THE SPECIFIC CONDUCTANCE

OF

FUSED CRYOLITE--ALUMINA BATHS

A Thesis

By

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PREFACE

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K. K. Cherian.

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INTRODUCTION

General Introduction.

Canada ranks among the leading countries of the world in the production and exportation of aluminium. In addition, Canadian enterprises operate aluminium plants in several parts of the world. It is rather surprising, therefore, to find relatively little research in Canadian universities dealing with problems in aluminium production. Difficulties associated with high temperature investigations have undoubtedly contributed to this situation, particularly corrosion, contamination and temperature measurement. This thesis represents an attempt to approach the problem without the usual expensive platinum equipment.

Since the development in 1886 of the Hall-Heroult process for aluminium production (1) the position of this metal has risen from laboratory curiosity to one of leadership among the non-ferrous metals. The process consists essentially of the electrolytic reduction of alumina dissolved in cryolite. The power consumed in this process is afactor of major importance, being greater in terms of production than for any other electrolytic industry. (3).About one quarter of this power is dissipated in the resistance of the electrolyte, amounting to a loss of 6000 K.W.H. per ton of aluminium produced, or a total of 15,000 million K.W.H. for an estimated world production of 2.5 million tons of aluminium in 1954.

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This fact alone suggests a need for investigation of the conductance of fused cryolite baths used in aluminium production. Further, increased conductance of the bath would permit greater distance between the electrodes for a given power consumption. This is desirable to minimize reoxidation of the cathode aluminium.

Also, impurities introduced by the utilization of new types of raw materials, both for the alumina and the electrode, have created new problems in the electrolytic reduction practice. A knowledge of the specific effects of such impurities is necessary for an intelligent approach to these problems, and will undoubtedly contribute to improvements in the efficiency of the process.

Finally the direct deposition of aluminium alloys in the electrolytic cell would minimize the cost of preparing such alloys by melting and mixing in the usual way. Here again information concerning the behaviour of cryolite baths with various additives is of vital importance. Such information can only be obtained by a systematic study of the various factors affecting the operation of molten salt cells.

Conductance is one such factor, and this research constitutes an attempt to determine trends in the conductance of cryolite - alumina melts on addition of various salts.

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Theoretical

Conductance C and specific conductance k are the reciprocals of resistance R and specific resistance ρ . The term specific conductivity has also been used, presumably with respect to specific conductance. In electrolytic studies a quantity called the equivalent conductance has found widespread use. It is defined, for ageous solutions, as the conductance of a quantity of solution containing one equivalent of the solute. For molten salts and their mixtures it is defined as the conductance of one equivalent of the salt or solution. Hence we have

 Λ (aqueous solution) = 1000 k/c

 Λ (molten salt) = We. k/d

 Λ (molten salt solution) = (We₁ · f₁ + We₂ · f₂) · k/d

where

c = concentration in eq./l. We= equivalent weight in g./ eq. d = density in g./ cc. f = weight fraction

and subscript numerals refer to components.

The modern concept of electrolytic conductance suggests the existence in all electrolytes of charged particles called ions. The passage of electric current through such materials involves only the movement of these ions in the applied potential field. There must also occur, across the interface between the electrolytic conductor and the electronic conductor (electrode), a transfer of charge. This results in oxidation at the anode and reduction at the cathode. The anodic and cathodic processes and ionic movement all contribute to concentration

(5)

changes within the electrolyte.

Specific conductance is determined experimentally by measuring the resistance of the electrolyte between two electrodes, whence

k = K/R

where K, a function of the electrode geometry, is known as the cell constant. It is usually determined experimentally using an electrolyte of known specific conductance. Resistances are measured with modified forms of the Wheatstone Bridge developed to overcome difficulties peculiar to electrolytic measurements.

The bridge method is essentially a comparison of resistances by the potentials developed across them under given current conditions. Errors peculiar to electrolytic measurements are usually associated with extra potentials developed within the electrolytic cell by the chemical action of the bridge current. The term polarization is used to indicate any condition in which the e.m.f. of such a cell differs from the normal value. It is usually the result of one or more of the following factors:

(1) transfer voltage arising from the transfer of charge across the electrode interface.

(2) concentration changes in the electrolyte.

(3) ohmic resistance of solid products of electrolysis formed over the surface of the electronic conductor.

(4) specific electrode effects such as a slow stage in the formation and evolution of gas bubbles at gas electrodes etc. The last factor is often quite distinct from the first three, and is distinguished from them by pertinent names such as hydrogen overvoltage, oxygen overvoltage, etc. The size of such overvoltage depends on the gas evolved, and also on the nature and surface finish of the metal conductor.

Polarization errors are effectively reduced by using the a-c bridge. This eliminates widespread changes in concentration as well as the

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deposition of high resistance films on the electrode surfaces. However, the relatively small effects produced during each half cycle of the alternating current are sufficient to cause significant polarization even when fairly high frequencies are used to reduce the charge passed in each half-cycle. Polarization does decrease as the frequency is raised, but an upper limit is imposed by increasing errors due to stray capacitances and non-resistive impedance in the bridge components. Frequencies of 60 c.p.s. and 1,000 c.p.s. have found widespread use, although much higher frequencies have been used in some investigations.

