STUDIES ON ALTERNATING CURRENT

ELECTROLYTIC CELLS

By

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PART I

The Effects of Concentration on Polarization Capacity
and Polarization Resistance in Ferrocyanide-Ferricyanide Cells
with Platinum Electrodes

By: A. Edward Remick and Herbert W. McCormick

The results of this research have already been reported
in our Technical Reports No. 1 and No. 2. There is no need,
therefore, to do more here than outline the objectives, the
method used and the conclusions. Literature references will
be given by using the Roman numerals I and II to refer respec-
tively to our Technical Reports No. 1 and No. 2 and Arabic
numerals will be used to indicate the reference numbers used
in our previous bibliographies.

Objectives

Our ultimate objective is three fold. (1) We wish to
analyse the behavior of an electrode in an alternating
current electrolytic cell into its component properties.
The result of such an analysis can be represented graphically
by an equivalent circuit consisting of both conventional and
unconventional circuit elements. (2) We wish to establish the
fundamental nature of the unconventional circuit elements.
(3) We wish to apply this fundamental knowledge to the eluci-
dation of the mechanism of electrochemical redox reactions.

An excellent start toward our goal has been made by
Rozental and Ershler (II-2), Randles (II-3,7), Grahame (II-4)

and Gerischer (II-5). Their mathematical theories and equivalent circuits are closely similar but Grahame's theory is the most complete and we have therefore concentrated our efforts on collecting experimental data with which to check his theory. Specifically we have studies the influence of frequency, depolarizer concentration and ionic strength on the equivalent series capacitance (C_s) and resistance (R_s) of an alternating current electrolytic cell and on the equivalent series capacitance (C_s^*) and resistance (R_s^*) of the faradaic branch of the equivalent circuit of said cell. These measurements were made using very small current densities. A little work was also done at high current densities for the purpose of furthering the studies of Shaw and Remick (I-1) which give us valuable qualitative "tools" for the investigation of electrode mechanism.

Experimental Method

The electrolytic cell was fitted with platinum electrodes arranged so that the interelectrode distance could be varied and measured. A piece of glass tubing was slipped over the two electrodes with the upper end projecting above the surface of the liquid; this was done to insure a uniform cross-sectional area of the conducting path. The electrolyte always contained equimolar concentrations of potassium ferrocyanide and ferricyanide and usually contained also potassium sulfate or sodium benzene sulfonate as supporting electrolytes; it was always freed of dissolved oxygen by a stream of pure

nitrogen. Sinusoidal alternating current was passed through the cell. Measurements of resistance and capacitance were made on an impedance bridge using an oscillograph for a detecting instrument. Measurements were carried out at $30^{\circ} \pm 0.1^{\circ}$.

Conclusions

(1) Reproducible results can be obtained with platinum electrodes if they are cleaned by a series of alternate cathodic and anodic electrolyses in an alkaline cyanide solution.

(2) Hysteresis is observed at sufficiently high current densities. It's probable cause is the collection of electrolytic gases on the surfaces of the electrodes.

(3) When C_S and R_S are plotted against current density, a "capacitive depression point" and a "resistive elevation point" are observed at the same current density. An explanation readily emerges from Grahame's theory.

(4) There is a frequency-independent component of the cell resistance in addition to the electrolytic resistance (R_Φ). We tentatively call it "the electrode layer resistance" and symbolize it as R_L. We may therefore write

$$R_S = R_\Phi + R_L + R_\Delta \qquad (1)$$

where R is the frequency dependent component of R_S.

(5) R_L is always positive. It increases as the depolarizer concentration increases and decreases as the concentration of the supporting electrolyte increases, other things

being equal.

(6) Our improved method of cleaning electrodes makes a constant contribution to R_L whereas four other cleaning methods gave four values of R_L, other things being equal. In the latter case, a rough parallelism was observed between R_L and C_s.

(7) C_s increases with the ionic strength slightly and with the depolarizer concentration markedly.

(8) Experiments made with potassium sulfate and sodium benzenesulfonate as supporting electrolytes showed that the quantity $(R_L + R_A)$ is accurately the same at a given value of the ionic strength independent of the kind of supporting electrolyte used, other things being equal. This indicates that the effect of the supporting electrolyte on $(R_A + R_L)$ is an ionic strength effect, not a mere concentration effect.

