INVESTIGATION OF THE POSSIBLE APPLICATION OF HIGH AND LOW FREQUENCY CONDUCTANCE MEASUREMENTS TO THE ANALYSIS OF POLY-COMPONENT SYSTEMS

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CHAPTER I

INTRODUCTION

As early as 1875 Kohlrausch (1) demonstrated by means of a single measurement of conductance, the analysis of a two-component system in which one component, the solute, was an electrolyte and the other component, the solvent, was a non-electrolyte. This work was extended and modified by numerous others (2). For example, Noyes (4) measured conductances at high temperatures and Jones, who measured conductances for ninety-six electrolytes at concentrations from 0.05 normal to 0.00048 normal at temperatures from zero degrees centigrade to sixty-five degrees centigrade (3). Two-component systems have also been analysed by means of conductance titrations. The fundamental techniques employed in this method may be found in nearly all instrumentalanalysis texts. On the other hand, for systems containing more than two components, analysis by means of conductance measurement has been accomplished only through successive titrations.

The use of high-frequency capacitance measurement for the analysis of two-component systems has several advantages over low-frequency conductance measurement. Low-priced, commercially available capacitance instruments, such as the

Sargent Model V Oscillometer, allow measurements to be read to one part in seven thousand, while conductance apparatus of equal price allow readings to about one part in three hundred. Furthermore, the high-frequency measurements eliminate direct contact between the electrodes and the solution, thus avoiding many undesirable effects such as polarization, electrodeposition, electrode attack, and solution contamination. Single measurements of high-frequency capacitance may be utilized not only for the analysis of two-component systems in which one component is conductive, but also for the analysis of two-component systems in which neither component is conductive. Titrations similar to conductance titrations may be carried out with the high-frequency instruments and may be used for the analysis of poly-component systems as well as two-component systems. A bibliography of such methods is available from one manufacturer (5).

In using either low-frequency conductance or highfrequency capacitance measurements for poly-component systems,
it is to be noted that the existing methods of analysis, consist entirely of titration techniques. Such titrations are
relatively tedious and have the added disadvantage that separate portions of sample must be removed and are of no further
value after analysis. It would seem desirable to have a
method for analyzing poly-component systems by means of a
small number of measurements on the sample unaccompanied by
the introduction of sample contaminants, such as titrants.

The object of this research was the development of such a method.

It was realized that the relationships involved were extremely complex and that it was probably for this reason no apparent previous attempts had been made. It was hoped that a study of these relationships would lead to a sufficient simplification of the procedures and calculations so as to lead to an analytical method of practical value. Toward this end the immediate goal of this thesis was the analysis of a three-component system whose major component was water. This analysis was to be the result of a procedure which could be readily extended to more complex systems.

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CHAPTER II

THEORY

Throughout a considerable range of concentrations encountered in analytical work the theoretical principles of conductance are considered to be well known. The basis for these principles is the theory of ionization presented in 1887 by Svante Arrhenius (1), which states that the majority of strong electrolyte molecules in solution are in a dissociated state as free ions. Under the influence of a potential gradient these ions migrate toward the pole of opposite charge, carrying a unique portion of the current. The extent of this migration is modified through the effect of the forces acting between the ions. Thus, an ion will be surrounded by an "ionic atmosphere" composed of more oppositely charged ions than of like charged ions. The "ionic atmosphere" is disturbed by the movement of the central ion and must continually reestablish itself. The result is that the "ionic atmosphere" becomes unsymmetrical around an ion in motion for, as its relocation must follow the movement of the ion, its mean charge density, as compared with that when the ion is stationary, undergoes a decrease in front of the moving ion and an increase behind it. Since the "ionic atmosphere" must have a net charge which is equal and opposite to that of

the central ion, this asymmetry means that there is an excess of opposite charge behind a moving ion. This excess charge exercises an electrostatic retarding force, and consequently the mobility of the central ion is reduced below the value which it has in infinitely dilute solutions, where interionic effects can be neglected. This effect is commonly known as the "relaxation effect". The oppositely charged ions which predominate in the "ionic atmosphere" migrate together with their solvent sheaths, in a direction opposite to the central ion. Thus, the central ion travels in a medium which is moving in the opposite direction and this introduces a viscous drag in excess of that which would be experienced if no "ionic atmosphere" existed. This effect is known as the "electrophoretic effect".

