NOISE IN ELECTRODE SYSTEMS

by

WILLIAM R. SILL

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Signature of Author ______________________
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Certified by ______________________
Thesis Supervisor

Accepted by ______________________
Chairman, Departmental Committee on Graduate Students

ABSTRACT

Title: Noise in Electrode Systems

Author: William R. Sill

Submitted to the Department of Geology and Geophysics in April, 1963 in partial fulfillment of the requirements for the degree of Master of Science at the Massachusetts Institute of Technology.

Measurements were made of the noise voltage and impedance on silver-silverchloride, lead, copper, aluminum and platinum electrodes. The measurements were made in the frequency range of .02 to .2.0 cps. Certain of the electrodes (Ag-AgCl and Pb) were found to have a near inverse frequency (f^{-1}) power spectrum. The frequency dependence of the noise voltage squared for the other electrodes fell in the range, f^{-1} to f^{-3}.

The possible noise sources are investigated in Chapter 4. These sources are; thermal noise, shot noise, current modulation noise and noise caused by fluctuations in concentration and temperature. It is shown that the shot noise is equivalent to the thermal noise of the reaction resistance and that the concentration

fluctuation noise is equivalent to the thermal noise of the warburg impedance. The total thermal noise (reaction resistance, warburg impedance and solution resistance) is well below the level of the observed noise over most of the frequency range. The power spectrum of this noise is proportional to $f^{-\frac{1}{2}}$. As current modulation mechanism is set up which gives rise to an inverse frequency (f^{-1}) spectrum. An investigation of the values of the parameters involved indicates that this mechanism is capable of producing noise of the observed magnitude.

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TABLE OF CONTENTS

List of Tables

List of Figures

CHAPTER I

Introduction

Many types of geophysical techniques utilize electrodes to measure natural and artificial electric potentials. In certain of these investigations the signals measured are small in comparison to the background noise and methods of eliminating and reducing the noise level must be employed. One source of noise in these measurements is the spontaneous fluctuations in potential of the electrodes. The purpose of this work was to measure the magnitude and the frequency dependence of these noise levels in various electrodes and to investigate their possible sources.

Measurements of noise voltage and impedance were made on silver-silver chloride, copper, lead, aluminum and platinum electrodes. The measurements were made with a variety of electrolytes (distilled watter, aqueous Na Cl, aqueous $Cu\ SO_4$) and in most cases both with and without a small net D.C. current. The noise voltages for the silver-silver chloride and lead electrodes were the smallest measured ($<.1\mu v$). The noise power in these two electrodes exhibits a dependence on frequency which is of the form f^{-1} to $f^{-1.5}$.

Copper and platinum have slightly higher noise levels (.1-.5μv) and aluminum exhibited the largest noise voltages (100 μv). The noise power in these electrodes had a dependence on frequency of the form $f^{-1.5}$ to f^{-3} . Allowing a net D.C. current to pass through the system caused little or no increase in noise. In most cases no significant increase was noted until the magnitude of the D.C. current approached the order of the exchange current.

Spontaneous fluctuations in systems are a common phenomena. Two familiar examples are the fluctuations in density of a gas and Brownian motion. Fluctuations and their effects are readily observable as in the scattering of light by density fluctuations. Another common and easily observed effect is that of the thermal noise voltage produced in resistors by the random thermally excited motion of electrons. Any thermodynamic system if observed under high enough resolution will be seen to undergo small, but macroscopic, fluctuations. In this work we will investigate the details of these fluctuations.

In light of the above discussion, one possible cause of electrode noise is the fluctuations in concentration of the active ion species. These fluctuations are analogous to the fluctuations of density in a gas. The processes involved in generating noise by this mechanism are investigated and the spectrum of this type of noise is found to be of the type $f^{-\frac{1}{2}}$.

Another mechanism investigated is one that causes a modulation of the exchange current. This mechanism might involve the adsorption of an atom or ion that affects the reaction rate and thus the conductivity. The spectrum of this noise is of the relaxation type but a proper superposition of spectra of this kind can give rise to a f^{-1} spectrum. The importance of this mechanism depends of course, on the magnitude of the exchange current.

Noise associated with current flow and with a f^{-1} frequency dependence is encountered in many electronic devices. The "Flicker effect" in tubes and "excess noise" in semiconductors are two examples. No really satisfactory explanation has yet been found for this type of noise in these devices.

The thermal noise of the electrode-electrolyte resistance as well as the "shot noise" associated with the exchange current are also investigated as noise sources. Both of these sources of noise have flat spectra for the frequencies of interest here.

The experimental results of this work show that the noise power has a strong frequency dependence of the form f^{-n} where n is in the range 1 to 3. As stated previously, the treatment of concentration fluctuations results in a $f^{-\frac{1}{2}}$ dependence and the thermal and shot noise have flat spectra. The mechanism involving the modulation of exchange current can be made to yield a f^{-1} spectrum by the superposition of elementary spectra and by a proper choice of limits.

CHAPTER II

Experimental Study of Electrode Noise

Experimental Procedure

In preliminary work it was noted that mechanical motions, surface waves and stirring of the electrolyte gave rise to large potential fluctuations. In an effort to avoid these effects, the electrode holder and tank system was made mechanically rigid and the tank could be filled to the exclusion of all air. Convection was inhibited by placing fiberglass in the electrolyte path. The size of the tank (approximately 1 liter) was large enough so that no rapid temperature changes could take place. The electrode geometry was fixed by sealing the electrodes in a lucite holder with epoxy resin.

The electrodes were kept reasonably clean though no special care was taken in this respect. The lead and aluminum electrodes were physically cleaned at first but then allowed to oxidize, thereafter the oxide layer was not removed. The copper electrodes were polished to begin with and were occasionally cleaned with acid. The silver-silverchloride electrodes were prepared by anodic deposition on silver wire gauze in a .1n HCl solution at a current density of $1 ma/cm^2$. The geometries of the electrodes are as follows:

	Area	Separation
Ag-Ag Cl	3.0 cm^2*	1.5 cm^2
Pb	2.7	1.5
Al	2.7	1.65
Pt	3.0	1.4

*Not accurate, probably larger

The measurements were taken and recorded using a Keithly (Model 150) D-C microvoltmeter, a Krohn-Hite low frequency band pass filter and a Sanborn two channel recorder. The general measurement technique used was to amplify the electrode signals with the D-C amplifier and then band pass the amplified signal and record it on one channel of the Sanborn recorder. The unfiltered output of the Keithly amplifier was recorded on the second channel. In this way a permanent record was made of both the filtered and unfiltered noise. The measurements were made in four band passes: (1) .02-.06; (2) .06-.2; (3) .2-.6; (4) .6-2.0 cps.

The impedance measurements were made with a Krohn-Hite oscillator (.01-10^3cps) and a Tektronix oscilloscope. The oscillator was used to drive a current through a large resistor in series with the electrodes. The voltage developed across the electrodes was displayed on the horizontal sweep of the scope and the driving voltage was displayed on the vertical sweep. Measurements made on the Lissajou pattern developed give the magnitude and the phase angle of the impedance.

Noise Data

In the following tables the measured noise voltages ($\frac{1}{2}$ peak to peak) are given for the four bands measured. All voltages are in microvolts (10^{-6} volts) and the current measurement data are given in terms of current densities ($\mu a/cm^2$).

Noise Measurements

Ag-Ag Cl

Distilled Water

band (cps)				
.02-.06	.03-.07 μv	.05-.10 μv	.05-.07 μv	.015-.03 μv
.06-.20	.03-.05	.05-.10	.05-.07	.015-.03
.20-.60	.05-.07	.05-.10	.04-.05	.015-.03
.60-2.0	.05-.10	.05-.10	.03-.05	.015-.02

	.01n NaCl	0.1n NaCl	
.02-.06	.002-.005 μv	.005-.007μv	.005-.01 μv
.06-.20	.002-.010	.002-.005	.005-.010
.20-.60	.002	.001-.002	.002-.007
.60-2.0	.001	.001-.002	.001-.002

Net Current

Distilled Water

I(μa/cm²)	0.0	0.53	4.5	28.0
.02-.06	.05-.10 μv	.05-.10 μv	.10-.20 μv	.30-.75 μv
.06-.20	.03-.05	.05-.07	.10-.15	.45-.60
.20-.60	.03	.05	.05-.07	.20-.30
.60-2.0	.03-.05	.05	.05-.10	.15-.30

Noise Measurements

Cu

Distilled Water

band (cps)				
.02-.06	.20-.30 μv	.50-.70 μv	.60-1.00 μv	.30-.60 μv
.06-.20	.10-.15	.20-.30	.50-.60	.15-.20
.20-.60	.08-.12	.05-.08	.15-.30	.07
.60-2.0	.07-.10	.05-.06	.05-.06	.07

.01n Na Cl

.02-.06	.30-.50 μv
.06-.20	.40-.50
.20-.60	.05-.10
.60-2.0	.03

0.1n Na Cl

.10-.40 μv	.15-.25 μv
.10-.30	.10-.15
.07-.15	.02-.10
.05	.02

.01n Cu SO_4

.02-.06	.015-.030 μv	.010-.025 μv	.015-.022 μv	.015-.030 μv
.06-.20	.007-.015	.005-.010	.015-.020	.008-.015
.20-.60	.007	.003-.005	.008-.015	.008
.60-2.0	.003	.002	.007	.007

.01n Cu SO_4

.02-.06	.010-.015 μv	.010-.020 μv
.06-.20	.008-.010	.005-.020
.20-.60	.008	.005-.008
.60-2.0	.005	

Noise Measurements

Cu

Net Current - Distilled Water

I($\mu a/cm^2$)	0.0	0.43	3.1	7.7
.02-.06	.40-.70 μv	.60-.80 μv	2.0-2.5 μv	5.0-10.0 μv
.06-.20	.15-.30	.30-.40	1.0-2.0	2.5-3.0
.20-.60	.05-.10	.15-.20	.3- .4	.3-1.0
.60-2.0	.05	.08-.15	.1-.15	.6- .7

	40.0	67.0
.02-.06	20.0-25.0 μv	1500-3000 μv
.06-.20	3.0-6.0	750-1000
.20-.60	1.5-2.0	300-600
.60-2.0	1.5-2.0	300-400

I($\mu a/cm^2$)	0.0	0.43	3.7	43.0
.02-.06	1.5-3.0 μv	5.0-7.5 μv	2.0-2.5 μv	7.5-10.0 μv
.06-.20	.4- .8	1.0-1.5	1.0-1.5	3.0- 5.0
.20-.60	.3- .6	.3-. 5	.5-1.0	3.0- 5.0
.60-2.0	.07- .1	.07	.25	1.5-3.0

I($\mu a/cm^2$)	0.0	.43	3.7	24.0
.02-.06	.30-.60 μv	.20-.60 μv	.30-.60 μv	.50-.80 μv
.06-.20	.15-.20	.20-.50	.30-.60	.30-.60
.20-.60	.07	.07-.15	.15-.30	.30-.45
.60-2.0	.07	.07-.15	.15-.30	.30-.45

Noise Measurements

Cu

Net Current - .01n Na Cl

I(μa/cm^2)	0.0	0.43	3.7	20.0
.02-.06	.80-1.50μv	.75-1.00μv	.75-1.00μv	1.00-1.50μv
.06-.20	.30-.60	.15-.30	.15- .30	.50-1.00
.20-.60	.08-.15	.15	.15	.25-.50
.60-2.0	.08	.10	.15	.20

0.1n Na Cl

I(μa/cm^2)	0.0	0.43	3.7
.02-.06	.60-.75μv	.75-1.00μv	.75-1.50μv
.06-.20	.30-.40	.30-.60	.30-.45
.20-.60	.15	.15	.15
.60-2.0	.07	.07	.10

.01n Cu SO_4

I(μa/cm^2)	0.0	0.43	3.7
.02-.06	.015-.030μv	.015-.030μv	.030-.050μv
.06-.20	.008-.015-	.007-.015	.020-.35
.20-.60	.008	.008	.008-.015
.60-2.0	.007	.007	.008

0.1n Cu SO_4

I(μa/cm^2)	0.0	0.43	3.7
.02-.06	010-.020μv	.008-.015μv	.030-.060μv
.06-.20	.005-.020	.008-.015	.015-.030
.20-.60	.005-.008	.008-.015	.007-.015
.60-2.0	.005	.005	.005

Noise Measurements

Pb

Distilled Water

.02-.06	.05-.10 μv	.05-.10 μv	.05-.08 μv
.06-.20	.05-.07	.03-.05	.03-.04
.20-.60	.03-.07	.03	.02
.60-2.0	.03-.07	.03	.025-.03

	.01n Na Cl		0.1n Na Cl	
.02-.06	.30-.60 μv	.30-.45 μv	.30-.45 μv	.30-.45 μv
.06-.20	.30-.45	.30-.45	.20-.30	.15-.30
.20-.60	.15-.25	.15-.30	.08-.15	.07-.15
.60-2.0	.07-.15	.07-.10	.08-.15	.07-.10

Distilled Water - Current

I(μa/cm²)	0.0	0.48	4.1	27.0
.02-.06	.070 μv	.10-.15 μv	.10-.15 μv	.20-.50 μv
.06-.20	.025	.05-.07	.05-.07	.30-.50
.20-.60	.025	.03-.05	.05	.15-.40
.60-2.0	.025	.03-.05	.05	.15-.40

	.01n Na Cl		0.1n Na Cl	
I(μa/cm²)	0.0	0.48	0.0	0.48
.02-.06	.30-.60 μv	.60-.80 μv	.30-.45 μv	.30-.45 μv
.06-.20	.30-.45	.30-.60	.15-.30	.15-.30
.20-.60	.15-.25	.30-.45	.07-.15	.07-.15
.60-2.0	.07-.15	.30-.45	.07-.15	.07-.15

Noise Measurements

A1

Distilled Water

Band

.02-.06	400-700 μv	800-1500 μv	750-1000 μv	500-750 μv
.06-.20	300-500	450-600	300- 600	300-500
.20-.60	70-150	300-600	150- 300	100-200
.60-2.0	25	50-100	30- 40	25- 50

.02-.06	750-1100 μv	750-1500 μv
.06-.20	300- 450	400- 100
.20-.60	50- 100	75- 100
.50-2.0	30	50

	.01n Na Cl		0.1n KCl	
.02-.06	750-1000 μv	300-600 μv	300-600 μv	400-750 μv
.06-.20	300-800	150-300	300-450	300-600
.20-.60	300-600	150-300	200-300	150-300
.60-2.0	300	150-200	150-300	150-200