Certain precautions are necessary in the design and location of components for an a-c bridge in order to minimize errors due to such phenomena as eddy currents, skin effect, stray capacitance and nonresistive impedance in the windings.

Special resistors are now available for construction of a-c bridges. The a-c resistance of these units is within 0.001% of the d-c value in the audio frequency range. This close tolerance is made possible by winding the resistors in a special pattern weave.

The nature and magnitude of the resistance of electrolyte depends largely on the design of the electrolytic cell. Inter-electrode and other cell capacitances, never completely eliminated, can be balanced by a like quantity in the adjacent arm of the bridge. Edge effects, due to current paths extending beyond the volume between the electrodes, are effectively removed by using concentric hemispherical electrodes filled with electrolyte. This arrangement ensures that all current passes directly between the electrodes, and thus permits calculation of the cell constant from geometry. An approach to this condition is possible with concentric cylindrical electrodes which have a small edge to area ratio. However, neither these designs is satisfactory when polarization is appreciable.

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According to Kohlrausch, polarization error depends upon the quantity $P^2/\omega R^2$, where P is the polarization e.m.f. and ω is the frequency. To reduce polarization errors, therefore, R must be made quite large, which is impractical with the two arrangements mentioned. The resistance between hemispherical electrodes is given by

$$R = \frac{P(r_{o} - r_{i})}{2\pi(r_{o} \cdot r_{i})}$$

and that between cylindrical electrodes by

$$R = \frac{\rho}{-1} \cdot \ln \frac{r_0}{r_1}$$

where r_i and r_i are the radii of inner and outer electrodes, h is the immersed height of the cylindrical electrodes, and ρ is the specific resistance of the electrolyte. Since r_0 is usually limited by the size of the crucible or furnace available, R can be increased only by decreasing r_i . But this defeats the original purpose because polarization e.m.f. is increased by the high current density resulting at the inner electrode.

When only relative values of conductance are required and the range of resistance to be measured is not extensive, edge effects can be neglected. Under these conditions high resistances can be obtained using widely spaced parallel plate electrodes of fairly small area.

In recent years, the vacuum tube oscillator has become the most popular a-c source for conductance work. The main advantages of the vacuum tube oscillator are inexpensive construction, silent operation and a sinusoidal output of constant frequency. It is fully adequate for even the most precise conductance measurements provided stray capacitance in the bridge circuit is avoided by suitable grounding. Telephone ear-pieces are usually employed as detectors. Currents as low as 10^{-9} amp. can be detected with such equipment when it is properly tuned, and even greater sensitivity is possible, when a tuned audio frequency amplifier is added. The use of such an amplifier also helps to stabilize the effects of stray capacitances introduced by the presence of the operator.

The effects of interaction between various bridge components and ground not eliminated in the design of the bridge can be effectively reduced by careful shielding and grounding of certain critical points. Shielding is not always easily accomplished, and unless **r**arefully handled it may actually introduce error. One of the most effective grounding devices is the "Wagner earth ", which permits indirect grounding of the detector unit without connecting either terminal directly to ground. This simple precaution gives sufficient accuracy for many purposes, particularly molten salt determinations where temperature measurements, **c**omposition and polarization are all difficult to control.

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Historical Introduction.

Published data on the conductivities of pure cryolite and mixtures of cryolite, sodium fluoride, aluminium fluoride, calcium fluoride and alumina are very meager and unduly variant. Although reports have appeared from time to time since the beginning of this century, absolute values of the conductances from different sources are in very poor agreement; deviations as high as 50 percent are found and even the results of recent investigations differ by 20 to 30 percent. This divergence in results appears to be due mainly to difficulties associated with the proper design of a conductivity cell for use with molten fluorides. The type of cell usually employed for measurements with fused salts is unsuitable due to the extremely corrosive nature of the fluorides. The choice of material for construction of the cell and electrodes is a problem still unsolved.

There are very few substances that can resist serious attack by fluorides at high temperatures, and of these, many are too porous for use as containers for the molten material. Platinum, carbon (and graphite), fused magnesia, and powdered carborundum sintered at 2000 deg. C. have been tried. Platinum appears to be the best of these, but considerable difficulty is experienced due to polarization effects. Platinum black is quite effective in reducing these effects, but at the high temperatures encountered the coating is rapidly converted to grey platinum with greatly reduced ability to depolarize. Carbon materials are relatively inert in liquid cryolite, but suffer attack by oxygen and fluorine gas at high temperature. The resulting ash and carbon dust contaminate the melt. Magnesia and carborundum suffer rapid chemical attack leading to short cell life and contamination of the electrolyte.

Difficulties are also encountered due to the formation of a solid crust on top of the liquid or surrounding the electrodes. This is caused by surface cooling or the conduction of heat from the liquid by the electrodes. At higher temperatures, dissociation of the electrolyte with subsequent volatilization

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of some constituents becomes excessive with attendant changes in composition.

The work done by Richards (22) and by Pascal and Jouniaux (20), prior to 1915, did not yield any reliable results. In 1920 Jaegar and Kapma (16) suggested the design of a cell for electrolytic conductance measurements at temperatures up to 1600 deg.C. In the same year Edwards and Taylor (10) used a modification of this cell to determine conductances of cryolite baths. Hemispherical platinum electrodes were used, the outer one acting as container. The height of electrolyte in the cell was calculated from cell dimensions and the weight and density of the charge. Platinum black was applied to the electrode surfaces before each experiment to minimize polarization, but a slow definite drift was found in the resistance of the cell and their results were not published at that time.