At low concentration (i.e. less than 0.0001 normal in aqueous solution) the equation:

$$(1) L = Ac$$

in which L is the specific conductance, c is the concentration and A is a constant, gives good quantitative agreement with the experimentally measured values of L and c. In aqueous solutions above 0.0001 normal, in order to take into account the effects of interionic attraction, a modification of this relationship to the form of Onsager's equation is necessary. The relation is now of the form:

(2)
$$L = Ac - Bc^{32}$$

in which B is an additional constant term. This equation has been derived from theoretical considerations and proven to hold experimentally. The constant A is peculiar to the electrolyte considered and is dependent upon the temperature and the solvent. Any change in the temperature changes the mobility of the ions, thus changing A. Any change of viscosity resulting from a change of solvent, also changes the mobility of the ions and changes A. The constant B is a function of the dielectric constant and the viscosity of the solvent.

When the dielectric constant is high, as in the case of water, the forces between particles will be relatively low, and they will be extensively dissociated by thermal vibrations. Electrolytes dissolved in such solvents will consist for the most part of ions, and their conductance will be relatively large. On the other hand, if the dielectric constant of the solvent is low, particles carrying opposite charges will have strong attraction for one another, and thermal vibration will be able to separate only a small proportion of them. In any case, the proportion existing as ions will be greater at low concentration, for the chance that an ion will encounter another of opposite charge is smaller than when more solute ions are present and the distance between ions will be considerably increased, which is to say, the forces acting between ions will be considerably decreased.

It is for this reason that the conductance of any fixed weight of solute will increase with decreasing concentration. In solutions with solvents of very low dielectric constant, where interionic attraction is not negligible even at quite low concentration, the situation is probably complicated by the presence of complexes involving the undissociated electrolyte and its ions. The constant B is inversely proportional to viscosity, dielectric constant and temperature, but the viscosity and dielectric constants are also inversely proportional to temperature, so that B becomes a more complex function of the temperature. At the temperatures being considered in this work, however, the effect is such as to cause a decrease in B with an increase in temperature. This in turn brings about an increase in conductance. At more elevated temperatures a maximum value of conductance is reached and for temperatures above this point a decrease in conductance is noted.

If the interionic forces between ions of two separate compounds are ignored, equation (2) may be extended to a system of a solvent and two electrolytes and it will take the form:

(3) Ac,
$$-Bc_1^{32} + Dc_2 - Bc_2^{32} = L$$

c₁ and c₂ refer to the concentration of the different electrolytes involved while A, B, D, and E are constants as in equation (2). Of course, the neglect of interionic forces

between ions of compound 1 and ions of compound 2 will make equation (3) an approximation and this can only be tolerated in the instance that the usefulness of the results gained from the added simplicity will outweigh their inaccuracy.

Extension of equation (2) to higher concentrations involves the addition of a square term:

(4)
$$Ac - Bc^{3/2} + Fc^2 = L$$

in which F is an empirical constant.

For salts of greater than 1,1 valencies the extension of equation (2) requires a further term as shown below:

(5) Ac - Bc
$$^{3/2}$$
 + Fc 2 + Gc log G = L

In equation (5) F and G are empirical constants.

Equations (4) and (5) apply to concentrations which are above the range necessary in many analytical procedures and they are too complex to lend themselves to easy simultaneous solution, so, for these reasons, their application will not be further pursued.

The Sargent Model V Oscillometer gives a response reading in units of capacitance, which may be represented by the following equation:

(6)
$$c_{a} = \frac{c_{g} (R^{2} c_{s}^{2} W^{2} + 1)}{R_{s}^{2} W^{2} c_{g} c_{s} + R_{s}^{2} W^{2} c_{s}^{2} + 1}$$

Ca = Capacitance of the solution

Cg = Capacitance of the glass

 $G_S = G_O K$

Co = Capacitance of the empty cell (with air)

K = Dielectric constant of the solvent

 $R_s = R_o/L$ (Resistance of Cell with Solution)

 $R_o = 0.885/C_o$ (Resistance Due to Cell Geometry)

L = Specific conductance at low frequency

 $W = 2\pi f$

f = Frequency of current

This theoretical equation has been derived (3) for solutions which exhibit significant conductance (i.e. aqueous solutions of electrolytes) and, while it is suitable for present purposes, does not permit general application.

