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FREQUENCY DISPERSION OF IMPEDANCE IN A MOLTEN ELECTROLYTE

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CHAPTER 1

INTRODUCTION1.1 The Problem

It is an experimental fact that the impedance of an electrolyte as usually measured (by conductance bridge in a two electrode cell) is dependent on the frequency of the applied voltage.

A quantity of fundamental physical significance in the elucidation of the structure of an electrolyte is the mobility of the conducting species. In order to know the mobilities of conducting species it is necessary to know the resistance of the particular electrolyte.

However in order to establish the nature of the electrolyte i.e. its structure, resistance measurements are required which are precise and accurate and the variation of resistance (conductance) with temperature must be accurately known.

Modern instrumentation gives a high degree of precision in such measurements but the accuracy of many published figures is somewhat doubtful. Variations among different workers publishing relatively recently, all claiming accuracy in the region of 0.1% are often greater than 2%, e.g. [1] and [2] for molten KBr. Temperature derivatives of conductance vary by even greater amounts.

That errors of measurement or interpretation are present is apparent and it must be established whether the dominant errors are in such things as the purity of the electrolyte, the instrumentation

and experimental set-up or in the interpretation of the impedance measured.

Some workers e.g. Buckle and Tsacoussoglou [1], have paid close attention to details of instrumentation and experimental method and it seems that while such attention is necessary it is not lack of it that is the major reason for the doubtful accuracy mentioned above.

It is noticeable in the literature of conductance measurements that whereas the basic principles of determining conductance are the same, there is little uniformity in allowing for the variation of measured impedance with measuring frequency. Perhaps this is because the concept of frequency dispersion of impedance is not one with which physical chemists are familiar as there is but sparse reference to these considerations in modern undergraduate texts. This problem is highlighted in a recent paper by Braunstein and Robbins [3] wherein is also described the necessity for capacitive balance in even the simplest bridge measurements.

Usually errors in interpretation of conductance measurements are not apparent because the raw data and methods of calculating parameters are not published.

The purpose of the present work is to establish the problem and investigate the factors contributing to this frequency dispersion of impedance in the case of an ionic liquid, a molten salt.

Some contributions will arise from the nature of the electrolytic cell used, the nature of the electronic instrumentation and its direct effect on the electrolyte. However what is really

needed is to decide whether the frequency dispersion is an intrinsic property of an electrolyte or can be accounted for completely by a knowledge of the experimental setup and the electrode parameters. For example, is the assumption that an electrolyte obeys Ohm's Law and can be considered as a pure resistance always justified and can a correction always be applied to allow for the variation with frequency?

It is well established that there are methods and formulae which can be used to nullify or correct for the effect of measuring frequency often to a very good approximation and adequate for many purposes.

The most common method of nullifying the effect of uncertain electrode characteristics is to arrange the experimental setup so that the resistance contribution from the electrolyte is far larger than the impedance contribution from electrode effects i.e. by using a cell of high cell constant (capillary cell). This method is not always convenient however and there are dispersion formulae which are used to make a correction. The most widely used is that which involves plotting of the series components of impedance, R_s and C_s against the square root of the inverse of the frequency and taking the intercept (infinite frequency) to be the true resistance (or impedance).

In the past there have been several different approaches to the problem and these will be considered in detail in subsequent chapters.

1.2 Historical

1.2.1 Frequency dispersion of impedance before 1940.

Even from the nineteenth century the problem of the apparent variation of conductance with measuring frequency has been appreciated and theories were proposed [4] and techniques developed to explain and minimise the effect.

Warburg [5,6] proposed and developed the idea that diffusion is responsible for the partial irreversibility of electrode reactions in aqueous electrolytes. He considered Fick's laws of diffusion with appropriate boundary conditions and concluded that polarisation causes a capacitance in series with the cell resistance, that the phase change across the electrolyte - electrode interface is 45° and that the capacitance is inversely proportional to $\omega^{\frac{1}{2}}$. This was tested experimentally at the time and found to hold at least approximately [7].

Warburg's mathematical analysis was subsequently improved [8] but perhaps the most reliable experimental work done was that by Grinnell Jones and coworkers [9-15] as part of a series of publications on the precise measurement of the conductance of aqueous electrolyte solutions.

These authors [14] set out to determine the resistance and capacitance at an electrode due to "galvanic polarisation by alternating current". They concluded that each electrode is equivalent to a series resistance and capacitance, the resistance proportional to $\omega^{-\frac{1}{2}}$ and the capacitance decreasing with increasing frequency. This polarisation resistance and capacitance were found to be dependent

on electrode material, electrolyte and temperature but independent of current density and electrode separation. At this time, since the main object was precise measurement of conductance, compensation for and elimination of this polarisation effect was most desirable and when this was done (empirically) the electrode process was not studied further.

Concurrently during the time before 1940 theories were developed on other aspects of electrode processes.

Progressive refinements to the simple double layer theories of Helmholtz [16] had by this time led through the theories of Gouy [17] and Chapman [18] to the combined theory of Stern [19] which eliminated many of the unsatisfactory features of the earlier models. So at this time the electrolyte side of the electrical double layer in dilute aqueous solutions was understood to be made up of a fixed (Helmholtz) layer of charge on the electrode surface and a diffuse (Gouy) layer of charge in the solution.

An analysis of frequency dispersion of impedance in the bulk of the electrolyte was made by Falkenhagen and Debye [20] in the early nineteen thirties and this is summarised in Falkenhagen's book [21]. They considered the effect of an alternating electric field applied to the electrolyte by an analysis of the forces between the various ions. There was found to be a significant effect for frequencies above 1 MHz where conductance was found to increase with increasing frequency.

It seems strange that in publications up to 1940 there was no linking of work on the various effects contributing to the apparent

variation of conductance with frequency.

1.2.2 Electrode processes causing frequency effects. The impedance method

The first use of a relaxation method, the next significant advance in the study of electrode processes, was the use of an impedance method by Delin and Erahler [22-34] who were determining the rate of hydrogen ionisation at a platinum electrode. By measuring the impedance of a cell they were able to obtain a rate constant for the reaction $\text{H}_3\text{O}^+ + (\text{Pt}) + e \rightleftharpoons \text{Pt}(\text{H}) + \text{H}_2\text{O}$, in various electrolytes. The theory of this method was later developed by Randles [25], Gerischer [26], and Grahame [27].

Randles [25] was studying a system of an aqueous solution with a small concentration of a reducible ion and a large volume of a supporting electrolyte. Account was taken of diffusion of the reducible species to or from the electrode (Hg), the rate of the charge transfer reaction at the electrolyte-electrode interface and the double layer capacitance. The last of these effects was considered as in parallel with a series combination of the other two effects. This was the first 'equivalent circuit' approach to the problems of electrode processes. The Randles treatment was extended to allow for adsorption of reactants on the electrode surface [26].

A far more complete analysis of the mathematical theory of the electrode impedance is that of Grahame [27] in which equivalent circuits for many different types of electrolyte solutions are devised and the

name of 'Warburg' impedance is introduced for the diffusion dependent impedance. Equivalent circuit models relevant to the molten salt case will be considered in a subsequent chapter.

From this time forward, the problem of frequency dispersion of impedance in liquid electrolytes became more clearly divided into two parts.

1.2.3 Dispersion within the electrolyte

First, effects arising in the bulk of the electrolyte. This includes the Falkenhagen-Debye effect mentioned earlier, significant at very high frequencies and with large electric fields, and also a 'space charge polarisation' effect which has been analysed for the molten salt case by Baker and Buckle [28] whose treatment was later criticised and simplified by Macdonald [29]. Macdonald has made an analysis [31] with equivalent circuits to explain frequency dispersion in pure molten salts with ideal polarised electrodes. Warburg ($Z \propto \omega^{-1/2}$) behaviour has been noted [32] in such cases. Frequency effects arising in the bulk of the electrolyte are how Buckle and Tsacoussoglou [24] and Baker and Buckle [30] explained their experimental results for the conductance of molten KBr. It is often considered that much of the measured frequency dispersion of impedance and errors in conductance values arise from spurious causes, e.g., poorly designed cells, bridge errors, impure electrolyte, frequency dependence of cell constant [13], incorrect analysis. Buckle and Tsacoussoglou [1] made a study of conductance in a pure salt melt designed to eliminate all such

spurious effects by careful experimenting. Their approach is unusual in that they reject the possibility of a faradaic process occurring in such a system and thus the possibility of any $\omega^{-1/2}$ dependence. This implies that the electrode is ideally polarisable and acts as a pure capacitor without leakage and that any frequency dispersion of the measured impedance arises within the electrolyte. They have subsequently published [33] conductance results for salts measured by their "a.c.-dispersion plateau" method.

Baker and Buckle [20] working with KCl and AgBr melts observed some unusual frequency dispersion trends (e.g. capacitance $\propto f^{-3/2}$) which are as yet unexplained.

In general however frequency effects within the electrolyte are small compared to frequency effects of the various electrode processes.

1.2.4 Dispersion at the electrode interface

Second, effects arising at electrode-electrolyte interface. The problem is the elucidation of the behaviour of all components of the system at the interface. This involves a detailed knowledge of the behaviour of the electrical double layer, diffusion close to the electrode, electrical migration close to the electrode, adsorption of various species on the electrode surface, the mechanism of charge transfer, the kinetics of charge transfer and the kinetics of any other (chemical) reactions which occur near the interface. The number of studies contributing knowledge to these processes in the last twenty

years is large and only a general introduction to some of the experimental methods is given here.

Refinements have been made to the theories of the structure of the electrical double layer with changes in the interfacial potential and concentration [34]. However the nature of the electrical double layer is less well established for molten salts. The double layer is likely to be rather diffuse if there are no specifically adsorbed charges and could possibly be treated as a space charge [28,32].

1.2.5 The impedance method

The impedance method, based on the formulae and equivalent circuits given by Grahame [27], has been applied to molten salts with limited success. Some kinetic parameters have been obtained in molten nitrates [35] and in certain metal-metal ion systems [36]. Results tending to agree with simple theory were obtained at solid electrodes by Hills and Johnson [37] and Hill et al [38]. Throughout these measurements there were difficulties arising, possibly from adsorption of some of the ions on the electrode surface. Some of the difficulty undoubtedly arises in the mathematical analysis, e.g. the measured series or parallel capacitance is a complicated function of the double layer capacitance and the diffusion dependent Warburg capacitance. Independent values for the ohmic resistance of the electrolyte and the double layer capacitance should therefore be determined in order that this method be used. The impedance method

has been used several times (e.g. 35,36,39) to determine electrode kinetic parameters (i_0 and α) for some dilute solutions of metal ions in molten salts (usually alkali metal halide mixtures).

1.2.6 The current step method

Another method for determining electrode parameters is the current step method. For this relaxation method the electrode being studied is subjected to a current step and the potential response of the electrode is observed, usually on an oscilloscope. The first analysis of this method in terms of the electrode parameters was given by Bergins and Delahay [40] (single pulse method) with refinements by Gerischer and Krause [41] (double pulse method). The double pulse method involves the application of a preliminary current pulse (perhaps 1 microsecond) to charge the double layer followed by the second, longer pulse for which the potential response is examined. This enables response to purely faradaic processes to be examined after very short times. These galvanostatic pulse methods have been successfully used on molten salt systems for determining electrode parameters [42,43].

Another relaxation method is the potential step method in which the electrode is subjected to a potential pulse or potential step and the current response is examined [43,44].

Modern concepts used for analysing the experimental potential and current responses from these methods have made the experimental requirements more flexible e.g. analysis of current and voltage steps is essentially the same and it is not necessary that the steps be absolutely abrupt [45,46].

Other methods that have been used are coulometric relaxation [47], faradaic rectification [48].

There have been refinements to all the above methods, some of which will be discussed in the following chapters. There have been several review articles published which outline these [49-51].

1.3 Object of this Work

It is proposed in this project to examine a molten salt system by an impedance method and as a lesser part of this, to examine the salt by a transient, single pulse method.

CHAPTER 2

THE IMPEDANCE METHOD. EQUIVALENT CIRCUITMODELS OF ELECTRODE IMPEDANCE

Before any analysis of a conductance measuring system can be made it is necessary to have a model - some concept of the physical nature of the system.

A convenient way of expressing the response of an electrode is to devise a combination of electronic components to which the electrode-electrolyte system is equivalent. This equivalent circuit approach has been much used in attempts to elucidate electrode processes.

The processes for which electrical equivalents are sought are the faradaic processes (charge transfer at the electrode interface), diffusion of reacting species to and from the electrode, adsorption of some species on the electrode surface and the charging of the electrical double layer at the interface.

We will first consider a system of an electrolyte and one electrode. The electrolyte will at first be supposed to behave as an ohmic resistance, R_o . The effect of this assumption is discussed in paragraph 2.3. This assumption that frequency dispersion of impedance is not an intrinsic property of an electrolyte is widely used.

2.1 The Simplest Model

The first comprehensive invention of models of the equivalent circuit type were those of Grahame [27] (1952) in which such concepts as 'Warburg' impedance were introduced and various cases were considered for the different types of electrode-electrolyte interfaces and reactions. Grahame considered aqueous electrolytes at metal electrodes with several special or limiting cases considered e.g. (non-electro-) chemical reactions occurring at the surface, but the mathematics was developed for small applied sinusoidal voltages only.

The basic equivalent circuit was made up of (a) the electrolyte resistance, R_o , (b) the electrical double layer, which, since it involves storage of planes of charge, is regarded as an electrical capacitor. In parallel with this non-faradaic charge storage is a series combination of impedances attributable to the processes associated with the faradaic reaction, the charge transfer and the diffusion of reactants.

This simple circuit is shown in Figure 1. The various components are described below.

2.1.1 The Double Layer Capacitance

In this model the double layer is represented as a pure capacitance. This is the simplest way to treat it but it is possibly more realistic to account for it as a generalised impedance dependent on frequency [52]. (See Section 6.6). The double layer capacitance is also potential dependent and will also be at least a small amount dependent on the faradaic processes.

FIGURE 1

Simple Equivalent Circuit.

2.1.2 The Charge Transfer Resistance

θ is the linearised charge transfer resistance, an impedance due to the existence of charge transfer overpotential i.e. it is the resistance to the passing of charge through the electrolyte-electrode interface in order that a faradaic process might proceed. This resistance is thus a measure of the kinetics of the electrode reaction(s) and will be small for a fast reaction.

It will be shown that

$$\theta = \frac{RT}{n^2 F^2 A c_O (1-\alpha) c_R^\alpha k_s} \quad (1)$$

Consider an electrode reaction represented by

where O and R are both species dissolved in the electrolyte and the reaction has one rate determining step. Then

$$i = nFA \{ c_O k_f \exp[-\alpha nFE/RT] - c_R k_b \exp[(1-\alpha)nFE/RT] \} \quad (2)$$

[ref. 34, Chapter 8] where i is the net current, positive for a cathode reaction,

k_f , k_b are the formal rate constants at $E = 0$ for the forward and backward reactions respectively,

α is the transfer coefficient,

E is the electrode potential, referred to some standard.

At the equilibrium potential, E_o , $i = 0$, $c_O = c_O^o$, $c_R = c_R^o$ so

$$c_O^o k_f \exp[-\alpha nFE_o/RT] = c_R^o k_b \exp[(1-\alpha)nFE_o/RT] \quad (3)$$

We note the appropriate Nernst equation,

$$E_e - E^0 = \frac{-RT}{nF} \ln(c_R^0/c_O^0) \quad (4)$$

When $c_R^0 = c_O^0$, $E_e = E^0$. E^0 is the standard potential for the system
 $O + ne^- = R$.

Then from (3)

$$k_F \exp[-\alpha nFE^0/RT] = k_B \exp[(1-\alpha)nFE^0/RT] = k_s \quad (5)$$

This defines k_s , a new rate constant expression.

By eliminating E^0 from (4) and (5), the quantities equated in (3) are seen to be equal to

$$c_O^0(1-\alpha) c_R^0{}^\alpha k_s$$

Equation (2) can be rewritten now to include k_s as the only rate constant expression

$$1 = nFk_s A c_O^0(1-\alpha) c_R^0{}^\alpha \left\{ \frac{c_O}{c_O^0} \exp[-\alpha nF(E-E_e)/RT] - \frac{c_R}{c_R^0} \exp[(1-\alpha)\frac{nF(E-E_e)}{RT}] \right\} \quad (6)$$

If the system is such that E differs from E_e by only a small amount, i.e. $|E - E_e| \ll RT/\alpha nF$ then (6) can be linearised and c_O/c_O^0 and c_R/c_R^0 can be equated to 1. Thus

$$\begin{aligned} 1 &= nFAk_s c_O^0(1-\alpha) c_R^0{}^\alpha \left\{ 1 - \alpha nF(E-E_e)/RT - 1 - (1-\alpha)nF(E-E_e)/RT \right\} \\ &= -nFAk_s c_O^0(1-\alpha) c_R^0{}^\alpha (nF/RT)(E-E_e) \end{aligned} \quad (7)$$

The negative sign arises because of the sign convention that a negative potential difference gives rise to a positive current. The required resistance is given by $-1/(di/dE)$. Thus

$$\theta = \frac{RT}{2.2 n F A c_0^0 (1-\alpha) c_R^0 k_s} \quad (1)$$

as required.

The exchange current density, i_0 , is given by

$$i_0 = n F A c_0^0 (1-\alpha) c_R^0 k_s \quad (8)$$

So a simpler expression for θ is

$$\theta = \frac{RT}{n F A i_0} \quad (9)$$

This treatment is not dissimilar to that given in the introduction of Damaskins monograph [49] except for the linearisation. Note that this derivation gives θ as a pure ohmic resistance, independent of potential and frequency.

There are some important points to note when using $\theta = RT/(n F A c_0^0 (1-\alpha) c_R^0 k_s)$. It is important that the electrode process is of right type. That is, species O and R must be defined and there must be only one rate determining step.

For the linearisation approximation to be valid it is necessary that

$$|E - E_0| \ll RT/\alpha n F \quad (10)$$

If $T = 700K$, $\alpha = 0.5$, $n = 2$ then $RT/\alpha n F \approx 50 \text{ mV}$.

Therefore we require $|E - E_0| < 0.5 \text{ mV}$ for 0.005% agreement
 $< 5 \text{ mV}$ for 0.5% agreement.

2.1.3 The Diffusion or Warburg Impedance

$-W$ is a frequency dependent impedance which is not equivalent to any finite combination of aperiodic (frequency independent) components. This impedance, often referred to as the Warburg impedance has series resistance and capacitance components usually expressed in the form:

$$R_w = \frac{RT}{n^2 F^2 \omega} \sum_i \frac{\nu_i^2}{\bar{c}_i \sqrt{D_i}} \quad (11)$$

$$C_w = \frac{n^2 F^2}{RT \omega} \left(\sum_i \frac{\nu_i^2}{\bar{c}_i \sqrt{D_i}} \right)^{-1} \quad (12)$$

where ν_i are stoichiometric coefficients for depleting components in the overall electrode reaction, $\bar{c}_i$ is the bulk concentration of component i , $(c_i(\omega, t))$. All other symbols represent quantities as defined in the Glossary.

Most of the following derivation has been known for about seventy years [5-8] although the experimental testing of the above equations was not first undertaken until 1947 [25]. The following derivation follows that given by Vetter [53].

We are considering an electrode-electrolyte system in which the reaction rate is dependent on the diffusion of a component i . A

small sinusoidal current is passed through the system. Let the current density be given by

$$i = I \sin \omega t. \quad (13)$$

Since a certain time is required after the establishment of a steady current for the establishment of a steady state concentration gradient (considering the concentrations of the reacting species) there will be a concentration distribution which varies with time, and which is dependent on the frequency of the current. Thus we require an expression for c_1 as a function of x , the distance from the electrode surface, and t , time.

Take Fick's Second Law

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} \quad (14)$$

The solution of (14), considering (13) and the boundary condition (which is Fick's First Law at $x = 0$)

$$\left. \frac{\partial c_1}{\partial x} \right|_{x=0} = \frac{-I \gamma_1 \sin \omega t}{nFD_1} \quad (15)$$

is

$$c_1(x, t) = \bar{c}_1 + B \exp(-x/x_0) \cdot \sin(\omega t - 2\pi x/\lambda + \beta) \quad (16)$$

which represents a damped concentration wave in the electrolyte with a phase shift β at $x = 0$. x_0 and λ can be determined by partially differentiating (16) and substituting in (14). The result is

$$x_0 = \lambda/2\pi = +\sqrt{2D_1/\omega}$$

x_0 is seen to be the penetration of the concentration wave where its amplitude is $1/e$ of the amplitude at $x = 0$ and λ is the wavelength.

The concentration wave is very strongly damped.

