THE TRANSPORT NUMBER OF SILVER FLUORIDE

USING A PULSATING CURRENT.

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INTRODUCTION.

It was thought probable that the transport number of an electrolyte is different when using a pulsating current, than when using a steady current, on account of the difference of inertias of different ions, due to their difference in masses. It was considered on sufficient interest to justify the work outlined in this paper.

THEORY.

An electrolyte is a substance which conducts electricity, but in so doing undergoes some chemical change at the electrodes.

According to the theory of electrolytic dissociation, an electrolyte is assumed to be dissociated into ions. The electricity is assumed to be carried by the movement of these ions toward the electrodes. Those which carry positive electricity move toward the cathode and are called cations. Those which carry negative electricity move toward the anode, and are called anions. The sum of the quantity of electricity carried by the cations and the quantity carried by the anions is necessarily equal to the total quantity passed.

The fraction of the total quantity of electricity passed, which is carried by the anion is Hittorf's transport number for the anion. When the term transport number is used in this paper it refers to the transport number for the anion.

The transport number may be determined in the following way. Suppose we have a cell divided into three compartments by two partitions, which prevent mechanical diffusion but do no interfere with

1.

the movement of the ions. In the two end cells are silver electrodes. The cell contains silver nitrate solution.
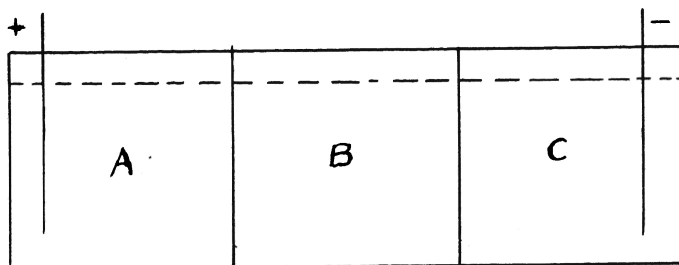

Figure 1

Pass one faraday of electricity through the cell. If X is the transport number, the following changes take place in A.

1 equivalent of Ag^+ formed from anode.

(1 - X) equivalents of Ag^+ pass to B.

X equivalents of NO_3^- enter from B.

In B.

(1 - X) equivalents of Ag^+ enter from A.

(1 - X) equivalents of Ag^+ pass to C.

X equivalents of NO_3^- enter from C.

X equivalents of NO_3^- pass to A.

In C.

(1 - X) equivalents of Ag^+ enter from B.

1 equivalent of Ag^+ is discharged on the cathode.

X equivalents of NO_3^- pass to B.

Summing up these changes there are the following changes in content of the ions in the different cells.

-2-

In A.

$+1$ equivalent of Ag^+ $+X$ equivalents of NO_3^-
$-(1-X)$ equivalents of Ag^+
_____
$+X$ equivalents of Ag^+ $+X$ equivalents of NO_3^-

There is a gain of X equivalents of $AgNO_3$ in A.

In B.

$+(1 - X)$ equivalents of Ag^+ $-X$ equivalents of NO_3^-.
$-(1 - X)$ equivalents of Ag^+ $+X$ equivalents of NO_3^-
_____
0   0

There is no change in the content of $AgNO_3$ in B.

In C.

$+(1 - X)$ equivalents of Ag^+ $-X$ equivalents of NO_3^-
$- 1$ equivalent of Ag^+
_____
$- X$ equivalents of Ag^+ $-X$ equivalents of NO_3^-

There is a loss of X equivalents of $AgNO_3$ in C.

So the transport numbers may be determined
by analysing the solution before passing the current,
and that in either A or C after passing the current.
The gain or loss of $AgNO_3$, expressed as equivalents,
divided by the number of faradays passed, is the
transport number.

Since one gram equivalent of any ion carries
one faraday of electricity, the rates, with which
different ions conduct, are directly proportional
to their respective average velocities. So the trans-
port number of the anion is the average velocity of
the anion, divided by the sum of the average vel-
ocity of the cation, and the average velocity of the

anion, both the velocities being taken with the same potential gradient.

When a potential gradient is applied to a cell, the ions begin to move toward the corresponding electrodes with an accelerated velocity. If a gram equivalent of one ion has a larger mass than that of the other, the acceleration of the one with the larger mass is smaller than that of the one with the smaller mass. For the force is proportional to the mass times the acceleration. The force on each ion is the same, for each carries the same amount of electricity. So, the acceleration of the one with the larger mass must be smaller than that of the one with the smaller mass.

Each ion will reach a maximum valocity when the resisting force is equal to the applied force. This maximum velocity is independent of the mass, for some ions of small masses have greater velocities than the ones with larger masses, and some with smaller mass have smaller velocities than the ones with larger masses. So, the transport number corresponding to the starting velocities is not in general the same as the transport number corresponding to the maximum velocities.

Similarly, when the circuit is broken, the transport number, corresponding to the stopping

velocities, is different from that corresponding to
the maximum velocities.

The object of this work was to determine
the transport number using a pulsating current,
which is an alternation of starts and stops, and to
compare it wibh the transport number for the maximum
velocities.

METHOD OF PERFORMANCE.

To determine experimentally the effect of a
pulsating current on the transport number, a solution
of silver flouride was used. It was chosen because
the ions have about the same mobility, and on account
of the difference in mass of gram equivalents of the
ions. It dissociates into silver ion and flouride ion.

$$AgF = Ag^+ + F^-$$

A gram equivalent of silver ion is 107.9
grams, and a gram equivalent of flouride ien is
19 grams. There is a considerable difference, so if
there is a difference in transport number due to
starting and stopping effects, it should be shown by
this electrolyte.

The silver flouride solution was prepared
from silver nitrate solution. The silver nitrate sol-
ution was treated with an excess of a solution of
potassium hydroxide. This precipitates the silver as

silver oxide.

$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O$$
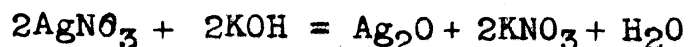
The precipitated silver oxide was washed repeatedly by decantation. It was then transferred to a platinum dish and partly dissolved in hydroflouric acid.

$$Ag_2O + 2HF = 2AgF + H_2O$$
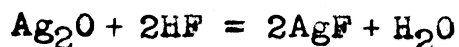
An excess of silver oxide was used in order to insure the solution being neutral. The excess silver oxide is so slightly soluble that the alkalinity due to it is negligible. The silver flouride solution formed was filtered and diluted to approximately .015 normal. The solution was kept in a covered bottle in a dark locker.

