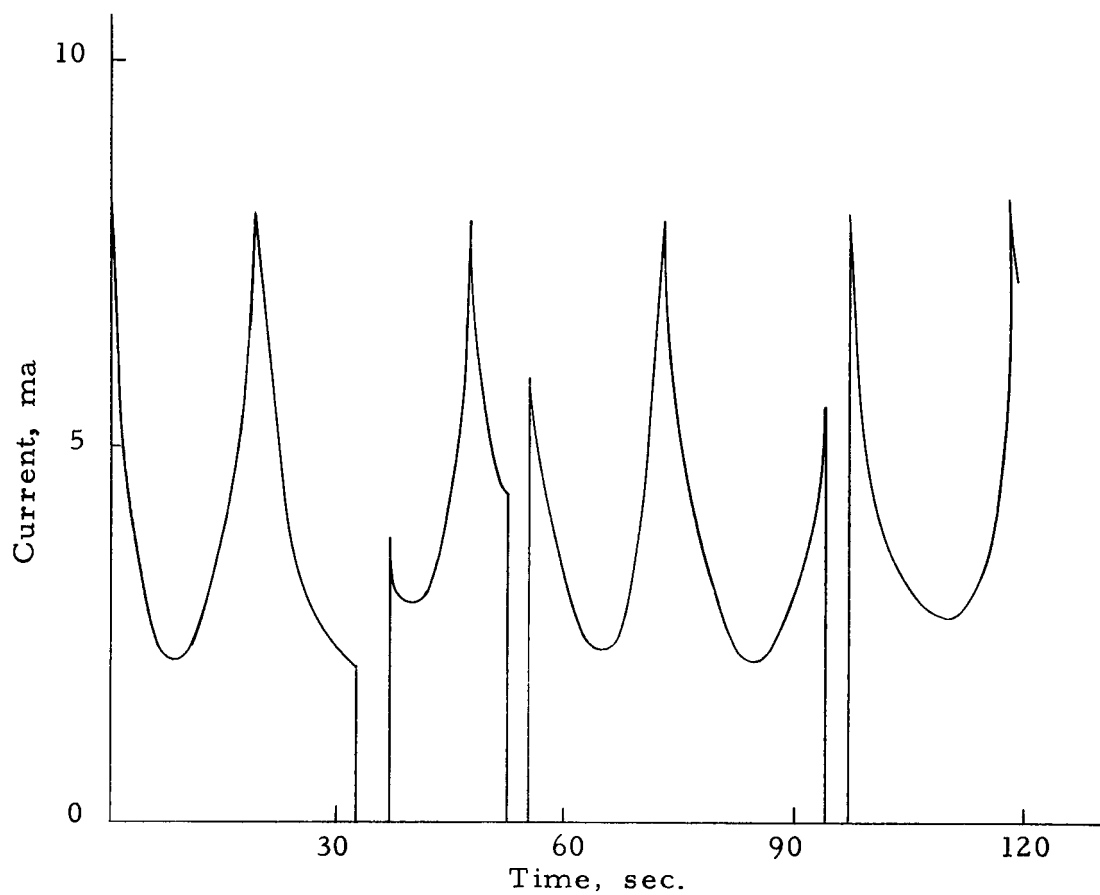


Figure 5. Oscillation when the circuit was opened for a moment. (Temperature, 20°C . Conc. of NaF, 2.38×10^{-2} moles/l. Conc. of H_2SO_4 , 6N. External Resistance, 88 ohms)

It was impossible to trace exactly the same oscillation currents on successive experiments even when the same conditions are repeated. The main causes of poor reproducibility are thought to be reaction (3) and the surface condition of the zirconium electrode. Previous history of the zirconium electrode may influence the results strongly.

DISCUSSION

Observations on Anodic Zirconium

The theory which is proposed should be consistent with all of the following observed phenomena.