By evaluation of $\partial c_1/\partial x$ at $x = 0$ from (16) and comparing coefficients with (15), B and β are determined.

$$B = \frac{I \gamma_1}{nF \sqrt{D_1 \omega}} \quad \text{and} \quad \beta = -\pi/4$$

$$\text{Thus } c_1(x,t) = \bar{c}_1 + \frac{I \gamma_1}{nF \sqrt{D_1 \omega}} \exp\left(-\sqrt{\frac{\omega}{2D_1}} x\right) \sin\left(\omega t - \sqrt{\frac{\omega}{2D_1}} x - \pi/4\right) \quad (17)$$

This equation will only apply when $x_0 \ll \delta$, the diffusion layer thickness. For very low frequencies special treatment is needed.[8]

A diffusion overvoltage arises because of the concentration difference, $\bar{c}_1 - c_1(0,t)$, which is given by

$$d = \frac{1}{nF} RT \ln(c_1/\bar{c}_1) \quad (18)$$

This supposes that the activity coefficient of 1 remains constant through the diffusion layer so it is necessary that

$$|\bar{c}_1 - c_1(0,t)| \ll \bar{c}_1.$$

Substitute (17) into (18) with the further assumptions, for the purpose of simplification, that

$$I \ll \bar{c}_1 nF \sqrt{\omega D_1} / \gamma_1 \quad \text{and} \quad x \ll x_0 \quad \text{i.e. } \exp(x/x_0) \approx 1.$$

We are considering the overvoltage very close to the electrode.

$$\eta_d = \frac{IRT}{2.2} \frac{v_1^2}{c_1 \sqrt{D_1} \omega} \cdot \sin(\omega t - \pi/4) \quad (19)$$

or, if there are two depleting substances, O and R,

$$\eta_d = \frac{IRT}{2.2 \sqrt{\omega}} \frac{v_1^2}{c_1 \sqrt{D_1}} \cdot \sin(\omega t - \pi/4) \quad (20)$$

$$= \frac{IRT}{2.2 \sqrt{\omega}} \left(\frac{v_O^2}{c_O \sqrt{D_O}} + \frac{v_R^2}{c_R \sqrt{D_R}} \right) \cdot \sin(\omega t - \pi/4) \quad (21)$$

The diffusion impedance is given by $\eta_{d, \max}/I.A.$

$$Z_w = \frac{RT}{AnF \sqrt{\omega}} \left(\frac{v_O^2}{c_O \sqrt{D_O}} + \frac{v_R^2}{c_R \sqrt{D_R}} \right) \quad (22)$$

The impedance Z_w may now be considered as a series combination of a resistance, R_w , and a capacitance, C_w . Since, from (21), the overvoltage lags the current by $\pi/4$, we know that $\omega C_w R_w = 1$.

$$\text{Also } Z_w^2 = R_w^2 + (1/\omega C_w)^2.$$

So

$$R_w = Z_w / \sqrt{2} \quad \text{and} \quad 1/\omega C_w = Z_w / \sqrt{2}$$

Thus

$$R_w = \frac{RT}{AnF \sqrt{2\omega}} \left\{ \frac{v_1^2}{c_1 \sqrt{D_1}} \right\} \quad (23)$$

$$C_w = \frac{AnF}{RT} \cdot \sqrt{2/\omega} \cdot \left(\frac{v_1^2}{c_1 \sqrt{D_1}} \right)^{-1} \quad (24)$$

Further simplification can be made. For example, for a diffusion dependent reaction, $O + ne^- = R$, we will suppose that

$$D_O = D_R = D.$$

Then (22) becomes

$$Z_w = \frac{RT(c_O + c_R)}{An F^2 c_O c_R \sqrt{\omega D}} \quad (25)$$

and R_w and C_w can be similarly simplified. If, further, $c_O = c_R$ then the form used by Randles [25] and others [37,54] results. This latter form differs only by a factor of two from that when $c_O \gg c_R$, a form which may apply to the present work in molten salts.

2.2 Improvements to Simplest Model

2.2.1 The Transmission-line Model for Diffusion Impedance

It should be noted from the derivations of the impedance parameters given in the preceding section in terms of electrode parameters that with the assumptions noted all the impedances are 'real' i.e. they are derived directly from a microscopic physical model, the double layer is a capacitor which can store charge, the charge transfer impedance is a resistor with ohmic characteristics. However it is not necessary to keep the model so closely related to a physical model of the electrode system and an example of this is an equivalent circuit for the Warburg impedance using only aperiodic components.

A transmission line in which one of the conductors has zero and the other a finite resistance per unit length and between which there is a uniform capacitance per unit length has the same overall impedance properties as the Warburg impedance i.e. impedance inversely proportional to the square root of frequency and an impedance phase angle of $\pi/4$. The transmission line concept in this context was first postulated by Barker [55] and has been discussed by Parsons in a review [54] and Birke [46]. This concept effectively makes an analogy between the process of mass diffusion to or from an electrode under the influence of an alternating electric field and the migration of charge along the length of an infinite transmission line under the influence of an alternating voltage, a valid analogy in an ideal case.

Consider a transmission line with one conductor of resistance R_t per unit length and the other conductor of zero resistance with a shunt capacitance C_t per unit length between them. This fulfils the aperiodic requirements.

The equation for diffusion of charge in such a line is [54]

$$\partial V(x,t)/\partial t = (1/R_t C_t) \partial^2 V(x,t)/\partial x^2 \quad (26)$$

where V is the voltage at time t at a distance x along the line.

This is analogous to the equation for linear diffusion of a reactant in a semi infinite medium as given by Fick's second law of diffusion.

$$\partial c_1(x,t)/\partial t = D_1 \partial^2 c_1(x,t)/\partial x^2 \quad (27)$$

By calculating the impedance of the transmission line (see Appendix) and comparing it with that of the Warburg impedance (equation 22) it is seen that they both have equal R and $1/\omega C$ components directly proportional to $\omega^{-1/2}$. Identifying the coefficients we have

$$C_{t,1} = An^2 F^2 \bar{c}_1 / RT \nu_1^2 \quad \text{and} \quad R_{t,1} = RT \nu_1^2 / An^2 F^2 D_1 \bar{c}_1 \quad (28)$$

This analogy can be carried further [51].

Thus the transmission line is a mathematically, rather than a physically based model.

Since at an electrode subjected to alternating voltage, reduction and oxidation are occurring alternately at the interface and from equation 22 if c_o and D_o differ from c_R and D_R the overall diffusion impedance should be represented by two transmission lines in series (cf. equation 22), one representing the oxidation process and the other representing the reduction process. The series combination of these two transmission lines is still an impedance with the frequency and phase properties of the Warburg impedance. See Figure 2. If $C_o \gg C_R$ it can be seen from equation 22 that the impedance representing the oxidation process can be neglected.

2.2.2 The Adsorption Impedance

If there is adsorption of a reacting species on the electrode surface there must be modification of the equivalent circuit. Since adsorption involves charge storage it is represented by a capacitive

shunt on the appropriate transmission line (oxidation or reduction) and the relationship between the capacitance is given by (of equation 28)

$$C_{ad,1} = (n^2 F^2 / RT) \Gamma_1 \quad (29)$$

where Γ_1 is the surface concentration of the adsorbed species.

Thus a complete aperiodic equivalent circuit model as is shown in Figure 2.

2.3 Another Equivalent Circuit Model

Most other equivalent circuit models involve but minor modifications to that of Figure 1 or 2 and depend on similar basic assumptions e.g. that all processes of interest occur close to the working electrode, that electromigration and geometric capacitance of the cell are unimportant, that electroneutrality holds throughout the bulk of the electrolyte (no space charge), that the bulk of the electrolyte can be regarded as an ohmic resistor and that ordinary diffusion equations can be applied to charged species. Often an excess of indifferent electrolyte is required for the model to hold. In many circumstances, such as the present work, these assumptions lead to a model which fits closely to a real situation but the model may be inadequate to describe the behaviour of the system at extremes of frequency and for some particular types of electrolyte.

Macdonald [32] devised a model to overcome the above deficiencies for some ideal situations. The situations considered were a pair of identical plane parallel electrodes completely blocking (no charge

FIGURE 2

Equivalent Circuit with Transmission Lines and Capacitances Representing Adsorption.

crosses the electrode-electrolyte interface) or partially blocking (charge of one sign only is freely discharged at the electrodes). No adsorption is postulated and only a unimivalent electrolyte was treated. The electrolyte can be either solid or liquid.

The equivalent circuit for a cell of this type is given as in Figure 3a in which, for the partially blocking case (most relevant to the present work) C_g is the geometric capacitance of the cell,

$$\epsilon A/4\pi l$$

$$R_F = l/\mu_n en_0 A, \quad R_C = l/\mu_p en_0 A \quad (30)$$

and R_{si} and C_{si} are frequency dependent.

The frequency variable used by Macdonald is a normalised frequency $\omega = \omega_D \tau_D$, where τ_D is the dielectric relaxation time, $\epsilon/4\pi en_0(\mu_p + \mu_n)$, ϵ is the permittivity of the electrolyte, μ_p, μ_n are the mobilities of the positive and negative charge carriers. e is the protonic charge. l is the electrode spacing. Note that $en_0(\mu_n + \mu_p)$ is the limiting high frequency conductance of the electrolyte.

n_0 is the equilibrium homogeneous concentration of positive and negative charge carriers, i.e. no. of particles/unit volume.

Electrolyte and cell systems are considered as classifiable by a parameter $M = l/2L_D$ where L_D is the Debye length, $(\epsilon kT/8\pi e^2 n_0)^{1/2}$ and different equivalent circuit parameters arise for different ranges of this M parameter.

For a molten salt system, as considered in the present work,

FIGURE 3

Examples of the Whole Cell Equivalent
Circuits of Macdonald (reference 32).

$\epsilon = 3\epsilon_0$ (ϵ_0 is the permittivity of a vacuum) and for $T = 700K$

$L_D = 7 \times 10^{-12} m$ and for $l = 5mm$, $M = 4 \times 10^8$.

$\tau_D = 10^{-13} s$ so the normalised frequency range for $\omega = 10^3$ to 10^5 Hz is $\omega = 10^{-10}$ to 10^{-8} .

Thus in a conventional impedance method treatment M falls in the upper limits of the various cases treated by Macdonald and ω is well below most cases treated.

In the model, Figure 3a, the frequency response of R_{sl} and C_{sl} is given by Macdonald as the conventional Warburg response for $(10/M)^2 \leq \omega \leq 0.1$ which is the present situation and R_C and R_P are equal to $2R_0$. C_g , which is only about $10^{-14} F$ in a molten salt cell, can be neglected in this frequency range.

We note that there is no specific double layer capacitance and any such capacitance is incorporated in ~~W~~ as a space charge capacitance. A specific double layer capacitance is only added to the equivalent circuit for the case when an indifferent electrolyte is present as in parallel to the model of Figure 3a with an associated resistance R_B (see Figure 3b).

This equivalent circuit model differs from that of Figure 1 in several ways. Minor differences are that (a) C_g , the geometric capacitance is introduced. This is significant in electrolytes with high dielectric constants and at high frequencies ($\omega \gg 1$) and (b) θ a charge transfer resistance is not considered. According to Macdonald this would occur in series with R_P . More important differences arise from (a) the finite cell length approach which

leads to Warburg impedance only in certain frequency ranges, and (b) the way in which the solution resistance is considered, i.e. the limiting high frequency resistance (the usual definition of R_e) is the parallel combination of R_F , R_C , R_B . ($R_e = R_B$ in a supporting electrolyte case). Thus this is an equivalent circuit that would have different frequency characteristics to that of Figure 1. It has not yet been experimentally tested in any of the various forms detailed by Macdonald. Molten salts (KCl and AgBr) in cells of high cell constant (up to 6000 cm^{-1}) have been examined for frequency dispersion of impedance by Baker and Buckle [30] and space charge relaxation has been suggested as the source of the $\omega^{-3/2}$ frequency response observed.

2.4 Applicability of models to the present molten salt case

The present work has been conducted in high conductivity, low permittivity liquids, without an inert electrolyte, with low cell constants and at (low) frequencies where dielectric and space charge effects are sufficiently small to be neglected. The model that seems most applicable to this system is that of Figure 1 or 2, and the experimental results are analysed in terms of this model.

CHAPTER 3

IMPEDANCE METHOD: ANALYSIS OF IMPEDANCE MEASUREMENTS3.1 Parameters of Model in Terms of Measured Quantities

Comprehensive treatments relating experimental data to particular models have been available for some time, e.g. [56]. In consideration of the nature of frequency dispersion of impedance in conductance cells there has been general agreement, e.g. [57,58,54], on the equivalent circuit of a cell. Information about various parameters can be derived from measurements of R_s and C_s , the equivalent series resistance and capacitance, or from R_p and C_p , the equivalent parallel resistance and capacitance. For the purpose of this treatment we will replace the transmission lines of Figure 2 with the Warburg impedance and will not consider the complicating possibility of adsorption, i.e. the model is that of Figure 1. R_w and C_w are given by equations 23 and 24 and can be expressed as

$$R_w = \sigma / \omega^{1/2} \quad (31)$$

$$C_w = \sigma / \omega^{1/2} \quad (32)$$

where

$$\sigma = \frac{RT(c_o + c_R)}{n^2 F^2 A c_o c_R / 2D} \quad (33)$$

$$D = D_o = D_R \text{ if } D_o = D_R$$

$$D = D_R \text{ if } c_R \ll c_o.$$

The SI units for σ are $\Omega^{-1} s^{-1/2}$ or $F^{-1} s^{1/2}$.

Note that σ is defined as the inverse of our σ in some published work, e.g. [57,58].

We also have an expression for θ (equation 1) and since the exchange current density is directly related to θ , i_0 is available from the intercept and σ (or D) from the slope of a plot of $R_w + \theta$ versus $\omega^{-1/2}$ using this model [43].

θ becomes significant only if R_0 is small (of the order of 10 ohms or less). If it is possible to disregard θ , R_s is not in general a linear function of $\omega^{-1/2}$ but follows a concave curve upwards since from the circuit of Figure 1

$$R_s = R_0 + \frac{\sigma}{(1 + 2\sigma C_d \omega^{-1/2} + 2\sigma^2 C_d^2 \omega) \omega^{1/2}} \quad (34)$$

R_s will approximate to a linear function of $\omega^{-1/2}$ for low values i.e. $\sigma C_d \omega^{-1/2} \ll 1$ and/or for very small C_d values (which are very likely in pure molten salts). The capacitive component in this case is given by

$$C_s = C_d + \frac{1}{\sigma \omega^{1/2}} \left[\frac{1 + C_d \sigma \omega^{1/2}}{1 + 2C_d \sigma \omega^{1/2}} \right] \quad (35)$$

which indicates that C_s will tend to C_d at high frequencies

Linear extrapolation to $\omega = \infty$ of R_s versus $\omega^{-1/2}$ to determine R_0 leads to negative errors in R_0 the relative significance of which depends on the absolute value of R_0 .

Hill and Djordjevic [57] and Crawford [58] plotted $R_s - R_e$ versus $\omega^{-1/2}$ for various likely values of C_d and σ for several molten salts. The curves are linear at low values of ω but extrapolation does not lead to the correct value at $\omega = \infty$. The error in the intercept of linear extrapolation of low frequency data is given by

$$\begin{aligned} \Delta R &= \frac{\sigma}{\omega^{1/2}} - \frac{\sigma}{\omega^{1/2}} \left(\frac{1}{1 + 2C_d\sigma\omega^{1/2} + 2C_d^2\sigma^2\omega} \right) \\ &= \frac{2\sigma^2C_d + 2C_d^2\omega^{1/2}\sigma^3}{1 + 2\omega^{1/2}C_d\sigma + 2\omega C_d^2\sigma^2} \end{aligned} \quad (37)$$

and for $\omega < 1$ kHz and low C_d (R_s versus $\omega^{-1/2}$ linear), $\Delta R = 2C_d\sigma^2$.

The absolute value of ΔR may be as large as 0.1Ω thus ΔR becomes important for $R_e < 10 \Omega$. All the above treatment supposes that $\theta = 0$, i.e. a very fast electrode reaction is present.

Although C_d values in most cases are not accurately known, Hill and Djordjevic [57] have shown their calculated ΔR values to be in reasonable agreement with observed differences (by comparison of data from capillary and non-capillary cells).

If $\theta = 0$ and Z_w is an impedance with magnitude proportional to $\omega^{-1/2}$ with phase angle $\pi/4$, the simple expressions (34) and (35) hold. By eliminating σ from these equations one gets

$$C_d = C_p^* (1 - \omega C_s [R_s - R_e]) \quad (38)$$

where C_p^* is the parallel equivalent capacitance to the series

combination of $(R_s - R_o)$ and C_s . This equation has been used by Hills and Johnson [37] to give results for C_d in nitrate melts close to those obtained by other methods. Their definition of C_p' seems confused with that of C_p [54].

If $\theta \neq 0$, the equivalent expressions for R_s and C_s in terms of the cell parameters are very much more complex and the corresponding expression for C_d is

$$C_d = C_p' \left[1 - \omega C_s (R_s - R_o) \frac{1 \pm \sqrt{4C\omega\theta - 4C^2\omega^2\theta^2 + 1 - 2C\omega\theta}}{1 \pm \sqrt{4C\omega\theta - 4C^2\omega^2\theta^2 + 1 + 2C\omega\theta}} \right] \quad (39)$$

where $C = \omega C_p' C_s (R_s - R_o)$.

This can be rearranged to

$$\theta = \frac{C_d - C_p' + \omega C_s (R_s - R_o) C_p'}{(C_d^2 - 2C_d C_p' + C_s C_p')} \quad (40)$$

Note that $\omega C_s (R_s - R_o) \geq 1$ for $\theta \geq 0$ since denominator of (3) is positive always and $\theta = 0$ implies equation (3.8) above.

In terms of series components, $C_p' = C_s / [1 + \omega^2 C_s^2 (R_s - R_o)^2]$ i.e. $C_p' > C_p$.
(41)

3.2 Outline of Experimental Difficulties

From the preceding paragraphs, one sees that in order to know accurately the difference between R_o and R_s it is imperative to know C_d .

The determination of C_d is beset by many difficulties on account of the two effects, double layer capacitance and faradaic impedance

being inextricably combined with each other and with space charge relaxation [32]. We must recognise that the simple equivalent circuit model is simple.

Hills and Johnson [37] determined C_d of platinum and other electrodes in various nitrate and chloride melts. They found that C_d was almost independent of temperature and cations present but depended on the nature of anions present. Information about the structure of the melt may be obtained from C_d values. Hills and Djordjevic, giving quantitative examples to illustrate the ΔR formulae, plotted calculated frequency dispersion of impedance versus $\omega^{-1/2}$ for $\sigma = 4 \times 10^{-8} \text{ s}^{-1}$ and several C_d values. They used C_d values from Hills and Johnson [37] to correct conductivity figures for KNO_3 , Na_2CO_3 and CdCl_2 melts for which non-conflicting data exists. Comparison of these conductivity values with those obtained independently in capillary cell measurements gives agreement within order of magnitude.

Also, in seeking to provide kinetic data (e.g. i_0 and α , intensive properties) from C_s and R_s (extensive properties) from impedance measurements, when electrode area cannot be determined exactly, difficulties arise. A technique such as measurement of faradaic rectification (which is the study of the response of an electrode to ac by measuring dc potential resulting from partial rectification [ref. 53, p.372; 59]) would not have this difficulty although the apparatus is necessarily somewhat more sophisticated. Faradaic rectification has been measured for some molten salts by Barker et al [60].

Thus in general even when only faradaic polarisation is considered, the relationship between ω and $R_s - R_e$ is considerably more complex than $\omega^{-\frac{1}{2}} \propto R_s - R_e$.

In order to evaluate the frequency dispersion of impedance for the type of experimental set-up usually used it is necessary to determine some of the electrode parameters first.

The most convenient methods of determining C_d and the kinetic parameters i_0 , k_s , α , involve pulse techniques. References to several potentiostatic and galvanostatic methods are given in Section 1.2.6.

In this work a single pulse galvanostatic method is to be tried to evaluate C_d and kinetic parameters for the electrode systems studied. In this case a current 'impulse' or a current step function is applied through a two electrode electrolytic cell. The working electrode, of which the kinetics are to be studied is made much smaller than the counter electrode which can then be regarded as non-polarisable.

Information is obtained by observing the potential response of the working electrode with time.

Berzins and Delahay [40] gave the first comprehensive analysis of the situation for the single galvanostatic pulse method for an electrode system in which the double layer capacitance and diffusion overpotential must be taken into account.

The methods described by Berzins and Delahay require prior accurate evaluation of C_d and R_e in order to determine kinetic parameters but methods have been developed since [42] where these

parameters can be determined directly from a potential-time transient.

More recent publications, particularly those of Pilla [45] and Birke [46] have taken the generalised equivalent circuit models and made analysis of their behaviour under the influence of impulse current or potential functions with sufficient generalisation to include the possibility of non-ideal step functions. See Chapter 7.

3.3 Testing of the Model by the Impedance Method

Measurements on a suitable electrode-electrolyte system for which parameters such as A , n , T , b , are known can be made in the conventional way (in a two electrode cell with a bridge type apparatus) applying a small sinusoidal voltage across the cell and measuring the parallel (or series) components of the impedance. The analysis of the frequency response can be done in a classical [25,27,56] way or by the complex plane method [89]. Recent comparison of the two methods [96] indicated little difference in the final results (for kinetic parameters) so the classical approach has been used in this work. To analyse the frequency response in terms of the model of Figure 1, some of the frequency independent components of the model must be known. We will consider that $C_{ad} = 0$ (see Section 10.2.2) and determine or estimate C_d , R_e , D_1 , c_1 before the measurements.

If the model holds then C_d and θ can be determined by graphical extrapolations but in order to test the model these ought to be confirmed by other methods.

CHAPTER 4

IMPEDANCE METHOD: EXPERIMENTAL EQUIPMENT AND TECHNIQUE4.1 The Molten Salt Studied

The salt studied in this work is cadmium iodide.