The apparatus used to determine the transport number is sketched in Plate I. It consists of a glass cylinder about five centimeters in diameter and about twenty centimeters high. Inside the cylinder is a large test tube with a small hole about fifteen centimeters from the bottom. Outside the test tube and inside the cylinder is a glass tube about twenty centimeters long open at both ends. The test tube is the anode chamber corresponding to A in Figure 1. At the bottom of the test tube is the silver anode. As first used it was a disk of silver foil with ahole in the middle, thru which was a glass tube. A platinum wire
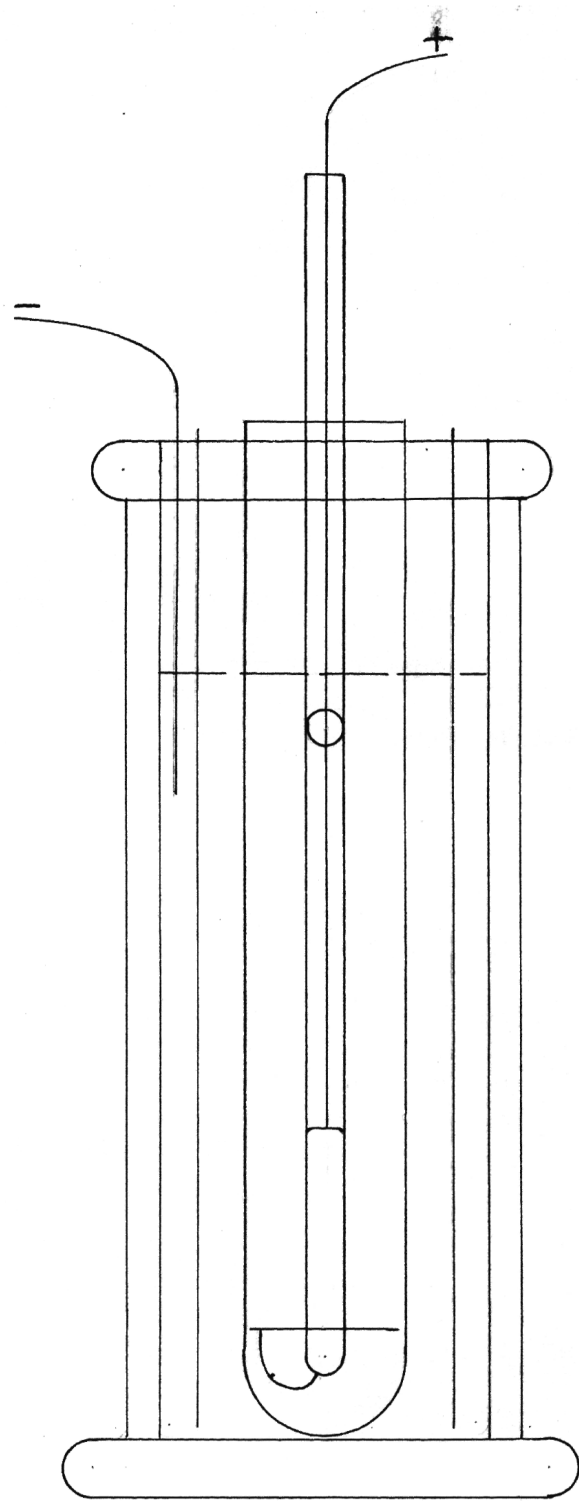
PLATE I
APPARATUS FOR TRANSPORT NUMBER

was welded to the silver foil and sealed thru the end
of the glass tube. Electrical connection was made thru
the glass tube.

This anode was unsatisfactory, for, when the
current was passed, a few bubbles of gas, probably
oxygen, accumulated on it. In other words the silver
would not go into solution fast enough. To remedy this
the anode as described above was silver-plated before
using. This coating of silver dissolved better, for
no gas appeared on the anode when the current was
passed.

The cathode was a piece of silver foil about
one by five centimeters. It was placed inside the
cylinder and outside the open glass tube, at about
the same height as the small hole in the large test
tube.

The apparatus was filled with silver flouride
solution to just above the hole in the test tube. The
current passed from the anode up the test tube, out
through the hole, down inside the open tube, and up
outside the open tube to the cathode. The test tube
corresponds to compartment A, in Figure 1, and it is
from the increase in silver flouride in this tube,
that the transport number is calculated.

Two pieces of transport apparatus as just
described were connected in series so as to get
duplicate results.

The quantity of silver flouride was determined
by titrating it with standard ammonium thiocyanate.
Ferric alum was used as indicator. A standard silver
nitrate solution was used to titrate back. The ammon-
ium thiocyanate solution and the silver nitrate sol-
ution were standardized against pure dried silver
nitrate.

The quantity of electricity passed was meas-
ured in an iodine coulometer. A sketch of it is shown
in Plate II. It is very similar to the transport ap-
paratus described above. The difference is in the
electrodes and in the solution used. The anode is a
piece of platinum foil about one by three centimeters.
The cathode is a platinum wire.

In operation the coulometer was filled to
above the hole in the test tube with a ten per cent
solution of potassium iodide. Then five cubic centi-
meters of a fifty percent solution of potassium iodide
was introduced into the bottom of the test tube with a
pipette. The anode was then put in. The platinum foil
was immersed in the fifty percent potassium iodide sol-
ution, which remained at the bottom of the tube. When a
current is passed through this coulometer, iodine is
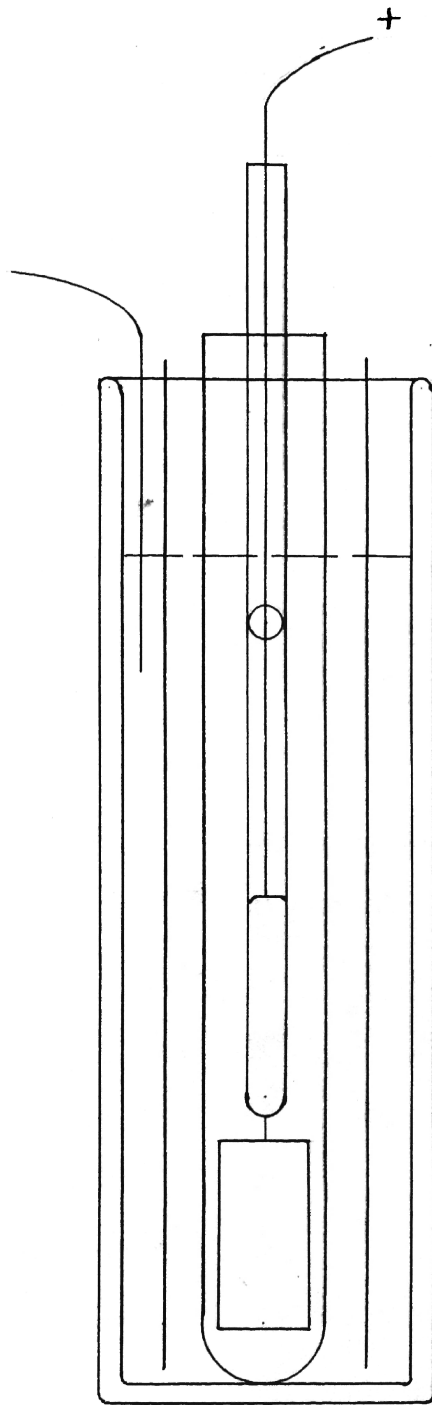liberated quantitatively at the anode.

PLATE II

IODINE COULOMETER

The iodine liberated was diluted, acidified with ten cubic centimeters of dilute sulphuric acid, and titrated with a standard sodium thiosulphate solution, using starch as an indicator. The sodium thiosulphate solution was frequently standardized against a standard solution of potassium iodate. This solution is made up by dissolving a weighed quantity of C.P. potassium iodate and diluting it to a known volume. It is a permanent solution and does not alter in strength.