1. Current and potential oscillations.
2. At the point of maximum current the electrode became white from a coverage of minute gas bubbles.
3. The common mineral acids and a number of organic acids were successfully used with a range of fluoride concentration
4. Removing dissolved oxygen from aqueous electrolytes by bubbling N_2 did not effect the oscillations.
5. Oscillations were obtained only when a trace of water was added.
6. As the fluoride concentration was increased it was found necessary to increase the load in order to maintain the oscillations.
7. The effect of rapid stirring was much the same as the effect of increasing fluoride concentration. The frequency, amplitude and peak current were all markedly increased by vigorous stirring.
8. Addition of hexafluorozirconate ion to an oscillating system

lengthened the period, while not influencing the maximum and minimum currents (Table 4).

Table 4. Effect of addition of $ZrF_6^{=}$ to an Oscillating Cell.

$[NaF] = 2.38 \times 10^{-2}$ moles/l	Current density			
	$[ZrF_6^{=}] \times 10^2$ (mole/l)	Max. (ma/cm ²)	Min.	Period, sec.
0		3.3	0.9	21.6
0.78		3.3	0.8	31.2
1.56		3.2	0.8	40.8
2.34		3.3	0.8	48.0
3.12		3.3	0.9	55.2
4.58		3.3	0.8	72.0

9. A simultaneous comparison of potential and current fluctuations indicated they oscillated in phase.
10. At fixed external resistance maximum current was decreased and minimum current was increased slightly by increase of fluoride concentration (Table 2).
11. When zirconium electrode which had been shaved with a blade or immersed in hydrofluoric acid solution was immersed in sulfuric acid solution, instantaneously a large current flowed and decreased to zero. The electrode was washed with distilled water and then immersed in the same solution again. There was no current drawn through the circuit.
12. When zirconium electrode which had been anodized in

sulfuric acid solution (in observation 11) was immersed in NaF-H₂SO₄ solution, current rose very slowly at first to a maximum and then decreased to a limiting current when the NaF concentration was above 1.19×10^{-2} moles/l. In case its concentration was below 1.19×10^{-2} moles/l, no maximum current appeared.

13. The circuit was suddenly opened during oscillation for a while and closed again. The oscillation always started at a higher current than existed at the time of opening (Figure 5).
14. Much vigorous stirring lifted the oscillation above the maximum current and gave an irregular oscillation with decreased amplitude.

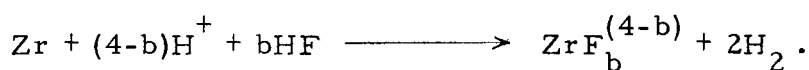
Observations 1 through 9 have been made previously (3; 4).

Factors Influencing Current Oscillations

Observation 11 reasonably supports the supposition that reaction (1) is the electrochemical reaction. Zirconium oxide is insoluble in water and forms a film on the electrode. Reaction (1) stops when almost all of the zirconium reactant on the electrode surface is consumed and is converted into zirconium oxide film. This was also assumed by Shatalov and Bondareva (1; 11) in their paper on "Anodic behavior of zirconium, niobium, and vanadium." Moreover only reaction (1) is electrochemical among proposed reactions, so that its

rate can be controlled by means of external resistance in the circuit.

Reaction (3) was studied by Smith and Hill (12). They introduced this reaction in general form:



However, they concluded that the majority of fluorozirconate complex is in form of ZrF_3^+ , among other forms whose concentrations were calculated from the equilibrium constants reported by Connick and McVey. The fluorozirconate complexes are soluble in water.

Furthermore, Broene and deVries (2) give the following data on the equilibrium constant of HF.

	Temperature °C	12	15	25	35
$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	$K_1 \times 10^4 =$	8.3	7.9	6.7	5.6
$\text{HF} + \text{F}^- \rightleftharpoons \text{HF}_2^-$	$K_2 =$		3.92	3.96	4.33

According to these data, almost all of the added sodium fluoride in acid solution is converted into undissociated hydrofluoric acid species, i. e., $[\text{NaF}] = [\text{HF}]$. Observation 2 suggests that reaction (3) occurs during oscillation. Reaction (2) is proposed because in order to maintain further flow of current, the dissolution of the oxide film must take place. Observation 12 and 13 suggest that reaction (2) may be non-electrochemical and initially slow. Comparison of the rates of the three reactions and of diffusion of HF at any time might

give a solution to oscillation mechanism.