Noise Measurements

Al

Net Current - Distilled Water

$I(\mu a/cm^2)$	0.0	0.48	4.8	52.0
.02-.06	500-700 μv	300-1000 μv	1500-3000 μv	750-3000 μv
.06-.20	250- 400	250- 700	1500-3000	1000-2000
.20-.60	100-200	250- 400	1500-3000	750-1000
.60-2.0	30	100- 150	750-1000	600- 750

	520
.02-.06	800-1000 μv
.06-.20	250- 500
.20-.60	150- 250
.60-2.0	100- 200

.01n Na Cl

$I(\mu a/cm^2)$	0.0	0.48	4.1	27.0
.02-.06	300-600 μv	300-600 μv	300-600 μv	300-600 μv
.06-.20	150-300	300-600	300-600	300-600
.20-.60	150-200	300	300-450	300-450
.60-2.0	150 -200	150-300	150-300	200-300

0.1n Na Cl

$I(\mu a/cm^2)$	0.0	0.52	4.1	21.0
.02-.06	300-600 μv	300-600 μv	300-600 μv	300-450 μv
.06-.20	300-450	300-600	150-300	150-350
.20-.60	200-300	150-300	150-250	150-300
.60-2.0	150-300	150	150-250	150-300

Noise Measurements

Pt

Distilled Water

Band		
.02-.06	.15-.30 μv	.10-.20 μv
.06-.20	.15	.07-.10
.20-.60	.07	.05-.10
.60-2.0	.07-.10	.05

Net Current - Distilled Water

I(μa/cm²)	0.0	0.57	5.2	43.0
.02-.06	.10-.30 μv	1.0-2.0 μv	1.0-1.5 μv	2.0-3.0 μv
.06-.20	.07-.15	1.0-1.5	1.0-1.5	1.5-3.0
.20-.60	.05-.10	1.0-1.5	1.0-1.5	1.5-2.0
.60-2.0	.05-.10	1.0-1.5	1.0	1.5-3.0

Discussion of Experimental Data

Ag-Ag Cl Electrodes

The Ag-Ag Cl electrodes in distilled water exhibit a near f^{-1} dependence for the noise voltage squared. This dependence increases slightly ($f^{-1.5}$) in Na Cl solutions and at the same time is accompanied by a drop in noise voltage by a factor of 10^{-1}. The impedance data shows that the concentration of the reacting species increases in the Na Cl solutions causing an increase in exchange current. With a net current passing through the system there is no significant increase in noise except at a current density of 28 $\mu a/cm^2$.

Pb Electrodes

In distilled water the noise power has a dependence on frequency of the form $f^{-1.3}$. The impedances are small and the noise voltages are comparable to those of the Ag-Ag Cl electrodes. In the Na Cl solutions the impedance increases as well as the noise voltages. As a result of the increase in impedance, we see that the concentration of active ions has decreased.

The current measurements in distilled water show little increase until a current density of 27 $\mu a/cm^2$ at this point the frequency dependence is almost f^{-1} . In .01n Na Cl, there is a slight increase for .48 $\mu a/cm^2$ in the lower frequency bands (.02-.06 and .06-.20) and a larger increase at the two higher bands (.20-.60 and .60-2.0).

Cu Electrodes

The frequency dependence of the squared voltage in the various solutions are, distilled water -- $f^{-1.5}$ to f^{-3}, .01n Na Cl $-f^{-2}$ to f^{-3} , .1n Na Cl $-f^{-2}$ to $f^{-2.5}$, .01n Cu SO_4 - $f^{-1.5}$ to f^{-2}, and .1 Cu SO_4 $-f^{-1.5}$. There is little difference in the noise voltages in distilled water and Na Cl solution, even though the concentration of active ions increases in the salt solutions. There is, however, an order of magnitude drop in the noise level in Gu SO_4 solutions. The current measurements in distilled water show significant increases for 3 $\mu a/cm^2$. The measurements with salt solutions show slight increases in noise for current densities above 3 $\mu a/cm^2$.

Al Electrodes

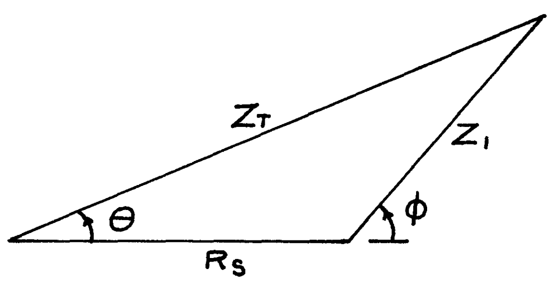
The noise voltages for the Al electrodes are at least two orders of magnitude larger than that observed for the other electrodes. In the salt solutions there is no significant increase in noise for the low frequency bands, (.02-.06 and .06-.20) but there is generally some increase in the bands (.20-.60 and .60-2.0). The result of this is to change the frequency dependence from f^{-2} in distilled water to $f^{-1.5}$ in the salt solutions. Crude measurements on aluminum foil electrodes showed a large increase in noise in salt solutions, but as noted above, this effect was not observed here. The impedance measurements show that there is little or no difference in the concentrations of active ion species in distilled water and salt solutions. The noise voltages in distilled water show some increase above a current density of 4.8 $\mu a/cm^2$. The largest increases were in the high frequency bands (.20-.60 and .60-2.0). The salt solutions showed little increase even for a density of 27 $\mu a/cm^2$.

In conclusion, a few general remarks can be made about the nature of the noise in electrode systems. We see that the noise is smallest for those electrodes generally considered reversible, such as Ag -Ag Cl in Na Cl solutions, Cu in Cu SO_4 solutions and Pb in distilled water ($PbCO_3$ reversible with respect to $CO_3^=$ in solution). The frequency dependence for those electrodes is also near f^{-1}. With any particular electrode, the noise increases as the concentrations of active ion species (m_i) decreases.

IMPEDANCE DATA

In the following work the total measured impedance at 10^3 cps was assumed equal to the solution resistance. The phase angle θ (in degrees) is the total phase shift. The values of Z_1 at 1 cps (ϕ is generally near 45° at 1 cps) are taken as the values of the warburg impedance (at 1 cps). The values of Z_1 are calculated from the observed impedance Z_T and the phase angles θ. See figure 2.1.

Figure 2.1



Z_T = total impedance (in ohms)

R_S = solution resistance = $Z_T(10^3 \text{cps})$

θ = total phase angle

$$Z_1 = \left[R_S^2 + Z_T^2 - 2 R_S Z_T \cos\theta \right]^{1/2}$$

Impedance Measurements

Ag-AgCl

Distilled Water

freq.	Z_T	θ	Z_T-R	Z_T	Z_T	θ	Z_T-R_s	Z_1
10^3	28,300Ω	1.5°			31,800Ω	2.0°		
10^2	28,600	0.0	300Ω		32,700	1.5	900Ω	
10^1	28,600	0.0	300		33,000	1.5	1,200	
1	29,000	1.5	700	1,000Ω	33,700	3.0	1,900	3,200Ω
10^{-1}	31,400	4.3	3,100	3,800	35,200	6.0	3,400	4,500
10^{-2}	34,400	8.6	6,100	7,400	41,400	10	9,600	6,300

10^3	26,900Ω	0.0°	
10^2	27,100	0.0	200Ω
10^1	27,100	0.0	200
1	27,200	1.5	300
10^{-1}	27,200	1.5	300
10^{-2}	28,600	4.3	1,500

	.01n NaCl				.1n NaCl			
10^3	283Ω	1.5°			114Ω	7°		
10^2	303	2.8	20Ω	28Ω	141	9	27Ω	34Ω
10^1	328	4.3	45	55	167	10	53	60
1	364	5.7	81	90	182	10	68	72
10^{-1}	384	7.2	101	110	187	9	73	78
10^{-2}	394	7.2	111	120	187	7	73	70

Impedance Measurements

Cu

Distilled Water

freq.	Z_T	θ	$Z_T - R_s$	Z_1	Z_T	θ	$Z_T - R_s$	Z_1
10^3	12,500 Ω	6°			21,000 Ω	6°		
10^2	14,150	9	1,650 Ω	2,200 Ω	21,000	0		
10^1	19,700	19	7,200	8,000	22,000	3	1,000 Ω	1,700 Ω
1	34,400	24	21,900	22,000	26,500	6	5,500	6,300
10^{-1}	65,000	18	52,000	52,000	29,600	7	8,600	9,200
10^{-2}	77,800	10	65,300	65,500	34,600	6	13,600	13,200
10^3	4,700 Ω	0°			14,700 Ω	3°		
10^2	4,900	3	200 Ω	300 Ω	14,900 Ω	3	200 Ω	
10^1	5,400	9	1,200	1,300	15,400	7	700	
1	8,100	12	3,400	3,600	21,200	12	6,500	
10^{-1}	11,200		6,500	6,600	28,300	12	13,600	
10^{-2}	16,100	12	11,400	11,600	37,400	9	22,700	
	.01n NaCl				.1n NaCl			
10^3	198 Ω	10°			38 Ω	7°		
10^2	272	15	75 Ω	137 Ω	50	18	11 Ω	
10^1	404	22	206	275	92	32	54	62 Ω
1	718	30	520	600	182	32	144	162
10^{-1}	1,200	32	990	1,000	495	30	457	510
10^{-2}	2,600	26	2,440	2,500	1,000	26	962	

Impedance Measurements

Cu

	.01n $CuSO_4$				.1n $CuSO_4$			
freq.	Z_T	θ	$Z_T - R_s$	Z_1	Z_T	θ	$Z_T - R$	Z_1
10^3	323Ω	4°			67Ω	3°		
10^2	364	6	41Ω	54Ω	76	6	9Ω	12Ω
10^1	425	7	102	114	90	7	23	25
1	485	7	162	171	101	7	34	36
10^{-1}	595	5	273	276	106	6	39	41
10^{-2}	646	4	323	325	106	4	39	40

Pb

	Distilled Water				Distilled Water			
10^3	8,900Ω	0°			6,300Ω	0°		
10^2	8,900	0			6,300	0		
10^1	8,900	0			6,300	0		
1	9,100	1.5	200Ω	340Ω	6,460	0	100Ω	
10^{-1}	9,200	.7	300	360	6,670	0	312	
10^{-2}	9,400	0	500	320	6,870	1.5	510	550Ω

	.01n NaCl				.1n NaCl			
10^3	278Ω	12°			131Ω	44°		
10^2	606	30	328Ω	395Ω	445	30	314Ω	360Ω
10^1	1,070	24	792	830	585	7	454	484
1	1,720	22	1,442	1,470	636	12	505	540
10^{-1}	2,980	18	2,700	2,720	970	22	839	900
10^{-2}	4,950	15	4,570	4,580	1,720	20	1,590	1,580

Impedance Measurements

Al
Distilled Water

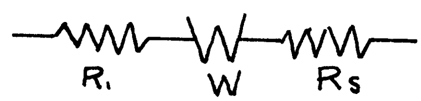
freq.	Z_T	θ	$Z_T - R_s$	Z_1	Z_T	θ	$Z_T - R_s$	Z_1
10^3	8,500Ω	3°			16,200Ω	0°		
10^2	8,700	4	200Ω	680Ω	16,200	1.5		
10^1	10,400	16	1800	3400	16,700	6	500Ω	
1	23,000	49	14000	19000	20,800	18	4600	7000Ω
10^{-1}	123,000	60	114000	130000	41,000	18	24800	30000
10^{-2}	341,000	10	332000	400000	62,000	10	36300	

	Distilled Water				.01n NaCl			
10^3	15,400Ω	7°			445Ω	7°		
10^2	15,700	2	300Ω		605	22	160Ω	256Ω
10^1	16,150	9	750		1,520	44	1,080	1,240
1	26,000	26	10,600	13,000Ω	5,550	39	5,100	5,000
10^{-1}	67,600	34	52,200	53,600	10,700	13	10,250	9,900
10^{-2}	129,000	12	113,600	114,000	12,100	7	11,660	11,700

	Al - .1n NaCl				Pt - Distilled Water			
10^3	53Ω	22°			39,000Ω	10°		
10^2	121	55	68Ω	240Ω	40,000	1.5	1,000Ω	
10^1	747	69	684	720	40,000	1.5	1,000	
1	4,140	49	4,090	4,550	43,400	13	4,400	
10^{-1}	8,370	15	8,320	8,500	75,600	39	36,600	
10^{-2}	12,100	6	12,050	12,000	185,000	43	146,000	

In this work we will assume a simple equivalent circuit for the electrode. The theory behind this representation of electrodes as a combination of circuit elements is worked out in full by Madden and Marshall (1959), For a brief review of their work see Appendix D. The electrode-electrolyte system is represented by the following circuit.

Figure 2.2



Where R_1 = the reaction resistance

W = the warburg impedance

R_s = the solution resistance.

The reaction resistance, as the name implies, is the result of the impedance to flow of current presented by the energy barrier of the reaction. The warburg impedance is associated with the diffusion of the reacting species to the electrode surface. The warburg impedance has a phase shift of 45° and is proportional to $f^{-1/2}$. The above representation (Figure 2.2) of the electrode impedance has then a dependence on frequency of the form $f^{-1/2}$ due to the warburg impedance. The impedance measurements made here show a frequency dependence of the form

$f^{-.2}$ to $f^{-.7}$ in the frequency range of interest here (10^{-2} to 1 cps). The circuit in Figure 2.2 is then at best, a rough approximation.

From a consideration of reaction rate theory we can evaluate the circuit elements. (Appendix D)

$$W = \frac{2.5\ 10^{-2}}{m_i\ f^{1/2}} \qquad 2.1$$

$$\frac{R_1}{W} = f^{1/2}\ 5.5\ 10^{-8}\ e^{\frac{\Delta G_0^{\ddagger}}{RT}} \qquad 2.2$$

$$i_0 = F\frac{kT}{h}\left(\frac{m_i\ 10^{15}}{55.5\ \ 6\ 10^{23}}\right) e^{-\frac{\Delta G_0^{\ddagger}}{RT}} \qquad 2.3$$

Where m_i = concentration of active ion species in moles/liter

i_0 = exchange current

$\Delta G_0^{\ddagger}$ = activation energy contains electric potential term

In their work, Madden and Marshall (1959) found a remarkably small range of values for the parameters R_1, $\Delta G_0^{\ddagger}$, W and m_i considering the wide variety of electrodes and conditions for which these parameters were measured. The reaction resistance was found to be quite small (1-100 Ω-cm^2) and for this reason they referred to it as the "catalyzed reaction resistance". They concluded that the reacting ion species is a minor constituent with a concentration of 1 to 10 x 10^{-5} moles/liter. The activation energy is similar for all the electrodes measured and is of the order of 7 Kcal/mole.