There are several reasons why this particular salt was chosen for a study of electrode impedances and frequency dispersion.

a) The cadmium halides are salts for which the various ionic species present are well established and for which reliable conductance data exists.

b) Dissolution of cadmium metal in the salt produces a simple ionic redox system.

c) The iodide was used because it is easy to handle and has a low melting point. Low conductivity is perhaps a disadvantage.

4.2 The Structure and Nature of CdI_2 and Solutions of Cd in CdI_2 4.2.1 The Structure

Considerable work has been done to determine the microscopic structure of cadmium halides and the solutions of cadmium in cadmium halides. Most of this work has been done with cadmium chloride systems but those published works although not conclusive have not detected or deduced significant deviations of kind between the chloride and the bromide and iodide systems.

X-ray studies were done on liquid CdI_2 in 1953 [62] which

indicated that this liquid at 400°C is a loose expanded form of the solid with short range order as CdI_6 octahedra and bonding as angular CdI_2 monomers.

The Cd/CdCl_2 system has had considerably more attention than Cd/CdI_2 and deductions as to the species present have been made from melting point depression [63], solubility [64], emf [58,65], and conductance measurements.

For Cd/CdCl_2 the available evidence can be summarised thus:

1956. Grothaus et al [63]. Cryoscopic data indicated the probability of dissolved Cd taking the form of Cd_2^{++} . However the results presented in this paper were later shown to be inconclusive because of a data error [64].

1960. Topol and Landis [64]. Solubility curves were determined and calculations made from cryoscopic data. The presence of subhalide forms such as Cd_4Cl_6 and Cd_3Cl_4 was postulated. The evidence is still inconclusive.

1960. Crawford [58]. Emf, density and conductance data were used to deduce that the predominant form of the dissolved metal is Cd_2^{++} .

1961. Corbett et al [66]. Cd_2^{++} isolated as solid $\text{Cd}_2(\text{AlCl}_4)_2$, thus giving extra evidence in support of Cd_2^{++} being present in Cd/CdCl_2 melts.

1961. Angell and Tomlinson [67]. In this paper associated ions were postulated, CdCl^+ and Cd_2Cl^+ . Data was from self-diffusion and electrical conductance measurements.

1963. Topol [65]. Emf measurements in a Cd/CdI_2 concentration cell gave evidence of a two electron process occurring at the electrodes (Nernst $n = 2$) which suggests the absence of any Cd^+ and the possibility of Cd , Cd_2^{++} or Cd_3^{4+} species. Evidence that Cd_2^{++} is very stable near the melting point of the salt.

1966. Crawford and Tomlinson [68]. The thermodynamics of the system were analysed from emf and volumes of mixing data. The most satisfactory explanation of the experimental data is given by the model of Cd dissolved as Cd_2^{++} .

1966. Grantham [69]. Conductance data indicates that Cd_2^{++} is stable to over 1000°C and evidence is given against the possibility of an electronic conduction mechanism.

1969. Staffanson [70]. This paper essentially confirms the thermodynamic evidence of Crawford and Tomlinson by measurements of the vapour pressure of Cd above the solution. This is strong support for the Cd_2^{++} ion theory.

How does all the above evidence relate to the Cd/CdI_2 system?

Topol and Landis [64] studied this system and from their solubility and cryoscopic data the iodide system seems similar to the chloride although the melting point and solubility of cadmium in the salt are rather lower for the iodide.

Grantham [69] gives conductance data for Cd/CdI_2 . This is consistent with Cd being dissolved as Cd_2^{++} but with considerable ionic association of pure CdI_2 at the lower densities associated with higher temperatures (around 1000°C).

4.2.2 Diffusion Data

There is no published data for the diffusion coefficients of Cd^{++} or Cd_2^{++} in CdI_2 . However, since there is no reason to expect that the character of the ions in CdI_2 is significantly different from their character in CdCl_2 a reasoned estimate can be made from CdCl_2 data available.

For example, if we consider that the deviation from the Nernst-Einstein equation is the same as that quoted by Angell and Tomlinson [67] for the CdCl_2 case for a similar temperature interval above the melting point, i.e. a factor of 1.89, we have

$$D_i = \Lambda_i RT / z_i^2 F^2 \quad (42)$$

Λ_i is the molar conductivity of the ion i and depends on the transport number of the ion. We will suppose that t_+ in CdI_2 to be the same or slightly greater than t_+ in CdCl_2 [71] (perhaps a rather gross assumption because of the different halide ion sizes) so that for $T = 680\text{K}$

$$\begin{aligned} D_{\text{Cd}^{++}} &= \frac{8.3 \text{ J/mol} \times 680\text{K} \times 230/12000 \text{ s}^{-1} \text{ m}^2 \text{ mol}^{-1} \times 1.89 \times 0.7}{4 \times (96500 \text{ C/mol})^2} \\ &= 4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

and if the inverse relationship between ionic radius and diffusion coefficients holds (Stokes-Einstein equation) then

$$D_{\text{Cd}_2^{++}} = 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}.$$

The variation with the relatively small temperature changes in the present work will be taken as having Arrhenius form:

$$D = D_1 \exp(-\Delta E_D/RT) \quad (43)$$

The value for ΔE_D for CdI_2 is $28.72 \text{ kJ mol}^{-1}$ [12] and by examining this quantity in relation to the literature value for ΔE_Λ (20.9 kJ mol^{-1}) [61] and observing that the relationship [73]

$$\Delta E_D = \Delta E_\Lambda + RT_m \quad (T_m \text{ is melting temperature}) \quad (44)$$

is fairly closely followed, certainly to much less than 10% error, we apply this equation to the literature value for ΔE_Λ in CdI_2 (see Section 4.2.3) whence $\Delta E_D = 58 \text{ kJ mol}^{-1}$ for CdI_2 . This value will be used in this work.

4.2.3 Physical properties of liquid CdI_2 from the literature

Formula: CdI_2

Molecular weight: 366.21

Melting point: 660K [74]

Boiling point: 981K [74]

Density: $(5133 - 1.117 T/K) \text{ kg m}^{-3}$, (680K - 920K) [75]

% volume change on fusion: 26.61% [76]

Vapour pressure: $\log(P/\text{mmHg}) = 8.8120 - 6012.4/T$ (77)

Enthalpy of fusion, ΔH_f : $20.71 \text{ kJ mol}^{-1}$ [78]

Specific heat, C_p : $100.4 \text{ J K}^{-1} \text{ mol}^{-1}$ [76]

Expansivity: 2.58×10^{-4} at 727.1K [79]

Equivalent conductance given by $\Lambda_{\infty} = 0.1109 \text{ S m}^2 \text{ equiv}^{-1}$

$$\Delta E_{\infty} = 26.7 \text{ kJ equiv}^{-1} [79]$$

Conductance: $K = -108.41 + 0.17574T/K + 0.2419(T/K)^2 \cdot 10^{-4} \text{ S m}^{-1}$

(sd = 0.002) [75,80] (also see Graph 2)

Solubility of Cd in CaI_2 [64]: 2.5 mole% at 673 K

15 mole% at 973 K

25 mole% at 1223 K

4.3 Apparatus for Impedance Method

4.3.1 Molten salt bath, temperature control and temperature measurement

For heating the conductance cells an isothermal molten salt bath was used. The salt mixture in the bath was that described as 'HTS' by Kirst et al [81] and used by others [82,83]. This is a mixture, not a eutectic, of NaNO_2 , NaNO_3 and KNO_3 in the ratio 40:7:53 by weight. This is a chemically stable mixture from its melting point of 415 K (142°C) up to over 780 K (500°C) at which temperature fuming becomes noticeable, and there is slow decomposition leading to a rise in freezing point. Other desirable features of this mixture are its chemical inertia and its low cost. The main precautions to be taken with this melt involve keeping it out of contact with organic matter on account of its vigorous oxidising characteristics and also out of contact with aluminium metal.

The bath was of stainless steel, cylindrical with a diameter of 60 cm and a depth of 60 cm. An outer stainless steel container was

separated from the inner container by 15 cm of Perlite. An insulated lid with holes for heaters, stirrer and insertion of samples was used.

The mass of salt used in the bath was about 170 kg.

For heating the salt bath an incoloy tube heater, 2 kW 110 V was used as control heater and a 2.3 kW, 230 V heater on a Variac was used as an auxiliary at temperatures above 620 K (350°C) as necessary.

Temperature control was achieved using a Melabs proportional temperature controller type CTC-1A. The probe in the bath is a platinum resistance (500 Ω at 273 K) in a stainless steel sheath and the controller can switch 20A at 100 V dc. In an ideal situation control to ± 0.001 K is possible.

Stirring of the salt in the bath is by a stainless steel shaft with two sets of propeller blades 12 cm in diameter (one set near bottom, the other about 35 cm higher) turned by an electric motor at 800 rpm.

Temperature measurement in the bath is by means of a chromel-alumel thermocouple (checked against a calibrated thermocouple) and the potential is measured to 1 μ V using a Tinsley 5590A potentiometer and a Tinsley M.R.4 galvanometer. In this particular work absolute temperature values are not regarded as particularly important. (1 μ V is equivalent to about 0.025 K with this thermocouple).

Measurements were made to test the isothermal quality of the bath. The limiting factor seems to be the rather inefficient stirrer configuration rather than deficiencies in the control or heater systems.

At one point, variation of temperature with time is

± 0.025 K (i.e. $\pm 1 \mu\text{V}$) for short term, $\sim \frac{1}{2}$ hour

with variations as much as 10 times this much over a whole day.

At one time, variation of temperature with position is less than 1 K from top to bottom of bath.

4.3.2 Conductance Cells

Design

The requirements for a cell to emphasise the frequency dispersion of impedance and the electrode effects are centered around the fact that the cell constant must be low. The electrolyte resistance must be small compared with the electrode impedance components.

A selection of cell and electrode designs is given by Graves et al [50].

A small electrolyte volume is desirable for uniform temperature but the electrodes must be sufficiently separated to allow free circulation of electrolyte.

Several trials were made with different types of glass cell. One particular design was chosen, an example of which is shown in the photograph. (Figure 4).

For this work it is necessary to have several variations of electrode configuration. Some cells have identical electrodes, and some have electrodes of vastly differing sizes. At least one cell of high cell constant is necessary to check electrolyte conductance values with the literature.

Tungsten is the best electrode material. It is chemically

Figure 4. Mark 6 Cell.

inert with respect to cadmium salt melts, it can be readily sealed into pyrex glass and is readily available in N.Z.

The cell must have provision for an inert atmosphere over the melt.

Three different types of cell were used which differed only in the electrode region.

- 1) 'Mark 4', the inter-electrode space was a horizontal capillary tube, diameter 1 mm, with about 13 cm between the uniform vertical cylindrical (rod) electrodes. Cell constant about 1400 cm^{-1} .
- 2) 'Mark 5' was a cell with vertical cylindrical rod electrodes parallel and close together. Typically the cell constant was about 2 cm^{-1} and the apparent electrode area was the same for all cells.
- 3) 'Mark 6'. This cell had two plane parallel electrodes, one the buffed end of a 1 mm diameter tungsten rod, the other a 1 cm^2 piece of tungsten sheet, 0.025 mm thick. The foil piece was welded to a tungsten rod sealed through the glass wall of the cell. Welding was done with a small arc in a reducing atmosphere (90% N_2 , 10% H_2) by a method similar to that described by Tomlinson et al for welding molybdenum [84]. The ratio of the electrode areas is about 100:1. The cell constant for this type of cell was typically about 2 cm^{-1} .

Cleaning of Cell after manufacture.

Cleaning the cell immediately after manufacture was done in several ways. However the most satisfactory method to clean the electrodes which were black ($W + WO_2$) after being heated in air during the electrode sealing process was [85] to fill the cell with 20% KOH and apply a potential of about 30v between the electrode being treated and a counter electrode inserted in the solution. The tungsten electrode was made the anode. Vigorous bubbling was allowed to continue for about 10 s whereupon light tapping caused the coating, now yellowish WO_3 , to flake off completely.

The cell was then rinsed with distilled water until the conductivity was about $10^{-4} S m^{-1}$ and the cell was dried in an oven at about 390 K.

Impedance of the Cell Leads

Lead capacitance was found by measuring with the bridge with the cell empty. This capacitance was very small and the bridge trim controls were adequate for compensation.

One cell was filled with mercury and the measured resistance taken to be the series lead resistance. This was about 0.05Ω and as it appears in series with the electrolyte resistance, R_e , in which the certainty is not as good as 0.05Ω , it is neglected in the present work.

4.3.3 Determination of the cell constant

Cell constants could be determined approximately from the geometry of the cells but standard solutions were used for accurate determinations.

1.000 Nermal KCl (71.1352 g KCl/kg soln, $\kappa = 0.111342 \text{ S cm}^{-1}$) [13] was prepared by careful weighing of pure KCl and water and this was the standard solution used for all cell constant measurements.

Conductance measurements were made with the cell in a thermostatted water bath at 25.00°C , using the Wayne Kerr signal generator, bridge and detector (see Section 4.3.5) to make impedance measurements over a frequency range 200 Hz to 20 kHz.

With some cells the electrodes were platinised at this stage for the cell constant measurement but the actual cell constant obtained was identical to that obtained using the unplatinised tungsten electrodes, the only difference being a smaller frequency dispersion of the impedance of the aqueous solution using platinised electrodes. This may be due to a change (increase) in the true electrode area (see equations 33,34) or a catalytic effect of the platinum on the electrode processes. Since the cell constant is determined by an extrapolation method greater precision was possible with platinised cells. After the cell constant measurement the platinum was removed with aqua regia and the cell rinsed to its earlier cleanliness with distilled water. Slight anodising of the electrodes in KOH was carried out also to clean the tungsten.

For frequencies above 2 kHz plots of the series resistance of the cell containing 1D KCl were linear functions of $\omega^{-\frac{1}{2}}$.

Extrapolation to infinite frequency was used to determine the electrolyte resistance.

Two methods for cell constant determination by direct measurement of the electrodes are outlined in the appendix.

When the cell was ready for the salt, the cell was weighed, the salt was added (about 15 g) and the cell was weighed again. The filling tube was sealed and the cell was evacuated via the sidearm and was left overnight on the pump. It is important to remove all oxygen as this would immediately oxidise the molten iodide to iodine. After overnight evacuation $1/3$ atmosphere of oxygen free nitrogen was admitted and the cell was sealed at the constriction.

4.3.4 The electrolyte

The CdI_2 salt used was BDH AnalaR grade. The cadmium metal was a pure sample obtained from Electrolytic Zinc Co., Australia, cleaned in dilute HCl as necessary.

4.3.5 Impedance measuring equipment

Impedance measurements were made with Wayne Kerr equipment. The bridge used is a transformer bridge - Universal Bridge B221 Mark 3, with an external source signal from AF Signal Generator S121 and as external detector the Waveform Analyser A321. This system operates satisfactorily over a frequency range of 100Hz to 20kHz and in the milliSiemens range most often encountered in this work precision is about 0.1%. The alternating potential applied across the cell is never more than 3 mV (peak to peak).

This equipment is nominally accurate to 0.1% over most of the range used. This was checked with standard components and performance was better than the maker's specifications. Discrimination is of the order of 0.01%. When the Wayne Kerr Low Impedance Adaptor Q221 is used (for $R_p < 10 \Omega$) the accuracy is nominally 1% which can be corrected for, and discrimination is as good as 0.02%.

Use was also made of the Autobalance Precision Bridge B331 for precise (0.01%) measurements at $\omega = 10^4$ Hz only.

4.3.6 Conduct of experiments

The cell was immersed deep in the molten salt bath and allowed to reach thermal equilibrium.

Parallel conductance and capacitance components were measured with the Wayne Kerr apparatus for a selection of bridge frequencies ranging from 200 Hz to 20 kHz. The temperature was monitored throughout by means of the thermocouple placed in a glass well very close to the salt sample. This includes random checking for reproducibility. A more precise value for the impedance at 1591.55 Hz could be obtained with the autobalance bridge, B331.

CHAPTER 5

IMPEDANCE METHOD. EXPERIMENTAL RESULTS5.1 Cell notation

E.g. 5H7. 5, type of cell (Mark 5)

H, 8th cell of this type

7, 7th set of measurements on cell 5H.

Since this notation was used throughout this work and in the data processing, it has been retained unchanged in this written account. Because some cells were rejected as unsatisfactory or broke in use there are gaps in the numbering of cells quoted in the following results.

5.2 Mark 4 cell. Cell constant and impedance results

This is a high cell constant cell for determining a frequency independent conductivity for the melt.

The cell constant was determined using two different 1.000 demal KCl solutions as $622.3 \pm 0.6 \text{ cm}^{-1}$.

An attempt was also made to measure the cell constant using a molten salt as a standard [86]. This was done with KNO_3 at 373.6°C but the result (631 cm^{-1}) is inconclusive on account of the reaction of the tungsten electrodes with the nitrate melt [87].

By measurement, the length of the capillary was 12 cm and its diameter $\sim 1.5 \text{ mm}$, giving an approximate cell constant of 680 cm^{-1} .

The cell was filled with pure CdI_2 under an atmosphere of oxygen free nitrogen (1 atmosphere as the cell was not sealed).

Temperature/°C	$G_p/\mu S$	G_p/nF	$k/S\text{ cm}^{-1}$		
			this work	ref. [80]	ref. [69]
406.0	358.4	0.01	0.223	0.223	0.225
402.0	345.0	0.01	0.214	0.215	0.215

The variation of the above conductance measurements with frequency is less than 0.1% over the range 100 Hz to 20 kHz. The conductance is about 0.1% lower at 20 kHz than 100 Hz but there is no measured variation from 100 Hz to 7 kHz. The literature values are found by linear interpolation of values quoted for slightly different temperatures. See Graph 2.

5.3 Mark 5 and 6 cells. Cell Constant

These are low cell constant cells, $< 5\text{ cm}^{-1}$, in which the evaluation of the cell constant is important for the evaluation of the electrolyte resistance.

The cell constants quoted below were obtained using 1.000 normal KCl solution at 25.00°C. Considerable frequency dispersion is observed but as a plot of R_g vs $\omega^{-1/2}$ is linear for frequencies $> 4\text{ kHz}$, the resistance obtained by extrapolating this plot to infinite frequency is taken to be the resistance of the electrolyte. This is a standard practice for dilute aqueous electrolyte. (See further comments on this, Section 6.1). A typical plot for the determination of cell constant is shown in Graph 1, which gives points for plain tungsten electrodes and for platinised tungsten electrodes.

53.(a)

GRAPH 2

Temperature Dependence of Conductivity.

Cell constants for cells used:

Cell	Cell constant/cm ⁻¹
5D	1.25
5H	1.32
5I	1.44
5J	2.06
5L	1.29
6A	2.4
6C	2.6

Because of the uncertainty of the extrapolation the values are possibly low by as much as 2% for Mark 5 cells and 5% for Mark 6 cells.

5.4 Mark 5 and 6 Cell. Impedance Results

In the impedance results which follow, f , G_p and C_p are the measured quantities (except in cells 5L and 5I where R_s and C_s are measured directly).

R_s and C_s are derived from G_p and C_p by these simple equations:

$$R_s = G_p / (G_p^2 + \omega^2 C_p^2)$$

$$C_s = (G_p^2 + \omega^2 C_p^2) / \omega^2 C_p \quad (\omega = 2\pi f)$$

All figures are significant in data and derived quantities.

