FLUCTUATIONS WITH A 1/f SPECTRUM IN THE
CONDUCTANCE OF IONIC SOLUTIONS AND IN THE
VOLTAGE OF CONCENTRATION CELLS

by F. N. HOOGE and J. L. M. GAAL

Abstract
The conductance of ionic solutions shows 1/f noise. The magnitude of
the noise is inversely proportional to the number of ions in the sample,
with a proportionality constant $\alpha$ that is $10^3$ to $10^4$ times higher than
for electrons in solids. The constant $\alpha$ is proportional to the electrolyte
concentration. The cell voltage of concentration cells also shows 1/f
voltage fluctuations. The same value for $\alpha$ is found from voltage fluc-
tuations and from conductance fluctuations.

1. Introduction and adaptation of the noise relations for ionic solutions

In a series of experiments we have shown that the 1/f noise of homogeneous
samples of metals and semiconductors can be expressed as

$$\left\langle \left( \frac{\Delta R}{R} \right)^2 \right\rangle = \frac{\alpha \Delta f}{N f}$$

(1)

where $R$ is the resistance, $\alpha$ is an experimental constant with the value $2 \times 10^{-3}$. $N$ is the total number of free charge carriers (not the concentration), $f$ is the
frequency, $\Delta f$ is the bandwidth $^{1,2}$.

Relation (1) holds good for electrons and holes in semiconductors and in
metals. In a recent preliminary publication we reported that if the 1/f noise of
electrolytic solutions is expressed by relation (1) one finds $\alpha_{\text{ion}}$ to be much
greater than $\alpha_{\text{electron}}$ and $\alpha_{\text{ion}}$ is now concentration-dependent $^3$). The purpose
of the present paper is
(a) to give more experimental details of the measurements briefly described in
the last-mentioned publication,
(b) to present results as to measurements of voltage fluctuations of concentra-
tion cells,
(c) to make a comparison between the 1/f noise in the conductance and in the
cell voltage.
Independent of this investigation, 1/f-noise studies have recently been carried out on ionic systems in connection with the voltage noise over nerve-cell membranes which was observed some years ago 4). In glass microelectrodes, often used as a physiological tool, spontaneous voltage fluctuations were observed, and further investigated, i.a. as a function of the KCl concentration inside and outside the microelectrode. The results, which are not in disagreement with ours, will be published soon by DeFelice and Firth 5).

The main experimental difficulty in studying the 1/f noise in ionic solutions lies in the necessity of using very small samples. This is so because the 1/f noise must be greater than the thermal noise over a reasonable frequency range. We put

$$\langle (\Delta V)^2 \rangle_{1/f} \geq \langle (\Delta V)^2 \rangle_{\text{thermal}}$$

at 1000 Hz. For a rectangular sample with length $l$ and cross-section $A$ and a concentration of $n$ charge carriers per cm$^3$ relation (1) and the relation for thermal noise $\langle (\Delta V)^2 \rangle = 4 kT R \Delta f$ leads to

$$\frac{V^2 \alpha \Delta f}{n l A f} = \frac{4 kT l \Delta f}{n e \mu A}.$$ (3)

For this comparison $n$, $A$ and $\Delta f$ are of no importance. For $f = 1000$ Hz, $T = 300$ °K and $\mu = 10^{-3}$ V$^{-1}$ cm$^2$ s$^{-1}$ we obtain

$$\frac{V^2 \alpha}{l^2} \geq 10^5 \text{V}^2 \text{cm}^{-2}.$$ (4)

Although $\alpha$ for ions can be about $10^4$ times higher than for electrons, i.e. $\alpha \approx 10$, it turns out that $l$ must be very small, since there is an upper limit for $V$. In our experiments $V$ could not be higher than several volts, since at higher voltages we always observed spectra steeper than 1/f. Taking $V = 1$ volt and $\alpha = 10$ leads to a maximum value for $l$ of $10^{-2}$ cm.