In the case that no external resistance is inserted in the circuit, a typical current-time plot is shown in Figure 2. The first pulse of current when the zirconium electrode was immersed in the $\text{NaF-H}_2\text{SO}_4$ solution was very similar to that of observation 11; therefore, it is supposed that the pulse current is due to reaction (1). In order to maintain the flow of current reaction (2) must occur. Reaction (2) is always followed by rapid reaction (1), so that the rate of reaction (2) is actually current-controlling. Thus the current curve after the pulse is a measure of the rate of reaction (2). In the case that the concentration of HF is above 1.19×10^{-2} moles/l, this curve possessed a maximum and finally leveled off. Therefore, it is concluded that at a concentration of 1.19×10^{-2} moles NaF/l, when the limiting current is reached, the rate of reaction (2) is balanced by that of HF diffusion. The limiting currents are listed in Table 3 and those for 2N H_2SO_4 are plotted vs. $[\text{NaF}]$.

In figure 6, it is shown that the limiting currents are proportional to $[\text{NaF}]$ and are also a function of temperature. For the reason that current decreases after maximum it is concluded that the rate of reaction (2) finally becomes larger than that of HF diffusion when the bulk concentration of HF is larger than 1.19×10^{-2} moles /l. The reason for the increase in rate of reaction (2) is unknown. On the basis of this concept the diffusion coefficients of HF species are