Polarization difficulties were also experienced by Arndt and Kalass (2) using a similar platinum cell. In this work the height of electrolyte was determined from solidified bath on a platinum rod. A specific conductance of 2.23 ohm $^{-1}$ cm. $^{-1}$ was reported for pure cryolite at 1000 deg. C.. The equivalent conductance of pure cryolite was roughly equal to that of sodium fluoride, and it was suggested that the sodium salt alone is responsible for conductance in cryolite. Conductance data obtained with cryolite - alumina melts containing up to 20% alumina were extrapolated and the conductance of pure alumina estimated to be zero. Hero alt later succeeded in depositing copper - aluminum alloy by electrolysis of alumina melts, and M. R. Galeau (14) later referred to this as evidence that molten alumina does conduct.

In 1936 Batashev (4) employed a dip-cell similar to that used by Arndt and Kalass. This cell was completely filled by submerging it in

(11)

molten electrolyte prepared in a larger platinum crucible. A conductance of 3.23 ohm⁻¹ cm.⁻¹ was reported for cryolite at 1000 deg.C.

In the same year Cuthbertson and Waddington (6) substituted a graphite container for the platinum crucible of Arndt and Kalass, but wide variations were found for supposedly identical experiments. Failure was attributed to the unsatisfactory nature of graphite for cell construction. Difficulty was also experienced in attempting to satisfy the requirements of Kohlrausch to avoid polarization errors; namely the area of the electrodes must be greater than 10/R sq. cm. In a further attempt, to reduce polarization, a long magnesia tube was used to hold the cryolite with electrodes situated at the ends. Solubility of magnesia caused poor reproducibility and results for similar experiments varied as much as 14%.

In 1950 the results of extensive work in this field were published by Dr. Vajna. His cell consisted of two concentric cylindrical platinum crucibles with hemispherical bottoms suspended by thick platinum wires. A brass framework held the outside crucible rigidly, while the inside one was fixed by a brass sleeve which guided the platinum wires. The sleeve and framework were insulated from each other by means of a fibrous material. Uncertainty in balancing the bridge, attributed to polarization effects, was listed as a source of appreciable error. A value of 2.36 ohm $^{-1}$ cm. $^{-1}$ was reported for the conductance of pure cryolite. This was lowered by additions of aluminium fluoride or alumina and raised by additions of sodium fluoride or calcium fluoride.

In 1952 and 1953 Edwards and Taylor and their collaborators (9) (10) published reports of conductance determinations on cryolite, with and without additions. Several different cells were used in an effort to obtain high accuracy. A quartz dip-cell was tried and discarded because of excessive attack by cryolite. Modifications of the partly filled platinum

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cell improved reproducibility, but results were subject to errors from volatilization and creep. Best results were obtained by immersing the electrodes in a large platinum vessel containing molten electrolyte. The large volume reduced errors due to volatilization, and complete filling eliminated errors introduced by density measurements. Concentric cylindrical platinum electrodes with hemispherical bottoms were supported by platinum rock rigidly fixed in two blocks of baked lavite. The outer electrode, with a 50 ml. volume, served as container. Conductance determinations were made by dipping this unit in molten electrolyte held in a 400 ml. platinum crucible.

Considerable care appears to have been taken in obtaining the purest available cryolite and other chemicals, and in determining the densities of the baths for calculation of equivalent conductances. To minimize polarization errors, their results were corrected to infinite frequency and zero elapsed time after melting. No allowance was made for volatilization during the melting period. Platinum black originally applied to the electrodes was quickly converted to grey platinum. The resistance of the well platinized electrodes decreased only 3% between 500 c.p.s. and infinite frequency. This decrease rose irregularly to 30% with continued use. An uncertainty of several percent in the conductance of pure cryolite was attributed to residual polarization.

The results of this work appear to be fairly reliable and include the following values at 1000 deg. C., ; 2.8 ohm⁻¹ cm.⁻¹ for the specific conductance of pure cryolite, 94 ohm⁻¹ cm.² eq.⁻¹ for equivalent conductance of pure cryolite, and 118 ohm⁻¹ cm.² eq.⁻¹ for the equivalent conductance of sodium fluoride. In their calculation of the equivalent conductance of mixed salts, weight fractions were used in place of equivalent fractions. The values obtained in this way are lower than those

(13)

FIGURE I

ELECTROLYTIC CONDUCTANCE OF CRYOLITE SYSTEMS RELATIVE

TO PURE CRYOLITE.



MEIGHT PERCENT OF ADDITIVE IN MIXTURE

ан • obtained by the definition given in this paper. The difference depends upon the difference in the equivalent weights of the two salts and their ratio in the mixture. It amounts to about five percent for a 60 : 40 mixture of cryolite and sodium fluoride.