It was found in this work that the concentrations of active ion species (m_i), calculated from the warburg impedances, fall in the range 10^{-4} to 10^{-6} mole/liter. The following table gives the average warburg impedance for 1 cm^2 of surface area at 1 cps. From these values of the warburg impedance the concentrations of the active ion species were calculated. The exchange currents were calculated assuming an activation energy of 7 Kcal/mole.

	warburg impedance at 1cps for 1cm^2	concentration of active ion $m_i\left(\frac{\text{moles}}{\text{liter}}\right)$	exchange current $i_0\left(\frac{\text{amp}}{\text{cm}^2}\right)$
distilled water			
Ag-Ag Cl	100-1000Ω	$2.510^{-4}-2.510^{-5}$	$10^{-1}-10^{-2}$
Pb	120Ω	210^{-4}	710^{-2}
Cu	1,200-7,400Ω	$210^{-5}-310^{-6}$	$1-810^{-3}$
Al	2,600-7,000Ω	$10^{-5}-410^{-6}$	$1-310^{-3}$
Pt	1,000Ω	1.410^{-5}	$5\ 10^{-3}$
.01n Na Cl			
Ag-Ag Cl	30Ω	$8\ 10^{-4}$	$3\ 10^{-1}$
Pb	550Ω	$5\ 10^{-5}$	10^{-2}
Cu	200Ω	10^{-4}	$4\ 10^{-2}$
Al	1900Ω	10^{-5}	$4\ 10^{-3}$
.1n Na Cl			
Ag-Ag Cl	25Ω	10^{-3}	$3\ 10^{-1}$
Pb	200Ω	10^{-4}	$4\ 10^{-2}$
Cu	50-150Ω	$1-5\ 10^{-4}$	$10^{-1}-5\ 10^{-2}$
Al	17000Ω	$1.5\ 10^{-5}$	$5\ 10^{-3}$
.01n Cu SO_4			
Cu	57Ω	$4\ 10^{-4}$	$1.3\ 10^{-1}$
.1n Cu SO_4			
Cu	12Ω	$2\ 10^{-3}$	$6\ 10^{-1}$

CHAPTER III

Inverse Frequency Noise

The experimental data shows that the noise voltage squared has a strong frequency dependence of the form f^{-n} where n varies from 1 to 3. Noise of this type with n=1 is common in a wide variety of electronic devices such as oxide coated valves, carbon microphones, carbon filiments and resistors, germanium filiments, thin metal films and rectifying barriers. The noise power in these devices is also proportional to the current and because of this it is generally considered as a result of conductivity fluctuations. Its widespread occurrence is an indication that it is associated with a basic property of current flow in semiconductors. This would lead one to look for some common mechanism in all these devices but there has not yet been a good explanation for any single one. Most of the elementary mechanisms proposed to modulate the conductivity give rise to a relaxation spectrum.

The frequency range over which f^{-1} noise has been observed is remarkable. At the low frequency end oberservations on devices have been made down to 10^{-4} cps with no deviation from a f^{-1} spectrum. At the upper limit the noise generally falls below the shot or thermal noise. The high frequency measurements extend to 10^6 cps. The range of f^{-1} noise then covers up to 10 decades.

Many theories of inverse frequency noise have been proposed, most of these give rise to a f^{-1} dependence only in a portion of the total spectrum and then only under certain conditions. (Schottky, 1926; Richardson, 1950; MacFarlane, 1950; Van der Ziel, 1950; du Pre, 1950) One method of deriving an inverse frequency spectrum is by the superposition of a distribution of relaxation spectra. This method will be outlined in the following sections.

Relaxation and Shot Noise Spectra

Given a random process f(t) the Wiener-Khintchine theorm gives the relation between the power spectrum and the auto-correlation function of the process.

$$\Phi_{11}(\omega) = \frac{2}{\pi} \int_0^\infty \phi_{11}(\tau) \cos \omega\tau \, d\tau \tag{3.1}$$

$$\phi_{11}(\tau) = \int_0^\infty \Phi_{11}(\omega) \cos \omega\tau \, d\omega \tag{3.2}$$

$$\phi_{11}(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_0^T f(t)\, f(t+\tau)\, dt \tag{3.3}$$

$$\phi_{11}(0) = \overline{f(t)^2} = \int_0^{\infty} \Phi_{11}(\omega)\, d\omega \tag{3.4}$$

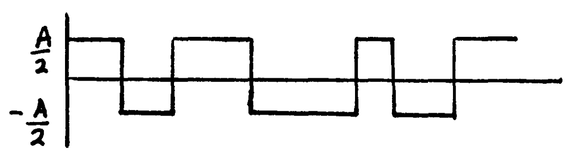
Where

$\Phi_{11}(\omega) \equiv$ Power density

$\phi_{11}(\tau) \equiv$ Autocorrelation function

For a function of time of the following form where the zero crossings have a Poisson distribution.

f(t)



The autocorrelation function is (Lee, 1960)

$$\phi_{11}(\tau) = \overline{f(t)^2}\; e^{-2K\tau} \tag{3.5}$$

$K =$ average number of zero crossings per second

$\overline{f(t)^2} = A^2/4$

If the function f(t) represents the fluctuations in conductivity of amplitude A/2 and of average length of time $\tau_c = 1/K$ then the power spectrum of these fluctuations is obtained by inserting equation (3.5) in (3.1).

$$\Phi_{11}(\omega) = \frac{2}{\pi}\int_0^\infty \overline{f(t)^2}\, e^{-2\tau/\tau_c} \cos\omega\tau \, d\tau$$

$$= \frac{2\overline{f(t)^2}}{\pi} \frac{\tau_c}{2(1+\omega^2\tau_c^2/4)} = \frac{2\overline{f(t)^2}}{\pi} \frac{2K}{(4K^2+\omega^2)} \qquad (3.6)$$

Spectra of this general type are known as relaxation or shot noise spectra. This spectrum is flat up to a frequency of $f_c \cong 1/\tau_c$ and then drops off as f^{-2}. Although the spectrum in equation (3.6) has the same form as a shot noise or a relaxation spectrum, it might be misleading to use these terms here because the characteristic time τ_c is defined differently and is not related to k. For a relaxation spectrum the form is

$$\Phi_{11}(\omega) = \frac{2\overline{f(t)^2}}{\pi} \frac{\tau_c}{(1+\omega^2\tau_c^2)} \qquad (3.7)$$

Where τ_c refers to the time to the time constant of the exponential wavelets, $g(t) \;\; A/\tau_c \exp(-\tau/\tau_c)$ and k is the average number of wavelets per second. In this case $\overline{f(t)^2}$ is a function of both k and τ_c.

In shot noise τ_c refers to the transit time of an electron and $k = \bar{i}/e$ and since the integral of each wavelet over all time must be equal to the electronic charge e, we have $A = e$. With this we can write for the spectrum of shot noise. (Equation 3.7)

$$\overline{i(\omega)^2} = \frac{e\,\overline{i}}{\pi}\;\frac{1}{(1+\omega^2\tau_c^2)} \tag{3.8}$$

Below the cutoff frequency we may write

$$\overline{i(f)^2} = 2e\,\overline{i}\,\Delta f \tag{3.9}$$

which is generally referred to as the full shot noise formula.

Derivation of f^{-1} Spectrum

Considering equation (3.6), if instead of a single relaxation time we have a distribution $g(\tau)$ of times, where the probability of a time between τ and $\tau + d\tau$ is

$$dP = g(\tau)\,d\tau$$

and

$$\int_0^\infty g(\tau)\,d\tau = 1 \qquad \text{(Normalization)}$$

We can then construct a new power spectrum by an integration over the distribution of relaxation spectra.

$$\Phi'(\omega) = \int_0^\infty \frac{\overline{f(t)^2}}{\pi}\;\frac{\tau\, g(\tau)}{(1+\omega^2\tau^2)}\;d\tau \tag{3.10}$$

It is possible to obtain a f^{-1} spectrum by the proper choice of $g(\tau)$ which proves to be

$$g(\tau) = \begin{cases} \frac{1}{\tau} \frac{1}{\ln \tau_2/\tau_1} & \tau_1 \ll \tau \leq \tau_2 \\ 0 & \text{outside the above interval} \end{cases} \qquad (3.11)$$

Substituting the above in equation (3.10) and integrating we have

$$\Phi'(\omega) = \frac{\overline{f(t)^2}}{\pi \ln \tau_2/\tau_1} \frac{1}{\omega} \left[\tan^{-1}\omega\tau_2 - \tan^{-1}\omega\tau_1\right] \qquad (3.12)$$

This function is independent of ω if $\omega\tau_2 \ll 1$ and varies as ω^{-2} if $\omega\tau_2 \gg 1$. The desired ω^{-1} dependence is obtained if $\omega\tau_1$ is so small that $\tan^{-1}\omega\tau_1$ approaches 0 and $\omega\tau_2$ is so large that $\tan^{-1}\omega\tau_2$ approaches ∞. These conditions can be stated alternatively as $\omega\tau_1 \ll 1 \ll \omega\tau_2$. By a proper choice of τ_1 and τ_2 the ω^{-1} region can be extended as far as is necessary. Within these limits we can rewrite equation (3.12)

$$\Phi'(\omega) = \overline{f(t)^2}/\ln \tau_2/\tau_1 \quad \frac{1}{\omega}$$

$$G'(f) = \overline{f(t)^2}/\ln \tau_2/\tau_1 \quad \frac{1}{f} \qquad (3.13)$$

If the time τ is dependent on an activation energy so that τ can be expressed in the form (Appendix B)

$$\tau = \tau_0 \ e^{E/KT} \tag{3.14}$$

Then a rather narrow distribution of energies may give rise to a wide distribution of times τ . With the aid of equation (3.14) we can rewrite equation (3.11) in terms of energies.

$$g(E) = \frac{KT}{\tau_0 (E_2 - E_1)} \ e^{-E/KT}$$

$$g(E)dE = \frac{dE}{(E_2 - E_1)} \tag{3.15}$$

The limits for a f^{-1} spectrum can then be written as

$$E_1 \ll KT \ln 1/\omega\tau_0 \ll E_2 \tag{3.16}$$

We can now investigate the restrictions placed on the activation energies if we wish to construct a f^{-1} spectrum. Stating the conditions on $\omega\tau_1$ and $\omega\tau_2$ as,

$$\omega\tau_1 \leqslant .1 \qquad\qquad \omega\tau_2 \gg 10$$

for the range 10^{-4} to 10^{6} cps we have

$$\tau_1 \leqslant 10^{-7} \text{sec} \qquad\qquad \tau_2 \gg 10^{5} \text{ sec}$$

With $\tau_0 = 1.66 \quad 10^{-13}$ (See Appendix B, equation B-15)
we can write for the activation energies.

$$E_1 \leqslant .35\,\text{ev}\ (8\ \text{Kcal/mole}) \qquad E_2 \gg 1.1\,\text{ev}\ (25\ \text{Kcal/mole})$$

We have here a derivation of a f^{-1} spectrum obtained by a superposition of a distribution of relaxation type spectra. It was further assumed that the distribution of characteristic times was the result of a distribution of the activation energies of some process. The results obtained here will be used in the following chapter to derive a f^{-1} spectrum for current modulation noise.

CHAPTER IV

Noise in Electrode Systems

Noise in electrode systems can be expected from a variety of sources. One would be the simple thermal noise due to the total resistance of the electrodes and the solution. We might also expect some noise similar to shot noise associated with any currents in the system. This applies to the exchange currents as well as any net currents flowing through the system. A reaction or any other mechanism, such as the adsorption of an ion, that modulates the exchange currents could also give rise to potential fluctuations. Fluctuations in concentration and temperature are another possible source of noise. In the next sections these noise sources will be investigated in greater detail.

Thermal Noise

Any resistance has a noise power characteristic of its temperature due to the thermal motion of the charge carriers. The spectrum of this noise is flat in so far as the resistance is not a function of frequency. The noise power is given by the Nyquist equation.

$$\overline{E^2} = 4\,KT\;R\,\Delta f \quad (\text{volts})^2$$

The noise voltage in micro volts is then

$$\Delta E = 1.29\;10^{-4}\left[R\,\Delta f\right]^{\frac{1}{2}} \quad \mu V \tag{4.1}$$

Noise voltages calculated from this formula are well below the observed values for low frequencies but at high frequencies is often of the same order of magnitude as that observed. We see then that the "excess noise" tends to fall below the level of the thermal noise at frequencies of the order of 1 cps. This is not true for the aluminum electrodes where even at the high frequencies the noise was three orders of magnitude greater than the thermal noise.