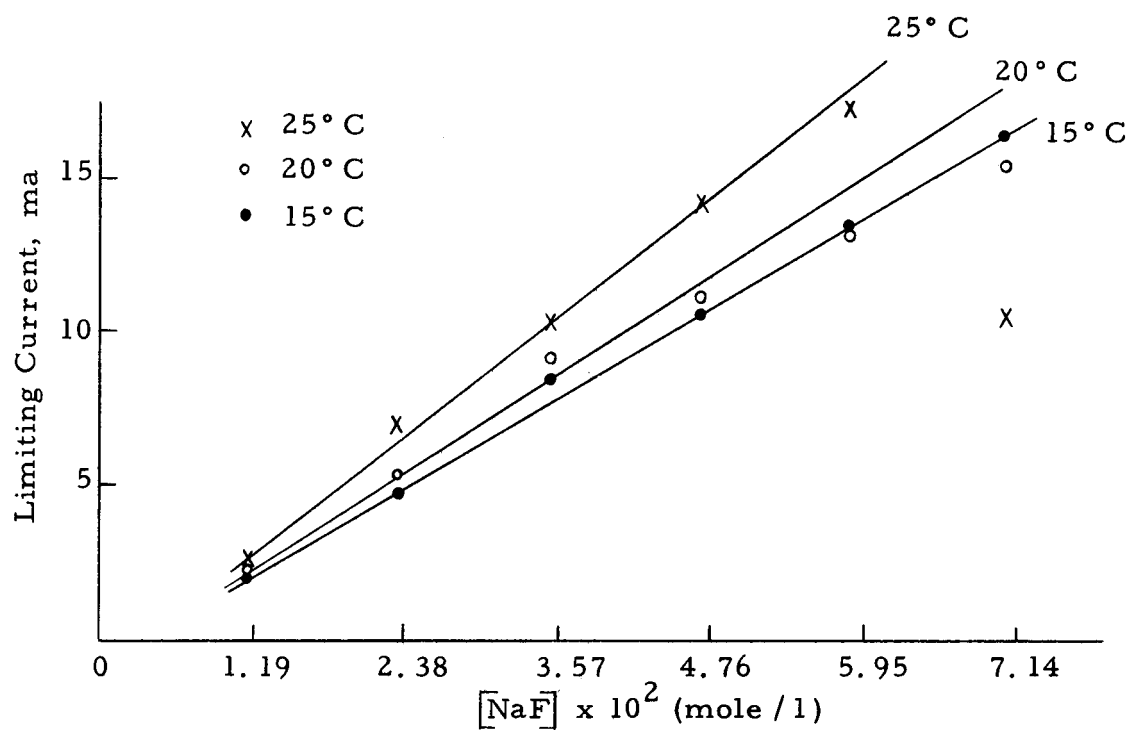


Figure 6. Plot of limiting current vs. $[\text{NaF}]$ in $2\text{N H}_2\text{SO}_4$.

calculated. From Fick's law and assumption of $C_o = C$ when $t = 0$ and $C_o \ll C$ when $t > 0$ (where C_o is the concentration of HF species at zirconium electrode and C is that of the bulk), the equation for current density at any time can be given:

$$i = nFAC \sqrt{\frac{D}{\pi t}} \quad (5)$$

where i is the current density, n is the number of faradays of electricity passed per mole of HF diffusing to the electrode, F is Faraday's constant, A is the area of the electrode, C is the bulk concentration and D is the diffusion coefficient of HF. The current densities at 30 seconds after maximum and calculated D values according to the equation (5) are listed in Table 3 and Table 5, respectively.

Table 5. Calculated Diffusion Coefficients of HF ($D \times 10^5 \text{ cm}^2 \text{-sec}^{-1}$).

Temperature [NaF] x 10 ² (mole/l)	15°C			20°C			25°C		
	[H ₂ SO ₄]			[H ₂ SO ₄]			[H ₂ SO ₄]		
	6N	4N	2N	6N	4N	2N	6N	4N	2N
1.19	--	1.1	1.2	--	1.4	1.5	1.7	2.5	1.9
2.38	1.5	1.9	1.4	1.9	2.1	2.1	3.6	3.7	3.2
3.57	1.5	1.8	1.5	2.0	2.1	2.0	3.4	4.1	3.2
4.76	1.9	1.8	1.8	2.1	1.9	2.2	--	2.0	3.4
5.95	--	--	1.9	--	--	1.9	--	--	3.1
7.14	--	--	1.9	--	--	1.7	--	--	0.8

There is no diffusion coefficient of HF available with which to compare but Kortum and Brockris supply the diffusion coefficients of

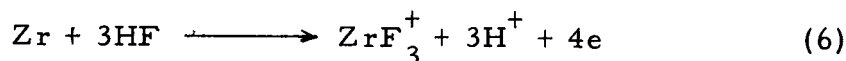
HCl and HBr (8). Those are listed in Table 6.

Table 6. Diffusion Coefficient at 25° C for Aqueous Solutions

moles/l	$D \times 10^5 \text{ cm}^2 \text{ - sec}^{-1}$	
	HCl	HBr
0	3.34	3.403
0.05	3.07	3.156
0.1	3.05	3.146
0.2	3.06	3.190
0.3	3.09	3.249
0.5	3.18	3.388
1.0	3.43	3.869

The values for HCl and HBr are close to those for HF at medium concentrations of HF, but not at low and high concentrations. As the concentration of HF is below 1.19×10^{-2} moles/l, the current depends on the rate of reaction (2) but apparently does not depend on the rate of HF diffusion. Therefore, the equation could not be applied at this concentration. Smaller D values at high concentrations are accounted for by reaction (3) which consumes HF. As a conclusion, this result supports the proposed concept.

The electrochemical reaction directly with HF species, that is,



is eliminated because maximum currents are linear in $[\text{NaF}]$ only up to medium concentrations and then level off at high concentrations.

This is shown in Figure 7.