Solving equation (6) for L the specific conductance:

(7)
$$L = \left[\frac{R_0 W^2 K}{C_0} \left(\frac{C_g C_a}{C_g - C_a} \right) - R_0^2 W^2 K^2 \right]^{\frac{1}{2}}$$

From equation (2) it is seen that;

(8) Ac - Be
$$^{-\sqrt{2}}$$
 = F(Ca)

F(Ca) is the function of L, the specific conductance, derived in equation (7). Upon further extension of this equation to a solution containing two electrolytes it becomes

(9)
$$Ac_1 - Bc_2^{3/2} + Dc_2 - Ec_2^{3/2} = F(Ca)$$

Thus, the high frequency capacitance measurement varies with changes in concentration of either or both electrolyte and

with changes in temperature or solvent in the same manner and for the same reasons as low frequency conductance. One new variable has appeared, however, and that is the frequency of the current applied to the sample cell.

Since the constants in equation (3) and (9) are dependent upon several variables, as already explained, it should be possible through variations of these quantities to obtain several independent equations whose simultaneous solution will allow calculation of c_1 and c_2 . The magnitude of the variation of constants and the accuracy of the instrument measurements as well as the practicality of variation of conditions, will all limit the accuracy, simplicity and application of the analytical method.

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CHAPTER III

EXPERIMENTAL PROCEDURE

All solutions were prepared from Baker's Analyzed Reagent grade chemicals. Samples were dried in an oven at two hundred degrees centigrade for two to three hours and kept in a desiccator until weighed. Distilled water, passed through a resin column, to effectively deionize it, was used in the preparation of all solutions. Solutions were stored in two hundred milliliter glass stoppered bottles prior to use. In each case the one normal solution was prepared from a weighed sample and all other dilutions were made volumetrically. Technical grade dimethyl formamide from The Matheson Company, boiling at 152-154 degrees centigrade, mixed volumetrically in a ratio of four to one with deionized water, was the auxiliary solvent used.

A Model RC Conductivity Bridge manufactured by Industrial Instruments, Incorporated, with a dip-type cell of platinized-platinum plate electrodes, was used for low frequency conductance measurements. The instrument was grounded and all contacts secured tightly to insure stability. A constant temperature bath, consisting of a clay crock filled with ten gallons of water, heated by a resistance heater in series with a Powerstat control and agitated with an electric

stirrer to insure uniformity, was used. Wooden racks fitted with thirty milliliter pyrex beakers suspended the solutions into the bath. Holes beside each beaker permitted the measurement of the temperature in very close proximity to the solution. Solutions were kept in the bath at least ten minutes prior to measurement. The dip-type cell was rinsed with a separate sample of the solution to be measured.

The cell constants were determined using measurements on a solution of potassium chloride of thirty-two liters per equivalent weight. Division of the dimensionless constant, Table I in appendix, by the instrument measurement gave the specific conductivity, which is the conductivity of one milliliter of solution as measured with electrodes one centimeter square and one centimeter apart.

A Model V Chemical Oscillometer, manufactured by E. H. Sargent, equipped with a ten milliliter rubidium coated cell and a type "A" cell holder was employed for high-frequency measurements. The room was air-conditioned at twenty-three degrees centigrade and maintained at constant humidity. The instrument was grounded and the cell holder assigned a marked area and kept in it throughout all measurements. A warm-up period of at least two hours was employed prior to adjustment of the zero setting with the dry cell. When erratic results or an oscillation of the resonance needle appeared, the cell holder was dismantled and all contacts cleaned thoroughly

with steel wool, dried and reassembled. The instrument operated at a frequency slightly less than five megacycles.