Shot Noise

Since currents are flowing across the electrode-electrolyte boundary we would expect this to give rise to "shot noise". This type of noise is caused by the random arrivals of individual charge carriers at the electrode. The spectrum of shot noise is flat out to the reciprocal of some characteristic time. The characteristic time in diodes is the flight time of the electron and by analogy we will use here the time it takes a charge carrier to cross the energy barrier. From Appendix B (Equation B.10 and B.12) we have that this time

Thermal Noise
Table 4.1

Elec-trode	band (cps)	Distilled Water		.01n NaCl		.1n NaCl	
		Thermal	Observed	Thermal	Observed	Thermal	Observed
Cu	.02-.06	.007	.25	.001	.50	.0006	.25
	.06 -.20	.012	.10	.002	.50	.0010	.15
	.20-.60	.017	.10	.003	.10	.0014	.10
	.60-2.0	.028	.08	.004	.03	.0022	.02
		.01n CuSO				.1n CuSO	
Cu	.02-.06	.0006	.030			.0003	.015
	.06-.20	.0012	.015			.0006	.010
	.20-.60	.0019	.008			.0009	.008
	.60-2.0	.0034	.007			.0015	.005

Thermal Noise[1]
Table 4.1

Electrode	band (cps)	Distilled Water Thermal Noise	Distilled Water Observed Noise	.01n NaCl Thermal Noise	.01n NaCl Observed Noise	.1n NaCl Thermal Noise	.1n NaCl Observed Noise
	.02-.06	.005	.07	.0005	.005	.0004	.010
Ag-AgCl	.06-.20	.009	.05	.0009	.010	.0006	.010
	.20-.60	.014	.07	.0015	.002	.0010	.005
	.60-2.0	.026	.07	.0029	.001	.0018	.002
	.02-.06	.003	.10	.002	.45	.001	.45
	.06-.20	.005	.07	.003	.45	.002	.30
Pb	.20-.60						
	.20-.60	.008	.07	.004	.30	.003	.15
	.60-2.0	.014	.07	.006	.10	.004	.10
	.02-.06	.012	700	.003	600	.003	600
	.06-.20	.017	600	.005	300	.004	450
Al	.20-.60	.017	500	.007	300	.006	300
	.60-2.0	.022	100	.010	200	.009	300

1. Calculated from equation 4.1 and the total measured impedance

is $\tau = [C^*]/[A] \times 10^{-5}$ sec. For all frequencies of interest here the spectrum is flat. The spectrum is given by

$$i(\omega)^2 = \frac{i_0 e}{\pi} \frac{1}{(1+\omega^2\tau^2)} \tag{4.2}$$

and below the cutoff frequency we may write

$$\Delta i^2 = 2 e i_0 \Delta f \tag{4.3}$$

If i_0 is the exchange current in amp/cm^2 and R_1 is the reaction resistance in Ω - cm^2, then the noise voltage squared is given by

$$\Delta E^2 = 4 e i_0 R_1^2 \Delta f \tag{4.4}$$

From the reaction rate theory of electrode impedances (Appendix D; D-40) we have for the reaction resistance $R_1 \cong RT/F i_0$. With this equation, 3 becomes

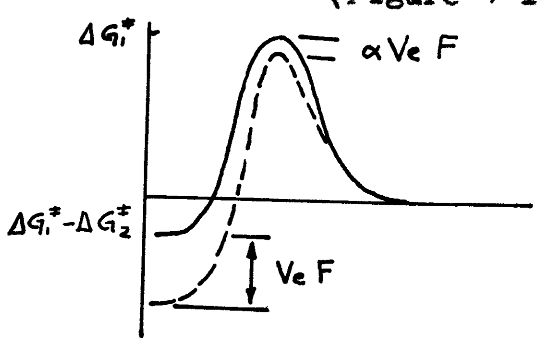
$$\Delta E^2 = 4 KT \ R_1 \Delta f \tag{4.5}$$

This we see to be just the thermal noise associated with the reaction resistance. Since the reaction resistances are small ($1 - 10^3\ \Omega\text{-}cm^2$) this noise is also small. As for magnitudes we can refer to the thermal noise calculations where the noise is determined for the solution resistance in series with the electrode reaction resistance.

Current Modulation Noise

For an electrode in equilibrium, the anodic and cathodic currents are equal and the exchange current which is equal to either one can be written

(Figure 4-1)



$$i_c = i_o = F \frac{KT}{h} a_o\, e^{-\frac{\Delta G_1^{\ddagger}}{RT} + \frac{\alpha V_e F}{RT}} \tag{4.6}$$

$$i_a = i_o = F \frac{KT}{h}\, e^{-\frac{\Delta G_2^{\ddagger}}{RT} - (1-\alpha)\frac{V_e F}{RT}} \tag{4.7}$$

Where a_o = activity at the surface of the electrode

$\Delta G_1^{\ddagger}$ = activation energy of cathodic reaction

$\Delta G_2^{\ddagger}$ = activation energy of anodic reaction

V_e = equilibrium potential associated with the activity a_o

Suppose the reaction is catalyzed by a mechanism that reduces the energy barrier by an amount βG^* in one direction and increases it by $(1-\beta)\, G^*$ in the other direction and that this effect acts uniformly over a small area σ. The anodic and cathodic currents are then

$$i_c = \sigma F \frac{KT}{h} a_o e^{-(\Delta G_1^{\ddagger} - \alpha V_e F - \beta G^*)/RT} \tag{4.8}$$

$$i_a = \sigma F \frac{KT}{h} e^{-(\Delta G_2^{\ddagger} + (1-\alpha) V_e F + (1+\beta) G^*)/RT} \tag{4.9}$$

The net current i_p will be given by the difference of these two currents.

$$i_p = \sigma F \frac{KT}{h} \left[a_o e^{-(\Delta G_1^{\ddagger} - \alpha V_e F - \beta G^*)/RT} - e^{-(\Delta G_2^{\ddagger} + (1-\alpha) V_e F + (1-\beta) G^*)/RT} \right]$$

$$= \sigma F \frac{KT}{h} a_o e^{-\frac{\Delta G_1^{\ddagger}}{RT} + \frac{\alpha V_e F}{RT}} \left[e^{\frac{\beta G^*}{RT}} - \frac{1}{a_o} e^{(V_o - V_e)\frac{F}{RT} - (1-\beta)\frac{G^*}{RT}} \right] \tag{4.11}$$

Where $$F V_0 = \Delta G_1^{\ddagger} - \Delta G_2^{\ddagger} \tag{4.12}$$

$$a_0 = \exp (V_0 - V_e) \frac{F}{RT}$$

Equation 4.11 can be rewritten with the aid of euqations 4.12 and 4.6.

$$\dot{z}_p = \delta \dot{z}_0 \left[e^{\frac{\beta G^*}{RT}} - e^{-(1-\beta)\frac{G^*}{RT}} \right] \tag{4.13}$$

If the current pulses are catalyzed by an atom diffusing onto the surface of the electrode, then the total increased current flow will depend on the number of atoms on the surface. Let n be the number of these atoms (catalyzed spots) on the surface at any moment and let $\bar{n}$ be the average number. The fluctuating current is then

$$\dot{z}(t) = (n - \bar{n}) \dot{z}_p$$

For a Poisson distribution of the number of atoms we have that

$$\overline{\delta n^2} = \overline{(n - \bar{n})^2} = \bar{n}$$

The autocorrelation function is then

$$\phi(\tau) = \bar{n} \dot{z}_p^2 \; e^{-\tau/\tau_c} \tag{4.14}$$

Where τ_c is the average length of a current pulse, or the average time spent by an atom on the surface. The spectrum of $i(t)$ is given by

$$i_p(\omega)^2 = \frac{2}{\pi}\int_0^\infty \bar{n}\, i_p^2\, e^{-\tau/\tau_c} \cos \omega\tau \, d\tau$$

Integrating and substituting from equation (4.13) the expression for i_p we have for the spectrum

$$i_p(\omega)^2 = \frac{2\bar{n}\, i_0^2\, \delta^2}{\pi}\left[e^{\frac{\beta G^*}{RT}} - e^{-(1-\beta)\frac{G^*}{RT}}\right]^2 \frac{\tau_c}{(1+\omega^2\tau_c^2)} \tag{4.15}$$

For G^* small compared to RT we can rewrite this as

$$i_p(\omega)^2 = \frac{2\bar{n}\, i_0^2\, \delta^2}{\pi}\left[\frac{G^*}{RT}\right]^2 \frac{\tau_c}{(1+\omega^2\tau_c^2)} \tag{4.16}$$

We have seen previously (Chapter III) that a distribution of time constants can give rise to a f^{-1} spectrum if the distribution is of the form

$$g(\tau) = 1/\tau \quad 1/\ln \tau_2/\tau_1 \qquad \tau_1 \leq \tau \leq \tau_2$$

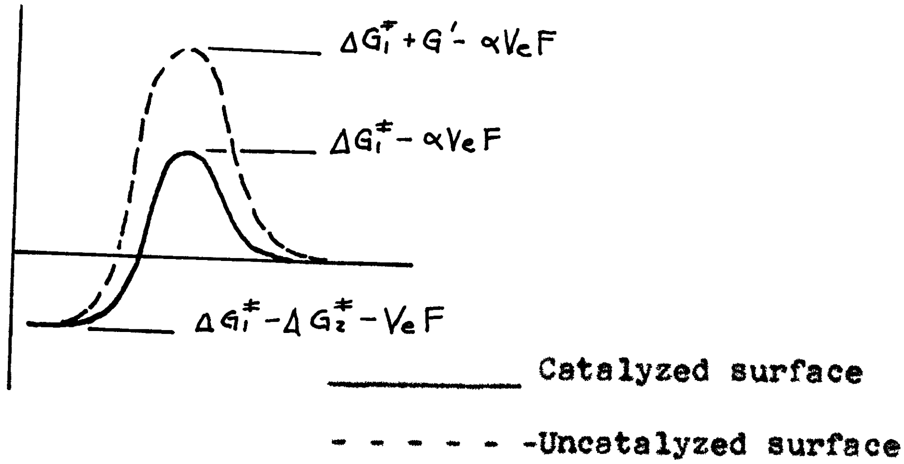
and if we remain within the limits $\omega\tau_1 \ll 1 \ll \omega\tau_2$.
With these restrictions we can write for the f^{-1} spectrum derived from equation 4.16.

$$i_P'(\omega)^2 = \frac{\pi \sigma^2 i_0^2}{\ln r_2/r_1} \left[\frac{G^*}{RT}\right]^2 \frac{1}{\omega} \tag{4.17}$$

In Chapter III we have seen that for the f^{-1} region to extend from 10^{-4} to 10^{6} cps we need to have a range of activation energies, for the catalyzing agent, from .35ev (8 Kcal/mole) to 1.lev (25Kcal/mole). It does not seem unreasonable to expect a range of activation energies of this magnitude. We have then that a proper distribution of activation energies for the mechanism that catalyzes the current pulses can give rise to a f^{-1} spectrum for the current fluctuations. The question now arises as to how the current fluctuations give rise to voltage fluctuations. This will be taken up in the following sections.

Let us consider the case where the electrode surface consists of a number of "hot spots" where the energy barrier is small compared to the rest of the surface. The energy barriers are as follows.

(Figure 4-2)



The exchange currents are:

Catalyzed:

$$i_c = i_o = F\frac{KT}{h} a_o\, e^{-\frac{\Delta G_1^{\ddagger}}{RT} + \frac{\alpha V_e F}{RT}} \tag{4.18}$$

$$i_a = i_o = F\frac{KT}{h} \quad e^{-\frac{\Delta G_2^{\ddagger}}{RT} - (1-\alpha)\frac{V_e F}{RT}} \tag{4.19}$$

Uncatalyzed:

$$i_c = i_o = F\frac{KT}{h} a_o\, e^{-(\Delta G_1^{\ddagger}+G')/RT + \frac{\alpha V_e F}{RT}} \tag{4.20}$$

$$i_a = i_o = F\frac{KT}{h} \quad e^{-(\Delta G_2^{\ddagger}+G')/RT - (1-\alpha)\frac{V_e F}{RT}} \tag{4.21}$$

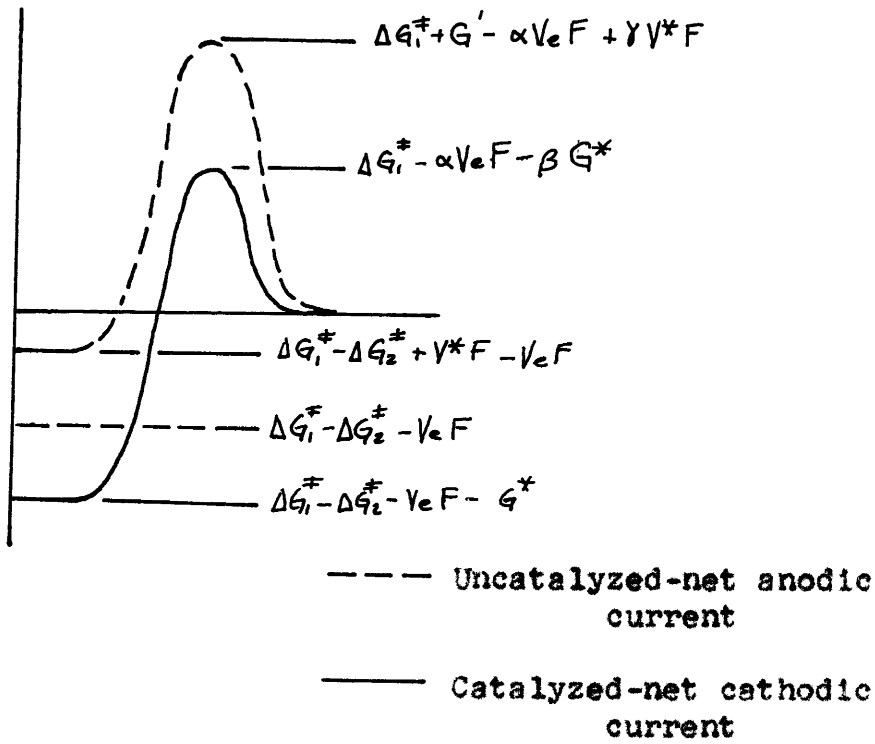
In both cases the anodic and cathodic currents are equal and no net currents flow. The potential V_c is then the equilibrium potential and it is found to be (Appendix C; C-4)

$$V_e = V_o - \frac{RT}{F}\ln a_o \tag{4.22}$$

Although both the catalyzed spots and the uncatalyzed surface give rise to the same equilibrium potential V_e, the current density i_o is larger for the catalyzed spots by a factor exp(G/RT). The total current carried by the catalyzed spots will depend however, on their total area. We see then that the importance of the "hot spots" in carrying current depends on how much the energy barrier is reduced (G') and on the total area catalyzed.