To standardize the sodium thiosulphate solution, a measured volume of the potassium iodate solution was added to three cubic centimeters of the fifty percent potassium iodide solution. Ten cubic centimeters of dilute sulphuric acid was added. Iodine is liberated according to the following equation:

$$K^+ + IO_3^- + 6K^+ + 6I^- + 6H^+ + 3SO_4^{--} =$$
$$3I_2 + 7K^+ + I^- + 3SO_4^{--} + 3H_2O$$
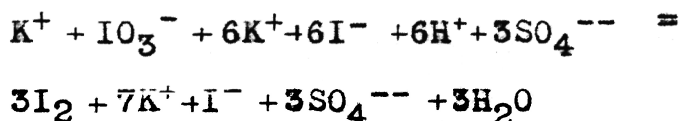
After standing three minutes the solution was diluted and titrated with the sodium thiosulphate solution.

The pulsating current was produced by an interrupter in series with the coulometer and transport apparatus. It was a brass disk attached to the shaft of a small motor in the place of the pulley. Twelve grooves were milled at regular intervals around the circumference of the disk. In the grooves were placed pieces of fiber, and the whole interrupter given a finishing cut on the lathe.

When finished the the circumference of the disk had alternating segments of brass and fiber. They were of the same width. Two brushes were used, one against the hub, and the other against the circumference of the interrupter.
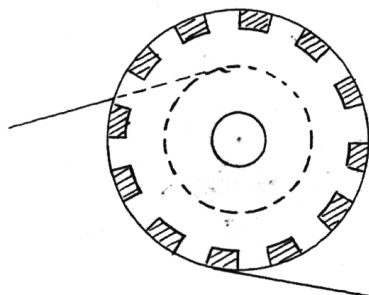
Figure 2

The brushes were connected in the circuit and the rotation of the interrupter produced a pulsating current. The motor which turned the interrupter ran at about 5000 R.P.M. This produced one thousand interruptions per second. At each pulsation the electromotive force was applied .0005 seconds.

Determination of the transport number was made both with and without the interrupter in order to find if there is a difference.

In making a determination, the two pieces of transport apparatus, the coulometer, and the interrupter, (if a pulsating current was desired), were connected in series with a 110 volt direct current circuit. Without the interrupter the current was approximately .01 ampere.

The anode tubes with the anodes were first weighed. Then the different pieces of apparatus were filled with the solution as described above. They were then connected in series and the current passed three or four hours. Then the circuit was broken. The anode tubes of the transport apparatus were removed with the solution in them, wiped dry on the outside, and weighed without removing the anodes. Then the solutions in them were filtered and titrated with the standard ammonium thiocyanate solution. The iodine, liberated in the coulometer, was diluted, acidified with ten cubic centimeters of dilute sulphuric acid, and titrated with the standard sodium thiosulphate solution.

DATA.

A number of determinations were made with both the steady and the pulsating current. The data obtained for the standardization of solutions, and for the determination of the transport number, together with the calculations and results are shown on the following pages. The method of calculation is evident from the arrangement. The symbols underlined represent the original data, and the others are calculations. The transport numbers obtained are underlined.

Table I.

Standardization of AgNO$_3$ and NH$_4$SCN solutions.

Date - Mar. 23, 1914.

$\underline{A}$ AgNO$_3$ $=$ 2.3619 gms. AgNO$_3$

$\underline{B}$ $\dfrac{107.9A}{169.9}$ $=$ 1.500 " Ag

$\underline{C}$ vol.of sol. $=$ 999.2 cc

$\underline{D}$ B/C $=$ .001500 gms. Ag/$_{c.c.}$ AgNO$_3$ sol.

$\underline{E}$ 1c..c. AgNO$_3$ $=$ .001500 gms. Ag.

$\underline{F}$ NH$_4$SCN $=$ 16.68 cc.

$\underline{G}$ AgNO$_3$ $=$ 23.31 c..c.

$\underline{H}$ $\dfrac{G \times E}{F}$ $=$ .002095 gms.Ag/c.c. NH$_4$SCN

$\underline{I}$ 1c..c. NH$_4$SCN $=$ .002095 gms. Ag

$\underline{J}$ $\dfrac{I}{E}$ $=$ 1.397

$\underline{K}$ 1c..c. NH$_4$SCN $=$ 1.397 c..c. AgNO$_3$

Table 2.

Standardization of KIO_3 solution.

Date - Mar. 23, 1914.

A KIO_3 = 3.0000 gms.

B   solution   = 1996. c.c.

C $\dfrac{6\ A}{214B}$ = .00004214 equiv. Iodine/c.c.

D   1 c.c. KIO_3 = .00004214   "   "

Table 3.

Standardization of $Na_2S_2O_3$ solution.

Date- Mar. 30, 1914.

A KIO_3 =   32.59   c.c.

B   1c.c. KIO_3 =   .00004214 equiv. Iodine[*]

C $Na_2S_2O_3$ =   35.39   c.c.

D $\frac{AB}{C}$ =   .00003882 equiv. Iodine/c.c.

E   1c.c. $Na_2S_2O_3$ =   .00003882   "   "

[*]D Table 2.

Table 4.

Standardization of AgF solution.

Date -Apr. 1, 1914.

A $\underline{A}$ NH_4SCN = 31.10 c.c.

$\underline{B}$ $AgNO_3$ = 1.94 "

C 1c.c. $AgNO_3$ = $\dfrac{1}{1.397}$ " NH_4SCN^*

D CxB = 1.39 "

E A-D = 29.71 " Net NH_4SCN

F 1c.c. NH_4SCN = .002095 gms. Ag^{**}

G ExF = .06224 " Ag

H $\dfrac{126.9\,G}{107.9}$ = .07 " AgF

$\underline{I}$ AgF sol. = 41.41 "

J I-H = 41.34 " H_2O

K $\dfrac{G}{J}$ = .001506 " Ag/gm H_2O

*K Table 1.

**I Table 1.

Table 5.

Transport Number.

Date Mar. 30, 1914.

Current Steady.
Determination I.

A	$Na_2S_2O_3$	=	31.54	c.c.	
B	1c.c. $Na_2S_2O_3$ =		.00003882	equiv. Iodine*	
C	BxA	=	.001170	"	"
D	107.9C	=	.13	gms Ag dissolve.	
E	NH_4SCN	=	58.97	c.c.	
F	$AgNO_3$	=	1.98	"	
G	1c.c.	=	$\frac{1}{1.397}$	" NH_4SCN**	
H	FxG	=	1.42	"	
I	E-H	=	57.55	" Net NH_4SCN	
J	1c.c. NH_4SCN =		.002095	gms Ag***	
K	IxJ	=	.12057	"	"
L	$\frac{126.9K}{107.9}$	=	.14	" AgF	
M	Wt.AgF sol.-D	=	42.81	"	
N	M-L+D	=	42.80	" H_2O	
O	AgF sol.	=	.001506	" Ag/gm H_2O****	
P	NxO	=	.06446	" Ag	
Q	K-P	=	.05611	" Ag excess.	
R	$\frac{Q}{107.9C}$	=	.4444	Transport Number.	

* E Table 3.   **K Table 1. ***I Table 1. ****K Table 4.

Table 6.

Transport Number.

Date   Apr. 7, 1914.
Current   Steady.
Determination II   Duplicate with III.

A $Na_2S_2O_3$ = 33.68   c.c.

B 1cc. " = .00003882   equiv. Iodine[*]

C AxB = .001307   "   "

D 1079.C = .14   gms. Ag dissolved.

E NH_4SCN = 59.58   c.c.

F $AgNO_3$ = .65   "

G 1cc. " = $\dfrac{1}{1.397}$ " NH_4SCN[**]

H FxG = .46   "

I E-H = 59.12   " NH_4SCN Net.