The easiest way to make such small samples is to use spreading resistances. When two large conducting bodies touch each other over a circular area with radius $a$ the spreading resistance is $6)$

$$R = \varepsilon / 2a.$$ (5)

The relation for the 1/f noise is then $7, 8)$

$$\left( \frac{(\Delta R)}{R} \right)^2 = \frac{\alpha \pi^2}{20 n \varepsilon^3} \frac{\Delta f}{R^3} = \frac{\alpha \pi^2 \Delta f}{160 n a^3 f}.$$ (6)

A comparison between 1/f noise and thermal noise, similar to (3), results in

$$\frac{V^2 \alpha \pi^2 \Delta f}{160 n a^3 f} \geq \frac{4 kT \Delta f}{n e \mu 2a}.$$ (7)
which leads to

$$\frac{V^2 x}{a^2} \geq 10^6 V^2 \text{ cm}^{-2}.$$  \hspace{1cm} (8)

For the same conditions $V = 1$ volt and $x = 10$ this leads to a maximum radius of the contact area $a_{\text{max}} = 30 \mu$.

![Fig. 1. Contact-noise arrangement for 1/f-noise studies of ionic solutions.](image)

Solutions are pre-eminently suited for contact-noise measurements when used in a cell as drawn in fig. 1. Here we do not encounter the difficulties we had with contact-noise measurements on solid bodies, where we had the theoretical difficulty of pressure-dependent resistivity and the experimental difficulty of possible surface layers at the contact between the two bodies. The only small complication we have is the finite thickness of the wall around the hole. In all experiments we used mylar film with a thickness of $6 \mu$. Instead of relation (5) we now expect

$$R = Q \left( \frac{1}{2a} + \frac{t}{\pi a^2} \right),$$  \hspace{1cm} (9)

t being the thickness of the wall. The radii of the holes were measured under a microscope, which showed the holes to be cylindrical. When relation (9) was used to determine $a$ from $R/Q$ we found values for $a$ that were about 20\% smaller than those from the microscope measurements. The latter radii are used in the following calculations, because these $a$ values were observed directly, whereas $a$ values from resistance measurements result from relation (9), which was derived for an ideal geometry of the hole. If radii from (9) were used all our $\alpha$ values would become smaller by a factor of $1.2^2 = 1.44$.

By adding $\langle (\Delta R)^2 \rangle$ of the two spreading resistances and the cylindrical channel we obtain for the 1/f noise:

$$\langle (\Delta R)^2 \rangle = \frac{\alpha \Delta f}{\beta n a^3 f'},$$  \hspace{1cm} (10)
where β is a numerical factor:

$$\beta = \left[ \frac{1}{4} + \frac{1}{\pi^2} \left( \frac{t}{a} \right)^2 + \frac{1}{\pi^4} \left( \frac{t}{a} \right)^4 \right] \left[ \frac{\pi^2}{640} + \frac{1}{\pi^2} \left( \frac{t}{a} \right)^2 \right]^{-1}.$$  \hspace{1cm} (11)

For very thin walls we obtain $\beta = 160/\pi^2 = 16$, as in relation (6). For the 6 $\mu$ thick film with radii between 5 $\mu$ and 14 $\mu$, $\beta$ is a slowly varying function with the values 14·4 for $a = 5 \mu$ and 14·0 for $a = 14 \mu$ and a minimum value in between of 13·5 for $a = 9·5 \mu$. So the finite thickness of the wall does not lead to important corrections, nevertheless relations (10) and (11) were used.

The next factor in the noise relation (10) that needs some attention is the concentration $n$, especially where the numbers of the positive and negative ions differ, as in Ni(NO$_3$)$_2$ and Cu(NO$_3$)$_2$, and in the case where the mobilities of the ions are different as in HCl. For solutions of $m$ molecules per cm$^3$ the values for $n$ given in Table I have to be used.

**TABLE I**

Values of $n$ to be used in relation (10) for solutions of $m$ molecules per cm$^3$

<table>
<thead>
<tr>
<th></th>
<th>$2m$</th>
<th>$\frac{5}{3}m$</th>
<th>$1·4m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNO$_3$, CuSO$_4$, NiSO$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$, Ni(NO$_3$)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
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Table I is obtained by the following analysis. Assume we have a solution of $m$ molecules per cm$^3$. The specific conductivities per ion are $g_+$ and $g_-$ and the concentrations of the ions are $n_+$ and $n_-$. We assume that the fluctuations of the conductances of the positive and negative ions are independent, each with its own $\alpha$, $\alpha_+$ and $\alpha_-:

$$\langle (\Delta G)^2 \rangle = \frac{\langle (\Delta G_+)^2 \rangle}{(G_+ + G_-)^2} = \left( \frac{G_+}{(G_+ + G_-)} \right)^2 + \left( \frac{G_-}{(G_+ + G_-)} \right)^2,$$  \hspace{1cm} (12)