Let us further suppose that in the process of catalyzing the reaction, the rate in one direction (cathodic) is favored with respect to reactions in the other direction (anodic). This corresponds to an energy reduction βG^* in the cathodic direction and an increase $(1-\beta) G^*$ in the anodic direction. There will be then a net cathodic current at the catalyzed spots. If no current is withdrawn from the system, the uncatalyzed surface must change its potential in such a manner that it can sustain a net anodic current. The magnitude of this change in potential (V^*) will depend on the areas of the catalyzed and uncatalyzed surfaces. The energy barriers under these conditions are shown in the following diagram:

(Figure 4-3)



If we have that

n = The number of catalyzed spots

σ = Average area of a catalyzed spot

A_T = Total area of the electrode

The currents are

Catalyzed:

$$i'_c = n \sigma F \frac{KT}{h} a_o \, e^{-(\Delta G_1^{\ddagger} - \alpha V_e F - \beta G^*)/RT} \tag{4-23}$$

$$i'_a = n \sigma F \frac{KT}{h} \, e^{-(\Delta G_2^{\ddagger} + (1-\alpha) V_e F + (1-\beta) G^*)/RT} \tag{4-24}$$

The net cathodic current is

$$i_{nc} = n\sigma F \frac{KT}{h}\left[a_0 e^{-(\Delta G_1^{\ddagger} - \alpha V_e F - \beta G^*)/RT} - e^{-(\Delta G_2^{\ddagger} + (1-\alpha) V_e F + (1-\beta) G^*)/RT}\right]$$

Uncatalyzed:

$$i_c' = (A_T - n\sigma) F \frac{KT}{h}\, a_0\, e^{-(\Delta G_1^{\ddagger} + G' - \alpha V_e F + \gamma V^* F)/RT} \tag{4.26-a}$$

$$i_a' = (A_T - n\sigma) F \frac{KT}{h}\, e^{-(\Delta G_2^{\ddagger} + G' + (1-\alpha) V_e F - (1-\gamma) V^* F)/RT} \tag{4.26-b}$$

The net anodic current is

$$i_{na} = (A_T - n\sigma) F \frac{KT}{h}\left[e^{-(\Delta G_2^{\ddagger} + G' + (1-\alpha) V_e F - (1-\gamma) V^* F)/RT} - a_0 e^{-(\Delta G_1^{\ddagger} + G' - \alpha V_e F + \gamma V^* F)/RT}\right] \tag{4.27}$$

Equating the two net currents (Equations 4.25 and 4.27)

we have

$$n\sigma\, a_0\, e^{-(\Delta G_1^{\ddagger} - \alpha V_e F)/RT}\left[e^{\frac{\beta G^*}{RT}} - \frac{1}{a_0} e^{(V_0 - V_e)\frac{F}{RT} - (1-\beta)\frac{G^*}{RT}}\right]$$

$$= (A_T - n\sigma)\, a_0\, e^{-(\Delta G_1^{\ddagger} - \alpha V_e F)/RT}\left[\frac{1}{a_0} e^{(V_0 - V_e)\frac{F}{RT} + (1+\gamma)\frac{V^* F}{RT}} - e^{-\frac{\gamma V^* F}{RT}}\right] e^{-\frac{G'}{RT}} \tag{4.28}$$

With the aid of Equation 4.22, we can rewrite this as

$$n\sigma\left[e^{\frac{\beta G^*}{RT}} - e^{-(1-\beta)\frac{G^*}{RT}}\right] = (A_T - n\sigma)\left[e^{(1-\gamma)\frac{V^* F}{RT}} - e^{-\frac{\gamma V^* F}{RT}}\right] e^{-\frac{G'}{RT}}$$

Equation 4.29 gives the relation between the areas involved and the change in potential V^* caused by the net cathodic current of the catalyzed spots. On the assumption that G^* and $V^* F$ are small compared to RT, we can rewrite Equation 4.29

$$n\sigma \frac{G^*}{RT} = (A_T - n\sigma)\frac{V^* F}{RT} e^{-\frac{G'}{RT}} \qquad (4.30)$$

With the final assumption that $n\sigma$ is small compared to A_T we can write for the potential change V^*

$$V^* = \frac{n\sigma}{A_T} \frac{G^*}{F} e^{\frac{G'}{RT}} \qquad (4.31)$$

Recalling from our previous work that the fluctuating current is caused by a change in area of the catalyzed surface, we see that the fluctuations in current will give rise to fluctuations in V^*. The fluctuations in V^* associated with the change in catalyzed area are

$$\Delta V^* = \frac{(n-\bar{n})\sigma}{A_T} \frac{G^*}{F} e^{\frac{G'}{RT}} \qquad (4.32)$$

The mean square deviation in voltage is then

$$\overline{\delta V^{*2}} = \frac{\bar{n}\sigma^2}{A_T^2}\left[\frac{G^*}{F} e^{\frac{G'}{RT}}\right]^2 \qquad (4.33)$$

and the autocorrelation function for this process is

$$\phi(\tau) = \frac{\overline{n}\,\sigma^2}{A_T^2}\left[\frac{G^*}{F}\,e^{\frac{G'}{RT}}\right]^2 e^{\tau/\tau_c} \tag{4.34}$$

Where the time constant τ_c is the same as that for the current fluctuations since the voltage fluctuations are caused by the current pulses. The spectrum in the f^{-1} region is then

$$E(\omega)^2 = \frac{\overline{n}\,\sigma^2}{A_T^2 \ln \tau_2/\tau_1}\left[\frac{G^*}{F}\,e^{\frac{G'}{RT}}\right]^2 \frac{1}{\omega} \tag{4.35}$$

Making use of Equation 4.31, we can write this in terms of the potential $\overline{V^*}$.

$$E(\omega)^2 = \frac{1}{\overline{n} \ln \tau_2/\tau_1}\;\frac{\overline{V^*}^2}{\omega} \tag{4.36}$$

Unfortunately we cannot substitute directly into Equations 4.35 and 4.36 and obtain an order of magnitude for the expected noise. We can, however, make use of the observed voltages and estimate the values of some of the parameters and see if the results are reasonable. Integrating Equation 4.36 for the noise in the band .02 to .06 cps, we have for the average number of catalyzed spots

$$\bar{n} \cong \frac{\overline{V^*}^2}{10\,\Delta E^2} \tag{4.37}$$

Where we have let $A_T = 1\ cm^2$ and $\ln r_2/r_1 = 10$. The observed voltage in this band is of the order of $.1 \mu v$. We have then for the average number of catalyzed spots

$$\bar{n} \cong 10^{13}\ \overline{V^*}^2 \tag{4.38}$$

With the aid of Equation 4.37 we can rewrite Equation 4.31 as follows

$$\frac{G^*}{RT}\, e^{\frac{G'}{RT}} = \frac{10\ \Delta E^2}{2.5\, 10^{-2}\ \sigma\ \overline{V^*}} \tag{4.39}$$

We are now in a position to evaluate some of the parameters involved. We have previously assumed that V^*F and G^* are small compared to RT. The potential V^* must then be small compared to 25 mv and G^* must be small compared to .6 Kcal/mole. The value assigned to σ in the following calculations is the same as the surface area of an adsorbed water molecule. This is probably a minimum for this parameter. For the case where the observed voltage $\Delta E(.02-.06\ cps) = 10^{-7}$ volts, the surface area $\sigma = 10^{-15}$ cm^2 and the potential $\overline{V^*} = 10^{-3}$ volts, we have

$$\bar{n} = 10^7 \qquad \bar{n}\sigma = 10^{-8}\ \text{cm}^2$$

$$G^* e^{G'/RT} = 2.38\ 10^6 \quad \text{Kcal/mole}$$

If G^* is .1Kcal/mole, then

$$G' = 10\ \text{Kcal/mole}$$

Under these conditions the total current carried by the uncatalyzed surface is five times greater than that carried by the total catalyzed surface. If $\overline{V^*}$ is greater, say 10^{-2} volts we have then

$$\bar{n} = 10^9 \qquad \bar{n}\sigma = 10^{-6}\ \text{cm}^2$$

$$G^* e^{G'/RT} = 2.38 \quad 10\ \text{Kcal/mole}$$

If G^* is .1 Kcal/mole then

$$G' = 8\ \text{Kcal/mole}$$

The currents for the catalyzed and uncatalyzed surfaces are then about equal. Both of these cases are in fair agreement with the work of Madden and Marshall (1958) in which they found the energy barrier $G_o^{\ddagger}$ to be approximately

7 Kcal/mole. In both of the above cases since the uncatalyzed and catalyzed currents are at least equal we should expect that measurements and calculations carried out to determine the energy barrier would give values close to $G_1^{\ddagger} + G'$. (The energy barrier for the uncatalyzed surface). Since G' (the difference in energy barriers between the catalyzed and uncatalyzed surfaces) is of the same order as $G_0^{\ddagger}$ given by Madden and Marshall (1958) we must have then that $G_1^{\ddagger}$ (the energy barrier of the catalyzed reaction) is small.

Noise Due to Fluctuations in Thermodynamic Quantities.

In considering the origin of the electrode noise, some contribution can be expected from the statistical fluctuations of the thermodynamic quantities involved. Fluctuations in temperature and concentration are statistically independent and it is these two quantities with which we will deal. In the following discussion we will, for the most part, consider the fluctuations in concentration but the development of the temperature fluctuations follows a parallel course.

If $\delta \hat{N}_1$ is the instantaneous deviation of the number of moles of solute from its average value $\bar{N}_1$ then the mean square deviation is given by (Appendix A)

$$\overline{(\delta \hat{N}_1)^2} = -K \frac{\partial N_1}{\partial F_1} \tag{4.40}$$

$$F_1 = \frac{\partial S}{\partial N_1} = -\mu_1 / T \qquad (4.41$$

For a dilute solution assumed to be ideal the chemical potential is

$$\mu_1 = \mu_0 + RT \ln x_1 \tag{4.42}$$

Where

$$x_1 \cong \frac{N_1}{N_2} \tag{4.43}$$

N_2 = Number of moles of solvent.

Inserting Equations 4.42 and 4.43 in Equations 4.40 and 4.41 we have

$$\overline{(\delta N_1)^2} = \frac{N_1}{N_A} \qquad N_A = 6.025\ 10^{23} \tag{4.44}$$

This can be rewritten in terms of concentration as

$$\frac{\overline{(\delta m_1)^2}}{m_1^2} = \frac{1}{m_1 V N_A} \tag{4.45}$$

Where the volume (V) is in liters and m_1 is in moles per liter. For any given volume and concentration we can then calculate the mean square deviation in concentration. Since the electrode potential is dependent on the concentration according to the relation

$$E = E_0 + 2RT/F \; \ln m_1 \tag{4.46}$$

We have for the voltage fluctuations, differentiating equation 4.46

$$dE = \frac{2RT}{F} \quad \frac{dm_1}{m_1} \tag{4.47}$$

This then is dependence of noise voltage on fluctuations in concentration. Making use of equation 4.45, we can write for the noise voltage

$$\delta E = \frac{2RT}{F} \frac{1}{[m_1 V N_A]^{\frac{1}{2}}}$$

This noise voltage (δE) is the total integrated noise produced by fluctuations in a given volume V. In the next section we will consider the frequency distribution of the concentration fluctuations.

Correlation of Fluctuations

The preceding treatment of thermodynamic fluctuations does not result in any knowledge of the frequency spectrum of the fluctuations. This can be investigated by considering the correlation of fluctuations in time. (Landau and Lifshitz; 1958) Consider that $\hat{x}$, a thermodynamic quantity, is some function of time X(t). Let $\delta X(t)$ be its deviation from the average value $\bar{X}$. The auto-correlation function and the spectral density $\delta X(\omega)^2$ of X(t) are defined in the usual manner.

$$\phi_{11}(\tau) = \overline{\delta X(t) \ \delta X(t+\tau)} \qquad (4.48)$$

$$\delta X(\omega)^2 = \frac{2}{\pi}\int_0^\infty \phi_{11}(\tau) \cos \omega\tau \, d\tau \qquad (4.49)$$

The spectral density $\delta X(\omega)^2$ can be determined providing that the correlation function is known.

In order to find the autocorrelation function $\phi_{11}(\tau)$ we make the assumption that at every moment of time the state of the body is determined by the value of X. Assume further that the quantity $\delta X(t)$ has at some time, a value which is larger than the root mean square deviation $[\overline{\delta X^2}]^{\frac{1}{2}}$. Then consistent with the assumptions made above the rate of change of δX will be determined by δX or that $\delta \dot{X} = \delta \dot{X}(\delta X)$. Expanding $\delta \dot{X}$ in powers of δX and retaining the linear term only.

$$\frac{d[\delta X]}{dt} = -\lambda \, \delta X \tag{4.50}$$

Integrating this equation, we obtain the two relations

$$\begin{aligned} \delta X(t) &= X_0 \, e^{-\lambda t} \\ \delta X(t+\tau) &= X_0 \, e^{-\lambda t - \lambda \tau} \end{aligned} \tag{4.51}$$

Substituting these in the equation for the correlation function

$$\phi_{11}(\tau) = \overline{\delta X(t)^2} \; e^{-\lambda \tau} \tag{4.52}$$

Inserting Equation 4.52 in 4.49, we have for the spectral power density

$$\delta X(\omega)^2 = \frac{2\,\overline{\delta X^2}}{\pi} \int_0^\infty e^{-\lambda \tau} \cos \omega \tau \, d\tau \tag{4.53}$$

Performing the integration we obtain

$$\delta X(\omega)^2 = \frac{2\,\overline{\delta X^2}}{\pi} \, \frac{\lambda}{(\lambda^2 + \omega^2)}$$

$$= \frac{2\,\overline{\delta X^2}}{\pi} \, \frac{\tau_c}{(1+\omega^2\tau_c^2)} \qquad \tau_c = 1/\lambda \tag{4.54}$$

Which is a relaxation type of spectrum. We recall that this spectrum is flat for frequencies below the cutoff $\omega_c \cong 1/\tau_c$.

The treatment thus far has been for any thermodynamic quantity X. With the substitution of the concentration m for X Equation 4.50 becomes

$$\frac{dm}{dt} = -\lambda m \tag{4.55}$$

Compare this to the ordinary diffusion equation.

$$\frac{\partial m}{\partial t} = -D \frac{\partial^2 m}{\partial x^2} \tag{4.56}$$

Or for small differences

$$\frac{\Delta m}{\Delta t} = -D \frac{\Delta m}{\Delta x^2}$$

The constant λ is then seen to be

$$\lambda = D/\Delta x^2 \tag{4.57}$$

Where D is the diffusion constant which for aqueous solutions is approximately 10^{-5} cm^2/sec.