RUN 5D2

Temperature 409°C

Electrolyte Pure CdI_2 under vacuum.

f/kHz	C_Y/nS	C_P/nF	R_E/Ω	C_E/nF
0.200	4.70	2.214	157.6	8.53
0.500	7.92	2.011	77.16	5.17
1.000	11.05	1.423	54.69	3.60
2.000	13.92	1.013	39.12	2.22
4.000	18.97	0.735	27.06	1.51
5.000	20.96	0.675	23.58	1.33
7.000	24.82	0.598	18.98	1.13
10.00	30.70	0.524	15.15	0.980
13.00	36.57	0.469	13.04	0.896
15.00	40.60	0.440	12.05	0.862
20.00	50.57	0.379	10.48	0.806

RUN 5H2

Temperature 405°C

Electrolyte. Pure CdI_2 under 1/3 atmosphere (at room temperature)
of oxygen free nitrogen.

f/kHz	G_p/mS	$C_p/\mu\text{F}$	R_g/Ω	$C_g/\mu\text{F}$
0.200	10.70	3.720	78.48	23.2
0.500	17.88	3.614	39.86	12.6
1.000	23.70	2.308	30.70	8.47
2.000	32.08	1.585	22.50	5.70
4.000	43.72	0.984	17.33	4.06
5.000	47.62	0.826	16.19	3.61
7.000	53.84	0.630	14.68	3.01
10.00	60.96	0.467	13.31	2.48
13.00	66.10	0.372	12.49	2.13
15.00	69.41	0.326	12.05	1.99
20.00	76.98	0.249	11.15	1.76

RUN 5H4

Temperature 407°C

Electrolyte. Pure CdI_2 under 1/3 atmosphere (at room temperature)
of oxygen free nitrogen.

f/kHz	G_p/mS	$C_p/\mu\text{F}$	R_g/Ω	$C_g/\mu\text{F}$
0.200	9.18	3.270	90.75	19.6
0.500	15.43	2.960	47.54	11.1
1.000	19.16	1.983	36.68	6.67
1.592	23.33	1.379	31.77	5.33
2.000	24.78	1.177	29.75	4.48
4.000	32.17	0.744	23.23	2.95
5.000	34.80	0.635	21.63	2.57
7.000	39.10	0.500	19.43	2.08
10.000	44.14	0.391	17.30	1.65
13.000	48.79	0.324	15.84	1.43
15.000	51.32	0.293	15.11	1.30
20.000	56.82	0.239	13.76	1.09

RUN 5H3

Temperature 407°C

Electrolyte. Pure CdI_2 under 1/3 atmosphere (at room temperature)
of oxygen free nitrogen

f/kHz	C_p/mS	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	9.22	3.160	91.49	20.2
0.500	15.74	2.944	47.23	11.5
1.000	19.40	1.813	38.33	7.07
2.000	24.84	1.171	29.80	4.51
4.000	31.92	0.729	23.56	2.94
5.000	34.43	0.624	21.93	2.55
7.000	38.54	0.493	19.71	2.05
10.00	43.50	0.387	17.52	1.63
13.00	48.09	0.322	16.01	1.40
15.00	50.50	0.292	15.27	1.28
20.00	55.96	0.239	13.87	1.07

RUN 5H5

Temperature 406°C

Electrolyte. Pure CdI_2 under 1/3 atmosphere (at room temperature)
of oxygen free nitrogen.

f/kHz	G_p/mS	$G_p/\mu\text{F}$	R_g/Ω	$C_g/\mu\text{F}$
0.200	9.27	3.290	89.98	19.8
0.500	15.67	2.980	47.03	11.3
1.000	19.15	1.980	36.72	6.67
1.592	23.43	1.374	31.76	5.37
2.000	24.71	1.221	29.21	4.39
4.000	32.22	0.739	23.30	2.96
5.000	34.78	0.630	21.72	2.58
7.000	39.10	0.498	19.47	2.08
10.00	44.11	0.388	17.37	1.66
13.00	48.96	0.321	15.87	1.44
15.00	51.53	0.291	15.12	1.32
20.00	56.71	0.238	13.80	1.09

RUN 5H7

Temperature 407°C

Electrolyte. Pure CdI_2 under $1/3$ atmosphere (at room temperature)
of oxygen free nitrogen

f/kHz	C_p/mF	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	15.59	4.28	57.32	40.2
0.500	24.56	3.48	33.98	21.0
1.000	28.74	2.09	28.81	12.1
2.000	35.16	1.300	23.39	7.32
4.000	44.00	0.770	19.04	4.75
5.000	46.82	0.644	18.00	4.09
7.000	51.40	0.490	16.55	3.27
10.00	56.58	0.378	15.03	2.52
13.00	60.88	0.296	14.19	2.17
15.00	63.34	0.264	13.68	1.97
20.00	68.54	0.209	12.72	1.63

RUN 517

Temperature 406°C

Electrolyte. Cd/CdI_2 mixture, 0.0960 mole % of Cd dissolved in the salt, under $1/3$ atmosphere (at room temperature) of oxygen free nitrogen.

For this set of measurements, the low impedance adaptor (Wayne Kerr Q221) was used. Absolute accuracy is only $\pm 1\%$ but discrimination can be as good as $\pm 0.02\%$. See page 51. R_s and C_s are the measured quantities.

f/kHz	R_s/Ω	$C_s/\mu\text{F}$
0.200	6.90	3600
0.500	6.811	2110
1.000	6.764	1550
1.592	6.739	1320
2.000	6.726	1320
3.000	6.708	1480
4.000	6.697	2600
5.000	6.689	3000*
7.000	6.678	3000*
10.00	6.667	3000*
20.00	6.635	3000*

* Lead inductance becomes dominant in these readings and these C_s values are estimates only.

RUN 5J2

Temperature 403°C

Electrolyte. Cd/CdI₂ mixture, 0.0087 mole % of Cd dissolved in the salt, under 1/3 atmosphere (at room temperature) of oxygen free nitrogen.

f/kHz	C_p/nF	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	79.00	12.00	12.21	341
0.500	87.18	3.797	11.26	207
1.000	92.14	1.546	10.73	141
1.592	94.69	0.808	10.48	112
2.000	95.73	0.575	10.39	102
3.000	97.38	0.310	10.23	86.4
4.000	98.36	0.196	10.14	78.3
5.000	99.04	0.133	10.08	74.9
7.000	99.94	0.069	10.00	74.9
10.00	100.77	0.026	9.92	99.0
13.00	101.20	0.008	9.88	191
15.00	101.44	< 0.001	9.86	
20.00	101.90	< 0.001	9.81	

RUN 5L4

Temperature 403°C

Electrolyte Cd/CdI₂ mixture, 0.0069 mole % of Cd dissolved in the salt, under 1/3 atmosphere (at room temperature) of oxygen free nitrogen.

Measurements made using low impedance adaptor, Wayne Kerr Q221.

f/Hz	R/ Ω	C/ μ F
0.200	9.700	570
0.500	8.550	174
1.000	7.950	122
1.592	7.654	95.1
2.000	7.531	85.8
3.000	7.361	68.8
4.000	7.249	59.3
5.000	7.166	53.3
7.000	7.058	46.2
10.00	6.953	41.5
13.00	6.886	39.4
15.00	6.846	40.2
20.00	6.773	48.7

RUN 6A1

Temperature 40.4°C

Electrolyte Pure CdI₂ under oxygen free nitrogen

f/kHz	G_p/mS	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	15.30	6.480	50.93	29.4
0.500	21.25	2.884	39.82	18.7
1.000	25.22	1.483	34.89	12.3
2.000	29.10	0.765	30.98	7.77
3.000	31.11	0.516	29.28	5.79
4.000	32.54	0.386	28.22	4.73
5.000	33.80	0.310	27.32	4.04
7.000	36.16	0.226	25.71	3.22
10.00	38.27	0.155	24.54	2.55
13.00	40.45	0.118	23.39	2.20
15.00	41.45	0.100	22.94	2.03
20.00	42.64	0.074	22.39	1.63

RUN 6A2

Temperature 428°C

Electrolyte. Pure CdI_2 under oxygen free nitrogen

f/kHz	G_p/mS	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	22.83	9.107	35.01	45.3
0.500	31.28	4.094	27.34	28.3
1.000	38.02	1.976	23.77	20.5
2.000	41.99	0.934	22.09	12.9
3.000	45.27	0.615	20.73	9.99
4.000	47.28	0.449	20.01	8.33
5.000	48.75	0.344	19.55	7.34
7.000	50.80	0.230	18.93	6.03
10.00	53.70	0.150	18.07	5.02
13.00	55.02	0.104	17.75	4.47
15.00	55.85	0.086	17.54	4.17
20.00	56.76	0.062	17.29	3.35

RUN 6A3

Temperature 438°C

Electrolyte. Pure CdI₂ under oxygen free nitrogen

f/kHz	G_p/mS	$C_p/\mu\text{F}$	R_p/Ω	$C_p/\mu\text{F}$
0.200	26.24	10.05	30.94	53.4
0.500	35.73	4.262	24.54	34.6
1.000	42.02	2.158	21.55	22.9
1.592	44.39	1.335	20.66	16.1
2.000	46.56	1.029	19.94	14.4
3.000	49.77	0.650	18.94	11.4
4.000	51.79	0.465	18.37	9.60
5.000	53.24	0.353	18.00	8.49
7.000	55.40	0.232	17.46	7.07
10.00	58.60	0.152	16.62	5.87
13.00	61.20	0.109	16.00	5.26
15.00	61.98	0.089	15.84	4.95
20.00	62.39	0.060	15.80	4.17

RUN 6A4

Temperature 463°C

Electrolyte. Pure CdI₂ under oxygen free nitrogen

f/kHz	G _p /mS	C _p /μF	R _s /Ω	C _s /μF
0.200	47.10	12	19.26	130
0.500	59.12	5.331	15.66	71.8
1.000	67.35	2.330	14.18	51.6
1.592	70.59	1.324	13.68	38.9
2.000	71.94	1.003	13.49	33.7
3.000	75.20	0.591	13.01	27.5
4.000	77.30	0.399	12.72	24.1
5.000	78.70	0.292	12.53	21.3
7.000	80.58	0.180	12.29	18.3
10.000	82.35	0.104	12.07	16.6
13.000	83.37	0.067	11.94	15.6
15.000	83.95	0.051	11.87	15.6
20.000	84.92	0.030	11.75	15.2

RUN 6A5

Temperature 465°C

Electrolyte. Pure CaI_2 under oxygen free nitrogen

f/kHz	C_p/mS	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	59	11	16.07	200
0.500	70.44	5.296	13.45	100
1.000	77.20	2.049	12.60	75.7
1.592	80.54	1.049	12.21	62.9
2.000	81.73	0.751	12.07	57.1
3.000	83.74	0.406	11.84	49.0
4.000	84.86	0.257	11.72	44.6
5.000	85.63	0.178	11.63	41.9
7.000	86.60	0.099	11.52	39.3
10.00	87.49	0.051	11.41	38.1
13.00	87.83	0.028	11.38	41.3
15.00	88.22	0.019	11.33	46.1
20.00	88.69	0.007	11.27	72

RUN 6A6

Temperature 444°C

Electrolyte. Pure CdI_2 under oxygen free nitrogen

f/kHz	C_p/nF	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	54	12	17.2	170
0.500	62.58	4.438	15.22	93.8
1.000	68.21	1.692	14.31	71.3
1.592	70.90	0.864	13.90	59.0
2.000	71.94	0.610	13.74	54.3
3.000	73.51	0.330	13.51	46.4
4.000	74.41	0.211	13.37	41.8
5.000	74.98	0.147	13.28	38.9
7.000	75.77	0.083	13.17	35.8
10.00	76.43	0.044	13.07	33.7
13.00	76.94	0.026	12.99	34.2
15.00	77.14	0.018	12.96	37.2
20.00	77.41	0.007	12.92	54.2

RUN 6A7

Temperature 418°C

Electrolyte. Pure CdI_2 under oxygen free nitrogen

f/kHz	G_p/mS	$C_p/\mu\text{F}$	R_s/Ω	$C_s/\mu\text{F}$
0.200	44.24	11.2	20.53	122
0.500	52.46	3.503	18.26	83.1
1.000	56.78	1.308	17.25	63.7
1.592	58.79	0.666	16.79	52.5
2.000	59.66	0.466	16.60	48.8
3.000	60.79	0.253	16.35	41.4
4.000	61.48	0.162	16.19	37.1
5.000	61.92	0.114	16.10	34.2
7.000	62.51	0.066	15.96	30.7
10.00	63.04	0.035	15.84	28.8
13.00	63.33	0.022	15.78	27.3
15.00	63.48	0.016	15.74	28.4
20.00	63.81	0.008	15.67	32.2

RUN 6C2

Temperature 402°C

Electrolyte. Pure CdI_2 under oxygen free nitrogen

f/kHz	G_p/mS	$C_p/\mu\text{F}$	R_g/Ω	$C_g/\mu\text{F}$
0.200	18.09	7.826	42.67	34.3
0.500	24.61	3.468	33.98	21.2
1.000	29.98	1.744	29.42	14.8
2.000	35.14	0.834	26.13	10.2
3.000	37.96	0.525	24.67	8.25
4.000	39.87	0.372	23.77	7.14
5.000	41.22	0.283	23.18	6.37
7.000	43.12	0.185	22.39	5.38
10.00	44.90	0.115	21.71	4.56
13.00	46.02	0.080	21.30	4.05
15.00	46.61	0.067	21.07	3.72
20.00	47.65	0.045	20.69	3.24

5.5 Evaluation of the foregoing results in terms of the model of Figure 1

If values of R_o , C_d , R_s , C_s are known, then for each value of ω , it is possible to calculate $R_W + \theta$ and C_W .

If this model is a true representation of the system studied a plot of R_s vs $\omega^{-1/2}$ should be concave upwards and approximately linear at low frequencies, and $R_W + \theta$ and $1/C_W$ vs $\omega^{-1/2}$ should be parallel straight lines, gradient σ , cutting the vertical axis at θ and zero respectively.

R_s and C_s and ω have been derived directly from the experimentally measured quantities. R_o values used are interpolated literature values (see Graph 2), together with measured cell constants.

The determination of C_d from this data is more complex. If θ is zero (electrode ideally non-polarisable, infinite exchange current) then equation 38 can be used. However, if $\omega C_s(R_s - R_o)$ is greater than 1 as is the case in almost all the measurements made, this equation clearly cannot be used and a value for θ must be determined for use in equation 39.

Since in general C_d will be less than the minimum value measured for C_s , a reasonable estimate can be made for the magnitude of C_d . The results have been plotted (Graphs 13 to 23) to determine the effect of treating C_d as a variable parameter.

The following plots illustrate the variations with $\omega^{-1/2}$ of R_s , $R_W + \theta$ ($RW + \text{THETA}$) and $1/\omega C_W$ ($1/WC$) with selections of R_o and C_d parameters.

Other variations introduced are R_d , a postulated resistance in series with C_d , temperature, cell design and concentration of dissolved cadmium.

Most of the plotting was done by computer. The facility used was an IBM 1130 system including a plotter. The fortran programs devised are in the appendix.

5.6 Comments on plots of R_g versus $\omega^{-1/2}$

Graph number	Run	Comments
3	6A5,6,7	Note effect of different temperatures. Plots are remarkably linear, upward curvature is greater at higher temperatures. Extrapolation to infinite frequency gives R_g as 11.0 Ω , 12.6 Ω , 15.3 Ω respectively. R_g is considerably less than that as the cell constant is about 2.6 cm ⁻¹ making R_g to be 6.4 Ω , 7.3 Ω , 8.9 Ω respectively.
4,5,6	6A5,6,7	R_g axis expanded. Curvature clearly seen.
7	5D2	Cell constant measurement gives R_g as 5.4 Ω but extrapolation of this plot to infinite frequency gives a negative resistance.
8,9	6C2,5J2	Remarkably linear.
10	5L1	Similar gradient to 5J2.
12	5I7	Little frequency dispersion. 20 kHz point doubtful on account of difficulty with capacitive balance.

5.7 Comments on plots of $R_w + \theta$ and $1/C_w$ versus $\omega^{-1/2}$.

Graph	Cell	Comments
13	6A4	The only effect of postulating different R_θ values seems to be the vertical displacement of the $R_w + \theta$ curve by the change in R_θ if $C_d = 0$ (trivial) and slightly more if $C_d \neq 0$. There is no measurable effect on $1/\omega C_w$.
14	6A5	
15	5L1	
16	6C2	
Change in C_d .		
17	6A5	Where the expected C_d is small, no marked effect on plots until C_d sufficiently large that $1/\omega C_w$ takes negative values at high frequencies.
18	6A6	
19	5H3	With larger C_d values (e.g. 5H3) the $R_w + \theta$ are higher and the gradient is reduced. $1/\omega C_w$ seems unaffected.
Change in R_d		
20	5H7	Effect at high frequencies only.
Change in cadmium metal concentration		
15	5L1	Gradient decreases with increasing cadmium concentration.
21	5J2	
22	5I7	
Changes with temperature		
23	6A5,6,7	Plots with expanded ordinate scales (Graphs 17,18) must be examined to determine differences.

In each case the lower of a pair of points at a particular frequency represents $1/\omega C_w$, and the upper point represents $R_w + \theta$.

80.

$(R_W + \theta) / \text{OHMS}$

 $(1/\omega C_w) / \text{OHMS}$

CHAPTER 6

IMPEDANCE METHOD: ANALYSES OF RESULTS6.1 The Determination of the Best Value for R_o

With reasonable literature values or measurements in cells of high cell constant the determination of R_o is almost entirely dependent on the quality of the determination of the cell constant of the cell used.

The conventional method involves the measurement of the resistance of a standard solution (e.g. 1D KCl) at a certain temperature and the high frequency limit of a plot of R_s against $\omega^{-1/2}$ is the solution resistance. In terms of the model of Figure 1 this is reasonable because a dilute aqueous solution $\theta \propto 1/i_o$ will be large.

Although this extrapolation can be done fairly accurately (e.g. Graph 1), it is not certain that the resistance at the intercept with $\omega = \infty$ is actually R_o , the solution resistance. Perhaps the neatest way to determine R_o would be to use a cell with variable electrode spacing and constant interelectrode cross-section area as the electrode impedance is independent of this. However the cells used in the present work were of constant dimensions and the extrapolated resistance was taken to be the solution resistance. Because this value of R_o is doubtful, the impedance parameters are in each case evaluated for a range of possible values of R_o .

We note that the extrapolated values at infinite frequency for R_s against $\omega^{-1/2}$ for the melt are always much higher than the

estimates for R_o based on the KCl measurement and the literature value for the conductivity of the melt. This is attributable to (a) the inaccurate measurement of R_o due to cell constant determination difficulties or (b) a large (compared with R_o) series resistance component of electrode impedance, probably due to a relatively small C_d value, i.e. even at high frequencies θ is not more than the same order of magnitude as $1/\omega C_d$. Considering (a), it will be seen that the inaccuracies are insufficiently great to be accounted for this way because always (in terms of the model of Figure 1) the measured R_s values will be greater than R_o which thus fixes a (rather high) maximum for our R_o estimate. The explanation (b) will be considered as causing this difference in further discussion.

6.2 The Determination of a Value for C_d by the Impedance Method

In order to determine the parameters θ , R_w and C_w it is necessary that C_d be known.

Various values of C_d have been used in order to determine the best fit with a model, the best value with the present model being that which gives the most linear plots of $R_w + \theta$ and $1/\omega C_w$ against $\omega^{-1/2}$. The two plots should have equal gradients and the plot of $1/\omega C_w$ should pass through the origin.

Extrapolation of the curve C_s versus $\omega^{-1/2}$ to $\omega = \infty$ will give an indication of the magnitude of C_d (see equation 35) and preliminary estimates have been made this way. Note that some of the high frequency C_p or C_s data are imprecise e.g. 5J2, 5I7, 6A5 and cannot be used in such an extrapolation.

These extrapolations, which have large uncertainties, lead to the following results:

6.3 Effect of Temperature on the gradient of $R_p + \theta$ vs $\omega^{-\frac{1}{2}}$.

The expression for σ (equation 33) contains several temperature dependent quantities i.e. T , D , c_o , c_R and their effect on σ is seen to be quite significant. The experimental effect is shown in Graph 23 but a gradient change is not immediately apparent. However with expanded ordinate scales the gradients are (taken at the low frequency ends of the plots) conveniently measured (e.g. Graphs 17, 18). A typical set of results is

Cell	Temperature/K	Measured $\sigma / \text{m.s}^{-\frac{1}{2}}$
6A7	691	160
6A6	717	142
6A5	738	130

Thus the experimental decrease in σ over this temperature range is $(23 \pm 3)\%$.

A calculation can be made on the basis of equation 33 to determine the variation of σ over this temperature range.

By the Arrhenius equation (43) and using the value 58 kJ/mol (see Section 4.2.2) for ΔE_D , we find that D will increase by 92% and $D^{\frac{1}{2}}$ by 39% over this temperature range. The temperature increase is 7% and the density decrease is 1.5%. Thus, considering only changes in T and D , σ will decrease by 23%. A small increase in σ , perhaps about the same magnitude as the density change, will be due to change in c_R with temperature.

Similar results are obtained by considering the changes in the gradients of plots of $1/\omega C_w$ vs $\omega^{-1/2}$ although in general the apparent values of σ are larger.

We note that the gradient decreases in the R_w plots are much greater than for the $R_w + \theta$ plots as other temperature dependent quantities, e.g. R_θ , θ are incorporated in the gradient (see equation 34).

6.4 The Effect of Concentration on R_w and $1/\omega C_w$

In terms of the model used, for a single electrode the gradient of a plot of $R_w + \theta$ or $1/\omega C_w$ versus $\omega^{-1/2}$ is (equation 33)

$$\sigma = RT(c_o + c_R)/n^2 F^2 A c_o c_R \sqrt{2D}$$

R , n , F are known quantities,

T is readily measured accurately.

c_R can be determined by the accurate weighing of a small amount of a reduced form (Cd metal) to the pure salt. Since $c_R \ll c_o$ in the case considered, $(c_o + c_R)/c_o c_R = 1/c_R$ is a good approximation, making σ inversely proportional to the minor redox species. This is a common situation in molten salts.

D is the diffusion coefficient D_R of equation 22 if $c_R \ll c_o$, and by the reasoning of Section 4.2.2 this can be taken as $3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for Cd_2^{++} in CdI_2 at 680 K.

A is a rather uncertain quantity. Here it is the true surface area of a single electrode (and is not in general related to that obtained

by dividing the interelectrode distance by the cell constant). A is rather larger than the macroscopic apparent area, the exact factor relating actual with apparent area probably depending on the history of the electrode. All the cells Mark 5 were constructed with two identical electrodes 5 mm long and 1 mm in diameter, a total (all around) apparent area of about $1.6 \times 10^{-5} \text{ m}^2$ per electrode. Interelectrode distances differed among the cells. For the cells with two identical electrodes the model (Figure 1) should still apply but any measured C_d will be half that at a single electrode and any measured Z_w or θ parameter will be twice that at a single electrode, i.e. σ measured for two identical electrodes in series is twice that for a single electrode.

In the present work A must be regarded as an adjustable parameter.