(Note: The values of R_A listed in Tables I-IV of our Technical Report No. 1 should be interpreted as $R_A + R_L$ in terms of our present definition of R_A.)

(9) The quantity $(R_A + R_L)$ decreases markedly as the ionic strength increases and is essentially independent of depolarizer concentration.

(10) C_s is a linear function of the depolarizer concentration in the presence of sufficient supporting electrolyte. The slopes of these curves are positive and are greater at lower frequencies, the half-wave area of the alter-

nating current being constant. The same conclusion
may be drawn about C_s^*.

(11) Grahame's theory leads to the equations

$$R_s^* = \eta / \sqrt{\omega} \qquad (2)$$

$$C_s^* = {}^1/\eta \sqrt{\omega} \qquad (3)$$

Eq.(2) involves the assumption that Grahame's θ is
zero. This is equivalent to the assumption that the
electron transfer reactions are rapid compared to the
period of the alternating current. Plots of the experi-
mental values of R_s^* and C_s^* against ${}^1/\sqrt{\omega}$ were found to
be linear passing thru the origin, as demanded by
Eq's. (1) and (2). Moreover, values of η calculated
from the slopes of the C_s^* and R_s^* curves agreed fairly
well and the equivalent requirement that $C_s^* R_s^* \omega = 1$
was accurately satisfied at frequencies up to 1000
c.p.s. if a sufficiently large excess of supporting
electrolyte is used. The dispersion studies here
involved were made at constant half-wave area of current,
i.e., they were "Q-dispersion" studies.

(12) From the standpoint of the effect of depolarizer con-
centration (C) on C_s^* and R_s^*, Grahame's theory leads to
the equations:

$$C_s^* = kC \qquad (4)$$

$$R_s^* = k'/C \qquad (5)$$

if we make the assumptions that: (a) equilibrium in the
electron transfer reaction is continuously established

between the electrode and the adjacent layer of electrolyte, and (b) using time-average values, the depolarizer concentrations at the electrode surface are the same as those in the bulk of the solution. Eq's. (4) and (5) demand a linear dependence between C_s^* and $1/R_s^*$, on the one hand, with C on the other hand. The predicted relations are found experimentally if a sufficient excess of supporting electrolyte is used.

The relationship between the constants of Eq's. (4) and (5) is:

$$k = 1/k'w$$

The experimental data is also in accord with this theoretical requirement.

(13) The concordance between theory and experiment cited in conclusion #12 was achieved only by taking R_L into account and thus furnishes additional evidence in favor of the reality of R_L.

(14) Consideration was given to the possibility that the resistance we have called R_L might more correctly be ascribed to a slow electron discharge step or, in other words, that $R_L = 0$ and Θ is finite. It was pointed out that the oscillographic studies made by Silverman and Remick (II-10) on the ferricyanide-ferrocyanide system furnished evidence that Θ is essentially zero. Furthermore, our method of evaluating R_L involved extrapolation of R_s to infinite frequency. In terms of Grahame's

theory the impedance of the faradaic branch of Grahame's equivalent circuit, including θ, is infinite when the frequency is infinite. It follows that the measured resistance which we have symbolized as R_L cannot be in the faradaic branch of the circuit and hence cannot be either wholly or partially accounted for as a resistance associated with the activation process, i.e., as θ.

(15) The accord achieved between experiment and Grahame's theory, using Grahame's equivalent circuit modified by the introduction of R_L, makes clear the fundamental nature of each of the circuit elements except R_L. Their nature is adequately described by Grahame's mathematical theory.

(16) An increase in ionic strength at constant concentration of depolarizer and constant frequency results in an increase of C_s^* while R_s^* usually rises slightly to a maximum and then falls comparitively rapidly. The maximum in the R_s^* curve may not be real.

There are apparent three ways in which the ionic strength might affect the values of C_s^* and R_s^*:
(a) Up to a point, an increase in ionic strength would diminish the effect of electrical migration. Let us call this the migration effect. (b) The conlombic interactions between the electrode and the depolarizer ions would be diminished by an increase in ionic strength in a manner reminiscent of the Brönsted-Christiansen-Scatchard equation

used in chemical kinetics. Let us call this the kinetic effect. (c) The activity coefficients of the depolarizer ions would be affected by interionic attractive forces and thus changes in ionic strength would alter the Nernst potentials which are associated with Grahame's   and hence with C_s^* and R_s^* by Eq's. (2) and (3). Let us call this the thermodynamic effect.