Activation energies for conductance in the various electrolytes were calculated according to the method described by Bloom and Heymann (5). The values reported show considerable variation from one material to another with **no** change as the concentration of one material is varied. Calcium fluoride addition was found to effect a substantial increase in activation energy which is in accord with the general rule that activation energies increase with increased size of the cation. The effect of other additives was slight decrease in activation energy values.

Variations of conductances of cryolite baths with additives based on the results of Dr. Vajna as well as of Edwards and colleagues are plotted in fig. 1. Disagreements are visible in all cases, though general trends are evident except in the case of calcium fluoride. Dr. Vajna reports increase of conductance with addition of calcium fluoride, in contrast to the decrease reported by Edwards et al.

The nature of cryolite - alumina melts:-

An explanation of conductance in fused salts must inevitably involve some consideration of the internal structure of such systems. Indeed, recent activitics in this field have produced a number of interesting suggestions and a brief review of this work follows.

Some investigators consider that all fused salts are completely ionised. However, the substantial reduction in conductivity caused by alumina additions to cryolite seems to indicate that such an assumption should be viewed with caution. The thermodynamic calculations of

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Pearson and Waddington (21) suggest that molten cryolite at 1000 deg. C. is about 15 to 20% dissociated into alumina and cryolite. But many of the data used in this calculation were estimated, owing to the lack of experimental values. Hence there is a possibility of considerable error in their results. A study of the densities of mixtures of sodium fluoride and aluminium fluoride supported the conclusion regarding molten cryolite which was considered to be a mixture of Naz AlF6, NaF, AlFz and their ions. The molar conductance of cryolite mixtures containing NaF, AlF3, CaF2 or Al2 O3; calculated from the data of Batashev (4) was found to vary linearly with mole percent additive. Pearson and Waddington note that extrapolation of these data yields zero conductance for pure alumina and very low conductance for calcium fluoride. Although such extrapolation is often misleading, it is interesting to note that a similar treatment of the results of Edwards and collaborators gives a negative value of conductance for pure alumina. Based on the low conductance of calcium fluoride and equivalent conductances of 107and 86 ohm -1 cm. 2 eq.-1 for cryolite and sodium fluoride respectively, Pearson and Waddington suggest that only a small fraction of the total current in an aluminium reduction cell is carried by the fluoride ion. The major part of the current is carried by the sodium ion, a view consistent with the considerable migration of sodium to the cathode during electrolysis. It is interesting to note that the values of equivalent conductance listed above are in direct contrast to those listed by Edwards et al.

Gadeau (14) attempted to produce aluminium from fluoride baths without sodium, namely from mixtures of aluminium, calcium and magnesium fluorides. The trials failed because the electrical conductivities of these baths were very low. They could not pass sufficient current

(16)

to produce the necessary heat for melting. A considerable increase in conductance resulted when sodium fluoride was added, indicating the important role played by sodium in the conductance of these mixtures.

For the solubility of alumina in cryolite, different authors have given different values. But many agree that the solubility at 1000 deg. C. is about 20% by weight and that the melting point of cryolite is lowered down to 935 deg. C. by the addition of 15% alumina by weight. According to Pyne (1), there is a minimum melting point of 915 deg. C. at 5% alumina which is not reported by any of the other workers, and hence may be in error. Anderson (1) mentions that the melting point of cryolite - alumina mixtures can be brought down to 800 deg. C. by adding suitable amounts of calcium fluoride.

Although substantial amount of alumina can be dissolved in cryolite, it is not soluble in other fused salts, especially in sodium fluoride (11). Hence the anion $AlF_6 = must be the Al_2O_3$ dissolving agent in cryolite, and it is thought that alumina reacts with the anions of cryolite to form oxy-fluoride anions as follows:

 $2 \operatorname{Na}_{3} \operatorname{AlF}_{6} + 2 \operatorname{Alo}_{23} \longleftrightarrow 6 \operatorname{Na}^{+}_{+} 3 \operatorname{Alo}_{224}$

Zintl and Morawietz (25), on examining radiographically the solid solution of cryolite and alumina, found each molecule of cryolite to be replaced by a double molecule of Al 0, corresponding to the formula 23 Al $3^{Al0}6$.

To explain the anomalies observed in the determination of the solubility of alumina in molten cryolite, Fedotiev (12) suggested the equilibrium reaction.

$$4 \text{ Al}_2^{0}$$
 + 2 Na₃AlF6 = 4 AlF₃ + 3 Na₂Al₂0₄

(17)

with subsequent decomposition of the aluminate the ions Na⁺and Al₂ θ_4 ⁼ or Al θ_2 . In this reaction the number of sodium ions does not change. The AlF₆⁼ ions are replaced by less mobile complex oxy-ions. This supports the fact of diminution of conductivity of cryolite on addition of alumina.

The linear relationship between molar conductance and mole percent for cryolite-alumina mixtures has been pointed out as evidence that alumina is an inert solute undissociated by the cryolite, which is itself dissociated and responsible for conductivity of the mixture. But Dr. Vajna has shown that the viscosity of cryolite is doubled by adding 20% alumina. The drop in conductivity could thus be attributed to a decrease in mobility of the ions which depends on the viscosity of the medium.

On the other hand, it (5) is reported that equivalent conductance is not a linear function of mole percent even when activity determinations reveal the mixture to be ideal. Deviations are normally negative and tend to be large for compositions corresponding to compound formation in the solid state. The only positive deviation on record was reported for the cadmium chloride lead chloride system.