A thermometer, calibrated against United States Bureau of Standard thermometers, gave readings reliable to ± 0.1 degree. The thermometer was introduced into the cell to a marked depth exceeding the mercury bulb. Cooling of the solutions, prior to measurement at lower than room temperature was accomplished with an ice bath in a Dewar flask. The entire bottle of solution was placed in the Dewar flask and allowed to attain a temperature of approximately five degrees centigrade. For measurement above room temperature, the solution was heated to about 65 degrees centigrade, a sample withdrawn and allowed to cool while taking readings at the desired temperatures. A sample of four milliliters was withdrawn and used to rinse the cell. This was discarded and an eight milliliter sample introduced into the cell for measurement. The cell was cleaned with deionized water and, when not in use, stored in a dessicator filled with silica gel.

To correlate equation (6) with experimental results, the constants Cg and Co were determined experimentally by the method outlined in the <u>Manual of Chemical Oscillometry</u> (1). Measurements on pure mercury and deionized water were used in the following simplified equations:

(10)
$$\frac{\text{Co}}{\text{Co}} = \frac{\text{Sw}}{\text{Kw(Shg - Sw)} - \text{Shg}}$$

(11)
$$C_g = \frac{Sw (C_g/C_0 + 1 + Kw(C_0/C_g + 1))}{Kw-1}$$

Sw = Reading for water

Shg = Reading for mercury

Kw = Dielectric constant for water

Substituting these values in equation (10) and utilizing these results in equation (11), $C_{\rm g}$ was found to be 134.3118 micro-micro-farads and $C_{\rm o}$ 3.85 micro-micro-farads.

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CHAPTER IV

DISCUSSION OF RESULTS

The data may be conveniently arranged into the following groups:

- 1. A demonstration of the validity of equation (2), Chapter II, for various electrolytes at several temperatures and in differing solvents.
- 2. A demonstration, with various electrolytes, of the relative change in magnitude of the constants A and B with temperature.
- 3. A demonstration, with various electrolytes, of the relative change in magnitude of the constants A and B with changing solvent.
- 4. A demonstration of the validity of equation (3), Chapter II, for various electrolyte systems at various temperatures.
- 5. A demonstration of the validity of equation (9) Chapter II.
- 6. A demonstration of the effect of frequency change upon conductance.

The conductance data were derived from two sources, measurements performed with a conductance bridge and measurements performed with an "Oscillometer".

Investigated initially were changes in temperature, since they are easier to achieve than changes in solvent or frequency of measurement. The data concerning solvent variation have been included for the reason that complex systems may require more equations than can be acquired through temperature variation on a single system.

Figure 1, together with Tables II, III, IV, V, VI, VII, and VIII in the appendix, illustrates the data which constitute the previously mentioned group 1. While the rates of increase of conductance with concentration increase (the slope of the curve) for sodium chloride and potassium chloride in aqueous solution are almost identical, barium nitrate and sodium chloride or potassium chloride show marked differences. Picking two points near each extremity of the curve for potassium chloride, two equations of the form of equation (2), Chapter II, were established. Solving for the constants, A and B, and applying them at different concentrations, good agreement between the theoretical conductance and experimental conductance was obtained and is graphically shown in Figure 2. Also shown in Figure 2 is the good agreement of barium nitrate, a bi-univalent electrolyte.

Changing the solvent from water to a mixture of 80 per cent dimethyl formamide and 20 per cent water causes a decrease in the conductivity. A rearrangement of the relative slopes has occurred with barium nitrate now higher than potassium chloride and cupric chloride now lower. This might

