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G. D. Robbins

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ELECTRICAL CONDUCTIVITY OF MOLTEN FLUORIDES. A REVIEW

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ABSTRACT/SUMMARY

A review of electrical conductivity measurements in molten fluoride systems covering the period 1927 to 1967 has been made, with particular emphasis on experimental approach. It is pointed out that the common practice of measuring resistance with a Wheatstone bridge having a parallel resistance and capacitance, R_p and C_p, in the balancing arm can result in considerable error if the relation $R_p = R_s[1 + R_p^2C_p^2(2\Pi f)^2]$ is not employed in determing the solution resistance, R_s. The frequency dependence of the measured resistance and the practice of extrapolating measured resistances to infinite frequency versus $1/\sqrt{f}$ is examined in terms of electrode process concepts. A summary of experimental approaches and results for 56 molten fluoride systems is presented.

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ELECTRICAL CONDUCTIVITY OF MOLTEN FLUORIDES. A REVIEW*

Introduction

Invesitgation of the electrical conductivity of molten salt systems has been an area of lively research in recent years, and a number of reviews have appeared which deal with this aspect of transport phenomena.[1-3] It will be the intent of this review to limit itself to the subject of conductance measurements in molten fluorides. The containment problems encountered with these materials set them apart from the other molten halides with respect to experimental difficulties and the consequent precision of measurement which can be expected. By limiting this review to fused fluorides, it is hoped that sufficient details may be presented to permit workers in the field to obtain a comprehensive survey covering the period 1927 to 1967. To our knowledge, no such review exists which addresses itself to the questions which we pose below.

Many investigations in the past have been concerned with cryolite-containing melts because of their relevance to the aluminum industry, and a review of these systems has been given by Grjotheim and Matiasovsky.[4] Renewed interest in the transport properties of fused fluorides in general has resulted from their use as fuel, blanket, and coolant materials in molten salt reactors.[5]

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Because of the high specific conductance of most molten salts (1-6 Ω^{-1} cm^{-1}),[6] experimental approaches have tended to fall into two groups[1]: (1) use of capillary-containing cells, which results in a cell constant of several hundred cm^{-1}, the capillaries being constructed from electrically insulating materials; or (2) use of metallic cells in which the container is usually one electrode, with a second electrode positioned in the melt. The latter type of cells have cell constants of the order of a few tenths cm^{-1}, requiring very accurate measuring bridges and determination of lead resistances. Since the value of measured resistance in such cells is less than 1Ω, errors due to temperature gradients, changes in cell constant with temperature, and polarization become a significant problem. Hence, cells of type (1) are clearly desirable for use in molten salts. However, electrically insulating materials for capillary construction which are resistant to attack by molten fluorides are scarce.

Measurement of electrical conductivity in molten salts differs from similar studies in aqueous solutions in several significant aspects. It is often the practice to employ some form of a Wheatstone bridge[7] (Figure 1) in which the two upper arms are matched, standard resistances, and the impedance of the cell in one lower arm is balanced by a variable impedance, Z, in the fourth arm. The balancing impedance is usually a variable resistance, R_p, and capacitance, C_p, connected in parallel. The solution resistance, R_s, and solution-electrode interfacial capacitances, C_s, in the cell are considered to be in series[8] (Figure 2). By requiring

one electrode to have a much greater area than the other, the impedance associated with such an electrode becomes negligible, and the equivalent circuit reduces to that shown in Figure 3. (Alternatively, one can employ electrodes of similar area and treat the capacitance resulting from their series combination as a single total capacitance, $\frac{1}{C_s} = \frac{1}{C_{s_1}} + \frac{1}{C_{s_2}}$.) The capacitance resulting from the electrode leads is in parallel across the entire cell shown in Figure 2. However, at frequencies ordinarily employed, and with some care in positioning, this capacitance can be neglected.

When a sinusoidal alternating potential is impressed across the cell, a sinusoidal alternating current results. If the potential is insufficient to cause electrochemical reactions to occur at the electrodes, the equivalent circuit of Figure 3 is valid, and the interfacial capacitance is charged and discharged during each half-cycle through the solution resistance. By employing an oscilloscope as the null detector, one can balance the cell impedance with the parallel combination of R_p and C_p shown in Figure 1. The two balance equations (when the standard resistances are matched) are

$$\frac{R_s}{R_p} + \frac{C_p}{C_s} = 1 \qquad (1)$$

and

$$R_s R_p C_s C_p (2\Pi f)^2 = 1 \qquad (2)$$

These may be combined into

$$R_p = R_s[1 + C_p{}^2 R_p{}^2 (2\Pi f)^2] \qquad (3)$$

It is often the practice to equate R_p (the value of the bridge dials) to R_s (the true solution resistance).[9,10] (In the case of unmatched standard resistors, their ratio is used.) This

is usually valid in aqueous solutions where R_s and C_s are such as to result in $R_p^2 C_p^2 (2\Pi f)^2$ being negligibly smaller than unity. However, in molten salts experimental conditions for the measurement of electrical conductance can result in considerable error if these equations are not considered when using parallel components in the balancing arm of a Wheatstone bridge. For example, on rewriting equations (2) and (3) in the form

$$R_p = R_s[1 + \frac{1}{C_s^2 R_s^2 (2\Pi f)^2}] \qquad (4)$$

it is evident that in molten salts, where R_s^2 may be smaller by a factor of 10^{10} that in aqueous solutions* (C_s having approximately similar values[13]), an awareness of these relations is necessary.