The variation of conductance with temperature is generally considered in terms of the Theory of Absolute Reaction Rates proposed by Stearn and Eyring (26). This treatment considers conductance in terms of ionic migration and proposes that activation energies for the two processes should be the same. As a result of this approach, conductance of a mixture containing two ions may be represented by

$$-C_{1}/RT -C_{2}/RT$$

$$k = A_{1} \cdot e + A_{2} \cdot e$$

(18)

where A_1 and A_2 are constants and C_1 and C_2 are the activation energies for ionic migration of the two species. When C_1 and C_2 are very nearly equal or when one is very much larger than the other, the expression may be simplified to read -C/RT

$$k = A_{e} e$$

where A is a constant and C combined activation energy.

A similar expression for the equivalent conductance has also been used in which

$$\Lambda = \Lambda^{1} e^{-C^{1}/RT}$$

where the primes are used merely to indicate equivalent conductance terms. Since Λ is proportional to k/d, it Follows that C¹ will differ from C by an amount which depends on the variation of density with temperature. In view of the logarithmic relationship and the normally small temperature coefficient of density for these mixtures, the difference between C and C¹ should not be very large.

EXPERIMENTAL

Apparatus

1. The electrolytic cell:-

Few materials can withstand chemical attack by molten fluorides. Platinum is very good in this respect, but it is expensive and contributes to polarization errors. Platinum black, so effective in reducing polarization at low temperature, is extremely unstable at temperatures necessary for melting fluorides. Most other metals are unsuitable because of high reactivity, low melting point or high cost. A consideration of the properties of the remaining metals indicated that molybdemum might prove satisfactory for use in this work. Its melting point is 2625 deg. C., and it is relatively inert in molten fluorides. It is reasonably inexpensive when purchased in standard forms, and was finally chosen for construction of the electrodes and container. Oxidation of the metal in air is quite severe at temperatures above 500deg. C because the oxide formed is light and fluffy with little tendency to adhere. However, this reaction may be satisfactorily controlled by preventing direct contact of the parts with large volumes of air.

A concentric cylinder dip-cell was designed in which the outer electrode was to be cut from a long 30 mm. I.D. molybdenum tube. The electrode proper, a relatively short piece of cylinder, was supported by two narrow strips left uncut in the original forming operation. The inner electrode was simply a piece of 10 mm. rod extending down the centre of the tube.

Machining the molybdenum tube was extremely difficult, and the design was finally modified to eliminate this operation. The outer electrode was merely a section of the tube with holes drilled for the inner electrode supports (fig. 2). Extra holes were drilled below this level

(20)

FIGURE 2.

CONDUCTIVITY CELL NO.I.

(SCALE-ACTUAL SIZE)



to ensure the escape of gases given off during operation of the cell. Positioning and insulation of the electrodes were accomplished by washers of AlSiMag 222, a machineable ceramic supplied by the American Lava Corporation. Concentricity was ensured by washers machined to fit snugly between the two electrodes. Vertical positioning was attained by a pin through the rod electrode. This pin, with AlSiMag sleeves, extended through the holes drilled in the wall of the outer electrode. It also served to govern the depth of immersion of the electrodes in the melt at about 5 mm. by resting on the AlSiMag crucible cover described below.

To prevent oxidation of the molybdenum crucible it was placed in a covered graphite container machined to a snug fit. A small lip served to position the cover and prevent ready access of air to the electrodes in the high temperature region just above the melt. An 'AlSiMag' disc, placed over the graphite cover and fixed with two short vertical pins served to support the electrode assembly which was inserted through a central hole in both lids. A small hole was drilled through the covers to hold the thermo-couple used for temperature determinations. Heavy copper wire was brazed around the top of each electrode for connection to the bridge. Kyanex refractory cement, applied to the graphite before each experiment decreased oxidation of the graphite and provided electrical insulation between the graphite crucible and the carbon blocks in the resistance furnace.

The resistance of molten cryolite using this assembly was about 0.06 ohms. Since the accuracy of measurement with the bridge available was about 0.001 ohms. an increase in cell resistance seemed to be desirable. This was accomplished in the parallel electrode assembly

(22)

FIGURE 3.

CONDUCTIVITY CELL NO.2.

(SCALE - ACTUAL SIZE)



shown in figure 3. Two small electrodes were made from the molybdenum rod by grinding the ends to rectangular cross sections 5 mm. square and 10 mm. long. Originally a single Al_Si_Mag disc was used to position. these electrodes with an immersion of about IO mm. and a separation of 27 mm. The method of assembly followed that of the previous cell where possible.

Some difficulty was experienced with heat conduction up these electrodes, and Al_Si_Mag discs were finally used to insulate the full length of exposed rod. When coated with the Kyanex cement this arrangement practically eliminated oxidation of the molybdenum rods. The resistance of cryolite using this assembly was about 0.2 ohms giving a relative accuracy of 0.5%.