For $\langle (\Delta G_+/G_+)^2 \rangle$ and $\langle (\Delta G_-/G_-)^2 \rangle$ we substitute relation (10). We obtain

$$\langle (\Delta G/G)^2 \rangle = \frac{\Delta f}{\beta a^3 f} \left[ \frac{\alpha_+}{n_+} \left( \frac{n_+ g_+}{n_+ g_+ + n_- g_-} \right)^2 + \frac{\alpha_-}{n_-} \left( \frac{n_- g_-}{n_+ g_+ + n_- g_-} \right)^2 \right].$$  \hspace{1cm} (13)

In view of the inaccuracy of our results we need not bother about the relatively small difference between $g_+$ and $g_-$ for the monovalent ions and between $g_+$ and $g_-$ for the divalent ions. We simply put $g_{\text{divalent}} = 2g_{\text{monovalent}}$. Only for
H⁺ ions do we use $g_{H^+} = 5g_{\text{monovalent}}$. From the noise measurements on one compound one cannot determine $\alpha_+$ and $\alpha_-$ from relation (13). Since the noise was equal for all compounds we studied, our results can be described by putting $\alpha_+ = \alpha_- = \alpha$ for all ions at the same molecular concentration.

It is possible in principle that all $\alpha_+$'s are equal, if $\alpha_+ \gg \alpha_-$ or that all $\alpha_-$'s are equal if $\alpha_- \gg \alpha_+$. Since $\alpha$ for ions is much higher than for electrons, we have wondered whether the mass of the charge carriers plays an important part: $m_{\text{ion}} \approx 10^5 m_{\text{electron}}$. Therefore we were interested in the 1/f noise of H⁺ ions, although one must realize that a hydrated H⁺ ion does not have such a small relative mass compared to other hydrated ions as a free H⁺ ion has compared to other free ions. Nevertheless the measurements on HCl were treated somewhat differently than those on the other compounds. Assuming $\alpha_{\text{Cl}} = \alpha_-$ and $g_{H} = 5g_{\text{Cl}}$ relation (13) leads to

$$\left\langle \frac{(\Delta G)^2}{G} \right\rangle = \frac{\Delta f}{\beta a^3 f} \left[ \frac{\alpha_{H}}{m} \left( \frac{5}{6} \right)^2 + \frac{\alpha_{-}}{m} \left( \frac{1}{6} \right)^2 \right].$$

(14)

We found $\alpha_{H}$ not significantly different from $\alpha$ at the same concentration. Therefore we no longer distinguished between $\alpha_{H}$ and $\alpha$. Relation (14) then goes over into

$$\left\langle \frac{(\Delta G)^2}{G} \right\rangle = \frac{0.72 \alpha \Delta f}{\beta a^3 m f}.$$

(15)

2. Experimental results of the noise measurements in the conductance

In the measurements of the conductance variations the two compartments of the cell of fig. 1 were filled with the same solution, of which the resistivity had been measured before. The electrodes were made of the metal of the positive ion, for HCl we used Cu. First we measured an $i-V$ characteristic. When we used electrodes that had been etched in diluted acid, the voltage at zero current was at the most a few mV. At high voltages of about 5 V the $i-V$ characteristic became non-linear. In the region where the noise measurements were done ($< 2$ V), the $i-V$ characteristic was always linear. The resistance derived from it was substituted in relation (9), which gave hole radii 20% lower than the optically determined radii that were used in the calculations.

The noise voltages were amplified by a factor of $10^5$ and then analyzed on a General Radio Corp. wave analyzer type 1900-A in the frequency range between 30 Hz and 50 kHz with a constant bandwidth of 10 Hz. The thermal noise was measured without applied voltage. It always agreed with the resistance from the $i-V$ characteristic. The measured noise decreased at frequencies above $10^4$ Hz when the resistance of the cell was 100 kΩ or higher due to the RC time of the cell. The cell with a diameter of 4.5 cm had a capacitance of 40 pF (included connections to preamplifier).
When a voltage was applied the noise at lower frequencies increased; see fig. 2. Subtraction of the thermal noise from the total noise gave a 1/f noise. At a given frequency we determined \( \langle (\Delta V/V)^2 \rangle \), put it equal to \( \langle (\Delta R/R)^2 \rangle \) and from relation (10) we calculated \( \alpha \). We always checked whether \( \alpha \) was independent of the applied voltage by measuring it at different voltages. Here we could not go to high voltages, because the spectra then became steeper than