J 1c.c. NH_4SCN = .002095   gms. Ag[***]

K IxJ = .12386   "   Ag

L $\dfrac{126.9K}{107.9}$ = .15   "   AgF

M Wt.AgF sol.-D = 40.88   "

N M-L+D = 40.87   " H_2O

O AgF sol. contains = .001506   "   Ag/gm H_2O[****]

P NxO = .06155   "   "

Q K-P = .06231   "   "   excess.

R $\dfrac{Q}{107.90}$ = .4419   Transport Number.

[*]E Table 3.   [**]K Table 1.   [***]I Table 1.   [****]K Table 4.

Table 7.
Transport Number.
Date Apr. 7, 1914.
Current Steady.
Determination III – Duplicate with 2.

A	$Na_2S_2O_3$	=	33.68	c.c.
B	1c.c. "	=	.00003882	Equiv. Iodine*
C	AxB	=	.001307	" "
D	107.9C	=	.14	gms. Ag dissolved.
E	NH_4SCN	=	61.53	c.c.
F	$AgNO_3$	=	2.03	c.c.
G	1c.c. "	=	$\frac{1}{1.397}$	" NH_4SCN**
H	FxG	=	1.45	"
I	E–H	=	60.08	" Net NH_4SCN
J	1c.c.NH_4SCN	=	.002095	c.c. Ag***
K	IxJ	=	.12587	" Ag.
L	$\frac{126.9K}{107.9}$	=	.15	" AgF
M	Wt.AgF sol.–D	=	42.51	"
N	M–L+D	=	42.50	" H_2O
O	AgF sol. contains		.001506	" Ag/gm H_2O****
P	NxO	=	.06401	" Ag
Q	K–P	=	.06186	" " excess.
R	$\frac{Q}{107.9C}$	=	.4386	Transport Number.

*E Table 3. **K Table 1. ***I Table 1. ****K Table 4.

Table 8.
Transport Number.
Date Apr. 9, 1914.
Current Steady.
Determination IV   Duplicate with V.

A $Na_2S_2O_3$ =   33.64 c.c.

B 1c.c. "   =   .00003882 Equiv. Iodine*

C AxB   =   .001306   "   "

D 107.9C   =   .14 gms. dissolved Ag.

E NH_4SCN =   60.92 c.c.

F $AgNO_3$ =   2.35   "

G 1c.c."   = $\dfrac{1}{1.397}$ " NH_4SCN**

H FxG   =   1.68   "

I E-H   =   59.24   "   Net NH_4SCN

J 1c.c.NH_4SCN =   .002095 gms. Ag ***

K IxJ   =   .12412   "   Ag

L $\dfrac{126.9K}{107.9}$ =   .15   "   AgF

M Wt.AgF sol.-D   =   41.63   "

N M-L+D   =   41.62   " H_2O

O Original AgF   =   .001506   "   Ag/gm H_2O****

P NxO   =   .06268   "   Ag

Q K-P   =   .06144   "   " excess

R $\dfrac{Q}{107.9C}$ =   .4359 Transport Number.

*E Table 3.   **K Table 1.   ***I Table 1.   **** K Table 4.

Table 9.

Transport Number.

Date Apr. 9, 1914.

Current   Steady.

Determination V Duplicate with IV.

$\underline{A}$ $Na_2S_2O_3$ = 33.64   c.c.

$\underline{B}$ 1c.c. " = .00003882 Equiv. Iodine*

C   AxB = .001306   "   "

D   107.9C = .14   gms. Ag. dissolved.

$\underline{E}$ NH_4SCN = 60.18   c.c.

$\underline{F}$ $AgNO_3$ = 1.02   "

G   1c.c. " = $\dfrac{1}{1.397}$ " NH_4SCN**

H   FxG = .73   "

I   E-H = 59.45   " Net NH_4SCN

J   1c.c.NH_4SCN = .002095   gms. Ag***

K   IxJ = .12455   "   Ag

L $\dfrac{126.9K}{107.9}$ = .15   "   AgF

$\underline{M}$ AgF sol.-D = 42.30   gms.

N   M-L+D = 42.29   " H_2O

O   AgF sol.contains   .001506 " Ag/gm. H_2O****

P   NxO = .06369   gms. Ag

Q   K-P = .06086   "   Ag excess.

R $\dfrac{Q}{107.9C}$ = .4319   Transport Number.

*E Table 3. **K Table 1. *** I Table 1. **** K Table 4

Table 10.

Standardization of AgF solution.

Date Apr. 10, 1914.

A $\underline{A}$ NH$_4$SCN = 59.80 c.c.

$\underline{B}$ AgNO$_3$ = 3.63 c.c.

C 1c.c." = $\dfrac{1}{1.397}$ " NH$_4$SCN*

D CxB = 2.60 "

E A-D = 57.20 " Net NH$_4$SCN

F 1c.c. NH$_4$SCN = .002095 gms. Ag**

G ExF = .1198 " Ag.

H $\dfrac{126.9G}{107.9}$ = .14 " AgF.

I Wt.AgF.sol. = 79.58 "

J I-H = 79.44 " H$_2$O

K G/J = .001508 " Ag/gm H$_2$O.

*K Table 1.

**I Table 1.

Table 11.

Transport Number.
Date Apr. 10, 1914.
Current Pulsating.
Determination VI.

A	$Na2S_2O_3$	=	26.48	c.c.
B	1c.c. "	=	.00003882	Equiv. Iodine*
C	AxB	=	.001028	" "
D	107.9C	=	.11	gms. Ag dissolved.
E	NH_4SCN	=	54.15	c.c.
F	$AgNO_3$	=	1.03	"
G	166 $AgNO_3$	=	$\dfrac{1}{1.397}$	" NH_4SCN**
H	FxG	=	.74	"
I	E-H	=	53.41	" NH_4SCN Net
J	1c.c. NH_4SCN	=	.002095	c.c. Ag***
K	IxJ	=	.11189	" "
L	$\dfrac{126.9K}{107.9}$	=	.13	" AgF
M	AgF sol.-D	=	41.91	"
N	M-L+D	=	41.89	" H_2O
O	AgF sol.	=	.001508	" Ag/gm H_2O****
P	NxO	=	.06317	" Ag
Q	K-P	=	.04872	" " excess.
R	$\dfrac{Q}{107.9C}$	=	<u>.4392</u>	Transport Number.

*E Table 3. ** K Table 1. *** I Table 1.   ****K Table 10.

Table 12.

Standardization of $Na_2S_2O_3$ solution.

Date Apr. 21, 1914.

A KIO_3 =   40.07   c.c.

B   1c.c.KIO_3 =   .00004214   Equiv. Iodine*

C $Na_2S_2O_3$ =   44.26   c.c.

D $\dfrac{AB}{C}$ =   .00003815

E   1c.c. $Na_2S_2O_3$ =   .00003815   Equiv. Iodine.

*D Table 2.

Table 13.

Standardization of AgF solution.

Date Apr. 22, 1914.

A NH_4SCN = 43.60 C,C.

B $AgNO_3$ = 1.09 c.c.

C 1c.c. $AgNO_3$ = $\dfrac{1}{1.397}$ " NH_4SCN

D CxB = .79 "

E A-D = 42.81 " NH_4SCN Net.

F 1c.c. NH_4SCN = .002095 gms. Ag**

G ExF = .08969 " Ag.