Use of equation (3) to calculate R_s is limited by the accuracy with which the values of the variable capacitance, C_p, and the frequency are known. Use of precision capacitors can be avoided by employing a bridge in which the balancing components are in series.[14] Then in the case of no electrochemical reaction, the value of R_s is well represented by the reading on the balanced bridge; however, this method does require the use of large capacitors.

When a sufficiently large a.c. potential is impressed on the cell that charge is transferred across the solution-electrolyte interfaces during part of each half-cycle, corresponding to an electrochemical reaction, the situation becomes considerably more complex. However, it is under these conditions

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*The measured resistance of 0.0005 m KCl in cells employed by Jones and Bollinger[11] was approximately 50,000 Ω. Cuthbertson and Waddington[12] report a measured resistance of approximately 0.5 Ω in molten cryolite.

that conductivity measurements are usually performed. Based on the work of Jones and Christian,[15] resistance in aqueous systems is generally measured at a series of frequencies and extrapolated to infinite frequency employing the functional form $f^{-\frac{1}{2}}$. Use of this particular functional form is attributed[15] to Warburg[16,17] and Neumann[18] who, on the basis of Fick's laws of diffusion, predicted that the polarization resistance (that part of the measured resistance due to electrode polarization) was inversly proportional to $\sqrt{f}$.

Applying the concepts resulting from electrode process studies,[19-21] one may envision the equivalent circuit shown in Figure 4 for an electrode-solution interface across which charge is being transferred. Z_r represents the impedance associated with the reaction, which is in parallel with the solution-electrode interfacial capacitance. Under the exacting assumptions of faradaic impedance studies, Z_r may be represented by a frequency-independent resistance, Θ, in series with a frequency-dependent impedance, -W-, the Warburg impedance. The latter is conveniently represented as a resistance and capacitance in series, R_r and C_r, at constant frequency (Figure 5). At a given frequency the impedances resulting from R_r and C_r are equal. However, both vary as $f^{-\frac{1}{2}}$.

The assumptions upon which the mathematical analysis which results in $f^{-\frac{1}{2}}$ dependance of R_r and $\frac{1}{2\Pi f C_r}$ rests include 1) semi-infinite linear diffusion of reactants and products and 2) a small amplitude a.c. potential superimposed on a net d.c. polarizing potential. These are not the conditions of conductivity measurements. However, during that part of each

half-cycle during which reaction is occurring at the electrodes, the equivalent circuit of Figure 4 is a useful concept, even though Z_r may not be treated rigorously according to Figure 5. That the above considerations lead to the same frequency dependence as that experimentally determined for many conductivity measurements[15] renders this conceptual analysis worth considering.

In brief, then, one may consider the equivalent circuit of Figure 4 as a rough analog of the solution resistance, electrode-solution interfacial capacitance, and reaction impedance (bearing in mind that Z_r cannot be represented exactly by any finite combination of resistance, capacitance, and inductance which will render it frequency independent). During that part of each half-cycle in which the potential is below that which results in an electrode reaction, the equivalent circuit of Figure 4 reduces to that of Figure 3, i.e., Z_r becomes infinite. It is also useful to consider the equivalent circuit of Figure 4 in view of the practice of extrapolating measured resistance to infinite frequency. It can be seen that at infinite frequency the impedance of C_s is infinitely less than that of Z_r, and Figure 4 again reduces to Figure 3.

It should be emphasized that while one measures resistance at a series of frequencies and extrapolates to infinite frequency, one does not make measurements at frequencies which approach infinity. In fact, very high frequency measurements (in the megahertz range) are to be avoided because of the increased admittance of the leads and the fact that at very high frequencies one ceases to measure a property assoicated with ionic

mobility and observes properties associated with dipole moments and polarizabilities. Hence the question of concern remains viz, what functional form of the frequency does one employ to extrapolate the measured resistance to infinite frequency?

Robinson and Stokes[22] consider this question in terms of electrode process concepts as applied to aqueous media and give balance equations for a bridge with a parallel-component balancing arm, assuming various relative magnitudes of R_s, Θ, and R_r. Under the conditions employed by Jones and Christian,[15] $f^{-\frac{1}{2}}$ dependence is predicted. Robinson and Stokes conclude that one should measure resistance as a function of frequency and extrapolate to infinite frequency in accordance with the observed behavior. This is also the conclusion of Nichol and Fuoss,[23] who observed a f^{-1} frequency dependence of resistance in methanol solutions.

In molten salts frequency dependence of the resistance has been reported at polarizing potentials much lower than required for faradaic processes.[24,25] Buckel and Tsaussoglou[26] have found that measured resistance vs. frequency plots show a plateau in the range 10-100 kHz in aqueous potassium chloride and molten potassium bromide. They suggest that extrapolation of resistance vs. $f^{-\frac{1}{2}}$ would lead to erroneous conductances and that one should study frequency dispersion in a particular apparatus and select a frequency-independent region for performing conductivity experiments. De Nooijer[27] reported that in molten nitrate melts plots of measured resistance vs. $f^{-\frac{1}{2}}$ were not linear, but approached linearity as the frequency approached infinity. His

values of measured resistance at 20 kHz only differed from values extrapolated to infinite frequency by about 0.1 %. Winterhager and Werner[28,29] have considered frequency dispersion in molten nitrate, chloride, and fluoride melts and have applied "electrical locus curve theory"[30] to their results obtained employing a Thomson-type bridge. They conclude that at sufficiently high frequencies measured resistance becomes independent of frequency, and they employ a measuring frequency of 50 kHz. Therefore, in this review particular attention will be given to the observed behavior of resistance with frequency and to the condition of the electrode surfaces, since in aqueous mdeia it is observed that frequency dispersion is less in cases of heavy platinization (increased C_s).[11]

In light of the foregoing discussion the following information was sought from each study which was consulted:

A. Cell material, its general design, and the resulting cell constant, (ℓ/a), or general range of measured resistance, $\{R\}$.