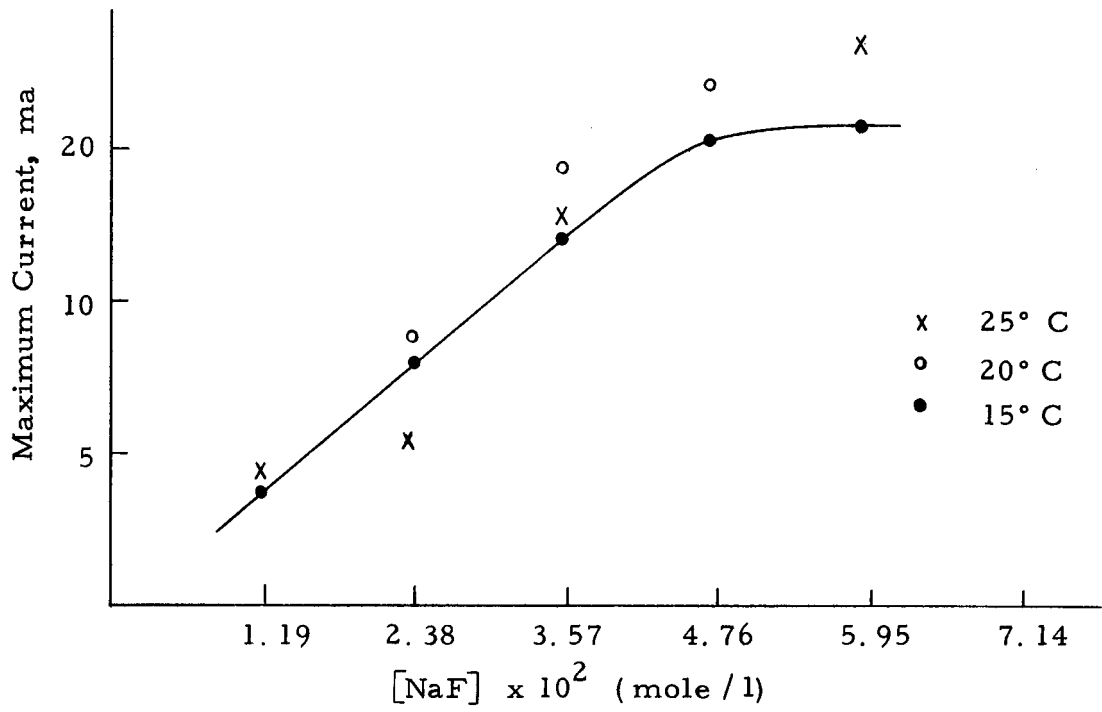


Figure 7. Plot of maximum current vs. [NaF] in 2N H₂SO₄.

Regular Oscillations

Figure 3 is a typical current-time plot of regular oscillations and their maximum and minimum currents are listed in Table 1. Plot of minimum currents vs. $[\text{NaF}]$ in Figure 8 shows that the minimum currents are a function of $[\text{NaF}]$ and also temperature. The temperature dependence of minimum currents implies that the current at the minimum is controlled by a process having an activation energy of about 18 Kcal/mole. This is too high for diffusion alone, which indicates that, while diffusion of HF to the electrode may be important in determining minimum current it is probably not the sole rate-determining process.

Consideration of the rates of three reactions and HF diffusion could explain the regular oscillation in Figure 3. After the zirconium electrode is covered with zirconium oxide film, current flows only when reaction (2) occurs. As shown in observation 12, the rate of reaction (2) is very small at first. Reaction (1) is a rapid reaction; however, after coverage by ZrO_2 is far advanced, the rate of reaction (1) is limited to be the same as that of reaction (2). As reaction (2) proceeds the rate of the reaction increases and thus current increases up to a maximum. Internal plus external resistance limits the maximum rate of reaction (1) and therefore the maximum current is fixed by the total resistance. The internal resistance was 10 to 15 ohms