2. The resistance bridge:-

A Leeds and Northrup Wheatstone bridge was modified for use with alternating current by the following changes. The variable resistor was shielded from the ratio resistors with aluminum foil. A Heathkit decade condenser, Model DC-1, was connected across the variable resistor. The tange of this unit was 100 μ μ f. to 0.111 μ f. in steps of 100 μ μ f. The alternating current was supplied by a Heathkit audio oscillator, Model AO-1, with a frequency range up to 20 k.c.p.s., and an output of ten volts maximum. It was coupled to the bridge through an impedance matching transformer. The galvanometer was replaced with a detector consisting of a Western Electric hearing aid, Model 64, with an impedance matching transformer substituted for the microphone. The entire detector unit was shielded with grounded aluminium foil. Wagner earth connections were made with a 25 k. ohm volume control. The circuit diagram for this bridge is given in figure 4.

(24)

FIGURE 4.

APPARATUS FOR MEASUREMENT OF RESISTANCE.

LEGEND :-

S		Oscillator.
^T I, ^T 2		Transformer.
R ₁ , R ₂ , R ₃	,R4	Resistances.
C		Conductivity Cell.
K		Condenser.
D		Detector Unit.
G _I ,G₂		Ground.



FIGURE 5.

CARBON RESISTANCE FURNACE.

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3. Auxiliary materials:--

A carbon resistance furnace (fig.5) was used to heat the melt during experiments. The frame consisted of a rectangular steel box, supported on four angle irons. It was lined with about 5 inches of insulating brick and 1 inch of fire brick, and filled with crushed graphite and carbon to serve as the heating element. Contact with the crushed material was made by means of two flat graphite blocks situated at the ends of the furnace. Current was supplied to the graphite blocks by two inch graphite rods which protruded from the furnace at either end. The ends of the rods were clamped in water cooled copper blocks which also served as terminal lugs for cables leading to a transformer.

A vertical cavity was prepared in the crushed graphite midway between the end blocks. The crucible was levelled in this cavity by placing it on a flat graphite brick laid in the bottom. Insulating brick coated with "Kyanex" was used around the top of the cell to reduce heat losses.

Considerable difficulty was experienced in heating the furnace from room temperature. The source of this trouble was finally located when complete failure occurred due to extreme oxidation of the graphite rod and block at one end of the furnace. To replace these the furnace had to be rebuilt, and an extremely hard deposit was found on the surface of the graphite block which caused poor contact with the crushed graphite at low temperatures. This deposit was probably formed from the binding material and the ash in the carbon, under the influence of alternating high and low temperatures. Replacement of one block and resurfacing of the other restored the furnace to reasonably good operation, but the crushed graphite was heated externally to save time when starting up a cold furnace. This occured on numerous occasions due to power failures and required interruptions when the power transformer was used for some other furnace. Once hot, the furnace operated in a satisfactory manner.

Power was supplied from a 550 volt line through a variac, an isolating transformer and a 15 kwa. step-down transformer. The output of the step-down transformer could be varied from 10 to 120 volts in 30 steps, and fine control was obtained with the variac. This equipment permitted a fairly constant temperature to be maintained for the short time needed to make a determination. Interference with the bridge operation made it necessary to turn the furnace off during final adjustment of the bridge.

Temperatures in the melt were determined with a platinum vs. platinum-13% rhodium thermocouple and a Leeds and Northrup portable potentiometer. The couple, introduced directly into the melt, usually lasted for three to four determinations before its operation was impaired beyond use. At this time, the tips were snipped off, and a new clean weld was made.

The cryolite used was of commercial grade having a rough analysis as follows:

Cryolite as NazAlF6	99•40 %
Total Iron as Fe ₂ 03	0.07 %
Lead sulphide as PbS	0.004%
Silica as SiO ₂	0.20 %
Other fluorides	0.30 %
Moisture as H ₂ 0	0.026%

Analytical or good technical grades of sodium fluoride, calcium fluoride and alumina were used.

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Procedures.

The resistance in cells of the type used in this work depends not only on the specific conductance of the electrolyte, but also on the depth of immersion of the electrodes. To ensure constant immersion from one experiment to another, the vertical position of the electrodes and the level of the electrolyte in the crucible must both be fixed. The former was arranged in the manner described in the preceding section. A constant electrolyte level was obtained by using a given weight of material for all experiments. The slight error introduced by this method due to density differences was within the limits required for this investigation.

The required amounts of materials were weighed into the molybdenum crucible. It was then placed in the graphite crucible with the cover in position and heated well above the melting point (about 1060 deg. C.). The AlSiMag lid and electrode assembly were set in position, and the thermocouple was inserted. Refractory brick was placed around the exposed superstructure to obtain slow cooling, and the furnace was turned off. Simultaneous determination of resistance and temperature was begun immediately and continued until the temperature dropped to below 1000 deg. C. The beginning of solidification was accompanied by a rise in resistance, and this was used as a signal to remove the electrode assembly and the thermocouple for the higher melting materials. Solidified bath on the electrodes was used to check the depth of immersion which was sufficiently constant for all experiments.

The bridge was balanced in the usual way, including the variable capacitance and the Wagner earth. A frequency of 1.5 k.c.p.s. appeared

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to give the best results, but this was not sharply critical. Interference from nearby machinery was considerable, and although it caused difficulty in obtaining a balance there was no significant effect on the result.

The resistance of the leads, determined by shorting the electrodes, was 0.02 ohms. This correction was applied to all values reported in this thesis.