Cell	5I	5J	5L
mole fraction of Cd added to salt	9.60×10^{-4}	8.7×10^{-5}	6.9×10^{-5}
$c_R / \text{mol m}^{-3}$	11.45	1.04	0.83
T/K	679	676	676
<u>σ calculated</u>	<u>5.4×10^{-4}</u>	<u>5.9×10^{-3}</u>	<u>7.4×10^{-3}</u>
$s^{-\frac{1}{2}}$	2A	2A	2A
<u>σ measured</u>	9.3	93	115
$s^{-\frac{1}{2}}$			
$10^5 A^* / \text{m}^2$	2.9	3.2	3.2

Gradient measurements were made on Graphs 15, 21, 22.

The density of the melt is not significantly affected by small additions of metal.

A^* is the area required in order that the formula for σ applies (equation 33).

The most striking feature of the tabulated results is that σ is directly proportional to $1/c_R$, i.e. the A required for the formula to hold is the same in each case. Uncertainties are large in the measured values of σ , perhaps $\pm 10\%$ and also in the calculated values of σ , which rely on an estimated diffusion coefficient.

The area A determined above is a reasonable figure for A , being about double the total apparent area of each electrode.

It is now of interest to derive a value for c_R in the pure salt. From Cell 5H7 (Graph 20) the measured value of σ is $1470 \text{ } \mu\text{s}^{-1/2}$. Taking A as $3.2 \times 10^{-5} \text{ m}^2$ we calculate c_R to be 0.065 mol m^{-3} . This figure unfortunately was not particularly reproducible and seemed to vary from day to day by as much as $\pm 10\%$, and over longer periods (months) the apparent value of c_R decreased with time.

This effect of decrease of frequency dependence by addition of a reduced species to a melt has been commented on before in a qualitative way [e.g. 58] but I am unaware of any quantitative experiments illustrating this property.

6.5 Evaluation of Electrode Kinetic Parameters from Impedance Data

6.5.1 Tabulation of θ values

In the case where plots of $R_w + \theta$ and $1/\omega C_w$ versus $\omega^{-1/2}$ are parallel, their separation is equal to θ , a resistance due to charge transfer, which if the measuring voltage is small is given in terms of a rate constant by equation 1 and in terms of the exchange current density, i_0 , by equation

$$i_0 = nFAc_0^{1-\alpha} c_R^\alpha k_s \quad (8)$$

$$\theta = RT/nFi_0 \quad (9)$$

Because C_d is very small (see Section 6.2) in the case of CdI_2 melts as treated in this work, the value of θ experimentally determined is virtually independent of C_d (Graph 18,22) (see equation 40) but it is necessary to have a reliable value for R_e . For $C_d = 0$, $\omega = \infty$,

$$R_s = R_e + \theta$$

Where $R_e \doteq R_s$, e.g. cell 5I, accurate determination of θ is difficult but in general in low cell constant cells and cells where $R_e < R_s$ it is a simple matter to determine θ and i_0 .

In the following table results are set out for several of the cells. The R_e values used, which are from the best cell constants determined previously, are not necessarily those for which results are plotted on the Graphs 13-23.

Cell	$(R_g \text{ at } \omega = \infty)/\Omega$	R_g/Ω	θ/Ω	T/K	i_0/mA	Graph No.
6A4	11.1	7.0	4.0	736	7.9	13
6A5	10.9	7.0	3.9	738	8.1	4, 14
6A6	12.5	7.9	4.6	717	6.7	6, 18
6C2	18.2	12.0	6.4	675	4.5	8, 16
5L1	6.45	5.95	0.6	676	50	10, 15
5I7	6.62	6.44	0.2	679	140	12, 22
5H7	8	5.9	2	680	14	20

Data for the Mark 6 cells was readily obtained from the graphs or by using single frequency data with equation 40, and the i_0 results are probably reliable within 10%. The linearity of plots from Mark 5 cells is poorer and θ cannot be read beyond one significant figure even for the best plots. θ becomes very low, less than 1Ω for the cells with cadmium metal added.

6.5.2 Variation of i_0 with temperature

The results for Mark 6 cells in the table above show a marked increase in exchange current with temperature. From equation 8 this is to be expected as i_0 is directly proportional to a chemical rate constant which will increase with temperature. Also the equilibrium concentrations of Cd^{++} and Cd_2^{++} will vary slightly with density changes.

6.5.3 Variation of i_a with dissolved metal concentration

Since α , the transfer coefficient, is characteristic of a particular charge transfer reaction at a particular interface, it can be determined from equation 8 by changing one equilibrium concentration and holding all other experimental parameters constant. This is done in the series of cells 5H7, 5L4, 5I7 (if the small temperature changes are neglected). Since θ is proportional to $1/c_R^0$ under these conditions, a plot of $\log \theta$ versus $\log c_R^0$ will have a gradient of $-\alpha$. Unfortunately the data for θ available in the present work is only to one significant figure and the c_R^0 value for the 5H case is a doubtful quantity (see Section 6.4 for an estimate of c_R). However such a logarithmic plot gives a gradient of -0.45 (Graph 24). This value has a large uncertainty associated with it and the best that can be said is that $\alpha = 0.5 \pm 0.2$ which, except that the real value of α lies in this range, cannot be regarded as a significant result.

With an accurate knowledge of the impedance quantities and the concentrations, α could be more precisely determined.

6.5.4 The exchange current density

The calculation of the exchange current density, a more fundamental quantity than the exchange current, requires that the electrode area be known.

For the Mark 6 cells, the apparent electrode surface area is 0.79 mm^2 , so i_0 for the pure salt at 736 K is

$$i_0 = \frac{8 \cdot 10^{-3}}{8 \cdot 10^{-3}} = 1.0 \text{ amp cm}^{-2}.$$

GRAPH 24

Plot to Determine the Transfer Coefficient.

The Gradient is $-\alpha$.

The exchange current for a single Mark 5 electrode (twice the i_0 value in the table) is six times that in the Mark 6 cell. This may seem anomalous because the (all around) area of the Mark 5 electrode is twenty times greater than the Mark 6 cell, but the current behaviour around the cylindrical electrode used here is not established and any results must have high uncertainty.

k_s , the rate constant characteristic of the electrode reaction can be calculated from equation 7a when c_O^0 , c_R^0 , and α have been found.

6.6 Effect of postulating a double layer resistance, R_d

The electrical double layer, although primarily a capacitance, must really be considered as a general impedance [52]. With this in mind the effect on the form of $R_w + \theta$ versus $\omega^{-\frac{1}{2}}$ plots with various constant values of R_d is investigated. Values of R_d from 0Ω to $100 \text{ k}\Omega$ were tried (Graph 20) but there seems to be slight effect only. Effect on the gradient was only noticeable at higher frequencies and the linearity of the $R_w + \theta$ was marginally improved for $R_d = 10 \Omega$. R_d and C_d should perhaps be considered as frequency dependent but a physical model is necessary to make any meaningful evaluation or analysis. The contribution to the equivalent circuit due to the deviation of the electrical double layer from pure capacitance is likely to be minor and cannot be considered further without definite information on all other electrode impedance parameters.

CHAPTER 7

THE CURRENT STEP OR SINGLE PULSE GALVANOSTATIC METHOD.THEORY7.1 Conventional treatments

This is the method developed by Berzins and Delahay [40] for determining electrode characteristics from observation of the potential response to a constant current step.

An electrode fitting the same model as in Figure 1 without R_o , is treated by Berzins and Delahay and the potential response for a current step at a single electrode is given as

$$E - E_o = \frac{i_t}{C_d(A-B)} \left\{ \begin{aligned} &\frac{A}{B^2} [\exp(B^2 t) \operatorname{erfc}(Bt^{1/2}) + 2B(t/\pi)^{1/2} - 1] \\ &-\frac{B}{A^2} [\exp(A^2 t) \operatorname{erfc}(At^{1/2}) + 2A(t/\pi)^{1/2} - 1] \end{aligned} \right\} \quad (45)$$

$$\text{where } \frac{A}{B} = \frac{i_o}{2nF} \left(\frac{1}{D_o^{1/2} C_o^o} + \frac{1}{D_R^{1/2} C_o^o} \right)^2 + \left[\frac{i_o^2}{4n^2 F^2} \left(\frac{1}{D_o^{1/2} C_o^o} + \frac{1}{D_R^{1/2} C_o^o} \right)^2 - \frac{nF i_o}{RT C_d} \right]^{1/2} \quad (46)$$

i_t is the total current (constant).

$E - E_o$ represents the potential change from an equilibrium value.

This potential-time relationship can under certain conditions be simplified [40,42], in particular for times greater than 50 μ s (in aqueous solutions) the potential-time relationship takes the form

$$E - E_0 = \frac{-RT}{nF} \left\{ \frac{2}{\pi^{1/2} nF} \left(\frac{1}{C_0 D_0^{1/2}} + \frac{1}{C_R D_R^{1/2}} \right) t^{1/2} - \frac{RT}{nF} \left[\frac{1}{nF} \left(\frac{1}{C_0 D_0^{1/2}} - \frac{1}{C_R D_R^{1/2}} \right) \right]^2 \cdot D_d + \frac{1}{i_0} \right\} \quad (47)$$

i.e. a plot of $E - E_0$ against $t^{1/2}$ is linear and i_0 is immediately available from the intercept if C_d is known and vice versa.

However more information is available from a potential-time transient. An advance in this direction was the work of Inman et al [42] who applied this single current pulse method to a molten salt system thereby making it possible, in suitable time ranges, to determine $i_t R_0$, the ohmic overpotential; C_d , the double layer capacitance; D , a diffusion coefficient from the slope of E versus $t^{1/2}$ at known current densities; and i_0 , the exchange current density.

The most notable features of the analysis described above are the complexity of the equations involved and also that these equations apply only to true current steps i.e. steps with zero rise time.

More recent works [45,46] have apparently overcome both these problems by a neat mathematical treatment which involves transformation of the data for electrode response obtained in the time domain into a complex frequency domain in which the parameters are more easily handled. The method is so general that finite rise times are easily handled.

7.2 The concept of operational impedance

The experimental parameters determined by the application of a (not necessarily abrupt) current step, $i(t)$, the excitation function, is a potential transient, $E(t)$, the response function. These time domain (t) functions can be transformed to a complex frequency domain by a Laplace transform defined as

$$\bar{f}(s) = \int_0^\infty f(t) \cdot e^{-st} dt \quad (48)$$

where s is a complex frequency variable, $s = \sigma + j\omega$, $j = (-1)^{\frac{1}{2}}$.

The above integration can be performed along the real axis, giving

$$\bar{f}(\sigma) = \int_0^\infty f(t) \cdot e^{-\sigma t} dt \quad (49)$$

or along the imaginary axis, giving (provided that $f(t) = 0$ for $t < 0$) the single sided Fourier transform

$$\bar{f}(\omega) = \int_0^\infty f(t) \cdot e^{-j\omega t} dt \quad (50)$$

This will converge only for certain time functions but most practical electrochemical systems give convergence of $\bar{f}(\omega)$, i.e. are physically realisable in this domain.

The Laplace or the Fourier transform can be used to transform equations and treat experimental data.

Knowledge of a transformed excitation function (in our case $\bar{i}(s)$) and the transformed response function, ($\bar{E}(s)$), allows us to consider their generalised relationship as for a linear system:

$$\bar{Y}(s) = \bar{H}(s) \cdot \bar{X}(s) \quad (51)$$

where $\bar{Y}(s)$ is the response function, $\bar{X}(s)$ is the excitation function and $\bar{H}(s)$ is the operational transfer function, which corresponds to the imittance (impedance or admittance) of the electrode process. In our particular case equation 51 becomes

$$\bar{E}(s) = \bar{Z}(s) \cdot \bar{i}(s) \quad (52)$$

$\bar{Z}(s)$ is the frequency domain impedance of the system. The form of $\bar{Z}(s)$ for an electrochemical system can be found by assuming a particular model, determining $\bar{Z}(s)$ for each element of the model and combining the series and parallel combinations of these circuit elements in the usual way. It is noted that in carrying out the process of building up an equivalent circuit model that the impedance of an element in the Laplace domain is most easily determined by using the familiar form of impedance from a.c. circuit theory, but substituting s for $j\omega$.

$$\begin{array}{lcl} \text{e.g.} & R & \longrightarrow R \\ & 1/j\omega C & \longrightarrow 1/sC \end{array}$$

The Fourier transform form is mathematically identical to the familiar complex frequency impedance but it must be remembered that we are considering non-sinusoidal conditions whereas the familiar form applies only to steady state sinusoidal conditions.

7.3 Operational Impedance for Present Model

For considering experimental results the same aperiodic model for the electrochemical system is used as for the impedance method (Figure 1 or 2).

Birke [46] gives a complete expression for the operational impedance, $\bar{Z}(s)$, of this model for the case including adsorption of oxidised and reduced species. We will consider the simpler case without adsorption, for which $\bar{Z}(s)$ is given by:

$$\bar{Z}(s) = \frac{R_o \left[s^{3/2} + \frac{Z_D}{\theta} s + \left(\frac{1}{\tau_o} + \frac{1}{\tau_s} \right) s^{1/2} + Z_D / \theta \tau_s \right]}{s^{1/2} \left(s + \frac{Z_D}{\theta} s^{1/2} + \frac{1}{\tau_o} \right)} \quad (53)$$

where $Z_D = RT/nFAD^{1/2}c = \sqrt{2} \sigma$, $c = c_o c_R / (c_o + c_R)$ as before, and $\tau_o = 1/\theta C_d$, $\tau_s = 1/R_o C_d$.

From this equation can be derived $\bar{E}(s)$ and $E(t)$ in a similar manner as that which Birke [46] uses to derive $\bar{i}(s)$ and $i(t)$ for the potential pulse case. Using the method of partial fractions, the denominator of the expression in equation 53 can be factorised so that

$$\bar{Z}(s) = \frac{R_o}{s^{1/2}} \left[\frac{K_1 s}{s^{1/2} + r_1} + \frac{N_1}{s^{1/2} + r_1} + \frac{K_2 s}{s^{1/2} + r_2} + \frac{N_2}{s^{1/2} + r_2} \right] \quad (54)$$

where r_1 and r_2 are the negatives of the roots of the quadratic in the denominator of 53, and

$$K_1 = (r_1 - z_D/\theta)/(r_1 - r_2)$$

$$K_2 = (r_2 - z_D/\theta)/(r_2 - r_1)$$

$$N_1 = \frac{z_D/\theta \tau_s - (1/\tau_0 - 1/\tau_s)r_1}{r_2 - r_1}$$

$$N_2 = \frac{z_D/\theta \tau_s - (1/\tau_0 - 1/\tau_s)r_2}{r_1 - r_2}$$

Combining equations 52 and 54 we have an expression for $\bar{E}(s)$ in terms of $\bar{i}(s)$ and the electrode parameters in a form which can readily be transformed by an inverse Laplace transform into the time domain if $\bar{i}(s)$ is known. If $i(t)$ is constant (ideal current step) then $\bar{i}(s) = i(t)/s$ and the inverse transformation of $\bar{i}(s)\bar{Z}(s)$ will be identical to the potential-time expression of Bersins and Delahay. Note in particular the complexity of the time domain response (equation 45) against the relative simplicity of the frequency domain response (equations 52 and 54).

If R_0 is known equation 53 can be simplified to give the operational impedance $Z^*(s)$ of the electrode only. $\sqrt{2\sigma}$ replaces z_D .

$$Z^*(s) = \frac{\sqrt{2\sigma} + \theta s^{\frac{1}{2}}}{s^{\frac{3}{2}} + \sqrt{2C_d}\sigma s + \theta C_d s^{\frac{3}{2}}} \quad (55)$$

If, as is likely in the present work

$$sC_d(\sqrt{2\sigma}/s^{\frac{1}{2}} + \theta) \ll 1 \quad (56)$$

i.e. if C_d is very small, or at low frequencies, equation 55 approximates to

$$\bar{Z}^*(s) = \sqrt{2\sigma}/s^{\frac{1}{2}} + \theta \quad (57)$$

The imaginary axis transform for the case where R_0 is known gives a real part

$$\operatorname{Re}[Z^*(j\omega)] = \frac{\sigma + \theta\omega^{\frac{1}{2}}}{\omega^{\frac{1}{2}}(1 + \omega^2 C_d^2 \theta^2 + 2C_d^2 \sigma^2 \omega + 2C_d \sigma \omega^{\frac{1}{2}} + 2C_d^2 \omega^{3/2} \theta \sigma)} \quad (58)$$

and an imaginary part

$$\operatorname{Im} Z^*[(j\omega)] = \frac{-(\omega^{3/2} \theta^2 C_d^2 + 2\omega \theta C_d \sigma + \sigma + 2\sigma^2 C_d \omega^{\frac{1}{2}})}{\omega^{\frac{1}{2}}(1 + \omega^2 C_d^2 \theta^2 + 2C_d^2 \sigma^2 \omega + 2C_d \sigma \omega^{\frac{1}{2}} + 2C_d^2 \omega^{3/2} \theta \sigma)} \quad (59)$$

If $\theta = 0$ then equation 58 is identical in form to the last term of equation 34 in the impedance method analysis and equation 59 is readily converted into a form identical with equation 35. If $C_d = 0$ i.e. in equation 56 holds then equations 58, 59 become

$$\operatorname{Re}[Z^*(j\omega)] = \sigma/\omega^{\frac{1}{2}} + \theta \quad (60)$$

$$\operatorname{Im}[Z^*(j\omega)] = -\sigma/\omega^{\frac{1}{2}} \quad (61)$$

7.4 Laplace transform Algorithms

Pilla [45] has also considered the examination of electrode impedances using an equivalent circuit model. In this paper the experimental method and analysis of results is established and described for simple circuits made up of ideal electronic components. The method involves the determination of current and potential transients simultaneously on an oscilloscope, digitising these (time domain functions) and making Laplace transformations separately along the real axis and the imaginary axis. The algorithm for the real axis case is

$$\bar{F}(s) = \sum_1 \left\{ \frac{[f(t_{1+1})\exp(-st_{1+1}) - f(t_1)\exp(-st_1)][t_{1+1} - t_1]}{\ln[f(t_{1+1})\exp(-st_{1+1})/f(t_1)\exp(st_1)]} \right\} + \frac{f(t_\infty)}{s} \quad (62)$$

where t_1 and t_{1+1} represent successive time points and the data points of $f(t)$ are sufficiently close that it is reasonable to assume exponential behaviour between consecutive data points.

t_∞ is the time at which the signal achieves a steady state. The corresponding algorithm for the imaginary axis transformation is:

$$\text{Re}[\bar{F}(j\omega)] = \sum_1 \frac{1}{a^2 + \omega^2} \left[\begin{array}{l} f(t_{1+1})[a \cos \omega t_{1+1} + \omega \sin \omega t_{1+1}] \\ - f(t_1)[a \cos \omega t_1 + \omega \sin \omega t_1] \end{array} \right] \quad (63)$$

$$\text{Im}[\bar{F}(j\omega)] = \sum_1 \frac{-1}{a^2 + \omega^2} \left[\begin{array}{l} f(t_{1+1})[a \sin \omega t_{1+1} - \omega \cos \omega t_{1+1}] \\ - f(t_1)[a \sin \omega t_1 - \omega \cos \omega t_1] \end{array} \right] - \frac{f(t_\infty)}{\omega} \quad (64)$$

where $a = \ln[f(t_{1+1})/f(t_1)]/(t_{1+1} - t_1)$.

Note the minor differences to those equations printed in reference [45].

$\bar{F}(j\omega)$ is taken to be $\bar{F}(j\omega) = \text{Re}[\bar{F}(j\omega)] + j \cdot \text{Im}[\bar{F}(j\omega)]$.

Computer programs have been devised to make transformations on experimental curves using the algorithms above and to derive frequency domain impedances, (appendix - TSC05, TSC06) and these have been tested on simple trial circuits as done by Pilla [45] with similar results.

CHAPTER 8

CURRENT STEP METHOD. EXPERIMENTAL TECHNIQUES

The methods described in chapter 4 up to Section 4.3.4 for the impedance method also apply to the current step method.

8.1 Circuit and Measuring Equipment

For the current step measurements the current pulse through the cell was provided by a function generator (Philips FM5168) which could provide a single voltage pulse of the order of 100 microseconds long. This was connected across the cell in series with a precision decade box (Sullivan dual dial non-reactive resistance 0.1% grade) to vary the current and a standard non-reactive resistor (Sullivan $200 \pm 0.1\%$ abs. Ω). The current through the cell (observed as the potential across the non-reactive resistor) and the potential across the cell were observed simultaneously on a double beam storage oscilloscope (Telequipment Oscilloscope type DM55A with plug-in amplifiers type A and type K or 43B and timebase type TD51). The single pulse from the function generator and the oscilloscope traces were simultaneously triggered using a twelve volt battery and a Morse key.

The circuit is shown in Figure 5.

This circuit is not strictly galvanostatic but variations in current are monitored and can be handled in the subsequent analysis. The rise time for the current pulse is about two or three microseconds

and observations are made on the current and potential response for times down to about 50 ns.

A circuit similar to that used by Mattsson and Bockris [88] was tried but difficulty was experienced with the relay 'bouncing' for many microseconds, even with a reed relay, so this circuit was abandoned as unsatisfactory.

The camera used was the Rolleicord twin lens Vb reflex model which is part of the set of the Philips multi-purpose photographic equipment type PM9300. Film used was Kodak VP120.

FIGURE 5

Circuit for Current Step Measurements.