H $\dfrac{126.9G}{107.9}$ = .11 " AgF

I AgF solution = 58.34 "

J I-H = 58.23 " H_2O

K G/J = .001540 " Ag/gm H_2O

*K Table 11.

**I Table 1.

Table 14.
Transport Number.

Date Apr. 20, 1914.

Current Steady.
Determination VII Duplicate with VIII.

<u>A</u>	$Na_2S_2O_3$	=	34.68	c.c.
B	1c.c. $Na_2S_2O_3$	=	.00003815	Equiv. Iodine*
C	AxB	=	.001323	" "
D	107.9C	=	.14	gms. Ag dissolved.
<u>E</u>	NH_4SCN	=	65.41	c.c.
<u>F</u>	$AgNO_3$	=	5.96	"
G	1c.c. $AgNO_3$	=	$\frac{1}{1.397}$	" NH_4SCN
H	FxG	=	4.26	"
I	E-H	=	61.15	" NH_4SCN Net.
J	1c.c. NH_4SCN	=	.002095	gms Ag***
K	IxJ	=	.12811	" Ag
L	$\frac{126.9K}{107.9}$	=	.15	" AgF
<u>M</u>	AgF sol.-D	=	42.30	"
N	M-L+D	=	42.29	" H_2O
O	Original AgF sol.	=	.001540	" Ag/gm H_2O****
P	NxO	=	.06513	" Ag
Q	K-P	=	.06298	" "
R	$\frac{Q}{107.9C}$	=	<u>.4412</u>	Transport Number.

*E Table 12. **K Table 1. ***I Table 1. ****K Table 13.

Table 15.
Transport Number.

Date Apr. 20, 1914.

Current   Steady.
Determination VIII - Duplicate with VII.

A	$Na_2S_2O_3$	=	34.68	c.c.
B	1c.c. $Na_2S_2O_3$	=	.00003815	Equiv. Iodine[*]
C	AxB	=	.001323	" "
D	107.9C	=	.14	gms. Ag dissolved.
E	NH_4SCN	=	61.90	c.c.
F	$AgNO_3$	=	3.32	"
G	1c.c. $AgNO_3$	=	$\dfrac{1}{1.397}$	" NH_4SCN[**]
H	FxG	=	2.38	"
I	E-H	=	59.52	" NH_4SCN Net
J	1c.c. NH_4SCN	=	.002095	gms. Ag[***]
K	IxJ	=	.12469	" Ag
L	$\dfrac{126.9K}{107.9}$	=	.15	" AgF
M	AgF sol.-D	=	41.10	"
N	M-L+D	=	41.09	" H_2O
O	Original AgF sol. =		.001540	" Ag/gm H_2O[****]
P	NxO	=	.06328	" Ag
Q	K-P	=	.06141	" " excess.
R	$\dfrac{Q}{107.9C}$	=	.4302	Transport Number.

[*]E Table 12.   [**]K Table 1.   [***]I Table 1.   [****]K Table 13.

Table 16.

Transport Number.

Date Apr. 21, 1914.

Current Pulsating.

Determination IX.

<u>A</u>	$Na_2S_2O_3$	=	39.76	c.c.
B	1c.c.$Na_2S_2O_3$	=	.00003815	Equiv. Iodine[*]
C	AxB	=	.001517	" "
D	107.9C	=	.16	gms Ag dissolved
<u>E</u>	NH_4SCN	=	65.29	c.c.
<u>F</u>	$AgNO_3$	=	.88	"
G	1c.c.$AgNO_3$	=	$\frac{1}{1.397}$	" NH_4SCN[**]
H	FxG	=	.63	"
I	E-H	=	64.66	" NH_4SCN Net
J	1c.c.NH_4SCN	=	.002095	gms Ag[***]
K	IxJ	=	.13546	" Ag
L	$\frac{126.9K}{107.9}$	=	.16	" AgF
<u>M</u>	AgF sol.-D	=	41.67	"
N	M-L+D	=	41.67	" H_2O
O	Orig. AgF sol.	=	.001540	" Ag/gm H_2O[****]
P	NxO	=	.06417	" Ag
Q	K-P	=	.07129	" "
R	$\frac{Q}{107.9C}$	=	<u>.4355</u>	Transport Number.

[*]E Table 12. [**]K Table1. [***]I Table 1. [****]K Table 13.

-28-

Table 17.

Standardization of $AgNO_3$ and NH_4SCN.

Date May 12, 1914.

			I	II
__A__	$AgNO_3$	=	12.92 c.c.	9.84 c.c.
__B__	NH_4SCN	=	9.62 "	7.39 "
C	B/A	=	1.343 "	1.332 "

Average = 1.338.

D	1c.c. $AgNO_3$	=	$\dfrac{1}{1.338}$ c.c. NH_4SCN

__E__	$AgNO_3$(solid)	=	.3983 gms.
__F__	NH_4SCN(solid)	=	121.06 c.c.
__G__	$AgNO_3$ (solid)	=	.99 "
H	GxB	=	.74 "
I	F—H	=	120.32 " NH_4SCN
J	$\dfrac{107.9E}{169.9I}$	=	.002107 gms Ag/c.c. NH_4SCN
K	1c.c. NH_4SCN	=	.002107 " "

Table 18.

Standardization of AgF solution.

Date May 12, 1914.

A NH_4SCN =   38.28   c.c.

B $AgNO_3$ =   3.07   "

C   1c.c. $AgNO_3$ = $\dfrac{1}{1.338}$ " NH_4SCN*

D   CxB   =   2.29   "

E   A-D   =   35.99   "   Net NH_4SCN

F   1c.c.NH_4SCN =   .002107 gms. Ag**

G   ExF   =   .07583   "   "

H $\dfrac{126.9G}{1079}$ =   .09   "   AgF

I   AgF sol.   =   53.23   gms.

J   I-H   =   53.14   " H_2O

K   G/J   =   .001427"Ag/gm H_2O

* D Table 17.

**K Table 17.

Table 19.

Standardization of $Na_2S_2O_3$ solution.

Date May 12, 1914.

A KIO_3 =   24.98 c.c.

B   1c.c. KIO_3 =   .00004214 Equiv. Iodine[*]

C $Na_2S_2O_3$ =   47.98 c.c.

D $\frac{AB}{C}$ =   .00002111

E   1c.c. $Na_2S_2O_3$ =   .00002111 Equiv. Iodine.

[*]D Table 2.

-31-

Table 20.

Transport Number.

Date May 12, 1914.

Current   Steady.

Determination X - Duplicate with XI.

A $Na_2S_2O_3$ = 63.65 c.c.

B 1c.c. " ≟ .00002111 Equiv. Iodine*

C AxB = .001344   "   "

D 107.9C = .15   gms. Ag dissolved.

E NH_4SCN = 60.04 c.c.

F $AgNO_3$ = .50 "

G 1c.c.$AgNO_3$ = $\dfrac{1}{1.338}$ " NH_4SCN**

H FxG = .37 "

I E-H = 59.67 " Net NH_4SCN

J 1c.c.NH_4SCN = .002107 c.c. Ag***

K IxJ = .12572 " Ag

L $\dfrac{126.9K}{107.9}$ = .15 " AgF

M AgF sol.-D = 40.84 "

N M-L+D = 40.84 " H_2O

O Orig. AgF sol. = .001427 " Ag/gm H_2O****

P NxO = .05828 " Ag

Q K-P = .06744 " " Excess

R $\dfrac{Q}{107.9C}$ = .4650 Transport Number.