At this point it may be in order to recapitulate some of the results obtained thus far. An expression for the mean square fluctuation as well as the spectral distribution of the fluctuations has been found. The mean square fluctuation we recall, is a function of the volume considered. This volume can be expressed as a product of an area and a length $V = AL$. The spectral distribution is also dependent on a length through the equation for the constant (Equation 4.57). For a small volume $(V = AL)$, where the dimensions of A are large compared to L, we can write

$$\delta \overline{m^2} = \frac{m\ 10^3}{A\ L\ N_A} \qquad \begin{array}{l} L \text{ in cm} \\ A \text{ in cm}^2 \end{array} \tag{4.58}$$

and

$$\lambda = D/L^2 \tag{4.59}$$

Any deviation in concentration in the volume composed of unit area and length L may be represented by the Fourier series.

$$\delta m(x) = \sum_{1}^{n} \left[a_n \cos \frac{n\pi x}{L} + b_n \sin \frac{n\pi x}{L} \right] \tag{4.60}$$

Integrating the fluctuations $\delta m(x)$ over the length $\ell \ll L$ we have

$$\int_0^\ell \delta m(x)dx = \sum_1^n \left[\frac{a_n L}{n\pi} \sin\frac{n\pi\ell}{L} + \frac{b_n L}{n\pi}\left(1-\cos\frac{n\pi\ell}{L}\right)\right] \tag{4.61}$$

For small $n\pi\ell/L$ (small n-low frequencies)

$\sin n\pi\ell/L \rightarrow n\pi\ell/L$ and $(1-\cos n\pi\ell/L) \rightarrow \frac{1}{2}(n\pi\ell/L)$

then

$$a_n \frac{L}{n\pi} \sin\frac{n\pi\ell}{L} \cong a_n \ell \tag{4.62}$$

$$b_n \frac{L}{n\pi}\left(1-\cos\frac{n\pi\ell}{L}\right) \cong b_n \frac{n\pi\ell^2}{2L} \tag{4.63}$$

For large n (high frequencies) the contributions to the summation are proportional to $\lambda_n = 2L/n$. Separating the summation in Equation 4.61 into two parts, the first over the high frequencies (n large) and the second over the low frequencies (n small) we have taking the dividing point where $\lambda \cong \ell$ or $n = L/\ell$.

$$\int_0^\ell \delta m(x)dx \cong \sum_{n=L/\ell}^{\infty} (a_n+b_n)\frac{L}{n} + \sum_0^{n=L/\ell}\left(a_n + b_n\frac{n\pi\ell}{L}\right)\ell \tag{4.64}$$

Since we are interested in the squares of the amplitudes (mean square deviation) we have from Equation 4.64

$$\left[\int_0^\ell \delta m(x)dx\right]^2 \cong \sum_{L/\ell}^{\infty} (a_n+b_n)^2\frac{L^2}{n^2} + \sum_0^{L/\ell}\left(a_n+b_n\frac{n\pi\ell}{L}\right)^2\ell^2 \tag{4.65}$$

The first sum on the right is small since the sum $\Sigma\ 1/n^2$ is a convergent series with a sum less than 2. In the second sum the terms associated with b_n are small since they contain term ℓ/L and $\ell \ll L$. We can then write

$$\int_0^{\ell} \delta m(x)\,dx \cong \sum_{0}^{n=L/\ell} a_n\,\ell \tag{4.66}$$

We have previously derived an expression for the mean square deviation (Equation 4.58)

$$\overline{\delta m(\ell)^2} = \frac{m\,10^3}{A\,\ell\,N_A} = \left[\frac{1}{\ell}\int_0^{\ell} \delta m(x)\,dx\right]^2 \tag{4.67}$$

Utilizing Equations 4.67 and 4.66 and letting the summation over n go into an integration, we have

$$\frac{1}{\ell^2}\int_0^{L/\ell} a_n^2\,\ell^2\,dn = \frac{m\,10^3}{A\,\ell\,N_A} \tag{4.68}$$

Differentiating with respect to the upper limit we have

$$\frac{d}{d\left(\frac{L}{\ell}\right)}\left[\frac{1}{\ell^2}\int_0^{L/\ell} a_n^2\,\ell^2\,dn\right] = \frac{m\,10^3}{A\,N_A}\,\frac{1}{L}\,\frac{d}{d\left(\frac{L}{\ell}\right)}\left[\frac{L}{\ell}\right] \tag{4.69}$$

$$a_n^2 = \frac{m\,10^3}{A\,L\,N_A} \tag{4.70}$$

The a_n's then have a white light spectrum. For any eigenfunction of the fluctuation, we have the correlation function

$$\phi_n'(\tau) = a_n^2 e^{-\alpha_n \tau} \tag{4.71}$$

Where $\alpha_n = D/\lambda_n^2 \qquad \lambda_n \cong L/n$

The total correlation function is a sum of terms as in Equation 4.71.

$$\phi(\tau) = \sum_n a_n^2 e^{-\frac{D\tau}{\lambda_n^2}} \tag{4.72}$$

The power spectrum is obtained in the usual manner.

$$\delta m(\omega)^2 = \frac{2}{\pi} \int_0^\infty \left[\sum_n a_n^2 e^{-\frac{D\tau}{\lambda_n^2}} \right] \cos \omega\tau \, d\tau$$

$$= \sum_n a_n^2 \frac{D/\lambda_n^2}{[(D/\lambda_n^2)^2 + \omega^2]} \tag{4.73}$$

Letting the summation over n go into an integration over λ we have $\quad dn = -L/\lambda^2 \, d\lambda \qquad$ limits: $n = 1;\ \lambda = L$
$n = \infty;\ \lambda = 0$

$$\delta m(\omega)^2 = \frac{2}{\pi} \int_0^L \frac{m\, 10^3}{A\, L\, N_A} \frac{L\, d\lambda}{\lambda^2} \frac{D/\lambda^2}{[D^2/\lambda^4 + \omega^2]} \tag{4.74}$$

$$= \frac{2\, m\, 10^3}{\pi\, A\, N_A} \frac{D}{\omega^2} \int_0^L \frac{d\lambda}{[D^2/\omega^2 + \lambda^4]}$$

By substituting $C^4 = D^2/\omega^2$ and $U^4 = \lambda^4/C^4$ and letting L go to infinity, we have for the integral in Equation 4.74

$$\int_0^\infty \frac{dU}{C^3(1+U^4)} = \frac{\pi}{2\sqrt{2}\,C^3} \qquad (4.75)$$

Equation 4.75 has been evaluated by integration in the complex plane. We can now rewrite Equation 4.74.

$$\delta m(\omega)^2 = \frac{m\,10^3}{\sqrt{2}\,A\;N_A\;D^{\frac{1}{2}}}\;\frac{1}{\omega^{\frac{1}{2}}} \qquad (4.76)$$

Recalling Equation 4.47 we have for the noise voltage caused by these concentration fluctuations

$$\delta E(\omega)^2 = \left(\frac{2RT}{F}\right)^2 \frac{1}{\sqrt{2}\,A\;m'N_A\;D^{\frac{1}{2}}}\;\frac{1}{\omega^{\frac{1}{2}}} \qquad (4.77)$$

Where m' is in moles/cm^3 and A is in cm^2.

With the aid of Equation D-42a, we can rewrite this in terms of the warburg impedance

$$\delta E(\omega)^2 = \frac{4KT}{\sqrt{2}}\,W$$

This then differs only from the thermal noise due to the warburg impedance by a factor $1/\sqrt{2}$.

We have seen previously that the total thermal noise (solution, reaction resistance and warburg) is less than the observed noise except at the higher frequency band passes. The concentration fluctuation noise or equivalently the warburg thermal noise is then a minor source of noise for most of the frequencies of interest here.

Thermal Fluctuations

The treatment of thermal fluctuations is parallel to that of the concentration fluctuations and we need not go into the details here. The mean square thermal fluctuation is (Appendix A, A-17)

$$\overline{\delta T^2} = \frac{KT^2}{N_{H_2O} C_P} = \frac{3\,10^{-19}}{V} \; (\mathrm{deg})^2 \tag{4.78}$$

Where $V = AL$ is in cm^3. Since we are dealing with thermal diffusion we replace, in the previous work, the diffusion constant D by the thermal diffusivity α^2. The final expression for the spectrum of the thermal fluctuations is then

$$\delta T^2(\omega) = \frac{KT^2}{\sqrt{2}\,A\alpha} \; \frac{1}{\omega^{1/2}} \tag{4.79}$$

Where

$$\alpha^2 = \frac{K}{C_P \rho} \cong 10^{-3} \; cm^2/sec \tag{4.80}$$

The temperature coefficient of many electrodes is of the order of 100 μV/deg. We can then write, with the aid of Equations 4.78; 4.79, and 4.80, for the noise voltage.

$$\delta E(f)^2 = 10^{-13} \frac{1}{A f^{1/2}} (\mu V)^2 \qquad (4.81)$$

We see then that the noise voltages due to thermal fluctuations are too small to be of any importance.

Conclusions

In the previous sections we have some interesting results. We have seen that the shot noise associated with the exchange current was equivalent to the thermal noise of the reaction resistance and that the concentration fluctuation noise was equivalent to the warburg impedance thermal noise. In retrospect these results are not surprising since both of the above treatments and that of the thermal noise are based on the statistical behavior of the charge carriers. If we allow the simple representation of the the electrode impedance as a reaction resistance and a warburg impedance in series with a solution resistance, then the total thermal noise power will have a $f^{-\frac{1}{2}}$ dependence on frequency due to the warburg impedance. In actual electrode systems the frequency dependence of the impedance is not as simple as our model would indicate and the equivalent circuit representation is more complicated. The observed frequency dependence of the impedance, in the range of interest here (10^{-2} to 1cps), was found to be from $f^{-.2}$ to $f^{-.7}$. We would expect then that the spectra of the thermal noise to exhibit a similar range of frequency dependancies. The magnitudes of the thermal noise as calculated from the observed impedance and Nyquists formula (Table 4.1) are well below the observed noise in the low frequency band passes. It is only for certain electrodes in the higher frequency band passes (.2-.6 and .6-2.0 cps) that the thermal noise becomes of the same order of magnitude as the observed noise. This type of noise probably sets a lower limit on the noise levels in electrode systems.

Only the postulated current modulation noise mechanism gives rise to an inverse frequency spectrum but here we cannot calculate the magnitude of the noise. As we have seen, the best that can be done is to show that the values of the parameters needed to produce the observed noise are not unreasonable.

All of the noise sources have a voltage squared which is inversely proportional to the area of the electrode. That this must be so can be demonstrated by considering the electrical power, $P = E^2/R$. In this case both E and R, the electrode resistance, are inversely proportional to the area so that the electrical power is independent of the area. If this was not the case (E^2 not proportional to A^{-1}) then two electrodes of different areas would have a net power transfer between them, a condition which is forbidden by the laws of thermodynamics.

In any future work it might be of interest to investigate this dependence of noise voltage squared on the area. The noise is also dependent on temperature. This dependence is linear for the thermal noise while the current modulation noise is dependent through the factor $\exp(G'/RT)$. The current modulation noise has then a strong temperature dependence. Other complications may arise in studying the temperature dependence of the noise such as a change in the reactions involved in carrying the current.

APPENDIX A

Fluctuations of Thermodynamic Quantities

The theory of fluctuations of thermodynamic quantities is dealt with in many works (Tollman, 1938; Landau and Lifshitz, 1958; Callen, 1960). The treatment of the topic as is given by Callen is particularly clear and it is his method and notation that will be followed here.

Consider a system described by two sets of extensive variables $\hat{X}_1$, $\hat{X}_2$, ...$\hat{X}_s$ and $\hat{X}_{s+1}$ ... X_t, The first group of variables undergo fluctuations and the circumflex indicates an instantaneous value. The variables of the second set are constant. The variables $\hat{X}_k$ fluctuate by transfers to and from appropriate reservoirs. The probability that $\hat{X}_1$ will be found in the range $d\hat{X}_1$, that $\hat{X}_2$ will be found in the range $d\hat{X}_2$, ... and that $\hat{X}_s$ will be found in the range $d\hat{X}_s$ is defined as

$$W \, d\hat{X}_1 \, d\hat{X}_2 \cdots\cdots d\hat{X}_s \qquad \text{(A-1)}$$

Where W is a function of $\hat{X}_1$ ... $\hat{X}_s$, X_{s+1} ... $\hat{X}_t$ and of the characteristics of the reservoirs.

We then postulate that there exists a function of the instantaneous extensive parameters of the system, $\hat{S}$ ($\hat{X}_1$ ...$\hat{X}_s$, X_{s+1} ... X_t) called the instantaneous entropy and having the following property. The probability, $W d\hat{X}_1 \ldots d\hat{X}_s$ that the instantaneous extensive parameters are in the ranges $d\hat{X}_1 \cdots d\hat{X}_s$ is given by

$$W = \Omega_0 \exp \frac{1}{K}\left(\hat{S} - \sum_0^s F_K \hat{X}_K - S_M\left[F_1^\circ \cdots F_s^\circ\right]\right) \tag{A-2}$$

Where

K = Boltzman's constant

$\hat{S}$ = instantaneous entropy

Ω_0 = normalizing constant such that

$$\int W \, d\hat{X}_1 \cdots d\hat{X}_s = 1$$

$F_K = F_K^r$ is the intensive parameter of the reservoir

$$F_K = \frac{\partial \hat{S}}{\partial X_K} \qquad F_K^\circ = \frac{\partial S}{\partial \bar{X}_K}$$

$S_M\left[F_1^\circ \cdots F_s^\circ\right]$ is the maximum value of

$$\hat{S} - \sum F_K \hat{X}_K$$

If the variables $\hat{X}_K$ are given their average values $\bar{X}_K$, the instantaneous entropy takes on a value S referred to as the equilibrium value.