C	Cell	P	Signal Generator
R1	Decade Box	CRO	Oscilloscope
R2	Standard Resistor	A, K ₊ , K ₋	Amplifier
B	12 Volt Battery		Terminals
M	Morse Key	T	Trigger Terminals

CHAPTER 9

CURRENT STEP METHOD. EXPERIMENTAL RESULTS9.1 Conduct of experiments

The apparatus described in Section 8.1 and Figure 5 was used to obtain a stored oscilloscope trace of current and potential through the cell when a current pulse with non-negligible rise time was applied across the cell. Current was readily adjustable and photographs were taken with various timebase and vertical amplifications on the oscilloscope. The photographs were traced under a photographic enlarger and digitised for computing. Large uncertainties arise at this stage mainly on account of the thick line of the stored oscilloscope traces and the consequent enlargements and the difficulty in determining the time origin for the curves. The possibility of gross errors arises close to the origin ($t < 1 \mu s$) which must be significant for a high value of frequency in the frequency domain transformation.

9.2 Experimental results

Once again it is necessary to have a reliable estimate for R_o (see Section 6.1) in order that that part of the measured potential due to the ohmic potential across the electrolyte can be subtracted from the total potential. For Cell 6C (used in this experiment) at $44.5^\circ C$ we take $R_o = 8.9 \Omega$.

Experimental current and potential curves for two different

applied current values, approximately 1 mA and 0.1 mA are shown in Graphs 25 and 26 and are tabulated below. The final column gives the corrected potential $E'(t)$ across the small electrode. The initial measured potential is zero and all changes occurring with current passed are attributed to changes at the electrolyte-electrode interface of the small electrode.

Tabulation of current step data

Cell 6C. $T = 718$ K. Current-time and Potential-time results.

High current case. See Graph 25.

Time/ μ s	$i(t)$ /mA	$i(t)R_{\Omega}$ /mV	$E(t)$ /mV	$E'(t)$ /mV
0	0	0	0	0
0.006	0.005	0.04	0.06	0.01
0.067	0.06	0.52	0.64	0.12
0.127	0.11	1.05	1.23	0.18
0.189	0.18	1.60	1.79	0.20
0.250	0.24	2.12	2.51	0.31
0.311	0.31	2.73	2.85	0.13
0.371	0.37	3.25	3.28	0.03
0.432	0.41	3.67	3.80	0.14
0.493	0.46	4.09	4.33	0.24
0.554	0.51	4.51	4.96	0.45
0.615	0.54	4.80	5.50	0.70
0.676	0.58	5.13	6.02	0.90
0.737	0.60	5.37	6.56	1.19
0.798	0.63	5.60	7.08	1.48
0.859	0.66	5.89	7.62	1.73
0.920	0.68	6.07	8.14	2.07
0.981	0.70	6.26	8.78	2.52

continued

Time/ μ s	$i(t)/\text{mA}$	$i(t)R_e/\text{mV}$	$E(t)/\text{mV}$	$E^*(t)/\text{mV}$
1.042	0.72	6.45	9.31	2.86
1.102	0.74	6.60	9.74	3.14
1.163	0.76	6.74	10.16	3.42
1.224	0.77	6.87	10.57	3.71
1.285	0.78	6.92	11.00	4.08
1.346	0.79	7.01	11.31	4.30
1.407	0.80	7.10	11.62	4.53
1.467	0.81	7.20	11.95	4.75
1.529	0.81	7.24	12.15	4.92
1.650	0.83	7.38	12.68	5.31
1.772	0.85	7.53	13.01	5.48
1.894	0.85	7.58	13.33	5.75
2.016	0.85	7.63	13.79	6.13
2.138	0.86	7.67	13.96	6.29
2.436	0.87	7.77	14.70	6.94
3.045	0.89	7.90	15.22	7.32
3.655	0.90	8.00	15.65	7.66
4.264	0.90	8.05	15.76	7.71
4.872	0.91	8.10	15.87	7.77
61.	0.936	8.33	17.03	8.70

Cell 6C. $T = 718$ K. Low current case. See Graph 26.

Time/ μ s	$i(t)/\text{mA}$	$i(t)R_e/\text{mV}$	$E(t)/\text{mV}$	$E'(t)/\text{mV}$
0	0	0	0	0
0.080	0.008	0.07	0.25	0.18
0.147	0.014	0.122	0.46	0.34
0.281	0.026	0.235	1.10	0.86
0.415	0.039	0.347	1.65	1.30
0.549	0.050	0.442	2.15	1.71
0.683	0.060	0.535	2.70	2.16
0.817	0.068	0.602	3.21	2.61
0.951	0.076	0.676	3.63	2.96
1.085	0.082	0.733	4.06	3.32
1.219	0.088	0.780	4.44	3.66
1.353	0.094	0.836	4.73	3.90
1.487	0.098	0.874	4.99	4.11
1.621	0.102	0.909	5.24	4.33
1.755	0.106	0.940	5.45	4.51
1.889	0.109	0.968	5.58	4.61
2.157	0.113	1.010	5.83	4.83
2.425	0.117	1.043	6.04	5.00
2.693	0.120	1.072	6.21	5.14
3.363	0.125	1.110	6.46	5.36
4.033	0.124	1.101	6.63	5.53
67.	0.123	1.091	7.01	5.92

GRAPH 25

Current Step Method. High Current Case.

Observed Current-Time and Potential-Time
Curves.

GRAPH 26

Current Step Method. Low Current Case.

Observed Current-Time and Potential-Time
Curves.

Systematic errors which almost certainly are present in these results (e.g. oscilloscope calibration) are regarded as unimportant in comparison with the larger errors due to determining the origin of the plots and digitising the graphs, particularly for times less than 1 μ s. Note a 'hump' in the $E(t)$ column. Presumably this is spurious and arises from a very small error in the digitising of the $E(t)$ or $i(t)$ data.

9.3 Tabulation of the transformed current and potential

Computation was done (programs TSC05 and TSC06) to produce the Laplace transforms along both the real and imaginary axes of the current and potential data $i(t)$ and $E^*(t)$. Values of s and ω were chosen over the rather wide range 10^2 to 10^9 Hz and tabulated on the following pages are some of the relevant parameters.

High Current Case. Transformation along real axis.

s/MHz	$\bar{I}(s)/\text{mA s}$	$\bar{E}(s)/\text{mV s}$	$\bar{Z}(s)/\Omega$
10^{-4}	9420	87500	9.289
0.001	990	9175	9.264
0.005	235	2160	9.181
0.01	135	1230	9.114
0.03	56.3	504	8.962
0.05	35.6	315	8.864
0.07	25.6	225	8.785
0.1	17.9	155	8.684
0.3	5.62	46.2	8.217
0.5	3.22	25.4	7.909
0.7	2.21	17.0	7.700
1	1.47	11.0	7.509
10	0.102	0.881	8.608
100	0.0094	0.0671	9.258
1000	0.00094	0.0067	9.292

High Current Case. Transformation along imaginary axis.

ω/kHz	$\frac{\text{Re}[i(j\omega)]}{\text{mA s}}$	$\frac{\text{Im}[i(j\omega)]}{\text{mA s}}$	$\frac{\text{Re}[E^*(j\omega)]}{\text{mV s}}$	$\frac{\text{Im}[E^*(j\omega)]}{\text{mV s}}$	$\frac{\text{Re}[\bar{Z}^*(j\omega)]}{\Omega}$	$\frac{\text{Im}[\bar{Z}^*(j\omega)]}{\Omega}$
0.0001	55.5	-9360	487	-87000	9.292	-0.003
0.001	55.4	-938	487	-8710	9.290	-0.029
0.005	54.6	-195	479	-1810	9.244	-0.130
0.01	52.0	-110	456	-1020	9.161	-0.188
0.03	28.8	-69.8	246	-637	9.030	-0.212
0.05	0.778	-55.5	-7.65	-500	9.017	-0.264
0.07	-12.8	-32.0	-127	-284	9.021	-0.375
0.1	-2.42	-9.19	-27.5	-77.1	8.588	-0.730
0.3	-2.31	-3.39	-26.3	-27.2	9.080	-1.557
0.5	-2.09	-2.41	-23.6	-18.1	9.130	-1.850
0.7	-1.80	-2.08	-20.0	-14.8	8.822	-1.953
1	-1.29	-1.88	-1.38	-12.8	8.072	-1.77
10	-4.44	-0.0012	-0.321	-0.104	7.288	2.14
100	0.006	-0.017	0.052	-0.156	9.203	-0.059
1000	-0.0001	-0.000	-0.001	-0.000	9.047	-0.255

Low current case. Transformation along the real axis.

s /MHz	$\bar{I}(s)$ /mA s	$\bar{E}^*(s)$ /mV s	$\bar{Z}^*(s)/\Omega$
0.0001	1230	59600	48.33
0.001	130	6290	48.22
0.005	31.4	1500	47.87
0.01	18.2	864	47.60
0.03	7.53	355	47.08
0.05	4.72	221	46.80
0.07	3.39	158	46.62
0.1	2.35	109	46.43
0.3	0.728	33.4	45.86
0.5	0.411	18.7	45.61
0.7	0.279	12.7	45.49
1	0.183	8.32	45.42
10	0.0130	0.611	47.18
100	0.0012	0.0592	48.341
1000	0.0001	0.00592	48.341

Low current case. Transformation along the imaginary axis.

ω/MHz	$\text{Re}[\bar{I}(j\omega)]$ mA s	$\text{Im}[\bar{I}(j\omega)]$ mA s	$\text{Re}[\bar{E}'(j\omega)]$ mV s	$\text{Im}[\bar{E}'(j\omega)]$ mV s	$\text{Re}[\bar{Z}'(j\omega)]$ Ω	$\text{Im}[\bar{Z}'(j\omega)]$ Ω
0.0001	8.13	-1220	376	59200	48.34	-0.013
0.001	8.12	-122	376	-5930	48.33	-0.133
0.005	7.98	-25.8	369	-1240	48.10	-0.557
0.01	7.53	-14.9	348	-717	47.73	-0.754
0.03	3.61	-9.92	162	-470	47.18	-0.764
0.05	-0.606	-7.31	-35.4	-343	47.04	-0.946
0.07	-1.85	-3.55	-91.8	-163	46.75	-1.400
0.1	0.383	-1.33	17.9	-59.8	45.08	0.472
0.3	0.279	-0.667	12.9	-30.3	45.68	0.338
0.5	0.112	-0.574	5.16	-26.3	45.85	0.0027
0.7	-0.0515	-0.472	-2.51	-21.6	45.86	-0.311
1	-0.176	-0.248	-8.28	-11.2	45.70	-0.851
10	-0.010	-0.020	-0.478	-0.960	47.37	0.531
100	0.001	-0.002	0.050	-0.090	49.28	-0.134
1000	0.000	-0.000	0.004	-0.010	48.27	0.067

9.4 Treatment of transformed current and potential

The Laplace transformations were also made with different values of R_0 postulated (from 7.0 to 9.5) but in every case the only observable effect on $\bar{Z}(s)$ and $\text{Re}[\bar{Z}(j\omega)]$ was a displacement by an amount equal to the change made in R_0 and no change was noted in $\text{Im}[\bar{Z}(j\omega)]$. The most likely explanation for this is that C_2 is very small (see Sections 6.2, 6.5) and can be taken as zero in which case equations 57, 60, 61, will hold. i.e.

$$\bar{Z}(s) = R_0 + \theta + \sqrt{2}\sigma / s^{\frac{1}{2}} \quad (65)$$

$$\text{Re}[\bar{Z}(j\omega)] = R_0 + \theta + \sigma / \omega^{\frac{1}{2}} \quad (66)$$

$$\text{Im}[\bar{Z}(j\omega)] = -\sigma / \omega^{\frac{1}{2}} \quad (67)$$

Thus the plots of $\bar{Z}(s)$ versus $s^{-\frac{1}{2}}$ and $\text{Re}[\bar{Z}(j\omega)]$ versus $\omega^{-\frac{1}{2}}$ should be linear with gradient σ and intercept θ and the plot of $-\text{Im}[\bar{Z}(j\omega)]$ versus $\omega^{-\frac{1}{2}}$ should be linear with gradient σ and intercept zero. These plots are made for both the high and low current cases (Graphs 27 and 28).

9.5 Analysis of transformed results

The tabulated results and the Graphs 27 and 28 are notable for their erratic nature. The irregularities at the high frequency ends of the curves arise because the transform (equations 48, 50) for high values of s or ω depends on accurate knowledge of $i(t)$ and $E'(t)$ at times of the order of $1/s$ or $1/\omega$. Since data for $t < 1 \mu s$ is very doubtful the results for s or ω greater than 1 MHz can have no

significance attached to them. For low values of s and ω the accuracy of the transformed variable depends on precise data for the small changes in $i(t)$ and $E'(t)$ being available right up to t_{∞} , the time beyond which $i(t)$ and $E'(t)$ are constant. It was not possible from the photographs made in the present work to get sufficiently accurate measurements of these changes for $t > 5 \mu s$.

It is unfortunate that for the low current experiment the gross uncertainties in the current-time and potential-time digitisations make the transformed functions unreliable for high frequencies down to the range where the low frequency errors predominate.

For the high current experiment it is most likely that, since the best data derives from the range 1 to 5 μs , the Laplace frequency range most likely to yield significant results is for s or ω being between 200 kHz and 1 MHz. In fact if the four points in this range are plotted with an expanded abscissa, the linearity of the $\bar{Z}'(s)$ versus $s^{-1/2}$ plot becomes apparent (Graph 29). The gradient of this plot is $900 \Omega s^{-1/2}$ and the intercept is 6.6Ω . From equation 65 $\sigma = 900/\sqrt{2} = 640 \Omega s^{-1/2}$ and $\theta = 6.6 \Omega$. From the impedance measurements with this cell (Graph 16) σ is apparently $900 \Omega s^{-1/2}$ at 675 K and at 718 K will be about 20% lower (see section 63) i.e. about $700 \Omega s^{-1/2}$. The impedance method gives θ as 6.4Ω at 675 K (and lower for a higher temperature).

Even in the most favourable frequency range the operational impedance functions derived by the Laplace transform with integration along the imaginary axis are erratic and although the general trend

GRAPH 29

Linear Portions of Graphs 27 and 28.

+ from Graph 27, $Z'(s)$ versus $s^{-1/2}$.

⊙ from Graph 28, $Z'(s)$ versus $s^{-1/2}$.

Add 39 to ordinate for lower plot.

of the real part function with frequency is as expected, no values for σ or θ can be determined.

The results from Graph 29 perhaps serve to illustrate that in circumstances where precise current-time and potential-time data are available, as much information can be derived from a single measurement as from a series of conventional impedance measurements using a sinusoidal excitation function at many different frequencies.

CHAPTER 10

GENERAL DISCUSSION10.1 Previous use of the Impedance Method for Investigating Electrode Processes

Several workers [e.g. 35, 36, 37, 38, 96] have made studies of molten salt systems using impedance methods. Liquid [35] and solid active and inert electrodes have been used on salt mixtures with a redox system established in a large bulk of inert electrolyte. In the present work it is supposed that the tungsten electrode is effectively inert (which is borne out by the effect on the impedance of changing the concentration of dissolved cadmium) so that except where cadmium metal has been added it is the pure salt that has been studied.

Hills and Djordjevic [57] carried out impedance measurements on pure molten salts and they report inter alia results for CdCl_2 at a molybdenum electrode for which they estimate a double layer capacitance of $80 \pm 20 \mu\text{F cm}^{-2}$ (assuming a value similar to that in molten alkali metal halides). σ is quoted as $14 \Omega \text{s}^{-\frac{1}{2}}$ for CdCl_2 at 868 K which, when corrections are made for the differing electrode areas, diffusion coefficients, temperature and density is certainly of the same order of magnitude as σ for CdI_2 in the present work.

The determination of the kinetic parameters i_0 and α for molten salts is reported in the literature only for redox systems at low concentrations in a supporting electrolyte with the reduced species usually being the solid electrode [e.g. 43, 37, 96]. Values

for the exchange current densities for this type of reaction are typically of the order of 1 A cm^{-2} .

More work has been done on the impedance method for the special case of aqueous solutions. Prominent amongst this work is an extensive series of papers by Sluyters et al in some of which [89,90,91] are outlined techniques of analysis of impedance data according to a model similar to that of Figure 2. They favour this simple model and are critical of the complications introduced by Batiste et al [92] treating the double layer as a general frequency dependent impedance. However, the double layer in aqueous solutions, with the bulk of the electrolyte being solvent dipoles is rather more complex than for molten salts where adsorption of ions on an electrode surface will be less important and the number of species identifiable in the electrolyte is smaller.

As mentioned earlier (Section 1.2.6) the current step method has been used successfully in molten salts, however the method is rather neglected and with the theory and the newer method of analysis devised [45,46] using frequency domain transformations interest in this method may be stimulated. I am unaware of any published results using the generalised excitation function and Laplace transform method with either aqueous electrolytes or molten salts.

The somewhat empirical treatment of impedance results, the 'a.c. dispersion plateau' method, used by Buckle and Tsacoussoglou [1,33] seems rather inadequate unless it can have theoretical backing, fitting it to some model of the electrode-electrolyte system. The conductances quoted by Buckle and Tsacoussoglou, being the result of

careful and well designed experiments, are probably reliable results but the generality of their treatment is in doubt until there is better reason for it than that it appears to work.

10.2 Validity of Model

All of the above analyses have depended on a model of the type in Figure 1 or 2. The particular equivalent circuit elements for the various electrode processes have been derived by using several assumptions and approximations which are considered here for the special case of the systems studied in the present work.

10.2.1 The electrical double layer

A fundamental problem that arises in the invention of an equivalent circuit model for an electrode process is that of a priori separation of the double layer processes from the faradaic processes [see e.g. 93]. This assumption of independence of the double layer capacitance on other equivalent circuit components can be shown to be a valid assumption where there is a supporting electrolyte and the double layer is composed almost entirely of non-reacting solvent ions (or dipoles) but the assumption is in general doubtful in the case of a pure molten salt. In the CdI_2 case studied the double layer admittance is small compared with the faradaic admittance implying that the double layer is diffuse, and whether or not it depends on the faradaic current flowing becomes unimportant.

The small value of the double layer capacitance in the CdI_2 melt suggests a lack of excess charge build-up close to the electrode surface. Since this implies a diffuse double layer it may possibly be better to account for it in the equivalent circuit on the basis of a space charge model as done by Baker and Buckle [28, 30] and Macdonald [32]. In the absence of a supporting electrolyte the equivalent circuit model of Macdonald (Figure 3a) does not include a double layer capacitance as a separate circuit element.

Also, because of the low value of the double layer capacitance in the present work, the potential dependence due to small potential changes during measurement can also be disregarded when determining values for other circuit parameters.

10.2.2 The adsorption capacitance, C_{ad}

Adsorption capacitance (or resistance) has been disregarded in the present work but since this capacitance would appear largely in parallel with the double layer capacitance i.e. as extra double layer capacitance, the very small apparent value of C_d seems to justify not considering adsorption of reactants at the surface.

Referring to Figure 2 we can consider $C_{ad,o}$ to be very large i.e. to have low impedance, since the Cd^{++} ions will almost certainly be against the interface, and $C_{ad,R}$ to be very small i.e. to have high impedance, because of the low concentration of these ions. The net effect of this is that, since the Warburg impedance representing the oxidation process is very small, the components $TL(0)$, $C_{ad,o}$ and $C_{ad,R}$ can be omitted from the circuit of Figure 2.

10.2.3 The charge transfer resistance, R

The major assumption that allows the charge transfer process to be treated as a pure resistor in the equivalent circuit is that the current due to charge transfer is a linear function of the potential deviation from equilibrium potential across the interface. As noted in Section 2.1.2 this is a good approximation for potential changes up to 5 mV which potential is not exceeded in the impedance measurements in this work.

10.2.4 The Warburg impedance, Z_w

The derivation of the expression for the Warburg impedance assumes, inter alia, that Fick's laws of diffusion apply to charged species in the absence of a supporting electrolyte. The CdI_2 case considered is perhaps unusual in that the CdI_2 can be considered as a supporting electrolyte for the Cd_2^{++} ions for which the diffusion equations are required to apply (for $\alpha_R \ll \alpha_0$). However, in general, it is probably more appropriate to use a model, e.g. that of Macdonald [32], in which electroneutrality in the melt and the validity of Fick's laws are not assumed. It is noteworthy that even in this model, an impedance with Warburg characteristics is still present. The experimental results in the present work (Chapter 5) which throughout give a strong indication of a Warburg style frequency dependence tend to justify the use of ordinary diffusion equations in this case.

10.3 Deficiencies in the present work

Perhaps the greatest difficulty in the present work was as discussed in Section 6.1, the estimation or determination of an accurate value for the electrolyte resistance. This becomes more important for cases where R_e is much greater than θ (e.g. in cell 5I) and in cases where C_d is not a negligible quantity.

The estimation of a diffusion coefficient and the effective electrode area are also problems not overcome in the present experimental work.