*E Table 19. **D Table 17. ***K Table 17.****K Table 18.

-32-

Table 21.
Transport Number.

Date   May 12, 1914.

Current Steady.

Determination XI- Duplicate with X.

<u>A</u>	$Na_2S_2O_3$	=	63.65 c.c.	
B	1c.c. "	=	.00002111	Equiv. Iodine*
C	AxB	=	.001344	" "
D	107.9C	=	.15	gms Ag Dissolved.
<u>E</u>	NH_4SCN	=	59.81	c.c.
<u>F</u>	$AgNO_3$	=	.78	"
G	1c.c. "	=	$\dfrac{1}{1.338}$	" NH_4SCN**
H	FxG	=	.58	"
I	E-H	=	59.23	" NH_4SCN Net
J	1c.c.NH_4SCN	=	.002107	gms. Ag***
K	IxJ	=	.12480	" "
L	$\dfrac{126.9K}{107.9}$	=	.15	" AgF
<u>M</u>	AgF sol.-D	=	39.96	" H₂O
N	M-L+D	=	39.96	" H_2O
O	Orig.AgF sol.	=	.001427	" Ag/gm H_2O****
P	NxO	=	.05702	" A
Q	K-P	=	.06778	" " Excess.
R	$\dfrac{Q}{107.9C}$	=	<u>.4673</u>	Transport Number.

*E Table 19. **D Table 17. ***K Table 17. ****K Table 18.

Table 22.

Transport Number.

Date   May 14, 1914.

Current   Pulsating.

Determination XII - Duplicate with XIII.

<u>A</u>	$Na_2S_2O_3$	=	35.08 c.c.	
B	1c.c. "	=	.00002111	Equiv. Iodine*
C	AxB	=	.0007405	" "
D	107.9C	=	.08	gms. Ag Dissolved.
<u>E</u>	NH_4SCN	=	45.72 c.c.	
<u>F</u>	$AgNO_3$	=	.87 "	
G	1c.c.$AgNO_3$	=	$\frac{1}{1.338}$ "	NH_4SCN**
H	FxG	=	.65 "	
I	E-H	=	.4507 "	
J	1c.c.NH_4SCN	=	.002107	gms Ag***
K	IxJ	=	.09496	" "
L	$\frac{126.9K}{107.9}$	=	.11	" AgF
<u>M</u>	AgF sol.-D	=	40.55 gms.	
N	M-L+D	=	40.52 "	H_2O
O	Orig. AgF sol. =		.001427 gms. Ag/gm H_2O****	
P	NxO	=	.05782	" "
Q	K-P	=	.03714	" " Excess.
R	$\frac{Q}{107.9C}$	=	<u>.4647</u>	Transport Number.

*E Table 19.   **D Table 17.   ***K Table 17.   ****K Table 18.

Table 23.

Transport Number.
Date   May 14, 1914.
Current   Pulsating.
Determination XIII- Duplicate with XII.

<u>A</u>	$Na_2S_2O_3$	=	35.08 c.c.		
B	1c.c. "	=	.00002111	Equiv. Iodine*	
C	AxB	=	.0007405	"	"
D	107.9C	=	.08	gms. Ag Dissolved.	
<u>E</u>	NH_4SCN	=	45.43 c.c.		
<u>F</u>	$AgNO_3$	=	.33 "		
G	1c.c. "	=	$\dfrac{1}{1.338}$ " NH_4SCN		
H	FxG	=	.25 "		
I	E-H	=	45.18 " NH_4SCN Net.		
J	1c.c. NH_4SCN	=	.002107	gms. Ag***	
K	JxI	=	.09519	"	"
L	$\dfrac{126.9K}{107.9}$	=	.11	" AgF	
<u>M</u>	AgF sol.-D	=	40.67	"	
N	M-L+D	=	40.64	" H_2O	
O	Orig.AgF sol.	=	.001427	" Ag/gm H_2O****	
P	NxO	=	.05809	" "	
Q	K-P	=	.03710	" " Excess.	
R	$\dfrac{Q}{107.9C}$	=	<u>.4643</u>	Transport Number.	

*E Table 19. **D Table 17. ***K Table 17. ****K Table 18.

Table 24.
Summary of Results.

Det.	Date			Nor.	Transport Number	
					Steady	Pulsating.
1	Mar.30	1914.		.014	.4444	
2	Apr.	7	"	.014	.4419	
3	"	7	"	.014	.4386	
4	"	9	"	.014	.4359	
5	"	9	"	.014	.4319	
6	"	10	"	.014		.4392
7	"	20	"	.014	.4412	
8	"	20	"	.014	.4302	
9	"	21	"	.014		.4355
10	May	12	"	.014	.4650	
11	"	12	"	.014	.4673	
12	"	14	"	.014		.4647
13	"	14	"	.014		.4643

DISCUSSION OF RESULTS.

The summary of results, Table 24, on the preceding page shows that the value of the transport number, obtained by the first nine determinations, usually decreases with each determination. These determinations were made with the original anodes used, which were not electroplated. As mentioned before there was a tendency for oxygen to be liberated on the anode. So, sufficient silver did not dissolve for the determination. Obviously, if some of it were more insoluble than the rest, the more soluble would dissolve first. Hence, with succeeding determinations, the silver left is more insoluble, so less of it dissolved and more oxygen liberated. Since less silver is dissolved in the later determination, the transport number as determined, decreases. For the calculation depends on the amount of silver in the anode tube.

The last four determinations were made with electroplated anodes. As mentioned before, no oxygen appeared to be liberated, so all the silver corresponding to the quantity of electricity passed, dissolved. Then the value of the transport number from these determinations should be larger than in the preceding cases. And they are considerably larger, as may be seen on Table 24.

Also, the duplicate determinations check much better than in the preceding determinations.

Compare the values found with a steady current with those with a pulsating current. Determination 10 with a steady current is within less than .1% of determination 12, using a pulsating current. The average of 10 and 11 (Steady current) is within .35% of the average of 12 and 13 (Pulsating current). It is easily possible that the experimental error was that great since the difference between the duplicates 10 and 11 is .5%.

So with the time of contact used, .0005 second, if the pulsating current makes a difference in the transport number of silver flouride, it is hidden by the experimental error.

MATHEMATICAL TREATMENT.

The conclusions above agree with the following general mathematical treatment of the subject.

As an electrolyte use a solution of a salt which dissociates into an anion A^- and a cation C^+. Let the equivalent weights of these ions be M_A and M_C, respectively. Use a potential gradient of one volt per centimeter.

Consider the starting conditions.

Let the average maximum velocity of A^- be U_A and of C^+ be U_C.

One volt is equal to $\frac{1}{300}$ of an electrostatic unit of potential. The potential difference (in electrostatic units) between two bodies is measuered by the number of ergs of work required to transport one electrostatic unit quantity of electricity from one of the bodies to the other. So, in the above case it will require $\frac{1}{300}$ of an erg to transfer one electrostatic unit quantity of electricity one centimeter.

One coulomb is equal to 3×10^9 electrostatic units. So, it requires $\frac{3 \times 10^9}{300}$ ergs to move one coulomb one centimeter.