The calculation of average or equilibrium values will be simplified if we assume that the distribution function W is so sharply peaked that the average and most probable values are nearly identical. The most probable values of $\hat{X}_K$ are these that maximize W. Since the exponential is a monotonically increasing function of its argument, the most probable values of $\hat{X}_K$ are those that maximize the quantity.

$$\hat{S} - \Sigma F_K \hat{X}_K - S_M[F_1^\circ \cdots F_S^\circ] \qquad (A\text{-}3)$$

The term $S_M[F_1^\circ \ldots F_s^\circ]$ is not a function of $\hat{X}_K$ so that the condition reduces to

$$\hat{S} - \Sigma F_K \hat{X}_K = \text{maximum} \qquad (A\text{-}4)$$

This condition will be satisfied when $\hat{X}_K = \overline{X}_K$. The condition on $S_M[F_1^\circ \ldots F_s^\circ]$ that it be the maximum of $\hat{S} - \Sigma F_K \hat{X}_K$ leads to the expression

$$S_M[F_K^\circ \cdots F_s^\circ] = S - \Sigma F_K \overline{X}_K \qquad (A\text{-}5)$$

Utilizing this relation we can rewrite equation (A-2) for the distribution function.

$$W = \Omega_0 \exp \frac{1}{K}\left(\hat{S} - S - \left[\Sigma F_K(\hat{X}_K - \overline{X}_K)\right]\right) \qquad (A\text{-}6)$$

Consider that X_K is the fluctuating variable then by definition

$$\overline{\hat{X}_K} \equiv \overline{X}_K$$

The average value of the deviation is defined as

$$\overline{\delta \hat{X}} \equiv \overline{(\hat{X}_K - \overline{X}_K)} = 0$$

The average value of the deviation is then zero. The mean square deviation or second moment is not zero and is given by

$$\overline{(\hat{X}_K - \overline{X}_K)^2} = \overline{(\hat{X}_K)^2} - 2\,\overline{\hat{X}_K \overline{X}_K} + \overline{X}_K^2 = \overline{(\hat{X}_K)^2} - \overline{X}_K^2$$

Adopting the notation $\delta\hat{X}_K$ for the deviation of $\hat{X}_K$

$$(\hat{X}_j - \overline{X}_j)(\hat{X}_K - \overline{X}_K) = \delta\hat{X}_j \; \delta\hat{X}_K$$

The second moment can be written as

$$\overline{(\delta\hat{X}_j \, \delta\hat{X}_K)} = \int (\delta\hat{X}_j \, \delta\hat{X}_K) W d\hat{X}_1 \cdots d\hat{X}_s \tag{A-7}$$

In order to carry out the integration we note that because of the form of W, as given in equation (A-6) we may write

$$\frac{\partial W}{\partial F_K} = -\frac{1}{K}(\hat{X}_K - \overline{X}_K)W = -\frac{1}{K}\delta\hat{X}_K W \tag{A-8}$$

With the aid of equation (A-8) we can now write equation (A-7) as

$$\overline{(\delta\hat{X}_j \; \delta\hat{X}_K)} = -K\int \delta\hat{X}_j \frac{\partial W}{\partial F_K} d\hat{X}_1 \cdots d\hat{X}_s \tag{A-9}$$

$$= -K\frac{\partial}{\partial F_K}\left[\int \delta\hat{X}_j \; W \, d\hat{X}_1 \cdots d\hat{X}_s\right]$$

$$+ K\int W \frac{\partial}{\partial F_K}\left[\delta\hat{X}_j\right] d\hat{X}_1 \cdots d\hat{X}_s \tag{A-10}$$

Since

$$\frac{\partial}{\partial F_K}\left[\delta\hat{X}_j\right] = \frac{\partial}{\partial F_K}\left[\hat{X}_j - \overline{X}_j\right] = -\frac{\partial \overline{X}_j}{\partial F_K} \tag{A-11}$$

Equation (A-10) can then be written as

$$\overline{(\delta \hat{X}_j \ \delta \hat{X}_K)} = -K \frac{\partial}{\partial F_K}\left[\overline{\delta \hat{X}_j}\right] - K \frac{\partial \overline{X}_j}{\partial F_K} \qquad \text{(A-12)}$$

The first term in equation (A-12) is zero because $\overline{\delta\hat{X}_j}$ vanishes independantly of F_K. The fluctuation moments are then given by

$$\overline{(\delta \hat{X}_j \ \delta \hat{X}_K)} = -K \left(\frac{\partial \overline{X}_j}{\partial F_K}\right)_{F_1 \cdots F_{K-1},\, F_{K+1} \cdots F_s} \qquad \text{(A-13)}$$

The case we wish to deal with has $\delta\hat{X}_j = \delta\hat{X}_K$ so that

$$\overline{(\delta \hat{X}_K)^2} = -K \frac{\partial \overline{X}_K}{\partial F_K} \qquad \text{(A-14)}$$

Making use of the following relations

$$F_{N_1} = \frac{\partial S}{\partial N_1} = -\frac{1}{T} \frac{\partial U}{\partial N_1} \qquad N_1 = \text{mole number}$$

$$\mu_1 = \frac{\partial U}{\partial N_1}$$

We have for the mean square fluctuation in mole number

$$\overline{(\delta \hat{N}_1)^2} = -KT \Big/ \frac{\partial \mu_1}{\partial N_1} \qquad \text{(A-15)}$$

For thermal fluctuations the general equation (A-14) becomes

$$\overline{(\delta \hat{T})^2} = -K \frac{\partial T}{\partial F} \qquad \text{(A-16)}$$

Where

$$F = \frac{\partial S}{\partial T} = N \frac{C_p}{T}$$

In dilute solutions we need only consider the mole numbers (N) and the heat capacity per mole (Cp) of the solvent. The thermal fluctuations are then

$$\overline{(\delta \hat{T})^2} = \frac{KT^2}{N\,C_P} \qquad \text{(A-17)}$$

Where in aqueous solutions

$$N_{H_2O} = \frac{10^3}{18} V(\text{liters}) \qquad \text{(A-18)}$$

$$C_p = 18 \text{ cal/deg-mole}$$

APPENDIX B

Reaction Rate Theory

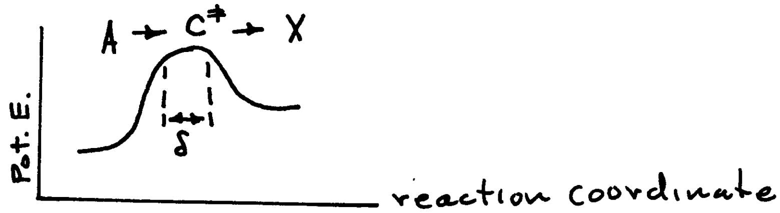
Let the reaction be represented by

$$A = X$$

further let us suppose that we have

$$A \rightleftharpoons C^{\ddagger} \rightleftharpoons X$$

and let $[\overrightarrow{C^{\ddagger}}]$ and $[\overleftarrow{C^{\ddagger}}]$ be the concentrations of activated complexes passing from left to right and right to left respectively.



Consider how just the case

$$A \rightleftharpoons C^{\ddagger} \tag{B-1}$$

So that

$$dN_a = dN_c \tag{B-2}$$

We have from elementary statistical thermodynamics that the partition function (Q) for a mixture of two gases.

$$Q = \frac{1}{N_a!\,N_c!} f_a^{N_a} f_c^{N_c} \tag{B-3}$$

Where N is the number of particles in the volume of the system and is the molecular partition function.

The Helmholtz free energy is given by

$$F = -KT \ln Q \tag{B-4}$$

And the condition for equilibrium is

$$\left(\frac{\partial F}{\partial N_c}\right)_{TV} = 0 \tag{B-5}$$

Utilizing equations (B-2), (B-3), (B-4), and (B-5) we have

$$\frac{N_c}{N_a} = \frac{f_c}{f_a} \tag{B-6}$$

Let $[C^{\ddagger}]$ be the number of molecules per unit volume and let $\phi_c' = f_c/V$ be the partition function per unit volume. We can then write

$$\frac{[C^{\ddagger}]}{[A]} = \frac{\phi_c'}{\phi_a'} \tag{B-7}$$

Recalling that the definition of the molecular partition function is

$$f = \sum_i W_i \, e^{-\frac{\epsilon_i}{kT}}$$

The lowest energy level can be factored out leaving

$$f_c = e^{-\frac{\epsilon_c}{kT}} \sum W_i \, e^{-(\epsilon_i - \epsilon_c)/kT}$$

$$= e^{-\frac{\epsilon_c}{kT}} \phi_c$$

Where $\phi_c = \sum W_i \, e^{-(\epsilon_i - \epsilon_c)/kT}$

Equation (B-7) can then be rewritten

$$\frac{[C^{\ddagger}]}{[A]} = \frac{\phi_c}{\phi_a} e^{-(\epsilon_c - \epsilon_a)/kT} = \frac{\phi_c}{\phi_a} e^{-\frac{\epsilon_0}{kT}} \tag{B-8}$$

Where ϵ_0 is the difference in the zero energy level of the reactants and the activated complex.

As is well known the partition function can be factored into products of translational, rotational and vibrational terms. With regard to the complex we will factor out of ϕ_c the translational term along the direction of the reaction coordinate δ . The translational partition function is of the type

$$f_{(trans)} = \frac{2l}{2h}\left(2\pi m K T\right)^{\frac{1}{2}}$$

So that we have

$$\phi_c = \frac{\delta}{2h}\left(2\pi m K T\right)^{\frac{1}{2}} \phi_c^{\ddagger} \qquad \text{(B-9)}$$

Where $\phi_c^{\ddagger}$ does not include the factor due the above mentioned translational motion.

Let $\bar{v}$ be the average velocity over the distance δ. The time of passage over the distance δ is $\tau = \delta / \bar{v}$. The forward reaction rate is then

$$\text{Forward reaction rate} = \overrightarrow{[C^{*}]}\, \bar{v} / \delta \qquad \text{(B-10)}$$

The mean velocity as given by elementary theory is

$$\bar{v} = \frac{\int_0^\infty v\, e^{-\frac{mv^2}{2KT}}\, dv}{\int_0^\infty e^{-\frac{mv^2}{2KT}}\, dv} = \left(\frac{2KT}{\pi m}\right)^{\frac{1}{2}} \qquad \text{(B-11)}$$

Combining equations (B-10)and (B-11)

Foward reaction rate = $\frac{KT}{h} \frac{\phi_c^{\ddagger}}{\phi_a} [A] e^{-\frac{\epsilon_o}{KT}}$ (B-12)

"Jump Frequency" $= \tilde{\nu} = \frac{KT}{h} \frac{\phi_c^{\ddagger}}{\phi_a} e^{-\frac{\epsilon_o}{KT}}$

Letting $\frac{\phi_c^{\ddagger}}{\phi_a} = 1$ and $\frac{KT}{h} = .6\ 10^{13}\ sec^{-1}$

We have

$$\tilde{\nu} = .6\ 10^{13} e^{-\frac{\epsilon_o}{KT}} \tag{B-13}$$

or

$$\tau = 1.66\ 10^{-13}\ e^{\frac{\epsilon_o}{KT}} \tag{B-14}$$

$\tilde{\nu}$ = Probability(per second) that a molecule passes over the energy barrier

τ = The average time before a molecule passes over the energy barrier

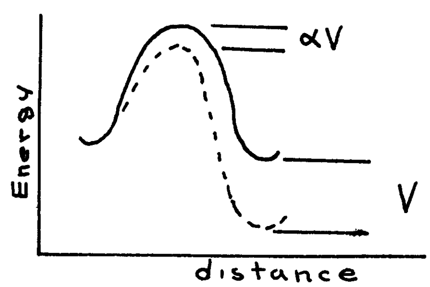
APPENDIX C

ELECTRODE POTENTIALS

From Glasstone Laidler and Eyring (1941)

Equilibrium Potentials

Consider the reaction at an electrode surface where the activity of the reacting ion in solution is a_o and the product of the reaction has unit activity. The reaction between a metal and its ion in solution is an example of the above.



The forward and backward rates may be written as:

$$\overleftarrow{rate} = a_o \frac{KT}{h} e^{-\frac{\overleftarrow{\Delta G}^{\neq}}{RT} + \alpha \frac{VF}{RT}} = a_o K_1 e^{\alpha \frac{VF}{RT}} \qquad 1$$

$$\overrightarrow{rate} = \frac{KT}{h} e^{-\frac{\overrightarrow{\Delta G}^{\neq}}{RT} - (1-\alpha)\frac{VF}{RT}} = K_2 e^{-(1-\alpha)\frac{VF}{RT}} \qquad 2$$

If V is the equilibrium reversible potential (V_e) the rates are equal and

$$e^{-\frac{V_e F}{RT}} = a_o e^{-\frac{\Delta G_o}{RT}} \qquad 3$$

Where

$$\Delta G_0 = \overleftarrow{\Delta G}^{\ddagger} - \overrightarrow{\Delta G}^{\ddagger} \qquad = \qquad \text{Std. Free Energy Change}$$

Therefore we may write from Equation 3

$$V_e = \frac{\Delta G_0}{F} - \frac{RT}{F} \ln a_0$$

$$= V_0 - \frac{RT}{F} \ln a_0 \qquad 4$$

This is the familiar equation for the potential of a reversible electrode at equilibrium.

Dynamic Electrode Potential

If there is a net flow of current at an electrode one rate of reaction exceeds the other. Since each ion carries a charge e we can write for the anodic and cathodic currents

$$i_c = F\, a\, K_1\, e^{\alpha \frac{VF}{RT}} \qquad 5$$

$$i_a = F\, K_2\, e^{-(1-\alpha)\frac{VF}{RT}} \qquad 6$$

Where V is the potential of the electrode when the net current is i_n . The net current assumed cathodic is the difference of the cathodic and anodic current.

$$i_n = i_c - i_a = F\left[a\, K_1\, e^{\alpha \frac{VF}{RT}} - K_2\, e^{-(1-\alpha)\frac{VF}{RT}}\right] \qquad 7$$

The activity a in the above equation is the activity in the vacinity of the electrode surface. The activity a will, in this case, be less than the activity a_o which exists in the bulk of the solution. The current carried by diffusion of the active species into the region of the electrode is

$$i_d = t\, i_n = \frac{FD}{\delta}\left(a_o - a\right) \tag{8}$$

Where t = effective transference number of all the other ions

δ = thickness of layer over which the gradient $(a_o - a)$ exists.

Utilizing Equation 8 we may rewrite Equation 7

$$i_n = \frac{F\left[a_o - e^{-(V-V_o)\frac{F}{RT}}\right]}{t\frac{\delta}{D} + \frac{1}{K_1} e^{-\frac{\alpha VF}{RT}}} \tag{9}$$

If K_1 is small, the discharge of ions is the rate determining step, and we have from Equation 9

$$i_n \cong F\left[a_o K_1 e^{\frac{\alpha VF}{RT}} - K_2 e^{-(1-\alpha)\frac{VF}{RT}}\right] \tag{10}$$

This is the same as Equation 7 except that a_o replaces a. This condition will hold only for small current densities.

The other case to be considered is where diffusion is the rate determining step. Here K_1 is large and we can rewrite Equation 9

$$i_n \cong \frac{FD}{\delta t}\left[a_o - e^{-(V-V_o)\frac{F}{RT}}\right] \tag{11}$$

From Equation 4 we have that the second term in the brackets in the above equation is equal to the activity a. We have then

$$\dot{z}_n \cong \frac{FD}{\delta t}\left[a_0 - a\right] \qquad 12$$

Which we see is equal to Equation 8.

We have then, that if diffusion is the rate limiting process, the dynamic electrode potential is equal to the equilibrium potential of an electrode in contact with an ion of activity a. The activity a being the value of the activity at the surface of the electrode.

APPENDIX D

ELECTRODE IMPEDANCES

The treatment of electrode impedances as outlined below is a simplified and condensed version of that developed by Madden and Marshall in their publication on Electrode and Membrane Polarization. For a more complete treatment, the reader is referred to their original work, (Madden and Marshall, 1959).