The reproducibility of some of the results is not very good. With one particular cell, or even between cells of the same type, reproducibility of impedance results was reasonable although frequency dispersion increased after long periods of time. However reproducibility between different types of cells was unsatisfactory. This may have been due to the differing histories of the electrodes i.e. this may have depended on how the surfaces had been treated during glassblowing and cleaning as these procedures were perhaps insufficiently standardised during this work. It is more significant, however, that there was no real knowledge of the microscopic nature of the electrode surface and the glass-tungsten seals. Cracks and depressions in the metal surface can contribute to frequency dispersion of impedance and this possibility has been treated theoretically by de Levie and others [94,95]. Imperfect electrode seal could cause stray capacitances which would be difficult to measure or eliminate. Some of the irregularities in the present work must be attributable to

this cause but this cannot be done quantitatively.

The erratic nature of the 5D2 results is probably due to the absence of an atmosphere in the cell which allowed the iodide of the melt to vaporise as iodine gas which was clearly visible in this cell.

The current step method as performed in the present work was done with a method and experimental setup of great simplicity. But the results are inadequate and do not justify this simple approach. The main difficulty was in transducing the oscilloscope signal to a digitised form, particularly at short elapsed times. Whereas the principles involved in this method are undoubtedly sound, better experimental results would be derived from a more ideal current step (with a rise time in the nanosecond region) or a current pulse (approximating a Dirac delta function [46]) for which R_o is unimportant after the end of the pulse. The current step method requires greater sophistication than in the present work and is almost certainly a major project in itself. In this work this method was used in an attempt to supplement and perhaps confirm information derived from the impedance method.

For the analysis of the potential response of an electrode to a current step by way of transforms to frequency domains the same assumptions and approximations are necessary as for the impedance method and the equations relating experiment to theory are essentially the same in each case, i.e. similar problems as arise in the impedance method analysis will also arise in an analysis of a current (or potential) step method.

10.4 Suggestions for further work

The problem of frequency dispersion in molten electrolytes is still far from solved. The electrode processes can only be analysed by making approximations and the nature of intrinsic frequency effects within the electrolyte is not well established.

The approach of the present work seems valid for contributing towards the elucidation of the nature of electrode processes in molten salts although the experimental methods could perhaps be refined.

The cell design used for studying the frequency dispersion is certainly not the ultimate although the Mark 6 cells used were satisfactory except for the difficulty in precise cell constant determination. A cell in which the cell constant is determined by an easily measured cell geometry (like a capillary cell) would be of more value in this work. Although practical complications would undoubtedly arise, a cell with variable electrode spacing in order to separate electrode and electrolyte effects could help in this problem.

A more sophisticated current step method should lead to confirmation of the impedance method results (see Section 10.3). If the problem of a suitable reference electrode could be overcome, then potential step methods, with the advantage of potential control of the electrode, could be used together with a similar analysis as that set out in this work for the current step method.

Perhaps, however, the most valuable experimental contribution that could be made in this field would be the experimental testing of

the model and equations of Macdonald [32] for the molten salt case or even for a wide range of different types of electrolytes (e.g. aqueous solution, liquid metal, solid, etc). Although in systems such as used in the present work space charge, cell length and geometric cell capacitance are not of great significance, it certainly has been shown [30], that at high frequencies with high cell constants, different frequency dispersion than that of the present work is observable in molten salts.

It would be desirable also, to extend the present work to impedance measurements on other molten salt systems. Presumably other cadmium halides (Cl, Br) would give similar characteristics throughout. Similar results would also be expected from such salts as ZnCl_2 , ZnBr_2 and PbCl_2 . (In the present work some preliminary experiments were done with cadmium chloride in a furnace but these were abandoned in favour of the more easily handled cadmium iodide at the lower temperatures attainable with the molten salt bath.)

Observations of both σ and θ over a wider temperature range could lead to more definite confirmation or rejection of a model.

It is even possible that a potential use of the measurement of impedance at various frequencies could be the determination of very small concentrations of an electroactive species by measuring σ . The method is fundamentally simpler than other electroanalytical techniques and if the components of an electrolyte are known it could be useful.

APPENDICESA1. Calculation of the cell constants of various cells from their geometry

In these calculations ideal conditions are assumed. Current density must be uniform over the whole surface of each electrode. Lines of current through the electrolyte are supposed to be straight. Since in real cases these conditions are not realised results obtained from these formula are not more than good approximations, and real cell constants will be lower than obtained from these formulae.

For a pair of parallel plane electrodes of widely differing size.

Consider electrodes of area a_1 (small) and a_2 (large), separation L . Consider a volume element of electrolyte enclosed between planes, separation δl parallel to and separated a distance l from the smaller electrode.

For the volume element, resistance δR is

$$\delta R = \frac{1}{\kappa} \cdot \frac{\delta l}{a} \quad \text{where } a = l a_2 / L \text{ if } a_1 \ll a_2$$

Thus total resistance R between the electrodes is

$$R = \frac{L}{K a_2} \int_{\frac{a_1 L}{a_2}}^L d\ell = \frac{L}{K a_2} \cdot \ln(a_2/a_1)$$

So cell constant b is given by $b = \frac{L}{a_2} \cdot \ln(a_2/a_1)$.

For two parallel vertical cylindrical electrodes

Consider electrodes of radius r , height h , separation of axes, $2L$.

Consider a volume element of electrolyte, height h , length the distance between the electrodes, thickness δx and displaced a distance x from the plane determined by the axes of the electrodes. Conductivity of electrolyte K .

For the volume element, conductance G is

$$\delta G = Kh \delta x / (2L - 2\sqrt{r^2 - x^2})$$

Thus total conductance between the electrodes is

$$G = Kh \int_0^r \frac{dx}{L - \sqrt{r^2 - x^2}}$$

So cell constant b is given by

$$b = \frac{1}{h \int_0^r \frac{dx}{L - \sqrt{r^2 - x^2}}}$$

from which

$$1/b = h \left[\frac{2L}{\sqrt{L^2 - r^2}} \cdot \arctan \frac{\sqrt{L^2 - r^2}}{L - r} - \pi/2 \right]$$

A2. Derivation for impedance of (Warburg) transmission line.

(See Section 2.2.1)

The transmission line is considered to have resistance and capacitance in small lumped increments, i.e. $n > 1$.

To determine Z_w

$$1/z'' = 1/(-jn/\omega C_t) + 1/z_w = (n + j C_t z_w)/n z_w$$

$$z_w = z'' + R_t/n = \frac{n^2 z_w + n R_t + j \omega C_t z_w R_t}{n^2 + j \omega C_t n z_w}$$

Cross multiply and take the limit as $n \rightarrow \infty$.

$$z_w = \sqrt{-j R_t / \omega C_t} = \sqrt{1/2} (1-j) \sqrt{R_t / \omega C_t}$$

$$\text{So } Z_w = \sqrt{R_t / \omega C_t}; \quad R_w = \sqrt{R_t / 2 \omega C_t}; \quad 1/\omega C_t = \sqrt{R_t / 2 \omega C_t}$$

$$\text{From equation 22, } \sqrt{R_t / \omega C_t} = R T \gamma_1^2 / A n^2 F^2 c_1 \sqrt{D_1 \omega}.$$

Also, identifying $1/R_t C_t$ with D_1 (from equations 26 and 27), we have

$$R_t = \gamma_1^2 R T / A n^2 F^2 c_1 D_1 \quad \text{and} \quad C_t = A n^2 F^2 c_1 / R T \gamma_1^2.$$

A3. COMPUTER PROGRAMS

Summary of programs.

TSC01

Data required:

experimental values of f , G_p , C_p .estimates of R_p , C_d , R_d .

Output tabulation:

 R_s , C_s , $\omega^{-1/2}$, $R_w + \theta$, C_w , $1/\omega C_w$.

TSC02

Data required:

as for TSC01.

Plots:

Plots against $\omega^{-1/2}$ of $R_w + \theta$, or R_s orboth $R_w + \theta$ and $1/\omega C_w$. Ordinate scalecan cover any range (≥ 1) within 0-999.

Range and label selection is made during

the calculation on the computer typewriter.

Minor changes to TSC01 and TSC02 enable data in R_s , C_s form to be handled.

TSC05

Data required:

experimental values of t , $i(t)$, $E(t)$.required selection of s values.

Output:

This program performs two Laplace transformations with integration along the real axis.

Tabulation of s , $\bar{I}(s)$, $\bar{E}(s)$, $\bar{Z}(s)$, $\bar{Y}(s)$, $1/s$.

If ohmic potential drop is to be allowed for then a value for R_o must be inserted at the appropriate place in the program.

TSC06

This program is the same as TSC05 except that ω rather than s must be inserted as the transform variable and integration is made along the imaginary axis.

Tabulation of ω , and the real and imaginary parts of $I(j\omega)$, $E(j\omega)$, $Z(j\omega)$, $V(j\omega)$.

The programs are listed on the following pages.

TSC01

PROGRAM TO CALCULATE AND TABULATE IMPEDANCE PARAMETERS FROM EXPERIMENTAL DATA

// FOR

*IOCS(CARD,1132PRINTER)

```

      DIMENSION RWT(100),CW(100),WHALF(100),W(100),RS(100),CS(100),
      QA(100),B(100),WABS(100),F(100),GP(100),CP(100),CPM(100),XC(100),
      XD(100),E(100)
999  READ(2,1003)CELL
      WRITE(3,1002)CELL
      J=0
      READ(2,1001)N
100  READ(2,1000)RE,CD
      READ(2,1000)RD
C    RE AND RD ARE IN OHMS, CD IS IN FARADS
      I=1
      IF (RE-99999.0)101,999,1013
1013 CALL EXIT
101  IF(J)102,1011,102
1011 READ(2,1000)F(I),GP(I),CPM(I)
C    F IS IN HERTZ, GP IS IN SIEMENS, CPM IS IN MICROFARADS
102  W(I)=2.0*3.14159*F(I)
      CP(I)=CPM(I)/1000000.0
      RS(I)=1.0/(GP(I)+W(I)*W(I)*CP(I)*CP(I)/GP(I))
      CS(I)=CP(I)+GP(I)*GP(I)/(W(I)*W(I)*CP(I))
      RSMRE=RS(I)-RE
      BOT=W(I)*W(I)*CS(I)*CS(I)*RSMRE*RSMRE
      BOTH=BOT+1.0
      A(I)=CS(I)/BOTH-CD
      B(I)=(1.0/BOT+1.0)*RSMRE
      IF(RD)3,4,3
3    D(I)=CD/(W(I)*W(I)*CD*CD*RD*RD+1.0)
      E(I)=RD+1.0/(W(I)*W(I)*CD*CD*RD)
      A(I)=A(I)+CD-D(I)
      B(I)=B(I)*E(I)/(E(I)-B(I))
4    WABS(I)=(W(I)*A(I)*B(I))**2
      CW(I)=(1.0/WABS(I)+1.0)*A(I)*1000000.0
      XC(I)=1000000.0/(W(I)*CW(I))
      RWT(I)=B(I)/(1.0+WABS(I))
      WHALF(I)=1.0/SQRT(W(I))
      I=I+1
      IF(N-I)105,101,101
105  WRITE(3,1015) RE,CD
      WRITE(3,1014)RD
      IF(J)110,110,120
110  WRITE(3,1010)
      WRITE(3,1016)(F(I),GP(I),CPM(I),W(I),RS(I),CS(I),WHALF(I),
      XWABS(I),I=1,N)

```

152.

```

120  WRITE(3,1018)
      WRITE(3,1020)(RWT(I),CW(I),XC(I),W(I),WHALF(I),I=1,N)
      J=1
      GO TO 100
1003  FORMAT(8F10.4)
1001  FORMAT(I2)
1002  FORMAT(1H1,'THE FOLLOWING ARE RESULTS FROM CELL ',A3)
1003  FORMAT(A3)
1014  FORMAT(/,'A DOUBLE LAYER SERIES RESISTANCE OF',F7.1,'OHMS IS POSTU
      XLATED')
1015  FORMAT(////////,' RE= ',F12.4,10X,' CD= ',E15.4,
1016  FORMAT(1H0,' F GP CPM W
      X RS CS WHALF WABS ')
1016  FORMAT(1H ,5F15.6,3E15.4)
1018  FORMAT(///,' RWT CW XC W
      X WHALF')
1020  FORMAT(5F15.4)
      END

```

TSC02
PROGRAM TO CALCULATE AND PLOT IMPEDANCE PARAMETERS FROM EXPERIMENTAL DATA

```
// FOR
*IOCS(CARD,1132PRINTER)
*ONE WORD INTEGERS
*IOCS(TYPEWRITER)
*IOCS(PLOTTER)
*IOCS(KEYBOARD)
      DIMENSION RWT(20),CW(20),WHALF(20),w(20),RS(20),CS(20),
      QA(20),B(20),WABS(20),F(20),GP(20),CP(20),CPM(20),XC(20),
      DD(20),E(20)
999  READ(2,1003)CELL
      WRITE(3,1002)CELL
      WRITE(1,400)
      READ(6,402)IZ,IR
      ORD=FLOAT(IR)
      RIZ=FLOAT(IZ)
      NORD=IR-IZ
      RRD=ORD-RIZ
      Y=15.0/RRD
      CALL SCALF(0.5,Y,0.0,RIZ)
      J=0
      READ(2,1001)N
      WRITE(1,7)
      READ(6,5)NAXIS
      WRITE(1,299)
      READ(6,1001)IMP
      IF (NAXIS)10,20,10
10    CALL FGRID(0,0.0,RIZ,1.0,30)
      IF(NORD-5)68,69,69
69    IF(NORD-50)70,70,71
70    CALL FGRID(1,30.,RIZ,1.0,NORD)
      CALL FGRID(2,30.0,ORD,1.0,30)
      CALL FGRID(3,0.0,ORD,1.0,NORD)
      GO TO 72
68    NORB=5*NORD
      CALL FGRID(1,30.0,RIZ,0.2,NORB)
      CALL FGRID(2,30.0,ORD,1.0,30)
      CALL FGRID(3,0.0,ORD,0.2,NORB)
      GO TO 72
71    NORA=NORD/10
      CALL FGRID(1,30.,RIZ,10.0,NORA)
      CALL FGRID(2,30.0,ORD,1.0,30)
      CALL FGRID(3,0.0,ORD,10.0,NORA)
72    IW=IR+1
      JW=NORD/5
      IF(JW)73,73,74
73    JW=1
74    IZI=IZ+1
```

```

DO 200 IY=IZI,IW,JW
  IL=IY-1
  FAC=FLOAT(IL)
  YVAL=FAC-0.008*RRD
  CALL FCHAR(-3.0,YVAL,0.4,0.4,0.0)
  WRITE(7,401)IL
200  CONTINUE
  S=RRD*0.84 +RIZ
  CALL FCHAR(2.0,S,0.4,0.4,0.0)
  WRITE(7,209)CELL
  SA=RRD*0.2 +RIZ
  CALL FCHAR(-4.0,SA,0.4,0.4,1.570796)
  IF (IMP)211,206,207
211  WRITE(7,212)
  GO TO 208
206  WRITE(7,204)
  CALL FCHAR(34.0,SA,0.4,0.4,1.570796)
  WRITE(7,205)
  GO TO 208
207  WRITE(7,204)
208  DO 210 IX=1,31,10
  IL=IX-1
  FAC=FLOAT(IL)
  XVAL=FAC-0.8
  SB=-0.04*RRD +RIZ
  CALL FCHAR(XVAL,SB,0.4,0.4,0.0)
  WRITE(7,1001)IL
210  CONTINUE
  SC=-0.12*RRD+RIZ
  CALL FCHAR(6.7,SC,0.4,0.4,0.0)
  WRITE(7,202)
  SD=-0.104*RRD+RIZ
  CALL FCHAR(12.0,SD,0.25,0.25,0.0)
  WRITE(7,203)
20  CONTINUE
100  READ(2,1000)RE,CD
  READ(2,1000)RD
  I=1
  IF (RE-99999.0)101,999,1013
1013 CALL EXIT
101  IF(J)102,1011,102
1011 READ(2,1000)F(I),GP(I),CPM(I)
  102  W(I)=2.0*3.14159*F(I)
  CP(I)=CPM(I)/1000000.0
  RS(I)=1.0/(GP(I)+W(I)*W(I)*CP(I)*CP(I)/GP(I))
  CS(I)=CP(I)+GP(I)*GP(I)/(W(I)*W(I)*CP(I))
  RSMRE=RS(I)-RE
  BOT=W(I)*W(I)*CS(I)*CS(I)*RSMRE*RSMRE
  BOTH=BOT+1.0
  A(I)=CS(I)/BOTH-CD

```

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```

      B(I)=(1.0/BOT+1.0)*RSMRE
      IF(RD)3,4,3
3     D(I)=CD/(W(I)*W(I)*CD*CD*RD*RD+1.0)
      E(I)=RD+1.0/(W(I)*W(I)*CD*CD*RD)
      A(I)=A(I)+CD-D(I)
      B(I)=B(I)*E(I)/(E(I)-B(I))
4     WABS(I)=(W(I)*A(I)*B(I))**2
      CW(I)=(1.0/WABS(I)+1.0)*A(I)*1000000.0
      XC(I)=1000000.0/(W(I)*CW(I))
      RWT(I)=B(I)/(1.0+WABS(I))
      WHALF(I)=1.0/SQRT(W(I))
      IF(IMP)300,303,306
300   IF (ORD -RS(I))307,308,308
307   RS(I)=ORD
      GO TO 306
303   IF(ORD -XC(I))305,305,306
305   XC(I)=ORD
306   IF(ORD -RWT(I))304,308,308
304   RWT(I)=ORD
308   I=I+1
      IF(N-I)105,101,101
105   WRITE(3,1015) RE,CD
      WRITE(3,1014)RD
      WRITE(1,8)
      READ(6,5)IP
      WRITE(3,6)IP
      DO 30 I=1,N
      WHALF(I)=WHALF(I)*1000.0
      IF (IMP)59,60,61
59    IF(J)30,58,30
58    CALL FPLOT(1,WHALF(I),RS(I))
      CALL FPLOT(-2,WHALF(I),RS(I))
      GO TO 62
60    CALL FPLOT(1,WHALF(I),XC(I))
      CALL FPLOT(-2,WHALF(I),XC(I))
      CALL POINT(IP)
61    CALL FPLOT(1,WHALF(I),RWT(I))
      CALL FPLOT(-2,WHALF(I),RWT(I))
62    CALL POINT(IP)
30    CONTINUE
      CALL FCHAR(0.0,RIZ,1.0,1.0,0.0)
      J=1
      GO TO 100
1000  FORMAT(8F10.4)
1001  FORMAT(I2)
1002  FORMAT(1H1,'THE FOLLOWING ARE RESULTS FROM CELL ',A3)
1003  FORMAT(A3)
1014  FORMAT(/,'A DOUBLE LAYER SERIES RESISTANCE OF',F7.2,' OHMS IS POST
      STULATED')
1015  FORMAT(/////////,' RE= ',F12.4,10X,' CD= ',E15.4 )

```

```

7      FORMAT(' KINDLY TYPE IN 1 IF YOU WANT A GRID AND 0 IF YOU DO NOT')
      )
8      FORMAT(' TYPE IN PLOTTING SYMBOL NUMBER IN FORMAT I1')
9      FORMAT (I1)
10     FORMAT(1H0,' PLOTTING SYMBOL IS ',I1)
299    FORMAT('TYPE -1 FOR A PLOT OF RS, 0 FOR A SERIES OF PLOTS OF RWT AND
      AND XC, AND 1 FOR PLOTS OF RWT ONLY')
205    FORMAT(' (1/WC)/OHMS ')
204    FORMAT(' (RW + THETA)/ OHMS ' )
202    FORMAT(' 1000*W / SECOND')
203    FORMAT( 1H ,'-1/2          1/2')
209    FORMAT(1H , 'CELL ',A3)
212    FORMAT( ' RS / OHMS' )
401    FORMAT(I3)
402    FORMAT(I2,1X,I3)
400    FORMAT('TYPE IN RANGE REQUIRED ON ORDINATE,FORMAT I2,1X,I3')
      END

```

IF DATA IS IN RS, CS FORM THEN THE FOLLOWING SIX CARDS REPLACE THE SIX CARDS IMMEDIATELY FOLLOWING STATEMENT 101 IN PROGRAMS TSC01 AND TSC02

```

1011 READ(2,1000)F(I),RS(I),CS(I)
C      F IS IN HERTZ, RS IS IN OHMS, CS IS IN MICROFARADS
102  W(I)=2.0*3.14159*F(I)
      CPM(I)=0.
      GP(I)=0.
      CP(I)=0.

```


TSC05

C THIS IS A PROGRAM TO MAKE LAPLACE TRANSFORMS ON TWO CURVES ASSUMING
C THAT THE CURVES ARE EXPONENTIAL BETWEEN THE DATA POINTS

// FOR

*ONE WORD INTEGERS

*IOCS(CARD,1132PRINTER)

DIMENSION S(30),T(100),FT(100),GT(100),DEL(100),EX(100),A(100),
BB(100),TRNSF(30),TRNSG(30),Z(30),Y(30),ST(30),THALF(100)

J=0

READ(2,100)N

READ(2,100)M

C N IS THE NUMBER OF S VALUES, M IS THE NUMBER OF T VALUES. N)31, M)101

11 J=J+1

READ(2,101)S(J)

C ENTER S IN MEGAHERTZ

I=1

IF(J-1)8,8,10

8 READ(2,107)T(I),FT(I),GT(I)

C ENTER T IN MICROSECONDS, FT IN MILLIAMPS AND GT IN MILLIVOLTS

C THE SET T(1) IS THE TIME DOMAIN

FT(I)=FT(I)/189.0

GT(I)=GT(I)+4.0

GT(I)=GT(I)*20.0/189.0

T(I)=T(I)*335.0/550.0

C THESE ARE SCALING FACTORS IF DATA ENTERED IN (E.G.) CENTIMETERS

GT(I)=GT(I)-FT(I)*8.0

C RS THE SOLUTION RESISTANCE IS ALSO ALLOWED FOR

THALF(I)=SQRT(T(I))

WRITE(3,103)

3 K=I+1

READ(2,107)T(K),FT(K),GT(K)

FT(K)=FT(K)/189.0

GT(K)=GT(K)+4.0

GT(K)=GT(K)*20.0/189.0

T(K)=T(K)*335.0/550.0

GT(K)=GT(K)-FT(K)*8.0

THALF(K)=SQRT(T(K))

10 K=I+1

DEL(I)=T(K)-T(I)

EX(I)=EXP(T(I)*S(J))

EX(K)=EXP(T(K)*S(J))

A(I)=(FT(K)/EX(K)-FT(I)/EX(I))*DEL(I)/ALOG(FT(K)*EX(I)/FT(I)/EX(K))

X)

B(I)=(GT(K)/EX(K)-GT(I)/EX(I))*DEL(I)/ALOG(GT(K)*EX(I)/GT(I)/EX(K))

X)

I=K

IF(J-1)20,20,9

20 IF(I-M)3,5,5