![Fig. 2. A typical example of the noise measurements; CuSO\(_4\), 0.6 mol/l, hole diameter 14 \( \mu \), bandwidth 10 Hz, applied voltage 1.16 V. Squares: with applied voltage; circles: without applied voltage; crosses: differences between squares and circles.](image)

1/f. This phenomenon is also often encountered in 1/f spectra of semiconductors. We are not sure whether in all cases the 1/f spectrum gradually becomes steeper, or whether a new noise with a 1/f\(^2\) spectrum is beginning to appear. In some cases at least, the latter is true, as can be seen in fig. 3. In the limited frequency range the measured points for 1.5 V will be interpreted as an \( f^{-1.2} \) spectrum. But for higher voltages, where a larger part appears above the thermal noise, it becomes clear that the low-frequency noise consists of two spectra, one 1/f, the other 1/f\(^2\). The extra 1/f\(^2\) spectra or the steeper-than 1/f spectra did not reproduce very well. It was our impression that cleaning the electrodes helps to reduce them.

First we shall analyze the results for 1-molar solutions. Then the influence of the concentration will be reported. We measured spectra of molar solutions of AgNO\(_3\), CuSO\(_4\), Cu(NO\(_3\))\(_2\), NiSO\(_4\), Ni(NO\(_3\))\(_2\) and HCl with several values of the applied voltage and with several hole diameters between 5 \( \mu \) and 15 \( \mu \). The factor 3 in the diameter gives a factor 3\(^3\) in \( \alpha \) in relation (10).

The voltage could in general be varied between 200 mV and 2 V, for lower values the 1/f noise disappeared in the thermal noise, for higher values the
noise no longer was \(1/f\). In the following analysis we used all \(\alpha\) values, obtained from good spectra. “Good” means here that the spectral region in which the \(1/f\) noise was observed was wide enough to make sure that the spectrum was \(1/f\) indeed. Only slopes between \(-1.0\) and \(-1.1\) were accepted. In all spectra the best fitting \(1/f^{1.0}\) line was drawn, from which \(\alpha\) was determined. “Good” does not mean that the resulting value must be close to the mean value. Once a spectrum had been accepted as a good \(1/f\) spectrum its \(\alpha\) value, however low or high, entered the analysis. In the 34 values for \(\alpha\) at 1 mol/l we saw no systematic dependence on hole diameter or nature of the ions. Therefore we treated them as a single Gaussian distribution around one mean value. Since \(\alpha\) was determined from plots of \(\log \langle (\Delta V)^2 \rangle\) versus \(\log f\) (e.g. fig. 2) we actually determined \(\log \alpha\), not \(\alpha\) itself. Hence we had to determine the mean value of \(\log \alpha\). Then we had to see whether the distribution of all \(\log \alpha\) values was gaussian around the mean. Figures 4 and 5 show that this is the case. The result for 1-molar solutions is
\[ \log \alpha = 1.0 \pm 0.6. \] (16)

The root-mean-square deviation of 0.6 in \( \log \alpha \), determined from fig. 5, corresponds to a factor of 4 around the most probable value \( \alpha = 10 \). Thus \( 2.5 < \alpha < 40 \). This does not exclude the possibility that each ion has its own characteristic value somewhere in the range from 2.5 to 40.

For the other concentrations we determined mean values of \( \log \alpha \) for each compound. The lowest concentration was determined by the highest resistance we could use, the highest concentration by the solubilities. Most points in fig. 6 are averages of 5 to 10 measurements of the given compound at that concentration. We draw a line proportional to the concentration through the mean value \( \alpha = 10 \) at 1 mol/l. The uncertainty factor of 4, determined at 1 mol/l.
was then applied over the whole concentration range, and drawn as two dashed lines in fig. 6. All experimental points turned out to be in the strip between the two dashed lines. If one were to draw a horizontal line at $\alpha = 10$ with horizontal dashed lines at $\alpha = 2.5$ and at $\alpha = 40$, then the agreement would be far worse. For the lower concentrations many points would lie below that strip, at higher concentrations HCl would be too high. Therefore we conclude that $\alpha$ is concentration-dependent; in all probability $\alpha$ is proportional to the concentration. The latter conclusion means that if for a given hole $N$ is varied by concentration variation the relative noise is constant. Expression (1), $\langle (\Delta R/R)^2 \rangle = \alpha N^{-1} f^{-1} \Delta f$, only makes sense for ions if $N$ is varied by variation of the hole diameter, i.e. by variation of the effective volume of the sample.