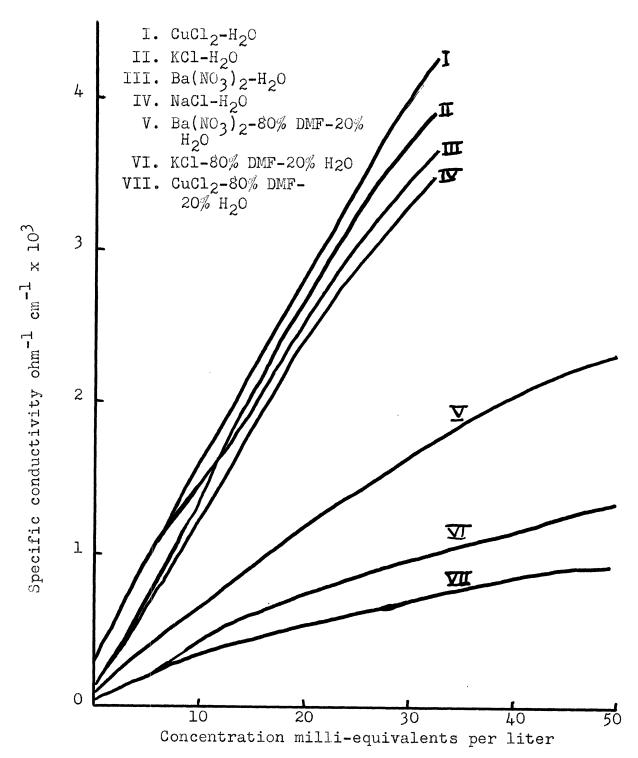


Fig. 1--Variation of conductance with concentration at 25° C.

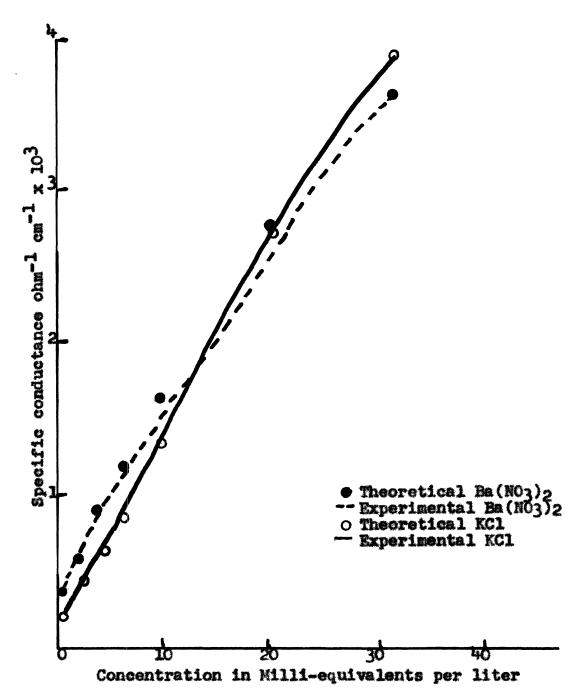


Fig. 2--Variation of conductance with concentration theoretical compared to experimental for KCl and $Ba(NO_3)_2$.

possibly be explained as a different solvent-solute association than with water. It is important to note that this solvent has achieved a considerable separation of the constants, A and B, for the electrolytes.

Figure 3, together with Tables II, III, IV, V, VI, VII, and VIII in the appendix, illustrates the data belonging to group 2 and demonstrates the relative change in magnitude of conductance with temperature change for various electrolytes at specific concentrations. In aqueous solution the conductance of electrolytes with similar valencies increase at similar rates with an increase of temperature. That is to say, in a mixture of such electrolytes the constants of equation (3). Chapter II. associated with each electrolyte change in a similar manner with temperature and the resulting equations are almost identical. However, electrolytes of dissimilar valencies show a variation with temperature and for these electrolytes the constants of equation (3), Chapter II. The rate of change of conductance with temperature, in a system whose solvent is 80 per cent dimethyl formamide and 20 per cent water is much less than a pure aqueous solution. An inversion is noted here as it was for the conductance-concentration relationship, indicating once again the point that similar electrolytes may possibly be differentiated by means of solvent variation, even though temperature variations would seem to have no effect.