We carried out a mathematical development based on the Debye-Hückel limiting law and Grahame's theory, which showed that the thermodynamic effect would operate in the opposite direction to that experimentally observed. The kinetic effect cannot be operative because θ is zero. Thus if any one of these three effects is the major cause of the observed influence of the ionic strength on the values of C_s^* and R_s^*, it must be the migration effect. It is possible, at least in principle, to expand Grahame's mathematical treatment to include the migration effect. This we have not yet attempted. It must be done before we can know whether or not the influence of the ionic strength observed experimentally can be explained on this basis.

The Determination of Thermodynamic Reduction Potentials
by an Alternating Current Technique

By: William K. Snead and A. Edward Remick

We have submitted no Technical Report on this research
work because no phase of it has been successfully concluded.
This report will deal, therefore, only with the guiding
principles we have employed, with the unsuccessful labora-
tory methods we have tried and with the method we are cur-
rently developing.

The objective of this phase of our research was a method
for measuring the thermodynamic reduction potentials of rever-
sible electron-transfer steps occurring in redox reactions
whose overall behavior would be described as irreversible.
An example would be a redox reaction having a Conant mecha-
nism:

$$AH_2 \rightarrow A + 2H^+ + 2e \qquad (fast)$$
$$A \rightarrow X + Y \qquad (slow)$$
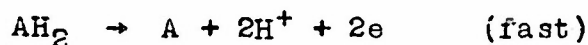
In this case the problem would be to measure the reduction
potential of the first step which involves the unstable inter-
mediate free radical A.

The method we originally used was essentially the method
of Silverman and Remick (I-17). We elected to study first
reversible redox systems whose potentials could be measured
potentiometrically, in this way hoping to establish the
validity of the method. This done, we reasoned that the
method could then be applied to irreversible oxidation or

reduction reactions to give the potential of the reversible
electron transfer step, if any.

The electrical circuit we employed was the one used by
Silvermand and Remick. A sinusoidal alternating current was
passed through a cell containing in aqueous solution one
component of a reversible redox system. One electrode of
this cell was of smooth platinum sealed in glass so that no
edges were exposed and had an exposed surface area of a few
tenths of a square contimeter. The instantaneous potential
of this electrode (under the influence of the exciting
current) was impressed on the vertical plates of a DC
oscilloscope, a standard electrode (saturated calomel elec-
trode) and salt bridge completing the circuit to the electro-
lyte. Of course, none of the impressed AC current flowed in
this oscilloscipe-standard electrode-salt bridge arm of the
circuit. The other electrode of the working cell was in most
cases somewhat larger than the working electrode (about
$2-3$ cm^2) and sometimes platinized.

The instantaneous potential at either of the two points
of an oscillogram where the current is zero we have designated
as e_0. Many years ago Reichenstein observed that as the r.m.s.
current through a cell in which water was being electrolysed
was increased, both the cathodic and anodic values of e_0
(measured between the two working electrodes) approached
limiting values. The difference between the two limiting
values he considered as being equal to the reversible
potential difference between a hydrogen and an oxygen

electrode. Silverman and Remick showed, however, that this potential difference included the corresponding overvoltages. We presumed that when reversible systems were used, and e_o corresponded to the potential difference between the working electrode and a reference half cell, the maximum value of the anodic e_o (in case the electrolyte was the reduced form of the redox system) should be the standard potential of the redox system against the given reference electrode, much as Reichenstein had originally imagined. This presumption was supported by the observation of Silverman and Remick that as the current was increased the oscillogram approached a condition wherein the part of the curve passing through the e_o value in question was linear for a considerable distance on each side of the e_o point. They advaned qualitative evidence to show that this linear region appeared when the current excursions became large enough to carry the system into the poised region. Thus the maximum value of e_o should occur when the redox ratio at the electrode surface is unity. Since the IR drop is zero at this point, e_o should be equal to the standard potential.