Take one gram-equivalent of ion, which carries 96,500 coulombs. So, to move one equivalent one centimeter requires $\frac{96,500 \times 3 \times 10^9}{300} = 96,500 \times 10^7$ ergs.

(1) Work = 96,500 x 10^7 ergs.

Work is equal to force times distance, so the force
on one gram equivalent under unit potential gradient is
96,500 x 10^7 dynes.

(2)   f = 96,500 x 10^7

There is also a resisting force which retards the
motion. This may be shown to vary directly as the velocity
of the ion. By Ohm's law, if the potential gradient is
increased n times, the current density is increased n
times. But increasing the potential gradient n times
increases the force on a gram equivalent of ion, n times.
When the velocity has reached its maximum value, the
acceleration is zero and the resisting force is equal
to the applied force. So the resisting force is increased
n times. Since the current density varies directly as the
velocity of the ions, this velocity has been increased
n times. So the resisting force varies directly as the
velocity.

(3)   f = KV

The motion of the ion is dependent on the
resultant of the applied force and the resisting force.
The resultant force is equal to the mass times the
acceleration.

            F = Ma

(4) 96,500 x 10^7 - KV = Ma

The acceleration is the derivative of the velocity
with respect to the time.

(5) $\qquad a = \dfrac{dv}{dt}$

Combining (4) and (5):

(6) $\qquad \dfrac{96500 \times 10^7 - KV}{M} = \dfrac{dv}{dt}$

(7) $\qquad dt = \dfrac{MdV}{96500 \times 10^7 - KV}$

(8) $\qquad t = \displaystyle\int \dfrac{MdV}{96500 \times 10^7 - KV} + C$

(9) $\qquad t = -\dfrac{M}{K} \displaystyle\int \dfrac{d(96500 \times 10^7 - KV)}{96500 \times 10^7 - KV} + C$

(10) $\qquad t = -\dfrac{M}{K} \ln(96500 \times 10^7 - KV) + C$

If $\quad t = 0$
$\qquad V = 0$

(11) $\qquad C = \dfrac{M}{K} \ln(96500 \times 10^7)$

(12) $\qquad t = \dfrac{M}{K} \ln \dfrac{96500 \times 10^7}{96500 \times 10^7 - KV}$

(13) $\qquad \dfrac{tK}{M} = \ln \dfrac{96500 \times 10^7}{96500 \times 10^7 - KV}$

(14) $\qquad e^{\frac{tK}{M}} = \dfrac{96500 \times 10^7}{96500 \times 10^7 - KV}$

(15) $\qquad V = \dfrac{ds}{dt}$

Combining (14) and (15):

(16) $\quad e^{\frac{tK}{M}} = \dfrac{96500 \times 10^7}{96500 \times 10^7 - K\dfrac{ds}{dt}}$

(17) $\quad e^{\frac{tK}{M}} \, 96500 \times 10^7 - e^{\frac{tK}{M}} \, K\dfrac{ds}{dt} = 96500 \times 10^7$

(18) $\quad - e^{\frac{tK}{M}} \, K\dfrac{ds}{dt} = 96500 \times 10^7 - 96500 \times 10^7 \, e^{\frac{tK}{M}}$

(19) $\quad \dfrac{ds}{dt} = \dfrac{96500 \times 10^7 \, (e^{\frac{tK}{M}} - 1)}{K e^{\frac{tK}{M}}}$

(20) $\quad ds = \dfrac{96500 \times 10^7}{K} \cdot \dfrac{(e^{\frac{tK}{M}} - 1)}{e^{\frac{tK}{M}}} \; dt$

(21) $\quad ds = \dfrac{96500 \times 10^7}{K} \left[dt - \dfrac{dt}{e^{\frac{tK}{M}}} \right]$

(22) $\quad s = \dfrac{96500 \times 10^7}{K} \left[t + \dfrac{M}{K} \dfrac{e^{\frac{tK}{M}}}{e} \right] + C$

(23) $\quad s = \dfrac{96500 \times 10^7}{K} \left[t + \dfrac{M}{K \, e^{\frac{tK}{M}}} \right] + C$

If $t = 0$
$\quad s = 0$

(24) $\quad C = - \dfrac{96500 \times 10^7}{K} \cdot \dfrac{M}{K}$

(25) $\quad s = \dfrac{96500 \times 10^7}{K} \left[t + \dfrac{M}{K \, e^{\frac{tK}{M}}} - \dfrac{M}{K} \right]$

$$(26) \qquad s = \frac{96500 \times 10^7 \, t}{K} + \frac{96500 \times 10^7}{K} \left[\frac{M - Me^{\frac{tK}{M}}}{K \, e^{\frac{tK}{M}}} \right]$$

$$(27) \qquad s = \frac{96500 \times 10^7 \, t}{K} + \frac{96500 \times 10^7}{K^2} \left[\frac{1 - e^{\frac{tK}{M}}}{e^{\frac{tK}{M}}} \right]$$

Equation (27) expreeses the relation between the time and the distance if the ion statrs from rest.

Now consider the conditions when, the ion being in motion, the circuit is broken. The applied force disappears and the ion is carried on only by its inertia.

As before, the force is equal to the mass times the acceleration.

$$(28) \qquad F' = M \, a'$$

The symbols will be primed to distinguish them from those in the previous discussion.

$$F' = K \, V'$$

The acceleration is negative, so

$$(29) \qquad K \, V' = - M \, a$$

$$(30) \qquad a' = \frac{d \, v'}{d \, t'}$$

$$(31) \qquad - \frac{K \, V'}{M} = \frac{d \, v'}{d \, t'}$$

$$(32) \qquad d \, t' = - \frac{M \, d \, v'}{K \, V'}$$

$$(33) \qquad t' = - \int \frac{M \, d \, v'}{K \, V'} + C$$

-43-

(34) $\qquad t' = -\dfrac{M}{K} \ln V' + C$

To find C take the instant the circuit was broken.

$\qquad t' = 0$

(35) From equation (5) $\dfrac{ds}{dt} = \dfrac{96500 \times 10^7}{K}\left[1 - \dfrac{1}{e^{\frac{tK}{M}}} \right]$

(36) $\qquad V' = \dfrac{96500 \times 10^7}{K} \cdot \dfrac{e^{\frac{tK}{M}} - 1}{e^{\frac{tK}{M}}}$

(37) $\qquad C = \dfrac{M}{K} \ln\left[\dfrac{96500 \times 10^7}{K} \cdot \dfrac{e^{\frac{tK}{M}} - 1}{e^{\frac{tK}{M}}} \right]$

(38) $\qquad t' = \dfrac{M}{K}\left[\ln\left(\dfrac{96500 \times 10^7}{K} \cdot \dfrac{e^{\frac{tK}{M}} - 1}{e^{\frac{tK}{M}}} \right) - \ln V' \right]$

(39) $\qquad t' = \dfrac{M}{K} \ln \dfrac{96500 \times 10^7 (e^{\frac{tK}{M}} - 1)}{K\, e^{\frac{tK}{M}}\, V'}$

(40) $\qquad V' = \dfrac{ds'}{dt'}$

(41) $\qquad t' = \dfrac{M}{K} \ln \dfrac{96500 \times 10^7 (e^{\frac{tK}{M}} - 1)}{K\, e^{\frac{tK}{M}}\, \dfrac{ds'}{dt'}}$