B. Electrode material, shape, size, and surface character.

C. Type of bridge employed.*

D. Frequency range employed.

E. Dependence of measured resistance on frequency.

F. Voltage applied to the bridge.

G. Results. Results are reported either in terms of the

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*The general types of bridge circuits employed are shown in Appendix I as an aid in description. The circuits actually employed were usually modified versions of those shown. For details of circuity, the reader is referred to the cited work.

specific conductance, κ, the equivalent conductance, Λ^{eq}, or the molar conductance, Λ^{m}. These quantities are defined as

$$\kappa = \frac{1}{R} (\ell/a) \tag{5}$$

$$\Lambda^{eq} = \kappa \cdot \frac{\text{equivalent weight}}{\text{density}} \tag{6}$$

$$\Lambda^{m} = \kappa \cdot \frac{\text{molecular weight}}{\text{density}} \tag{7}$$

These quantities are reported as functions of temperature for the minimum, maximum, and one intermediate value for pure salts. For binary mixtures a 3 x 3 grid also stating the extremes and one intermediate value of composition is employed where convenient. Conductivities of mixtures of more than two components are presented in a manner designed to convey maximum information.

The tabulation is ordered according to the system under consideration; and within each system, by date of publication, the earliest appearing first. Where one investigation has covered several systems, a cross reference is given. Additional values of κ and Λ may be found in Janz's Molten Salts Handbook[31] for many of the systems reported here. As previously stated, the primary concern of this review is topics A-F. The results presented herein are given for comparison and completeness and were, in all cases, taken from the original publications (exception: Appendix II).

It will be observed below that a number of publications have not addressed themselves to some of the questions raised above. If this review serves only to remedy this practice, it is considered justified.

TABULATION

#	System	Ref	Cell {R} or (ℓ/a)	Electrodes	Bridge (Detector)	f Range (kHz)	R vs. f	Vpp (v)	Results T(°C)	κ(Ω⁻¹cm⁻¹) or Λ(cm²Ω⁻¹eq⁻¹(mol⁻¹))
1	LiF	32	Pt crucible {R} ≃ 0.1 Ω	Pt crucible and platinized Pt foil (3 x 4 mm)	Wheatstone (telephone)	6	N.S. = Not Stated	N.S.	905 950 995	κ 20.3 23.4 27.2 (±5 to 10%)
2	LiF	33	Two Pt (80%) - Rh hemispheres (d = ¾" & 2"). These are also current electrodes.	Two Pt (80%) - Rh rods (d = .01"). These are potential-measuring electrodes.	Specially developed by E. Fairstein.(34) f range=.2-6 kHz R range=.01-10Ω (oscilloscope)	N.S.	N.S.	N.S.	847-1027	$\kappa = 3.805 + 1.004\times10^{-2}T(^{\circ}C) - 3.516\times10^{-6}T^2$ (σ=.008Ω⁻¹cm⁻¹)
3	LiF	35 36	Hot-pressured BN cylinder (id = 3/16") surrounded by graphite {R} ≃ 3-6 Ω. (ℓ/a) = 17-39 cm⁻¹	Inconel rod and inconel plate across ends of BN cylinder.	Wheatstone, no capacitors (oscilloscope)	2	"did not vary appreciably between 1 and 20 kHz	N.S.	900 Θ=1.05	κ = 8.43 Λ^{eq} = 128 (±1%)
4	LiF	28 29	Pt crucible (vol. = 39 cm³) (ℓ/a) ≃ 0.28 cm⁻¹	Two platinized Pt foils (10 x 10 mm)	Thomson-type (oscilloscope)	50	f-dependency at lower f, independent at 50 kHz	~.05	875 958 1037	8.663 9.058 9.306
5	LiF	37	Graphite crucible (id = 3.5", 5" deep) containing 2 BN cylinders (id = 3/16") encased in graphite and enlarged at top to accomodate electrodes.(ℓ/a) ≃ 100cm⁻¹	Two ¼" Mo tubes fitting into upper portions of BN cylinders	Jones (null detector)	10	f independent 1-20 kHz	N.S.	870-1010 Θ=1.2	$\kappa = 9.06 + 5.83\times10^{-3}(T-870^{\circ}C)$ Λ^{eq} = 160.8 (±1%)
6	NaF	38 39	Pt crucible (400 ml), (ℓ/a) = 0.0835cm⁻¹	Hemispherical Pt electrodes, platinized originally.	Kelvin	.6 to 4	$R \propto f^{-\frac{1}{2}}$ extrapolated to f = ∞	10	1000 1040 1080	κ 5.52 5.74 5.95 Λ^{eq} 118 (±several %)
7	NaF	40	Pt crucible (0.2 mm wall) {R} ≃ 0.02 Ω	Crucible and a Pt cylinder (area = 2 cm²), both platinized	N.S.	.15 to 8	N.S.	N.S.	997	$\kappa = 5.2_5$*
8	NaF	35 36	#3	#3	#3	#3	#3	#3	1020 Θ=1.05	κ = 5.15 Λ^{eq} = 113 (±1%)
9	NaF	28 29	#4	#4	#4	#4	#4	#4	1003 1086 1138	4.960 5.179 5.335
10	NaF	37	#5	#5	#5	#5	#5	#5	1030-1090 Θ=1.2	$\kappa = 5.29 + 5.64\times10^{-3}(T-1030^{\circ}C)$ Λ^{eq} = 156.6 (±1%)
11	KF	32	#1	#1	#1	#1	#1	#1	860 900 1000	κ 4.14 4.28 4.77 (±5 to 10%)
12	KF	33	#2	#2	#2	#2	#2	#2	869 1040	$\kappa = -3.493 + 1.480\times10^{-2}T(^{\circ}C) - 6.608\times10^{-6}T^2$ (σ=.009Ω⁻¹cm⁻¹)