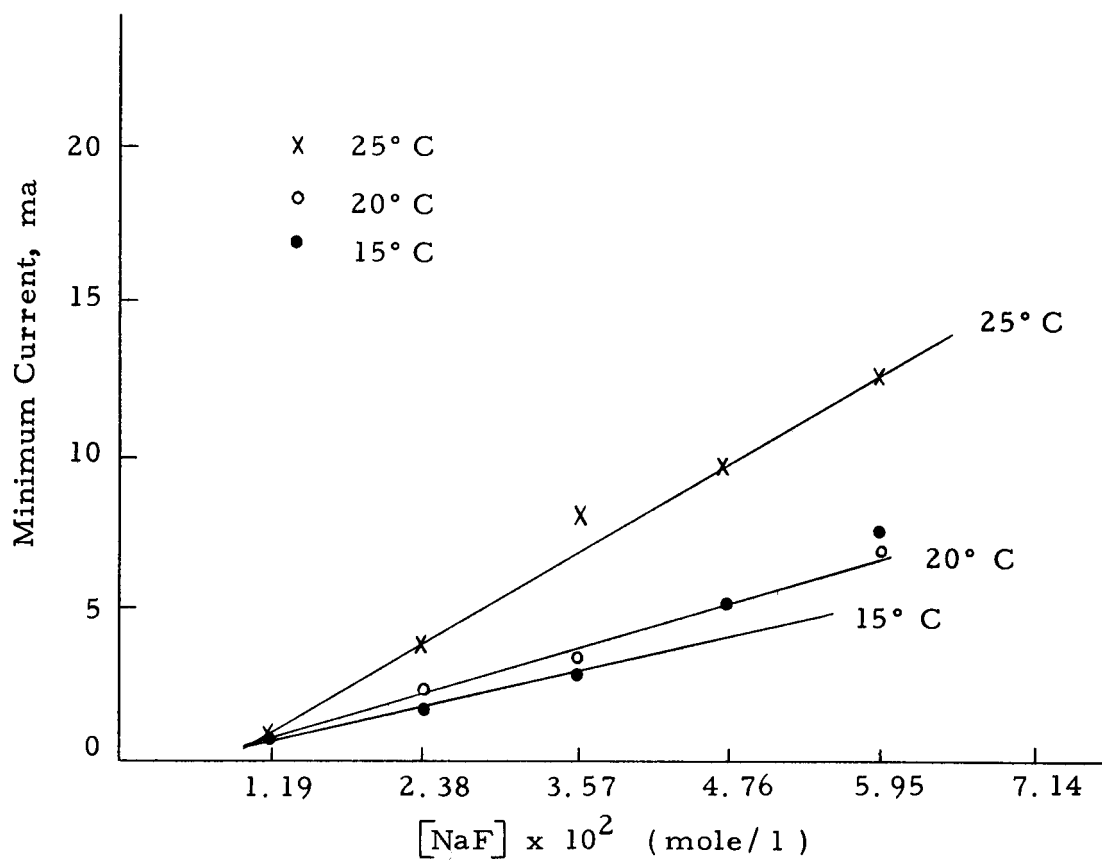


Figure 8. Minimum current vs. [NaF] plot in 2N H₂SO₄.

when the electrodes were separated in a distance of 10 cm in the solution. At the point of maximum current excess zirconium reactant on the electrode surface which is not used for reaction (1) can exist because the rate of reaction (2) now exceeds that of reaction (1). This excess zirconium reactant can be used for reaction (3) and produces hydrogen gas bubbles which is consistent with observation 2. Then the current quickly decreases. Minimum current is determined at least in part by diffusion of HF to the electrode. At the point of minimum current reaction (2) starts to occur, however; the rate at which HF is used is initially smaller than the rate at which HF is supplied by diffusion. This results in an increase of HF concentration at the electrode surface up to that of the bulk. If the minimum currents are limiting currents, they must satisfy the limiting current equation 7:

$$i_1 = \frac{nFA}{\delta} (C - C_o)D \quad (7)$$

where δ is thickness of diffusion layer. The calculated nFA/δ values must be constant at constant temperature. Those are given in Table 7. ($n = 4/3$. $C_o = 1.19 \times 10^{-2}$ moles/l because below this concentration the current does not depend on the rate of HF diffusion but depends on the rate of reaction (2). This is based on the lack of a maximum below 1.19×10^{-2} moles/l.)