The original parallel electrode assembly without extensive insulation was used in experiments with the following compositions:

100% cryolite
95% cryolite + 5% alumina (3 times).
95% cryolite + 5% calcium fluoride.

The final electrode assembly with insulation covering the external portion of the electrodes was used for the following compositions:

95% cryolite	+	5% alumina		
90% cryolite	+	5% alumina	+	5% sodium fluoride
90% cryolite	+	5% alumina	+	5% calcium fluoride
85% cryolite	÷	5% alumina	+	10% sodium fluoride
85% cryolite	+	5% alumina	+	10% calcium fluoride

The results obtained with the first parallel electrode assembly are plotted in figure.6. The general trend of these results shows a rise in resistance with decreasing temperature. This trend is in agreement with the results of other workers, and with the modern concept of conductance. The sudden sharp increase in the resistance of cryolite at about 1025 deg. C. is apparently caused by solidification. The mixtures exhibit this break in the curve at lower temperatures because of reduced melting points. The melting range of temperatures exhibited by such mixtures in place of a sharp melting point is evident in the more gradual nature of the break.

In the case of pure cryolite the break occurs at 1025 deg. C. as compared with the melting point of 1000 deg. C. accepted by most workers and listed in the supplier's specifications. This discrepancy is probably the result of surface cooling and heat conduction up the electrodes. A solid surface crust combined with solidified naterial on the electrode surfaces would certainly increase the resistance appreciably while the thermocouple continued to register temperatures in the still molten body of the material.

This possibility also offers an explanation for the decrease in resistance found on addition of either alumina or calcium fluoride to the cryolite. Most workers have reported an increase in resistance for such additions, and the reversed effect obtained in this work is explained as follows:

Pure cryolite at the highest temperature of measurement is still close to the freezing point, and heat conduction through the electrodes is sufficient to cause solidification of a film of cryolite

(31)

FIGURE 6.

RESISTANCE VS.TEMPERATURE CURVES.

(Data obtained with Conductivity Cell No.I)



over the electrode surface. The slope of the upper part of the curve for pure cryolite supports this view, and the resistance is therefore probably higher than it should be. Addition of calcium fluoride or alumina lowers the freezing point sufficiently to permit a completely liquid bath. The resulting decrease in resistance is more than enough to mask the increase caused by compositional changes.

Higher temperatures would eliminate this difficulty, but several factors oppose such a change. Higher temperatures cause faster volatilization of the melt, and faster oxidation of the molybdenum and carbon. Also, the results of other workers are pretty well confined to temperatures in the order of 1000 deg. C., and aluminum reduction cells operate at or below this value.

To prevent such solidification in the region of 1000 deg. C. a completely new cell would have to be designed and built. Lack of time and materials made such a move undesirable, and the following plan was adopted. In place of pure cryolite, a cryolite-alumina mixture was for chosen as the standard comparison. This decision was made on the basis that all electrolytic reduction cells for aluminium production contain alumina, and a solution of 5% alumina in cryolite melts considerably below 1000 deg. C. A further reduction of undesirable effects was obtained by insulating the exposed portions of the electrodes **as** described in the experimental section. The efficiency of this insulation is immediately evident from a consideration of the results platted in figures 6 and 7. The resistance of a 5% solution of alumina in cryolite dropped from about 0.33 ohms to 0.22 ohms.

Calculated cell constants are extremely unreliable for parallel electrodes of the type used in this work, and the values of specific

(33)

FIGURE 7.

RESISTANCE VS. TEMPERATURE CURVES.

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(Data obtained with Conductivity Cell No.2)



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conductance listed in Jable 1 are based on an experimental cell constant obtained from the specific conductance of a 5% solution of alumina in cryolite reported by Edwards et al. (9). The activation energies are calculated according to the formula

$$-C/RT$$
 k = A . e

suggested by Bloom and Heymann (5).

Calcium fluoride up to 10% causes a regular increase in the specific conductance of the cryolite-alumina mixture. Sodium fluoride also causes an increase in the specific conductance with a maximum occurring in the region below 10%. It is recalled at this point that for additions of calcium fluoride up to 10% in pure cryolite, Vajna reported a regular increase in conductance while Edwards et al. found a decrease. Also, for the mixture containing 5% alumina and 10% calcium fluoride Edwards' group found a decrease relative to the cryolite-alumina mixture. This is in contrast to the increase reported here.

It seems likely, after examination of the three sets of data, that some solidification occurred around the insulated electrodes used in the last set of experiments. Though less in amount than that occurring on the bare electrodes, it was still sufficient to give rise to considerable error. This view is supported by the activation energies which are much higher than those reported by Edwards and collaborators. This quantity is related to the change of conductance with temperature, and is larger for greater values of the temperature coefficient of

(35)

Table 1.