#	System	Ref	Cell {R} or (ℓ/a)	Electrodes	Bridge (Detector)	f Range (kHz)	R vs. f	Vpp (v)	Results T(°C)	κ(Ω⁻¹cm⁻¹) or Λ(cm²Ω⁻¹eq⁻¹(mol⁻¹))
13	KF	35 36	#3	#3	#3	#3	#3	#3	900 Θ=1.05	κ = 3.80 Λ^{eq} = 124 (±1%)
14	KF	28 29	#4	#4	#4	#4	#4	#4	859 938 1012	3.573 3.793 4.021
15	KF	41 42 43	MgO, single crystal, dip cell; Pt container	Container and Pt electrode	Jones	.5-10	varied <0.3% over f range	N.S.	905	3.77 (±2%)
16	CsF	33	#2	#2	#2	#2	#2	#2	725-921	$\kappa = -4.511 + 1.642\times10^{-2}T(^{\circ}C) - 7.632\times10^{-6}T^2$ (σ=.009$\Omega^{-1}cm^{-1}$)
17	CsF	42 43	#15	#15	#15	#15	#15	#15	737 784 852	2.51 2.73 3.03
18	AgF	28 29	#4	#4	#4	#4	#4	#4	590 670	4.0* 6.0*
19	BeF_2	44 45	Pt-Rh (20%) crucible (id = 2", ht. = 2½") (ℓ/a) = .11 or .28cm⁻¹	Crucible and Pt-Rh (20%) bob	"Wheatstone R-C bridge" (scope or VTVM)	2-10	f independent 2-10 kHz	N.S.	700 800 950	κ 0.71×10^{-5} 15.3×10^{-5} 236×10^{-5} (±10%)
20	CaF_2	46	Carbon crucible	Mo electrodes	N.S.	N.S.	N.S.	N.S.	1418	κ = 3.56
21	MnF_2	28 29	#4	#4	#4	#4	#4	#4	940 990	4.7* 5.0*
22	CuF_2	28 29	#4	#4	#4	#4	#4	#4	970 1110	2.2* 2.5*
23	ZnF_2	28 29	#4	#4	#4	#4	#4	#4	900 960	3.2* 3.7*
24	PbF_2	28 29	#4	#4	#4	#4	#4	#4	820 1000	5.1* 5.8*
25	KBF_4	28 29	#4	#4	#4	#4	#4	#4	545 569 652	1.052 1.126 1.245
26	Na_2TaF_7	28 29	#4	#4	#4	#4	#4	#4	702 733 814	1.165 1.396 1.595
27	K_2TiF_6	28 29	#4	#4	#4	#4	#4	#4	843 888 976	1.346 1.435 1.604
28	K_2TaF_7	28 29	#4	#4	#4	#4	#4	#4	747 800 887	0.7285 0.9193 1.0366