Table 7. Calculated $(nFA/\delta) \times 10^7$ coulomb-cm.

Temperature [NaF] x 10 ² (mole/l)	15°C [H ₂ SO ₄]			20°C [H ₂ SO ₄]			25°C [H ₂ SO ₄]		
	6N	4N	2N	6N	4N	2N	6N	4N	2N
1.19	--	--	--	--	--	--	--	--	--
2.38	1.1	1.0	0.9	1.5	1.0	1.1	0.9	0.8	1.0
3.57	1.1	1.5	1.2	1.9	1.6	1.4	--	1.1	1.0
4.76	--	1.0	1.2	2.5	1.4	1.5	--	--	1.3
5.95	--	1.0	1.2	--	1.5	1.3	--	--	1.2

If 1.2×10^{-2} coulomb-cm is adopted for an average nFA/δ , δ becomes 0.057 cm. Comparison of this value to that given ($\delta = 0.05$ cm) by Kortüm and Brockris (8) supports the view that the minimum currents are limited by diffusion.

Irregular Oscillations and Disappearance of Oscillation

When the external resistance was larger or smaller than that of regular oscillation, the oscillation becomes irregular but periodic, or disappears. Examples for this kind of oscillation are shown in Figure 4. In the case of larger external resistance, the maximum rate of reaction (1) decreases, so that the rate of reaction (2) also decreases because of decrease in $[ZrO_2]$ at the electrode surface. The rate of HF diffusion exceeds the rate of reaction (2) and results in the accumulation of HF species at the electrode surface. Therefore, current density curve is raised. However, reaction (3)

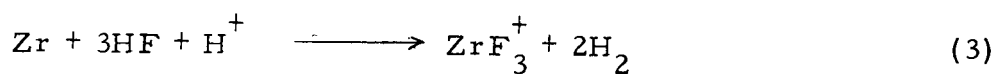
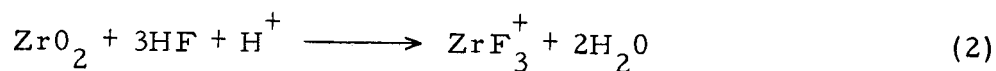
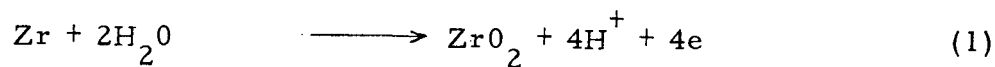
consumes HF species quickly and then decreases the current. Its curve does not trace exactly the same oscillation but nearly so. On the other hand, smaller external resistance accumulates zirconium oxide film on the electrode because reaction (2) does not remove all of zirconium oxide film on the electrode under this condition. Reaction (3) does not occur in this case because as soon as zirconium reactant on the electrode is exposed to the solution by reaction (2), it is consumed by reaction (1). This results in the disappearance of oscillation. The effect of stirring which is in accordance with observation 7 and 14 can be easily understood by consideration that the rate at which HF is supplied to the electrode is greatly increased by stirring. Variation of NaF concentration at fixed external resistance gave results similar to stirring. Addition of NaF, over that required for regular oscillation, makes an oscillation very similar to that of larger external resistance. Lower concentration of NaF makes an oscillation similar to that of smaller external resistance. This effect can be also explained by the proposed theory.

Effect of Acidity

The influence of acidity on the current oscillation is uncertain within the variation of acidity adopted for this study.

CONCLUSION

The current oscillation is interpreted in terms of the rates of three reactions and hydrofluoric acid diffusion.



and the diffusion of hydrofluoric acid to the electrode. The proposed theory in this paper is plausible but it still has some shortcomings. Further investigation should include a study of the potential oscillation which might give useful information concerning the role of resistive-layer formation.

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