Fig. 6. $\alpha$ versus concentration. The uncertainty factor of 4, represented by the dashed lines, was determined only at 1 mol/l in fig. 5. Dots: $\alpha$ from conductance fluctuations; open circles: estimates for $\alpha$ from voltage fluctuations of concentration cells.
3. Experimental results of measurements of noise in the cell voltage of concentration cells

A series of measurements was done in which the compartments were filled with solutions of the same compound but with different concentration in each compartment. Although this may seem an obvious next step after the experiments with equal concentrations, the historical order is the other way round. The first 1/f spectra on ionic systems were observed as voltage fluctuations over nerve-cell membranes 4).

Two series of experiments were done, one with CuSO₄ and Cu electrodes, and the other one with AgNO₃ and Ag electrodes. The cell voltages \(V_{\text{cell}}\) measured on the electrodes are built up by three contributions. There are two voltage jumps at the electrode-solution interfaces \(V_{\text{eleclr-c1}}\) and \(V_{\text{eleclr-c2}}\) and a diffusion voltage \(V_{\text{diff}}\) over the hole region, where a concentration gradient exists:

\[
V_{\text{cell}} = V_{\text{eleclr-c1}} + V_{\text{eleclr-c2}} + V_{\text{diff}}.
\]  (17)

From simple theory 9) it follows that

\[
V_{\text{cell}} = \left(1 + \frac{u_+ - u_-}{u_+ + u_-}\right) kT \ln \frac{c_1}{c_2},
\]  (18)

where \(z = 1\) for AgNO₃ and \(z = 2\) for CuSO₄; \(c_1\) and \(c_2\) are concentrations in the two compartments, for higher concentrations one should use activities; \(u_+\) and \(u_-\) are the mobilities of the positive and negative ions.

When four electrodes are used (fig. 1) we could apply an extra voltage over the two inner electrodes by passing a current through the outer ones. Then the measured voltage over the inner electrodes is \(V_{\text{total}}\):

\[
V_{\text{total}} = V_{\text{cell}} + V_{\text{extra}}.
\]  (19)

First the spectra of the fluctuations in \(V_{\text{cell}}\) were measured without extra applied voltages. One compartment was filled with a molar solution, the other one with a 1/300-molar solution. The cell voltages were about 45 mV for CuSO₄ and 110 mV for AgNO₃ in fair agreement with relation (18). The spectrum of the voltage fluctuation was white at higher frequencies from which we determined \(R_{\text{cell}}\), using the relation for thermal noise. A good 1/f spectrum was found when the thermal noise was subtracted from the measured noise at low frequencies.

It was our aim to investigate whether a relation similar to relation (1) applies to voltage fluctuations, in other words whether in relation (1) \(\langle(\Delta R/R)^2\rangle\) may be replaced by \(\langle(\Delta V/V)^2\rangle\). We therefore tried to estimate \(\alpha\) from cell-voltage fluctuations. These estimates for \(\alpha\) are rougher than from conductance measurements, because here \(N\) is much more difficult to determine. We did not integrate
over the concentration gradient in the hole region, but used effective average values. The resistance and the fluctuations are now mainly at one side of the hole: the lower-concentration side. Therefore, instead of relations (5) and (6) we now use

$$R = \frac{\rho_{\text{eff}}}{4a},$$

(20)

$$\left\langle \left( \frac{\Delta V}{V} \right)^2 \right\rangle = \frac{\alpha}{8 n_{\text{eff}} a^3 f} \Delta f.$$

(21)