Silverman and Remick were unable to test their theory quantitatively because they did not have a D.C. oscillograph. We therefore undertook the test using a Dumont type 304-H oscillograph and a Dumont oscillographic record camera. As depolarizers we used potassium ferrocyanide, hydroquinone, stannous chloride and ferrous sulfate respectively in four different groups of experiments. In order to locate the

maximum value of e_0 as accurately as possible we plotted e_0 against the r.m.s. current. In all cases the values of e_0 tended to level off but they never reached a maximum value or usually a point of inflection. They leveled off at values of the voltage close to the expected standard potential but obviously it was impossible to locate the point precisely. Some inflections were observed, however, but these were never reproducible nor retraceable because they occurred in the range of current density where hysteresis was operative.

The above work was done prior to the advent of Grahame's theory of the faradaic admittance (I-3). When we became acquainted with that theory it became evident to us that when the cell current (i_T) is zero, it by no means follows that the faradaic current (i_f) is also zero; hence our e_0 undoubtedly contained an iR drop. We thereupon set to work trying to devise a method, both experimental and mathematical, by which we could locate the point at which the redox ratio is unity and correct the corresponding potential for the iR drop in the faradaic part of the circuit. We devised an experimental means of automatically subtracting the $i_T R_T$ drop (where R_T is the electrolytic resistance) before the voltage was recorded on the screen of the oscillograph. We devised a number of different circuits involving square waves, triangular waves or sine waves to be used with the oscillograph and worked out their mathematical properties only to find that none of them gave unequivocal answers to our problem.

Incorporation of the effects of the electrical double
layer and of diffusion into the interpretation of the oscillo-
grams did yield one method which appeared to be theoretically
sound but it was considered to be unduly burdensome. Because
of the non-linearity of the electrode as a circuit element,
graphical and Fourier analysis of the oscillographic record
would be required to interpret it fully.

By making certain simplifying assumptions, including
the assumption that the impedance of the double layer is
essentially infinite, we developed from first principles
an equation which seems to be at least roughly valid. It is:

$$\exp \frac{e_o nF}{RT} = \frac{nFAC_{ox}}{a} \sqrt{2\omega D_{Red}} \exp (E^o nF/RT) - \frac{\sqrt{D_{Red}}}{\sqrt{D_{ox}}} \exp (E^o nF/FT)$$

Where A is electrode area, $\underline{a}$ is the alternating current ampli-
tude, D is a diffusion coefficient, ω is the angular frequency
of the alternating current, C_{ox} is the bulk concentration of
the oxidant (C_{Red} being zero) and E^o is the Nernst standard
potential. This equation predicts the experimentally observed
shape of the curve obtained by plotting e_o against current
density. When the quantity $\exp (e_o nF/RT)$ is plotted against
$1/a$, the points are rather widely scattered but a straight
line can be reasonably drawn through them. The frequency-
dependency of e_o called for by this equation is also roughly
satisfied. On the whole, the results indicate that the
equation is at least roughly valid but that our data are not
accurate enough for an adequate test. We propose to pursue

this line of approach further, improving our experimental
accuracy and our working equation if we can.

The difficulty in interpreting the cyclograms with cer-
tainty and also the experimental difficulty of hysteresis
has led us to consider an alternative alternating current
electrolysis method, namely the incremental (or differential)
method utilizing a small A.C. superimposed on D.C. and
employing an impedance bridge technique. This is the method
used by Grahame in his measurements of double layer capacities
and the one assumed in his theory of the faradaic admittance.

This method appears to offer to our case several advan-
tageous points. Hysteresis, which interfered with reproduci-
bility when using high alternating current densities, should
be considerably reduced by the incremental technique since
the AC excitation must be kept negligibly small; the direct
current also is generally quite small. Kinetic constants
for the electrode reaction are obtainable by Grahame's theory
of the Faradaic admittance directly from the bridge data and
the standard potential can be calcul ed from the ratio of
these constants. The disadvantage of this method is that it
is only applicable when the electron transfer step is suf-
ficiently slow so that the velocity constants can be measured
by this method with suitable accuracy.

We have begun construction of an exceedingly well shielded
bridge and suitably sensitive detector to test this method for
our purposes. Since currents are in the microampere range,
the shielding problem is difficult.