#	System	Ref	Cell {R} or (ℓ/a)	Electrodes	Bridge (Detector)	f Range (kHz)	R vs. f	Vpp (v)	Results T(°C)	κ($\Omega^{-1}cm^{-1}$) or Λ($cm^2\Omega^{-1}eq^{-1}(mol^{-1})$)
29	Li_3AlF_6	35 36	#3	#3	#3	#3	#3	#3	800 920	κ = 3.45* κ = 3.87*
30	Na_3AlF_6	12	Fused MgO tube (d = .99, ℓ = 10.3 cm) (ℓ/a) = .0752 cm^{-1}	Graphite plates across ends of tube	Wheatstone, R and C in parallel (telephone)	two f's	N.S.	N.S.	1020	κ = 1.5_7
31	Na_3AlF_6	39	#6	#6	#6	#6	#6	#6	1000 1040 1080	κ 2.80 2.90 3.00 $\Lambda^{eq} = 2.744 - \frac{980}{T(^\circ K)}$ (± several %)
32	Na_3AlF_6	40	#7	#7	#7	#7	#7	#7	1013	κ = 2.8_2*
33	Na_3AlF_6	35 36	#3	#3	#3	#3	#3	#3	1000 1060	κ / Λ^m 2.80* / 284 at 1010° 2.95* / 296 at 1040°
34	Na_3AlF_6	28 29	#4	#4	#4	#4	#4	#4	1025 1120	2.8* 3.0_5*
35	Na_3AlF_6	47	Pt hemisphere (od = 4 cm), (ℓ/a) = .386 cm^{-1}	Container and Pt rod (d = 3 mm)	Thomson plus phase indicator	5	N.S.	N.S.	1000 1040 1080	κ 2.84 2.92 3.00
36	K_3AlF_6	35 36	#3	#3	#3	#3	#3	#3	1000 1060	κ 2.22* 2.42*
37	LiF + ThF_4	37	#5	#5	#5	#5	#5	#5	LiF-ThF_4 96.8-3.2(m%) 78-22(m%) 50.2-49.8(m%)	 κ = 7.14 + 10.97x10^{-3}(T-880°C) Λ^{eq} = 117.2, for Θ = 1.2 κ = 2.50 + 7.58x10^{-3}(T-640°C) Λ^{eq} = 29.9, for Θ = 1.2 κ = 2.13 + 4.19x10^{-3}(T-820°C) Λ^{eq} = 31.0, for Θ = 1.2 (±1%)
38	LiF+UF_4	37	#5	#5	#5	#5	#5	#5	LiF-UF_4 95-5(m%) 60-40(m%) 40-60(m%)	 κ = 7.55 + 5.86x10^{-3}(T-900°C) Λ^{eq} = 99.3, for Θ = 1.2 κ = 2.17 + 5.68x10^{-3}(T-700°C) Λ^{eq} = 23.8, for Θ = 1.2 κ = 2.89 + 3.29x10^{-3}(T-900°C) Λ^{eq} = 33.5, for Θ = 1.2 (±1%)
39	NaF + CaF_2 (67 w%)	48	Pt crucible {R} ≃ 0.1Ω	Curcible and Pt rod, both platinized originally	Carey-Foster	1	N.S.	N.S.	900 1000 1100	κ 4.837 5.373 5.879 (±.5%)

#	System	Ref	Cell {R} or (ℓ/a)	Electrodes	Bridge (Detector)	f Range (kHz)	R vs. f	Vpp (v)	Results T(°C)	κ(Ω⁻¹cm⁻¹) or Λ(cm²Ω⁻¹eq⁻¹(mol⁻¹))
40	NaF + SrF_2 (67 w%)	48	#39	#39	#39	#39	#39	#39	900 1000 1100	κ 4.441 4.961 5.642 (±.5%)
41	NaF + BaF_2 (67 w%)	48	#39	#39	#39	#39	#39	#39	900 1000 1100	κ 4.027 4.602 5.319 (±.5%)
42	NaF + ZrF_4	49	Hot-pressed BeO tube in a cylindrical Pt crucible (ℓ/a) ≃ 24 cm^{-1}	Pt crucible across bottom of the tube and Pt rod at top	Wheatstone, R and C in parallel (oscilloscope)	1	N.S.	N.S.	NaF-ZrF_4 57-43(m%) 50-50(m%)	565°: κ = 0.82 730°: κ* = 1.27 885°: κ = 2.10 0.52, 0.92, 1.73 (±10%)
43	NaF + ThF_4	37	#5	#5	#5	#5	#5	#5	NaF-ThF_4 88-12(m%) 67-33(m%) 50-50(m%)	κ = 3.49 + 3.74x10⁻³(T-900°C) Λ^{eq} = 71.3, for Θ = 1.2 κ = 1.76 + 3.88x10⁻³(T-800°C) Λ^{eq} = 28.1, for Θ = 1.2 κ = 1.48 + 5.23x10⁻³(T-800°C) Λ^{eq} = 28.6, for Θ = 1.2 (±1%)
44	NaF + UF_4	37	#5	#5	#5	#5	#5	#5	NaF-UF_4 85-15(m%) 65-35(m%) 25-75(m%)	κ = 2.81 + 3.56x10⁻³(T-850°C) Λ^{eq} = 57.7, for Θ = 1.2 κ = 1.37 + 4.65x10⁻³(T-700°C) Λ^{eq} = 26.6, for Θ = 1.2 κ = 2.18 + 3.56x10⁻³(T-900°C) Λ^{eq} = 36.9, for Θ = 1.2 (±1%)
45	NaF + $NaBF_4$	50	Described in Ref. 51, not readily available	Pt electrodes	Wheatstone, with balancing R (oscilloscope)	5	N.S.	N.S.	NaF-$NaBF_4$ 60-40(w%) 40-60(w%) 10-90(w%)	450°: κ 650°: κ 800°: κ –, –, 6.502 0.905, 6.350, 14.105 2.408, 8.801, 14.978
46	NaF + Na_3AlF_6	38 39	#6	#6	#6	#6	#6	#6	NaF-Na_3AlF_6 76.9-23.1(m%) 50-50(m%) 35.7-64.3(m%)	1000°: κ, 1040°: κ, 1080°: κ, $\Lambda^{eq}_{1000°}$ 3.86, 4.00, 4.14, 109 3.19, 3.30, 3.41, 99 3.12, 3.23, 3.33, 100
47	KF + KBF_4	50	#45	#45	#45	#45	#45	#45	KF-KBF_4 70-30(w%) 40-60(w%) 10-90(w%)	450°: κ 650°: κ 800°: κ –, –, 5.001 –, 2.255, 11.495 0.281, 3.601, 12.703
48	MgF_2 + Na_3AlF_6	52	Pt cell	N.S.	Wheatstone, R and C in parallel (oscilloscope)	N.S.	N.S.	N.S.	(data taken from graphs) MgF_2-Na_3AlF_6 18-82(w%) 10-90(w%) 1-99(w%)	κ 1070° 2.8 2.2 2.8