From $R$, measured by the thermal noise, we determined an effective value for $\rho$, $\rho_{\text{eff}}$, using relation (20). For CuSO$_4$ and AgNO$_3$ we had already determined $\rho$ as a function of the concentration. Hence $\rho_{\text{eff}}$ gave $n_{\text{eff}}$ at the low-concentration side of the hole. From $n_{\text{eff}}$ and the values of $\left\langle (\Delta V/V)^2 \right\rangle_{\text{cell}}$ we determined $\alpha$ using relation (21). The estimates for $\alpha$ and the effective concentrations are plotted in fig. 6 as open circles. They agree well with the values from the conductance fluctuations, showing that for voltage fluctuations, $\left\langle (\Delta R/R)^2 \right\rangle$ in relation (1) may be replaced by $\left\langle (\Delta V/V)^2 \right\rangle$. In all our measurements with the concentration ratio 1 mol/l: 1/300 mol/l the effective concentration near the hole was between $3.10^{-2}$ and $7.10^{-2}$ mol/l with the average for AgNO$_3$ at $5.10^{-2}$ and for CuSO$_4$ at $6.5.10^{-2}$ mol/l.

Measurements with KCl also gave effective concentrations of $6.10^{-2}$ mol/l. Here we used calomel electrodes for which

$$V_{\text{electr} - c_1} = V_{\text{electr} - c_2},$$

so that $V_{\text{cell}} = V_{\text{diff}}$. For KCl $V_{\text{diff}}$ is very low, because of $u_K \approx u_{\text{Cl}}$. The measured value of $V_{\text{cell}}$ was about 2 mV. Nevertheless the absolute 1/f noise $\left\langle (\Delta V)^2 \right\rangle$ was of the same order of magnitude as in CuSO$_4$ and AgNO$_3$ cells. We shall come back to the KCl measurements in the discussion.

When an extra voltage is applied to the concentration cells a strong 1/f noise appears proportional to $V_{\text{extra}}^2$ independent of the sign of $V_{\text{extra}}$. Even for $|V_{\text{extra}}| < |V_{\text{cell}}|$ the 1/f noise dominates the 1/f noise. For CuSO$_4$ and for AgNO$_3$

$$\left\langle \left( \frac{\Delta V}{V} \right)^2 \right\rangle_{\text{extra}} = 8.10^{-9} \frac{\Delta f}{f^2}.$$

(22)

This made it impossible to determine with any accuracy whether the 1/f noise remained constant or whether it varied with $V_{\text{extra}}$.

4. Discussion

Since relation (1) proved so successful for describing 1/f noise in metals and semiconductors, we have used it for the presentation of the 1/f noise in ionic solutions. The relations for the noise of spreading resistances follows directly from (1) by simple geometrical considerations.
When the results of the conductance and cell-voltage experiments are presented by the relations

\[
\left\langle \left( \frac{\Delta R}{R} \right)^2 \right\rangle = \frac{\alpha(c) \Delta f}{N f} \tag{1}
\]

and

\[
\left\langle \left( \frac{\Delta V}{V} \right)^2 \right\rangle = \frac{\alpha(c) \Delta f}{N f} \tag{23}
\]

we have two problems to discuss:
(a) the high value and concentration dependence of \(\alpha(c)\),
(b) the same value of \(\alpha(c)\) in the relations (1) and (23).

(a) The constant \(\alpha\) for ionic solutions is much higher than in semiconductors and metals, and it is concentration-dependent. Both experimental findings point into the same direction: the ions are not independent. We think here of the independence of a positive ion with regard to the other positive ions, not of the independence of positive and negative ions, which played a role in the discussion of table I and relation (10). The factor \(N\) in the denominator of a relation of the type of (1) implies \(N\) independent particles, each giving the same average contribution to the noise. Here, however, we have used the total number of charge carriers. When there is an interaction, \(N\) in (1) should be lower than that. If we still use the total number the value of \(\alpha\) will be found too high. Errors in \(N\) are then converted into errors in \(\alpha\). The proportionality to the concentration lines up with this idea. On the other hand the order of magnitude of the factor of \(10^3\) to \(10^4\) is rather disturbing.

If one interprets \(\alpha\) as a measure for the independence of the ions, one is prompted to plot \(\alpha\) versus \(\Delta/\Delta_0\) for the equivalent conductance decreases at higher concentrations just because of the ion-ion interaction. Such a plot shows no direct dependence on \(\Delta/\Delta_0\). The fit to an average line is far worse than in fig. 6. The points for CuSO₄ and NiSO₄ with their low \(\Delta/\Delta_0\) values are far off. Also a plot of \(\alpha\) versus equivalents/l instead of mol/l is inferior to fig. 6.