```

9      IF(I-M)10,5,5
5      IF(J-1)7,6,7
6      WRITE(3,102)(T(I),FT(I),GT(I),THALF(I),I=1,M)
7      SUMA=0
      SUMB=0
      L=M-1
      DO 19 I=1,L
      SUMA=A(I)+SUMA
19     SUMB=B(I)+SUMB
      TRNSF(J)=SUMA+FT(M)/S(J)
      TRNSG(J)=SUMB+GT(M)/S(J)
      Z(J)=TRNSG(J)/TRNSF(J)
      Y(J)=1.0/Z(J)
      ST(J)=1.0/S(J)
      IF (J-1)12,12,13
12     WRITE(3,105)
13     WRITE(3,106)S(J),TRNSF(J),TRNSG(J),Z(J),Y(J),ST(J)
C      S IS IN MHZ, TRNSF IS IN MILLIAMPS, TRNSG IS IN MILLIVOLTS,, Z IS IN OHMS
C      Y IS IN MHOS AND ST IS IN MICROSECONDS
      IF(J-N)11,14,14
101    FORMAT(E9.3)
106    FORMAT(3(E13.7,1X),2F15.4,2X,E13.7)
105    FORMAT(1H1,' SFREQUENCY          SCURRENT          SPOTENTIAL          SIMP
IMPEDANCE          SADMITTANCE          1/SFREQUENCY')
102    FORMAT(4F15.7)
100    FORMAT(I2)
103    FORMAT('          TIME          CURRENT          POTENTIAL          THALF
LF ')
107    FORMAT(3F10.4)
14     CALL EXIT
      END

```

TSC06

C THIS IS A PROGRAM TO MAKE LAPLACE TRANSFORMS ON TWO CURVES ASSUMING
C THAT THE CURVES ARE EXPONENTIAL BETWEEN THE DATA POINTS

// FOR

*IOCS(CARD,1132PRINTER)

*ONE WORD INTEGERS

DIMENSION W(30),T(99),FT(99),GT(99),A(99),B(99),TRNSF(30),TRNSG(30),
X),E(99),CS(99),SN(99),C(99),D(99),RIMAF(30),RIMAG(30),F(99),ZRE(30),ZIM
30),ZIM(30),YRE(30),YIM(30)

J=0

READ(2,100)N

READ(2,100)M

C N IS THE NUMBER OF W VALUES, M IS THE NUMBER OF T VALUES

11 J=J+1

READ(2,101)W(J)

I=1

IF(J-1)8,8,10

8 READ(2,107)T(I),FT(I),GT(I)

C THE SET T(I) IS THE TIME DOMAIN

FT(I)=FT(I)/189.0

GT(I)=GT(I)+4.0

GT(I)=GT(I)*20.0/189.0

T(I)=T(I)*335.0/550.0

C RS THE SOLUTION RESISTANCE IS ALSO ALLOWED FOR

GT(I)=GT(I)-FT(I)*8.0

WRITE(3,103)

2 <=I+1

READ(2,107)T(K),FT(K),GT(K)

FT(K)=FT(K)/189.0

GT(K)=GT(K)+4.0

GT(K)=GT(K)*20.0/189.0

T(K)=T(K)*335.0/550.0

GT(K)=GT(K)-FT(K)*8.0

10 K=I+1

E(I)=ALOG(FT(K)/FT(I))/(T(K)-T(I))

F(I)=ALOG(GT(K)/GT(I))/(T(K)-T(I))

CS(I)=COS(W(J)*T(I))

CS(K)=COS(W(J)*T(K))

SN(I)=SIN(W(J)*T(I))

SN(K)=SIN(W(J)*T(K))

A(I)=(FT(K)*(E(I)*CS(K)+W(J)*SN(K))-FT(I)*(E(I)*CS(I)+W(J)*SN(I)))

// (E(I)*E(I)+W(J)*W(J))

B(I)=(GT(K)*(F(I)*CS(K)+W(J)*SN(K))-GT(I)*(F(I)*CS(I)+W(J)*SN(I)))

// (F(I)*F(I)+W(J)*W(J))

C(I)=(FT(K)*(W(J)*CS(K)-E(I)*SN(K))-FT(I)*(W(J)*CS(I)-E(I)*SN(I)))

// (E(I)*E(I)+W(J)*W(J))

D(I)=(GT(K)*(W(J)*CS(K)-F(I)*SN(K))-GT(I)*(W(J)*CS(I)-F(I)*SN(I)))

// (F(I)*F(I)+W(J)*W(J))

```

      I=K
      IF(J-1)20,20,9
20    IF(I-M)3,5,5
9     IF(I-M)10,5,5
5     IF(J-1)7,6,7
6     WRITE(3,102)(T(I),FT(I),GT(I),I=1,M)
7     SUMA=0
      SUMB=0
      SUMC=0
      SUMD=0
      L=M-1
      DO 19 I=1,L
      SUMA=A(I)+SUMA
      SUMC=SUMC+C(I)
      SUMD=SUMD+D(I)
19    SUMB=B(I)+SUMB
      TRNSF(J)=SUMA
      TRNSG(J)=SUMB
      RIMAF(J)=SUMC-FT(M)/W(J)
      RIMAG(J)=SUMD-GT(M)/W(J)
      ZRE(J)=(TRNSF(J)*TRNSG(J)+RIMAF(J)*RIMAG(J))/(TRNSF(J)*TRNSF(J)+RIMAF
      *MAF(J)*RIMAF(J))
      YRE(J)=(TRNSF(J)*TRNSG(J)+RIMAF(J)*RIMAG(J))/(TRNSG(J)*TRNSG(J)+RIMAF
      *MAG(J)*RIMAG(J))
      ZIM(J)=(RIMAG(J)*TRNSF(J)-TRNSG(J)*RIMAF(J))/(TRNSF(J)*TRNSF(J)+RIM
      *MAF(J)*RIMAF(J))
      YIM(J)=(RIMAG(J)*TRNSF(J)-TRNSG(J)*RIMAF(J))/(TRNSG(J)*TRNSG(J)+RIM
      *MAG(J)*RIMAG(J))*(-1.0)
C     THE COMPLETE IMAGINARY AXIS TRANSFORM IS GIVEN BY(TRNSF+J*RIMAF)
C
C     ZRE AND ZIM ARE THE REAL AND IMAGINARY PARTS OF THE COMPLEX IMPEDANCE,
C     Z(JW), FROM THE POTENTIAL AND CURRENT TRANSFORMED ON THE IMAGINARY AXIS.
C     I.E. Z(JW)=V(JW)/I(JW)    YRE AND YIM ARE THE CORRESPONDING ADMITTANCES.
      IF(J-1)12,12,13
12    WRITE(3,105)
13    WRITE(3,106)W(J),TRNSF(J),RIMAF(J),TRNSG(J),RIMAG(J),ZRE(J),ZIM(J),
      ,YRE(J),YIM(J)
      IF(J-N)11,14,14
107   FORMAT(3F10.4)
102   FORMAT(3F15.7)
100   FORMAT(I2)
101   FORMAT(E9.3)
103   FORMAT(1H1,'      TIME          CURRENT          POTENTIAL ')
105   FORMAT(1H1,'WFREQUENCY WRECURRENT WINCURRENT WREPOTL      WIMPOTL W
      WREIMPEDANCE WIMIMPEDANCE WREADMITTANCE WIMADMITTANCE ')
106   FORMAT(5(E10.3,1X),4F12.6)
14    CALL EXIT
      END

```

A4. Glossary of Symbols

These symbols which occur in the text only where they are defined are not included in the list. Where appropriate the SI unit for the quantity is given.

A	electrode surface area, m^2 .
C	capacitance, F. capacitance per unit area, F m^{-2} .
D	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$.
E	electrode potential, V. activation energy, J mol^{-1} , e.g. ΔE_D .
F	the Faraday, C mol^{-1} .
G	conductance, S.
R	the gas constant, $\text{J K}^{-1} \text{mol}^{-1}$. (with subscript) resistance, Ω .
T	temperature, K.
V	potential, V.
Y	admittance, S.
Z	impedance, Ω .
b	cell constant, m^{-1} .
c	concentration, mol m^{-3} .
$\bar{c}$	bulk concentration, mol m^{-3} .
c^0	equilibrium value of c, mol m^{-3} .
i	current, A. current density, A m^{-2} .
j	$(-1)^{\frac{1}{2}}$

k	rate constant, m s^{-1} .
n	the number of electrons involved in a charge transfer process.
s	Laplace transform variable, s^{-1} .
t	time, s.
x	distance from electrode, m.
z	number of electronic charges per ion.
ω	impedance operator, Ω .
α	transfer coefficient
κ	conductivity, S m^{-1}
ν	stoichiometric coefficient of species
σ	the Warburg coefficient, $\Omega \text{s}^{-\frac{1}{2}}$.
σ	the real part of the Laplace transform variable, s^{-1} .
ω	angular frequency, Hz.
ω	the imaginary part of the Laplace transform variable, s^{-1} .
θ	the linearised charge transfer resistance, Ω .
Λ	the equivalent conductivity, $\text{S m}^2 \text{equiv}^{-1}$.
Λ	the molar conductivity, $\text{S m}^2 \text{mol}^{-1}$.

The following are symbols used as subscripts. Examples are given.

ad	absorption, C_{ad} .
b	reverse reaction, k_b .
d	double layer, C_d .
e	electrolyte, R_e .
	equilibrium, E_e .
f	forward reaction, k_f .
i	species i.
o	at $E = 0$, i_o .
p	parallel, R_p .
s	series, R_s .
t	transmission line, R_t .
	total, i_t .
w	Warburg
O	oxidised species
R	reduced species

REFERENCES

1. E. R. Buckle and P. E. Tsacoussoglou, *J. Chem. Soc.*, 667 (1964).
2. I. S. Yaffe and E. R. van Artsdalen, *J. Phys. Chem.*, 60, 1125 (1956).
3. J. Braunstein and G. D. Robbins, *J. Chem. Ed.*, 48, 52 (1971).
4. F. Kohlrausch, *Wied. Ann.*, 49, 249 (1893).
56, 182 (1895).
58, 514 (1896).
60, 315 (1897).
- M. Wien, *Wied. Ann.*, 58, 37 (1896).
59, 267 (1896).
Ann Physik., 8, 372 (1902).
5. E. Warburg, *Wied. Ann.*, 67, 493 (1899).
6. E. Warburg, *Ann. Physik.*, 6, 125 (1902).
7. E. Neumann, *Wied. Ann.*, 67, 500 (1899).
8. T. R. Rosebrugh and W. L. Miller, *J. Phys. Chem.*, 14, 816 (1910).
9. G. Jones and R. C. Josephs, *J. Am. Chem. Soc.*, 50, 1049 (1928).
10. G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, 51, 2407 (1929).
11. G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, 53, 411 (1931).
12. G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, 53, 1207 (1931).
13. G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, 55, 1780 (1933).
14. G. Jones and S. M. Christian, *J. Am. Chem. Soc.*, 57, 272 (1935).
15. G. Jones and D. M. Bollinger, *J. Am. Chem. Soc.*, 57, 280 (1935).
16. H. L. Helmholtz, *Wied. Ann.*, 7, 337 (1879).
17. G. Gouy, *J. Phys. Radium*, 2, 457 (1910).

18. D. L. Chapman, *Phil. Mag.*, 25, 475 (1913).
19. O. Stern, *Z. Elektrochem.*, 30, 508 (1924).
20. P. Debye and H. Falkenhagen, *Phys. Z.*, 29, 121, 401 (1928).
Z. Elektrochem., 34, 562 (1928).
21. H. Falkenhagen, 'Electrolytes', English Translation, O.U.P. (1934),
page 182.
22. P. Dolin, B. Ershler, *Acta Physicochim. URSS*, 13, 747 (1940).
23. P. Dolin, B. Ershler, A. N. Frumkin, *Acta Physicochim. URSS*,
13, 779 (1940).
24. A. N. Frumkin, P. Dolin, B. Ershler, *Acta Physicochim. URSS*,
13, 793 (1940).
25. J.E.B. Randles, *Discuss. Faraday Soc.*, 1, 11 (1947).
26. H. Gerischer, *Z. Physik. Chem. (NF)*, 1, 278 (1954).
27. D. C. Grahame, *J. Electrochem. Soc.*, 99, 370C (1952).
28. C.G.J. Baker and E. R. Buckle, *Trans. Faraday Soc.*, 64, 469 (1968).
29. J. R. Macdonald, *Trans. Faraday Soc.*, 66, 943 (1970).
30. C.G.J. Baker and E. R. Buckle, *Trans. Faraday Soc.*, 66, 3121 (1970).
31. J. R. Macdonald, *J. Electroanal. Chem.*, 32, 317 (1971).
32. J. R. Macdonald, *J. Chem. Phys.*, 54, 2026 (1971).
33. E. R. Buckle and P. E. Tsacoussoglou, *J. Chem. Soc. Faraday I*,
68, 1024 (1972).
34. J. O'M. Bockris and A.K.N. Reddy, 'Modern Electrochemistry',
Macdonald, London (1970), Chapter 7.
35. J.E.B. Randles, W. White, *Z. Elektrochem.*, 59, 666 (1955).

36. H. A. Laitinen and H. C. Gaur, *J. Electrochem. Soc.*, 104, 730 (1957).
37. G. J. Hills and K. E. Johnson, *J. Electrochem. Soc.*, 108, 1013 (1961).
38. D. L. Hill, G. J. Hills, L. Young, J. O'M. Bockris, *J. Electroanal. Chem.*, 1, 79 (1959).
39. E. A. Ukshe and N. G. Bukam, *Zh. Fiz. Khim.*, 35, 2689 (1961).
40. T. Bersins and P. Delahay, *J. Am. Chem. Soc.*, 77, 6448 (1955).
41. H. Gerischer and M. O. Krause, *Z. Physik. Chem. (NF)*, 10, 264 (1957).
14, 184 (1958).
- S. K. Rangarajan, *J. Electroanal. Chem.*, 32, 329 (1971).
42. D. Inman, J. O'M. Bockris, E. Blomgren, *J. Electroanal. Chem.*, 2, 506 (1961).
43. H. A. Laitinen, R. P. Tischer, D. K. Roe, *J. Electrochem. Soc.*, 107, 546 (1960).
44. W. Vielstich and P. Delahay, *J. Am. Chem. Soc.*, 79, 1874 (1957).
45. A. A. Pilla, *J. Electrochem. Soc.*, 117, 467 (1970).
46. R. L. Birke, *Anal. Chem.*, 43, 1253 (1971).
47. e.g., W. H. Reinmuth, *Anal. Chem.*, 34, 1272 (1962).
48. e.g., P. Delahay, M. Senda, C. H. Weis, *J. Am. Chem. Soc.*, 83, 312 (1961).
49. B. B. Damaskin, 'The Principles of Current Methods for the Study of Electrochemical Reactions', English Edition, McGraw-Hill, New York (1967).
50. A. D. Graves, G. J. Hills, D. Inman, *Adv. in Electrochem. and Electrochem. Eng.*, 4, 117 (1966).
51. R. Parsons, *Adv. in Electrochem. and Electrochem. Eng.*, 7, 177 (1970).
52. A. M. Baticle, F. Perdu, P. Vennereau, *J. Electroanal. Chem.*, 24, 305 (1970).

53. K. J. Vetter, 'Electrochemical Kinetics', English Edition, Academic Press, New York (1967).
54. C. H. Liu, K. E. Johnson, H. A. Laitinen, in 'Molten Salt Chemistry', ed. M. Blander, Interscience, New York (1964).
55. G. C. Barker, Pure and Applied Chem., 15, 239 (1967).
56. H. A. Laitinen and J.E.B. Randles, Trans. Faraday Soc., 51, 54 (1955).
57. G. J. Hills and S. Djordjevic, Electrochim. Acta, 13, 1721 (1968).
58. G. A. Crawford, Thesis, Imperial College, London (1960).
59. K. B. Oldham, Trans. Faraday Soc., 53, 80 (1958).
60. G. C. Barker, R. L. Faircloth, A. W. Gardner, Nature, 181, 247 (1958).
61. P. L. Spedding, Rev. Pure and Appl. Chem., 21, 1 (1971).
62. R. E. Wood and H. L. Ritter, J. Am. Chem. Soc., 75, 471 (1953).
63. K. Grothaus, F. Gronvold, J. Krogh-Moe, J. Am. Chem. Soc., 77, 5824 (1955).
64. L. E. Topol and A. L. Landis, J. Am. Chem. Soc., 82, 6291 (1960).
65. L. E. Topol, J. Phys. Chem., 67, 2222 (1963).
66. J. D. Corbett, W. J. Burkhard, L. F. Druding, J. Am. Chem. Soc., 83, 5 (1961).
67. C. A. Angell and J. W. Tomlinson, Discuss. Faraday Soc., 32, 237 (1961).
68. G. A. Crawford and J. W. Tomlinson, Trans. Faraday Soc., 62, 3046 (1966).
69. L. F. Grantham, J. Chem. Phys., 44, 1509 (1966).
70. L. I. Staffansson, Acta Chem. Scand., 23, 1225 (1969).
71. H. Bloom and N. J. Doull, J. Phys. Chem., 60, 620 (1956).

72. M. K. Nagarajan, L. Nanis, J. O'M. Bockris, J. Phys. Chem.,
68, 2726 (1964).
73. R. L. Martin, J. Chem. Soc., 3246 (1954).
74. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe,
'Selected values of chemical thermodynamic properties.' Natl.
Bur. Std. (U.S.) (1952).
75. H. Bloom, I. W. Knaggs, J. J. Molloy, D. Welch, Trans. Faraday Soc.,
49, 1458 (1953).
76. J. O'M. Bockris, A. Pilla, J. L. Barton, Rev. Chim. Acad. Rep.
Populaire Roumaine, 7, 59 (1962).
77. H. Bloom, J. O'M. Bockris, N. E. Richards, A. Taylor, J. Am. Chem.
Soc., 80, 2044 (1958).
78. L. E. Topol and L. D. Ransom, J. Phys. Chem., 64, 1339 (1960).
79. G. J. Janz, 'Molten Salts Handbook', Academic Press, New York (1967).
80. J. O'M. Bockris, E. H. Crook, H. Bloom, N. E. Richards, Proc. Roy.
Soc., A255, 558 (1960).
81. W. E. Kirst, W. M. Nagle, J. B. Kastner, J. Am. Inst. Chem. Eng.,
371 (1940).
82. W. H. Bridges, J. V. Cathcart, G. P. Smith, J. Sci. Instr., 32, 139
(1955).
83. H. Bloom and I. A. Weeks, J. Chem. Soc. A, 2029 (1969).
84. J. W. Tomlinson, D. C. Lowe, G. W. Mellors, J. O'M. Bockris,
J. Sci. Instr., 31, 107 (1954).
85. C. J. Smithells, 'Tungsten', 3rd ed, Chapman and Hall, London,
(1952), page 112.

86. G. D. Robbins, J. Braunstein, J. Electrochem. Soc., 116, 1218 (1969).
87. e.g., F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, London (1962), page 778.
88. E. Mattsson and J. O'M. Bockris, Trans. Faraday Soc., 55, 1586 (1959).
89. M. Sluyters-Rehbach, B. Timmer, J. H. Sluyters, Rec. Trav. Chim., 82, 553 (1963).
90. B. Timmer, M. Sluyters-Rehbach, J. H. Sluyters, J. Electroanal. Chem., 18, 93 (1968).
91. M. Sluyters-Rehbach, B. Timmer, J. H. Sluyters, J. Electroanal. Chem., 19, 305 (1968).
92. A. M. Batiele and F. Perdu, J. Electroanal. Chem., 13, 364 (1967).
93. S. K. Rangarajan, J. Electroanal. Chem., 25, 344 (1970).
94. R. de Levie, Electrochim. Acta, 10, 113 (1965).
95. R. L. Birke, J. Electroanal. Chem., 33, 201 (1971).
96. D. L. Hill, K. W. Fung, S. Hsieh, H. L. Lee, J. Electroanal. Chem., 38, 57 (1972).

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