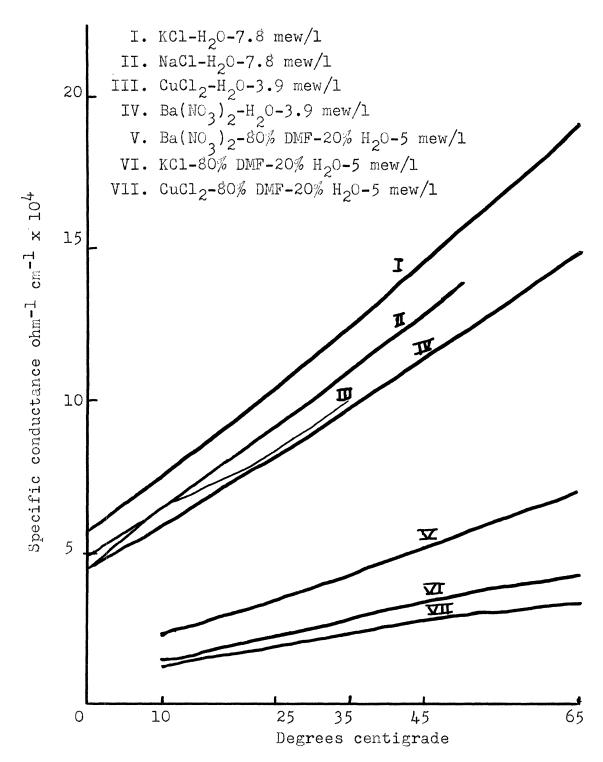


Fig. 3--Variation of conductance with temperature for specific concentrations.

Figure 4, taken from data in Tables II, III, IX, and X in the appendix, shows the relationship of experimentally determined high-frequency capacitance to experimentally determined low-frequency conductance. This curve was used as a working curve to convert high-frequency measurements to specific conductance.

The constants A and B were calculated using the limiting ionic conductances and the limiting slope values as described in Bockris (1). Constants for sodium chloride and potassium chloride from ten to twenty-five degrees centigrade are given in Table XIV in the appendix, and verify the conclusion based upon Figure 3 that each changes in a parallel manner to the other with changes of temperature. These constants were used in equation (3), Chapter II, and expected conductances of mixtures of sodium chloride and potassium chloride were calculated. The expected values are compared with experimental converted high-frequency measurements in Table XIII in the appendix. These results verify the postulate made in Chapter II that the conductance of a mixture of electrolytes in aqueous solution is equal to the sum of the conductances of the individual electrolytes.

In view of Figure 3 a mixture of barium nitrate and potassium chloride would give a greater variation of constants. Constants derived in the same manner as above and applied to mixtures of the electrolytes, show agreement to within 5 per cent of converted high-frequency

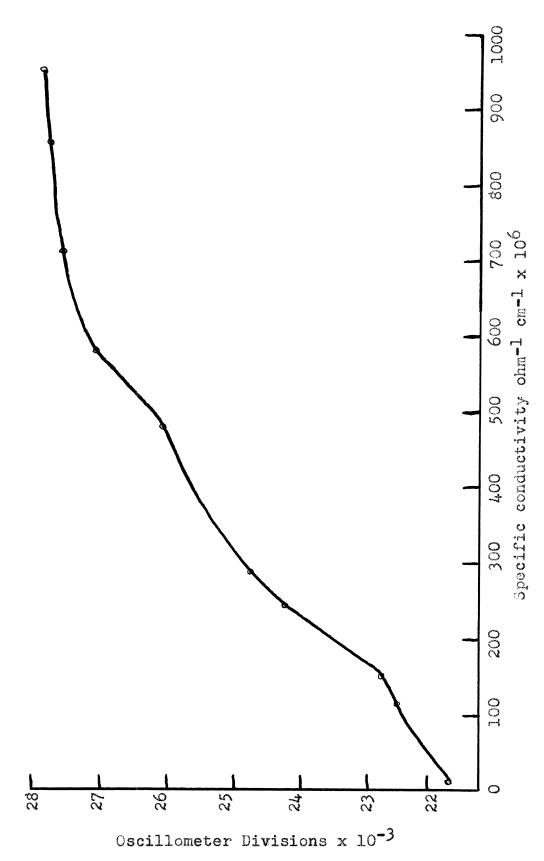
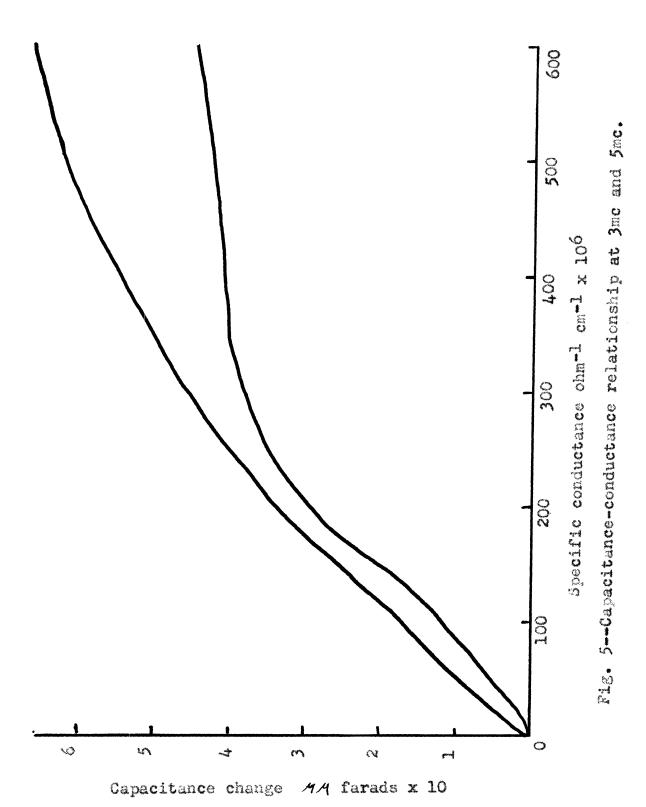