Composition of	Re	sistance	Speci:	fic conductance	Activation energy
the mixture.	ir	ohms.	ohma	s ⁻¹ cm. ⁻¹	K. cals./mole.
cryolite	95%				· ·
alumina	5%	0.220		2•55	
					10.0
cryolite	90%				· .
alumina	5%	0.117		4.80	٤.0
sodium fluoride	5%				
cryolite	90%				
alumina	5%	0.202		2.78	10. 0
calcium fluorid	ə 5%				
cryolite	85%				
alumina	5%	0.168		3• 34	č.č
sodium fluoride	10%				
cryolite	85%				
alumina	5%	0.13		4. 32	IO.5
calcium fluoride	e10%				

(36)

conductance. If solidification on the electrodes occurs, the amount will decrease with rising temperature. Conductance will then increase by two mechanisms. The first involves ionic mobility, the normal machanism of conductance in liquid electrolytes, and gives rise to the true activation energy. The second involves a decrease in the thickness of the solidified material around the electrode, and is not directly associated with the true activation energy. Conductance data determined under these conditions will yield high activation energies. Two other factors contribute somewhat to the difference in activation energies noted. The first concerns the use of specific conductance in this work for calculation of activation energy whereas equivalent conductance was used by Edwards and colleagues. Secondly, as noted in the introduction, equivalent conductance was calculated by Edwards! group using weight fractions in place of equivalent fractions. However, the logarithmic relationship for activation energy makes it relativaly insensitive to these errors which are small in any case. Solidification of electrolyte on the electrodes appears to be the major cause of high activation energies found in this investigation.

It is possible that some solidification of this type occurred in the cell employed by Vajna. The relative conductance curves calculated from his results are shown in figure 1 along with those of Edwards et al. In every case Vajna's curve lies above Edwards' except for sodium fluoride. An explanation of this trend is possible if it is assumed that some solidification occurred in Vajna's cell. This would be greatest with pure cryolite leading to the low value of conductance reported (2.36 as compared to 2.8 listed by Edwards). A decrease in solidification caused by lower melting points for the various mixtures would obviously cause high values for relative

(37)

conductance as seen in the figure. This is particularly notable for calcium fluoride which is known to have considerable effect on the melting point. Further evidence in support of such solidification is found in the high activation energies calculated from Vajna's results (about 8K.cals./ mole).

The dip-cell of Edwards et al, immersed in a relatively large bath of the molten electrolyte would be much lass likely to give rise to solidification of this type. However other sources of error are always present, and they have indicated the limitations of their results. Activation energies are reported with three significant figures, and it is rather surprising to find identical values for all concentrations of a given additive. The method used to obtain such consistent results is not obvious, particularly since calculations based on their conductance values indicate some uncertainty in the second figure of the activation energy. The reliability of their conductance values is supported because of the cell design and the nature of the curves discussed above rather than on the consistency of the activation energies reported.

Other sources of error are always present in measurements of this type, and a brief discussion of some of these follows.

Chemical attack of the electrodes and crucible by the electrolyte may introduce impurities into the melt, or alter its composition by reaction of certain components. Molybdenum appears to be satisfactory in this respect since the weight loss after numerous experiments was negligible.

Volatilization of certain components appears to be a problem if prolonged experiments are attempted. This was indicated in one case when a given mixture was repeated for two temperature cycles.

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Resistances were notably higher during the latter part of the experiment. Secondary effects introduced by volatilization include compositional changes, lowering of the liquid level and possible attack of some part of the apparatus not normally in contact with the electrolyte, by the gases evolved.

The determination of liquid level is essential if absolute values of conductance are to be determined unless totally immersed electrodes of fixed area are used. Relative conductances were deemed satisfactory for this investigation, and a constant electrolyte level was obtained using a constant weight of material. As indicated earlier this was subject to error resulting from density differences, but at most such error would amount to about 5%.

Polarization errors were fully discussed in an earlier section and it will only be pointed out here that this difficulty is not eliminated with molybdenum electrodes. However, its satisfactory behaviour in other respects and a relatively low cost suggest that further experiments with this metal should be made. Also, it is still possible that some improvement over platinum may be found in reducing polarization errors.

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SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE.

I) Factors concerning the design of conductivity cells and the choice of bridge components for resistance measurements of fused cryolite baths are discussed. The divergence of results obtained in previous investigations is noted in a brief review of the literature on conductance determinations in molten cryolite mixtures. Theoretical aspects of conductance in fused electrolytes are discussed, and the variation. of conductance with temperature is considered briefly in terms of the theory of absolute reaction rates.

2) A conductivity cell consisting of a molybdenum crucible for holding the molten cryolite and concentric molybdenum electrodes was designed and constructed. The total resistance of fused crycolite baths in this cell was too low for sufficiently accurate measurement with the bridge available.

3) A second cell was designed in which two parallel molybdenum rods served as electrodes. Severe oxidation of the molybdenum crucible was prevented by enclosing in a carbon crucible. Discs of AlSiMag 222 were used to insulate and position the electrodes.

4) The conductances of various mixtures of cryolite, alumina, sodium fluoride and calcium fluoride were determined at temperatures in the neighbourhood of IOOO deg. C. Accuracy of the results was affected by cooling and solidification of electrolyte in contact with the electrodes.

5) Experience gained by this work seems to indicate that Dr.Vajna's results may have been affected in a similar manner.Such solidification would be much less likely with the apparatus used by Edwards' group and their results are probably less affected by this type of error.

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6) Molybdenum is demonstrated as a possible material of construction for use in contact with fused cryolite.Oxidation at high temperatures can be curtailed by careful design, and further study of its use in this field is recommended.

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