#	System	Ref	Cell {R} or (ℓ/a)	Electrodes	Bridge (Detector)	f Range (kHz)	R vs. f	Vpp (v)	Results T(°C) κ(Ω⁻¹cm⁻¹) or Λ(cm²Ω⁻¹eq⁻¹(mol⁻¹))
49	CaF_2 + Na_3AlF_6	53 12	Graphite crucible {R} ≃ 0.5Ω	Carbon anode and molten Al cathode	Wheatstone, $\vec{R}$ and $\vec{C}$ in parallel (telephone)	two f's	N.S.	N.S.	CaF_2-Na_3AlF_6 $\Lambda^m_{1000°}$ 75-25(m%) 70 40-60(m%) 140 13-87(m%) 185
50	CaF_2 + Na_3AlF_6	38 39	#6	#6	#6	#6	#6	#6	CaF_2-Na_3AlF_6 1000° κ 1040° 1080° $\Lambda^{eq}_{1000°}$ 32.3-67.7(m%) 2.66 2.77 2.87 79 23-77(m%) 2.68 2.79 2.90 83 12.3-87.7(m%) 2.74 2.85 2.95 88
51	CaF_2 - Na_3AlF_6 (81m%)	35 36	#3	#3	#3	#3	#3	#3	T Λ^m 1010 232 1040 242
52	AlF_3 - Na_3AlF_6	52	#48	#48	#48	#48	#48	#48	AlF_3-Na_3AlF_6 κ 1070° 13-87(w%) 2.4 7.5-92.5(w%) 2.6 2.5-97.5(w%) 2.8
53	AlF_3 + Na_3AlF_6	38 39	#6	#6	#6	#6	#6	#6	AlF_3-Na_3AlF_6 1000° κ 1040° 1080° $\Lambda^{eq}_{1000°}$ 17.9-82.1(m%) 2.60 2.68 2.76 84 11.6-88.4(m%) 2.68 2.77 2.86 88
54	Li_3AlF_6 + Na_3AlF_6 (40w%)	35 36	#3	#3	#3	#3	#3	#3	740 2.12* 880 2.82*
55	LiF+NaF+KF(46.5-11.5-42 m%)	49	Hemispherical Pt crucible (ℓ/a) ≃ 0.162	Current electrodes: crucible and Pt sphere; potential electrodes: crucible and Pt cylinder surrounding sphere	No bridge: VTVM and ammeter	.5	N.S.	N.S.	565 1.18* 675 1.52* 815 1.80* (±10%)
56	NaF+ZrF_4+ UF_4	49	#55	#55	#55	#55	#55	#55	NaF-ZrF_4-UF_4 565° κ* 730° 885° 53.5-40-6.5(m%) 0.58 0.88 1.43 50-46-4(m%) 0.79 1.08 1.60 (±10%)

*Interpolated from a linear plot of κ vs. T

$^{+}\Theta = \frac{T \text{ measured } (°K)}{T \text{ melting } (°K)}$

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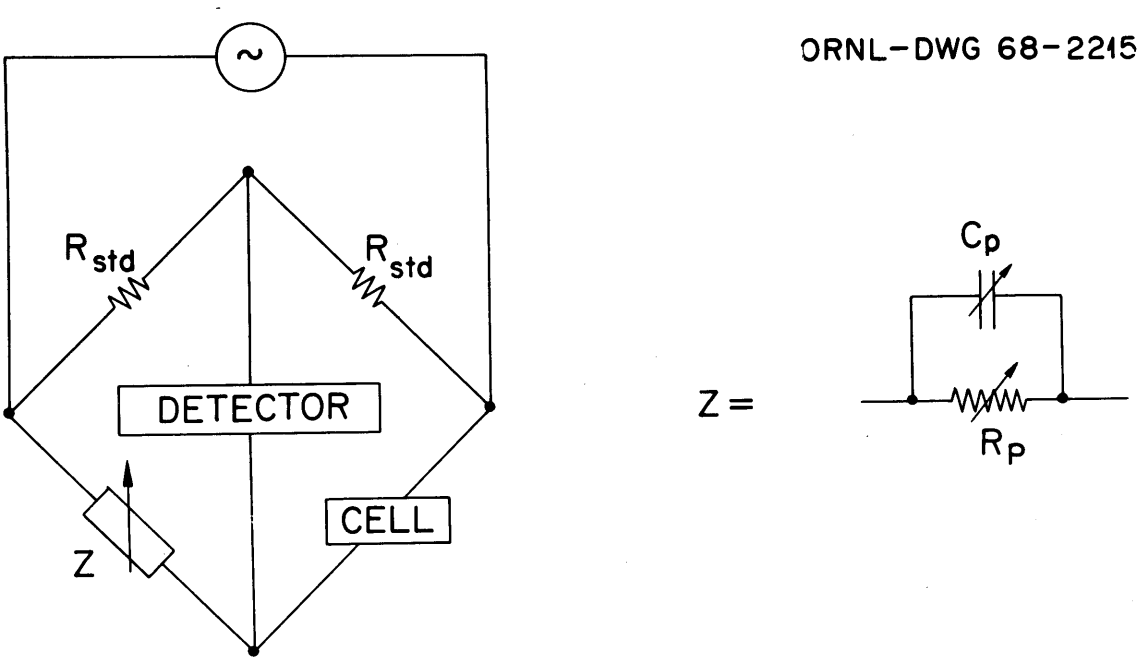

Figure 1: Wheatstone bridge: parallel-component balancing arm.