The model used here treats the ions of the diffuse layer as point charges moving through a viscous fluid under the influence of an electric field and concentration gradients. The equations of motion are

$$\frac{\partial P}{\partial t} = D_P \frac{\partial^2 P}{\partial x^2} - \mu_P \frac{\partial (PE)}{\partial x} \qquad \text{D-1}$$

$$\frac{\partial n}{\partial t} = D_n \frac{\partial^2 n}{\partial x^2} + \mu_n \frac{\partial (nE)}{\partial x} \qquad \text{D-2}$$

Where P = positive ion concentration

D = diffusion constant

μ = Mobility

E = electric field.

The condition on E from Poissons' equation is

$$\frac{\partial E}{\partial x} = \frac{F}{\epsilon} (P - n) \qquad \text{D-3}$$

Consider now the case where the electrolyte is a mixture of active ion species, those taking part in the electrode reactions, and an inert or supporting electrolyte.

Let P_2, n_2 be the active ion species concentration

P_1, n_1 be the supporting electrolyte concentration

$$D_{P_1} = D_{P_2} = D_{n_1} = D_{n_2} = D$$

$$\mu_{P_1} = \mu_{P_2} = \mu_{n_1} = \mu_{n_2} = \mu$$

$$P_1 = P_{01} + \Delta P_1$$

$$\Delta P_1 + \Delta P_2 \equiv P_3$$

$$\Delta n_1 + \Delta n_2 = n_3$$

$$P_1 + P_2 \equiv C \quad = \quad \text{Total salt concentration}$$

We can then rewrite Equations 1, 2, 3 in terms of P_3 and n_3

$$\frac{\partial n_3}{\partial t} = D \frac{\partial^2 n_3}{\partial x^2} + \mu \frac{\partial (n_3 E)}{\partial x} \qquad 4$$

$$\frac{\partial P_3}{\partial t} = D \frac{\partial^2 P_3}{\partial x^2} - \mu \frac{\partial (P_3 E)}{\partial x} \qquad 5$$

$$\frac{\partial E}{\partial x} = \frac{F}{\epsilon} (P_3 - n_3) \qquad 6$$

The solution of this set of equations, assuming sinusoidal time dependance is

$$P_3 = A_1 e^{-r_1 x} + A_2 e^{-r_2 x} \qquad 7$$

$$n_3 = -A_1 e^{-r_1 x} + A_2 e^{-r_2 x} \qquad 8$$

$$E = -\frac{2F}{\epsilon r_1} A_1 e^{-r_1 x} + E_\infty \qquad 9$$

Where

$$r_1^2 = K^2 = \frac{2CF^2}{\epsilon RT} \tag{10}$$

$$r_2^2 = \gamma = \frac{j\omega}{D} \tag{11}$$

The solution for E can be used in the flow equation for the active ion species.

$$\frac{\partial \Delta P_2}{\partial t} = D\frac{\partial^2 \Delta P_2}{\partial x^2} - \mu \frac{\partial (P_2 E)}{\partial x} \tag{12}$$

For sinusoidal time dependance we have

$$j\omega \Delta P_2 = D\frac{d^2 \Delta P_2}{\partial x^2} - \mu P_{o2}\frac{2F}{\epsilon}A_1 e^{-r_1 x} \tag{13}$$

Assuming a solution of the form

$$\Delta P_2 = M e^{-r_2' x} + N e^{-r_1 x}$$

We have

$$j\omega M = M D r_2'^2$$

and

$$r_2'^2 = \frac{j\omega}{D} = r_2^2 \tag{14}$$

$$j\omega N = N D r_1^2 - \mu P_{o2}\frac{2F}{\epsilon}A_1 \tag{15}$$

and

$$N \cong \frac{2\mu P_{o2} F}{D\epsilon r_1^2} A_1 \qquad \text{if } r_1^2 >> r_2^2$$

We have then

$$E = -\frac{2F}{\epsilon r_1}A_1 e^{-r_1 x} + E_\infty \tag{16}$$

$$n_3 = -A_1 e^{-r_1 x} + A_2 e^{-r_2 x} \tag{17}$$

$$\Delta P_1 = A_1(1 - P_{o2}/c)e^{-r_1 x} + (A_2 - M)e^{-r_2 x} \tag{18}$$

$$\Delta P_2 = \frac{P_{o2}}{c}A_1 e^{-r_1 x} + M e^{-r_2 x} \tag{19}$$

If only the P_2 species reacts at the electrode and α is the complex fraction of the total current carried across the boundary by P_2, the boundary condition will then be

at $x = 0$ flow of $P_2 = \alpha \dot{z}_\infty$

flow of $P_1 = 0$

flow of $n_3 = 0$

Where $\dot{z}_\infty$ = the total current. With the aid of Equations 16, 17, 18, and 19, these become

$$-\mu \frac{P_{02}\, 2F}{\epsilon D \tau_1} A_1 + \tau_2 M + \tau_1 \frac{P_{02}}{C} A_1 = \frac{\dot{z}_\infty}{DF}\left(\alpha - \frac{P_{02}}{2C}\right) \qquad 20$$

$$-\mu \frac{(C - P_{02})}{\epsilon D \tau_1} A_1 + \tau_1\left(1 - \frac{P_{02}}{C}\right)A_1 + \tau_2(A_2 - M) = -\frac{\dot{z}_\infty\,(C - P_{02})}{2DFC} \qquad 21$$

$$-\mu \frac{2FC}{\epsilon D \tau_1} A_1 + \tau_1 A_1 - \tau_2 A_2 = -\frac{\dot{z}_\infty}{2DF} \qquad 22$$

The solution of these equations gives

$$A_1 = \frac{\dot{z}_\infty}{2DF\tau_1\delta}\left[\alpha - 1\right] \qquad 23$$

$$A_2 = \frac{\alpha\,\dot{z}_\infty}{2DF\tau_2} \qquad 24$$

$$M = \frac{\alpha\,\dot{z}_\infty\left[2 - P_{02}/C\right]}{2DF\tau_2} \qquad 25$$

Where

$$\delta = \frac{\gamma}{K^2} = \frac{\tau_2^2}{\tau_1^2}$$

If the impedance of the electrode is linear for small current densities, we can express the faradaic current in a Taylor expansion. Let the concentration of the reacting species be C_i and the driving voltage acting across the fixed layer be V_F, then

$$\dot{z}_\alpha = f(C_i, V_F)$$

and in series form

$$\dot{z}_\alpha = \dot{z}_{\alpha 0} + \sum_i \frac{\partial [f(C_i, V_F)]}{\partial C_i} dc_i + \frac{\partial [f(C_i, V_F)]}{\partial V_F} V_F \tag{26}$$

Where for equilibrium $\dot{z}_{\alpha 0} = 0$

Consider the reaction $P \rightleftharpoons X$

Where the product X has unit activity and therefore the accumulation of this product does not influence the reaction. We have then considering Equation 26

$$\text{flow of } P_2 = \alpha \dot{z}_\infty = V_F / \theta - \beta \Delta P_2 \tag{27}$$

From Equations 19, 23 and 25 we have

$$\frac{\Delta P_2}{\dot{z}_\infty} = \frac{P_{02}(\alpha - 1)}{2 c D F \Gamma_1 \delta} + \frac{\alpha(2 - P_{02}/C)}{2 D F \Gamma_1 \sqrt{\delta'}} \tag{28}$$

The displacement current is given by

$$(1-\alpha)\dot{z}_\infty = j\omega C_F V_F \tag{29}$$

Where C_F = fixed layer capacitance.

The reaction impedance is

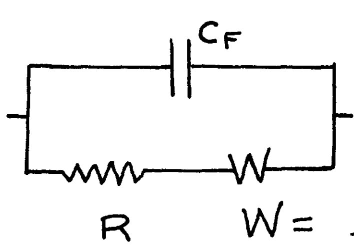
$$Z_\alpha = V_F / \alpha i_\infty \qquad \text{D-30}$$

From the solution of equations 27, 28, and 29 this can be rewritten as

$$Z_\alpha = R + \frac{\beta (2 - P_{O2}/c) R}{2F\sqrt{Dj\omega}} \qquad \text{D-31}$$

Where $$R = \frac{1}{\frac{1}{\theta} + \frac{P_{O2}\,\beta K C_F}{2CF}} \qquad \text{D-32}$$

The first term in Equation 31 is a pure resistance and the second is an impedance which is proportional to $\omega^{-\frac{1}{2}} e^{-\frac{i\pi}{4}}$. This term is referred to as a warburg impedance and is given the circuit symbol —W— . The warburg impedance is associated with diffusion phenomena. We can now represent the fixed layer impedance by the following circuit.



$$W = \frac{R\beta(2 - P_{O2}/c)}{2F\sqrt{Dj\omega}}$$

The equivalent circuit elements R and W are given in terms of the parameters θ and β . By considering the reaction rate theory for the electrode processes we can evaluate these two parameters.

Let the electrode reaction be represented by

$$A \rightleftharpoons C$$

The reaction rate theory gives us for the forward and backward rates

$$\overrightarrow{rate} = \frac{KT}{h} a_A e^{-\frac{\overrightarrow{\Delta G_0^\ddagger}}{RT}} \qquad \text{D-33}$$

$$\overleftarrow{rate} = \frac{KT}{h} a_C e^{-\frac{\overleftarrow{\Delta G_0^\ddagger}}{RT}} \qquad \text{D-34}$$

Where $\overrightarrow{\Delta G_0^\ddagger} = \Delta G_1^\ddagger + \alpha V_e F$

$\overleftarrow{\Delta G_0^\ddagger} = \Delta G_2^\ddagger - (1-\alpha) V_e F$

V_e = The equilibrium potential

The equilibrium rates in Equations 33 and 34 multiplied by F are referred to as the exchange currents and are given the symbol i_0 . For a driving voltage V_F we may rewrite Equations 33 and 34 in the form.

$$\overrightarrow{i} = F \frac{KT}{h} a_A e^{-\frac{\overrightarrow{\Delta G_0^\ddagger}}{RT} + \alpha \frac{V_F F}{RT}} \qquad \text{D-35}$$

$$\overleftarrow{i} = F \frac{KT}{h} a_C e^{-\frac{\Delta G_0^\ddagger}{RT} - (1-\alpha) \frac{V_F F}{RT}} \qquad \text{D-36}$$

Making an expansion of these currents about their equilibrium value $\dot{z}_o$ we have

$$\overrightarrow{\dot{z}} = \dot{z}_o + \dot{z}_o \frac{\Delta a_A}{a_A} + \dot{z}_o \frac{\alpha F}{RT} V_F \qquad \text{D-37}$$

$$\overleftarrow{\dot{z}} = \dot{z}_o + \dot{z}_o \frac{\Delta a_c}{a_c} - \dot{z}_o (1-\alpha) \frac{F}{RT} V_F \qquad \text{D-38}$$

If we allow $a_A = 1$ and $\Delta a_A = 0$ we have for the net current

$$\dot{z}_\alpha = \dot{z}_o \left[\frac{\Delta a_c}{a_c} + \frac{F V_F}{RT} \right] \qquad \text{D-39}$$

On comparison of this with Equation 27, we have for the parameters β and θ .

$$\theta = \frac{RT}{F \dot{z}_o} \qquad \text{D-40}$$

$$\beta = \frac{\dot{z}_o}{a_c} \qquad \text{D-41}$$

We can now investigate the dependence of the warburg impedance on the concentration of the active ion species $C_{\dot{z}}$. The calculations are simplified if we make the assumptions that $C_{\dot{z}} << C$ and $R \cong \theta$. From Equation 31 we have

$$W \cong \frac{RT}{F} \frac{1}{F C_{\dot{z}} \sqrt{D\omega}} \qquad C_{\dot{z}} \text{ in } \frac{\text{moles}}{cm^3} \qquad \text{D-42-a}$$

Upon substitution of the values for the constants and changing C_i from $\frac{\text{moles}}{\text{cm}^3}$ to $\frac{\text{moles}}{\text{liter}}$.

$$W \cong \frac{2.5\ 10^{-2}}{C_i\ f^{1/2}} \qquad C_i \text{ in mole/liter}$$

D-42-b

Assuming that the surface concentration of a species is proportional to its concentration and using 10^{15} molecules/cm^2 as the water molecule surface concentration we have for the exchange current (amp/cm^2).

$$i_0 = F\,\frac{kT}{h}\left(\frac{C_i\ 10^{15}}{55.5\ \ 6\ 10^{23}}\right) e^{-\frac{\overrightarrow{\Delta G}_0^{\ddagger}}{RT}}$$

D-43

C_i in $\frac{\text{moles}}{\text{liter}}$

With the aid of Equation 43 we can write for the reaction resistance.

$$R \cong \frac{1.4\ 10^{-9}}{C_i}\ e^{\frac{\overrightarrow{\Delta G}_0^{\ddagger}}{RT}}$$

D-44

C_i in $\frac{\text{moles}}{\text{liter}}$

and

$$\frac{R}{W} \cong f^{1/2}\ 5.5\ 10^{-8}\ e^{\frac{\overrightarrow{\Delta G}_0^{\ddagger}}{RT}}$$

D-45

REFERENCES

Callen, H.B., 1960. Thermodynamics, Chapter 15. John Wiley and Sons.

du Pre, F.K., 1950, A Suggestion Regarding the Spectral Density of Flicker Noise. Phys. Rev., 78, 615.

Glasstone, S., Laidler, K.J. and Eyring, H., 1941. The Theory of Rate Processes, Chapter 10. McGraw-Hill.

Landau, L.D. and Lifshitz, E.M., 1958. Course of Theoretical Physics Volume 5 - Statistical Physics, Chapter 12. Addison-Wesley

Lee, Y.W., 1960. Statistical Theory of Communication, Chapter 2, 53; Chapter 8, 340. John Wiley and Sons.

Mac Farlane, G.G., 1950. A Theory of Contact Noise in Semiconductors. Proc. Phys. Soc. B., 63, 807.

Madden, T.R. and Marshall, D.J., 1959. Electrode and Membrane Polarization, Interim Report for 1958 U.S. Atomic Energy Commission, Division of Raw Materials.

Richardson, J.M., 1950. The Linear Theory of Fluctuations Arising from Diffusional Mechanisms. Bell Syst. Tech. J., 29, 117.

Schottky, W., 1926. Small Shot Effect and Flicker Effect. Phys. Rev., 28, 74.

Van der Ziel, A., 1950. On The Noise Spectra of Semiconductor Noise and of Flicker Effect. Physica, 16, 359.