(42) $\qquad \dfrac{Kt'}{M} = \ln \dfrac{96500 \times 10^7 (e^{\frac{tK}{M}} - 1)}{K\, e^{\frac{tK}{M}}\, \dfrac{ds'}{dt'}}$

(43) $\qquad e^{\frac{Kt'}{M}}\, \dfrac{ds'}{dt'} = \dfrac{96500 \times 10^7 (e^{\frac{tK}{M}} - 1)}{K\, e^{\frac{tK}{M}}\, \dfrac{ds'}{dt'}}$

$$(44) \qquad e^{\frac{tK}{M}} \frac{ds'}{dt'} = \frac{96500 \times 10^7 \, \ell \, (e^{\frac{tK}{M}} - 1)}{K \, e^{\frac{tK}{M}}}$$

$$(45) \qquad ds' = \left[\frac{96500 \times 10^7 \, (e^{\frac{tK}{M}} - 1)}{K \, e^{\frac{tK}{M}}} \right] \frac{dt'}{e^{\frac{Kt'}{M}}}$$

$$(46) \qquad s' = \left[\frac{96500 \times 10^7 \, (e^{\frac{tK}{M}} - 1)}{K \, e^{\frac{tK}{M}}} \right] \int \frac{dt'}{e^{\frac{t'K}{M}}} + C$$

$$(47) \qquad s' = -\left[\frac{96500 \times 10^7 \, \ell (e^{\frac{tK}{M}} - 1) M}{K^2 \, e^{\frac{tK}{M}}} \right] \int e^{-\frac{Kt'}{M}} \, d(-\frac{Kt'}{M}) + C$$

$$(48) \qquad s' = -\frac{96500 \times 10^7 \, \ell (e^{\frac{tK}{M}} - 1) M}{K^2 \, e^{\frac{tK}{M}} \, e^{\frac{t'K}{M}}} + C$$

If $t' = 0$
  $s = 0$

$$(49) \qquad C = \frac{96500 \times 10^7 \, (e^{\frac{tK}{M}} - 1) M}{K^2 \, e^{\frac{tK}{M}}}$$

$$(50) \qquad s' = \frac{96500 \times 10^7 (e^{\frac{tK}{M}} - 1) M}{K^2 \, e^{\frac{tK}{M}}} \left[1 - \frac{1}{e^{\frac{Kt'}{M}}} \right]$$

If t' is infinite the ion stops.

$$(51) \qquad s' = \frac{96500 \times 10^7 \, (e^{\frac{tK}{M}} - 1) M}{K^2 \, e^{\frac{tK}{M}}}$$

Let D be the total distance covered in starting and stopping.

D = S + S' (See equations (27) and (51).

$$(52) \quad D = \frac{96500 \times 10^7}{K} t + \frac{96500 \times 10^7}{K^2} M \cdot \frac{1 - e^{\frac{tK}{M}}}{e^{\frac{tK}{M}}}$$

$$+ \frac{96500 \times 10^7}{K^2} M \cdot \frac{e^{\frac{tK}{M}} - 1}{e^{\frac{tK}{M}}}$$

$$(53) \quad D = \frac{96500 \times 10^7 \, t}{K}$$

This expression is perfectly general and applies to any ion. Of course, the constant K is different for different ions. It may be easily determined for any ion. The specific conductivity (c) of an electrolyte is defined as the number of coulombs per second which pass under a potential gradient of one volt per centimeter, in a tube of one square centimeter cross section.

Let n be the concentration of the dissolved salt expressed in equivalents per cubic centimeter.

Let y be the degree of dissociation.

Then ny is the number of equivalents of each ion per cubic centimeter. An equivalent of ion carries 96500 coulombs. Let the velocity of the ion be

V_A and V_C. Then the electrolyte will carry 96500 ny $(V_A + V_C)$ coulombs per second in a tube of one square centimeter cross section under unit potential gradient.

$$C = 96500 \text{ ny } (V_A + V_C)$$

The equivalent conductivity (A) is the specific conductivity divided by the concentration of the salt in equivalents per cubic centimeter.

$$(54) \qquad A = \frac{96500 \text{ ny } (V_A + V_C)}{n}$$

$$(55) \qquad A = 96500 \text{ y } (V_A + V_C)$$

The ionic conductivity (1) is that part of the equivalent conductivity due to the ion considered. It evidently is 96500 y V.

$$(56) \qquad 1 = 96500 \text{ y } V.$$

Suppose we have a salt in solution, which dissociates into an anion A^- and a cation C^+. Let 1_A be the ionic conductivity of A^- and 1_C of C^+. y is necessarily the same for both ions.

$$(57) \qquad y \ V_A = \frac{1_A}{96500}$$

$$(58) \qquad y \ V_B = \frac{1_B}{96500}$$

yV is the average velocity of the ion under unit potential gradient. As mentioned before, when an ion has reached its maximum velocity, the resisting

force is equal to the applied force. By equation (2) the applied force is 96500×10^7 dynes. By equation (3) the resisting force is equal to K times the maximum average velocity, So:

(59)
$$K_A \frac{1_A}{96500} = 96500 \times 10^7$$

(60)
$$K_A = \frac{(96500)^2 \; 10^7}{1_A}$$

Similarly,

(61)
$$K_C = \frac{(96500)^2 \; 10^7}{1_C}$$

K_A and K_C are the K of equation (7). The subscripts are used to denote anions and cations respectively.

Rewriting equation (53)

(62)
$$D_A = \frac{96500 \times 10^7 \; t}{\dfrac{96500 \cdot 10^7}{1_A}}$$

(63)
$$D_A = \frac{1_A \; t}{96500}$$

Similarly

(64)
$$D_C = \frac{1_C \; t}{96500}$$

D_A and D_C represent the distance traveled by the anion and the cation respectively, if unit potential gradient is applied for time t. Of course, t may be as small as we please. The transport number for the ion is from the definition, $\dfrac{D_A}{D_A + D_C}$

-48-

So if the transport number is x,

$$(65) \quad x = \frac{\dfrac{l_A t}{96500}}{\dfrac{l_A t}{96500} + \dfrac{l_C t}{96500}}$$

$$(66) \quad x = \frac{l_A}{l_A + l_C}$$

A pulsating current fulfills the above conditions if the time during which the potential gradient is cut off, is long enough to allow the ions to come to rest. So the transport number for the anion, using a pulsating current, is

$$\frac{l_A}{l_A + l_C} \; .$$

If a steady current is used the transport number is

$$\frac{y\,V_A}{y(V_A + V_C)} .$$

By equations (57) and (58) $\quad y\,V_A = \dfrac{l_A}{96500}$, and $y\,V_C = \dfrac{l_C}{96500}$

Then $\dfrac{y\,V_A}{y(V_A + V_C)} = \dfrac{\dfrac{l_A}{96500}}{\dfrac{l_A}{96500} + \dfrac{l_C}{96500}} = \dfrac{l_A}{l_A + l_C} \; .$

The transport number, using a steady current is

$$\frac{1_A}{1_A + 1_C}$$, the same as that using a pulsating current.

However, the transport number under conditions of starting and stopping are different and are different from that with a steady current. It is merely the resultant of the two that is equal to that with a steady current.

CONCLUSION.

The above considerations show that the transport number, using a pulsating current, should be the same as when using a steady current. The experimental results show the same thing. So, it may be safely stated that the transport number using a pulsating current is the same as that when using a steady current.