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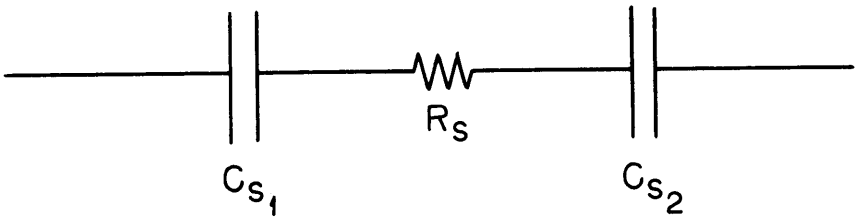

Figure 2: Equivalent circuit of cell in absence of reaction.

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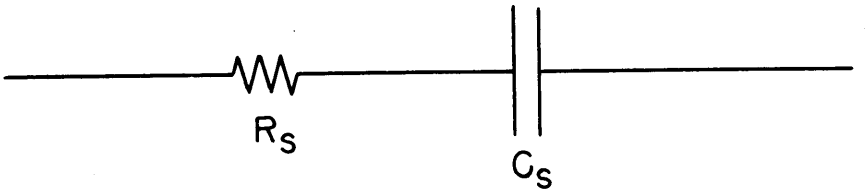

Figure 3: Equivalent circuit of solution resistance and electrode-solution interfacial capacitance in absence of reaction.

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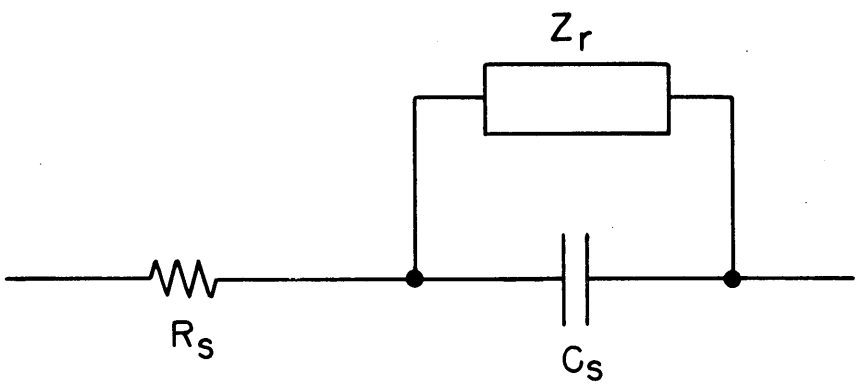

Figure 4: Equivalent circuit including reaction.

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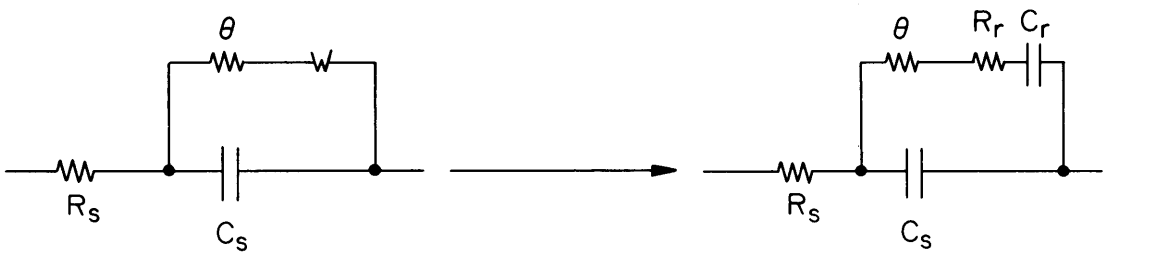


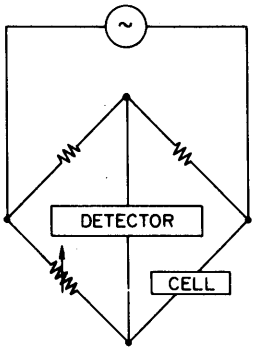
CONSTANT FREQUENCY

Figure 5: Equivalent circuit for faradaic impedance studies.

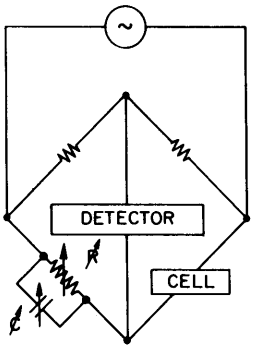
ORNL-DWG 68-2220

APPENDIX I
IMPEDANCE BRIDGES

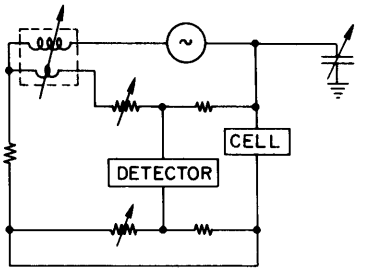
A. WHEATSTONE BRIDGE, NO CAPACITORS[54]