(b) Having accepted the high values of \(\alpha\) as an experimental fact, we still have the surprising correspondence of conductance fluctuations and cell-voltage fluctuations, (1) and (23). The resistance of the bridge between the compartments plays no part in the relation for the cell voltage. Then it would be rather strange if fluctuations in the bridge resistance would give rise to fluctuations in the cell voltage. Yet we have shown that the voltage fluctuations are determined by the properties of the bridge: hole diameter and effective concentration. Therefore we must now go back to relation (18):

\[
V_{\text{cell}} = \left( 1 + \frac{u_+ - u_-}{u_+ + u_-} \right) \frac{kT}{zq} \ln \frac{c_1}{c_2} \tag{18}
\]
The term with \( u_+ \) and \( u_- \) corresponds to the diffusion voltage. Often \( u_+ \approx u_- \), which means that this term can be neglected in the cell voltage. It is 19% of \( V_{\text{cell}} \) for CuSO$_4$ and 5% for AgNO$_3$. Neglecting that term we obtain

\[
V_{\text{cell}} \approx \frac{kT}{zq} \ln \frac{c_1}{c_2}.
\]  

(24)

Even if the diffusion voltage is low, its fluctuations determine the cell-voltage fluctuations since \( N \) is small only for the diffusion process near the hole, whereas the number of ions taking part in the electrode-solution exchange is many times higher. The diffusion currents of the positive and negative ions are nearly equal and practically compensate each other. But the fluctuations in the currents do not compensate and must be quadratically added. The contribution of the positive ions to the diffusion voltage is

\[
V_{\text{diff}+} = \frac{u_+}{u_+ + u_-} \frac{kT}{zq} \ln \frac{c_1}{c_2} \approx -\frac{1}{2} V_{\text{cell}}.
\]  

(25)

If now the 1/f noise in this voltage obeys a relation similar to (1), and if the same holds good for the negative ions, then these two noise contributions add in the same way as the contributions of the positive and negative ions to the conductance fluctuations. Hence the same numerical relations are found as in (13), which explains why relation (23) applies. The bridge properties determine the cell-voltage fluctuations, although in the cell voltage itself the bridge resistance has no influence at all, and the diffusion voltage hardly any. This view is confirmed by noise measurements on a KCl concentration cell with calomel electrodes, where \( V_{\text{cell}} = V_{\text{diff}} \). Here the factor \((u_+ - u_-)/(u_+ + u_-)\) is about 1/150, resulting in a very small value for \( V_{\text{diff}} \) of about 2 mV. The individual contributions are not \( \frac{1}{2} V_{\text{cell}} \) but roughly \( 150 \times \frac{1}{2} V_{\text{cell}} \), which is of the order of 150 mV. Using this inaccurate value for an estimate of \( \alpha \) we find \( \alpha \approx 0.9 \) for an effective concentration of \( 6.10^{-2} \) mol/l. The agreement is good, proving our view. This result has not been plotted in fig. 6, the inaccuracy being much higher than for the CuSO$_4$ and AgNO$_3$ cells.

The last and essential problem is now: why do fluctuations in the diffusion voltage obey the same relation as conductance fluctuations do? The answer must be that 1/f fluctuations are essentially voltage fluctuations or current fluctuations. For ohmic devices there is no difference in \( \langle (AV/V)^2 \rangle \), \( \langle (\Delta i/\bar{i})^2 \rangle \) or \( \langle (\Delta G/G)^2 \rangle \). There, 1/f noise can be interpreted as noise in the conductance. This is the base for the usual 1/f-noise theories, in which the conductance fluctuates because of fluctuations in the number of free charge carriers. But a non-ohmic device, such as a concentration cell immediately shows that the 1/f fluctuations are voltage or current fluctuations. Therefore, as a sequence to the concentration-cell experiments we are now studying the noise in the
thermal e.m.f. In both cases there is a voltage difference over the devices, but without particle current in the thermal-e.m.f. experiment, and with a continuous particle current in the concentration-cell experiments (the total electrical current being zero).

Our preliminary experiments show that there is no $1/f$ noise without particle current. Therefore the $1/f$ noise must be interpreted as a current noise, its magnitude being determined by the number of charge carriers.

Acknowledgement

We wish to express our sincere thanks to Dr E. P. Honig for this contribution to the discussion of the concentration-cell experiments.

Eindhoven, October 1970

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