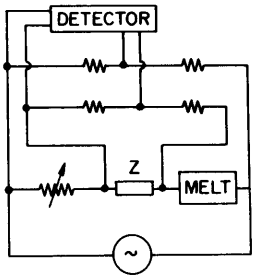
B. JONES BRIDGE[7,55] (WHEATSTONE BRIDGE, R AND C IN PARALLEL)



C. KELVIN BRIDGE[38]

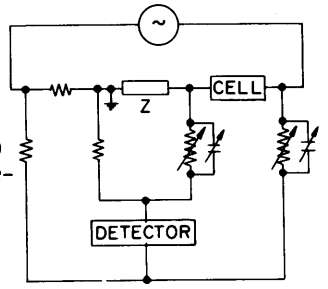


D. THOMSON BRIDGE[47]



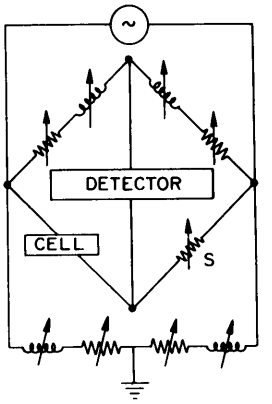
Z = IMPEDANCE OF CONNECTIONS

E. THOMSON -TYPE" BRIDGE[28,29] (EMPLOYED BY WINTER-HAGER AND WERNER)



Z = IMPEDANCE OF CONNECTIONS

F. CAREY-FOSTER BRIDGE[48] (CELL AND S ARE INTER-CHANGEABLE)



APPENDIX II

For the sake of completeness, references to those cryolite systems which could not be consulted in the original are listed in this appendix. An indication of their content, together with the secondary source, is given.

Batashev, K. and A. Zhurin, Metallurg, 10, 67 (1935); C.A., 30, 7018[9] (1936).

(κ of $KF-AlF_3$ system vs. T)

Batashev, K. P., Legkie Metally, 10, 48 (1936); ref. 4.

(κ of cryolite vs. T)

Batashev, cited by Mashovets in The Electrometallurgy of Aluminum (Russian), 1938; ref. 53.

(Λ^m of cryolite + NaF and cryolite + AlF_6)

Vayna, A., Alluminio, 19, 215 (1950); C. A., 44, 10,549d (1950) and ref. 4.

(κ of cryolite vs. T; κ of cryolite with additions of NaF, CaF_2, or AlF_3 near 1000^0C)

Abramov, G. A., M. M. Vetyukov, I. P. Gupalo, A. A. Kostyukov, and L. N. Lozhkin, "Teoreticheskie osnovy electrometallurgii alyminia," Metallurizdat, Moscow (1953); ref. 4.

(κ of cryolite vs. T)

Ponomarev, V. G., F. M. Kolomilskii, Yu. M. Putilin, Izvest. Vysshikh. Ucheb., Zavedenii, Tsvetnaya Met., 1958, No. 6, 78; C.A., 53, 14,670i (1959).

(κ of K_2TiF_6 vs. T)

Belyaev, A. I., Tsvetnye Metally, 31, No. 10, 61 (1958); C.A., 53, 6832i (1959).

(κ of cryolite with additions of LiF, NaF, BeF_2, MgF_2, CaF_2, BaF_2, or AlF_3)

Antipin, L. N., S. F. Vazhenin, and V. K. Shcherbakov, Nauch. Doklady Vysshei Shkoly, Met. 1958, 11; C.A., 55, 1241f (1961).

(κ of NaF/AlF_3 ratios of 1.6 to 3.9)

Antipin, L. N. and S. F. Vazhenin, Tsvetnye Metally, 31, No. 12, 56 (1958); C.A., 53, 7824e (1959).

(κ of cryolite with additions of CaF_2 or MgF_2)

Chu, Y. A. and A. I. Belyaev, Izvest. Vysshikh. Ucheb., Zavedenii, Tsvetnaya Met., 2, No. 2, 69 (1959); C.A., 54, 24,025i (1960).

(κ of cryolite and cryolite with additions of LiF or BeF_2)

Belyaev, A. I. and E. A. Zhemchuzhina, Tsvetnye Metally, 33, No. 4, 45 (1960); C.A., 55, 1242a (1961).

(κ of NaF/AlF_3 ratio of 2.2 to 2.78 with additions of MgF_2)

Kuvakin, M. A. and P. S. Kusakin, Trudy Inst. Met., Akad. Nauk. SSSR, Unal. Filial, 5, 145 (1960); C.A., 55, 2255i (1961).

(κ of cryolite)

Belyaev, A. I., "Elektrolit alyuminievykh vann," Metallurgizdat, Moscow, 1961; ref. 4.

(κ of cryolite with BeF_2 additions up to 17 wt. % at 1000°C)

Matiasovsky, K., S. Ordzovensky, and M. Malinovsky, Chem. zvesti, 17, 839 (1963); ref. 4.

(κ of cryolite vs. T)

Vakhobov, A. V. and A. I. Belyaev, "Vliamie razlichnykh solevykh komponentov (dobavok) na elektroprovodnost elktrolita alyuminievykh vann," in "Fizicheskaya khima rasplavlemykh solei," ed. by The Institute of General and Inorganic Chemistry of the Soviet Academy of Science., Metallurgizdat,

Moscow, 1965, pp. 99-104; ref. 4.

(κ of cryolite with additions of LiF, MgF_2, CaF_2, BaF_2, or AlF_3 up to 20 wt. % at 1000°C)

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