Fig. 4--Relationship of high-frequency capacitance to low-frequency conductance.

measurements and are indicated in Table XVII of the appendix.

Mathematical manipulation of four equations of the form of equation (3), Chapter II, using constants in Table XV and XVI in the appendix, indicate inconsistent equations. It is noted that the ratio of the constants for barium nitrate at twenty-five and forty-five degrees centigrade is 1.4700, while for potassium chloride at the same temperatures it is 1.4508. This difference is too small to allow for experimental error in the conductances and still have four solvable simultaneous equations.

Figure 5 is a graph taken from Reilley (2) indicating the capacitance-conductance relationship at two frequencies, three and five megacycles of current. These plots were made from theoretical considerations and verified experimentally by their author. As can be seen by equation (7), Chapter II, such a variation of frequency would give equations which were simple multiples of each other throughout. It is to be noted however, that a greater range of accuracy is obtainable at five megacycles than at three megacycles of current.



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CHAPTER V

CONCLUSION

A three-component system, such as two electrolytes in aqueous solution, follows equation (3), Chapter II, which is a summation of the relationship that each would exhibit alone at the same concentration. This equation, for a given set of conditions (i.e. temperature, frequency, solvent) has only two variables, the concentrations of the electrolytes. Ordinarily it would require only two such equations to solve for the concentrations, but since there is involved a fractional power along with an integral power of each concentration, it requires four sets of conditions to solve for the concentrations. (It could be possible to solve with a minimum of three by reduction to a cubic equation). The usable concentration range on the "Oscillometer" was found to lie between one and fifteen milli-equivalents per liter and thus further limited conditions.

Investigation of strong electrolytes shows that the constants, A, B, D, and E, vary with the electrolyte, solvent and frequency of measurement. The constants, A and D, are of primary importance and have a variation among strong aqueous electrolyte solutions at twenty-five degrees centigrade, of about 0.125 to 0.150 ohm⁻¹ cm². Independent

variation from one electrolyte to another, is necessary in order to obtain independent equations.

Investigation of temperature as a means of such variation indicated that the variations were present, but not of a magnitude allowing mathematical solution of the equations. This was shown using a mixture of sodium chloride and potassium chloride, whose constants differ markedly at one temperature but vary from one temperature to another in a very similar manner. Even electrolytes, whose conductance-temperature relationships cross graphically (barium nitrate and potassium chloride) do not lend themselves to such a mathematical solution. Both mixtures substantiated the summation principle and the capacitance-conductance relationship

In a preliminary investigation, variation of frequency, as a means of obtaining independent constants, appears not to have any advantageous effect.

Variation of the solvent, which would necessitate multiple samples, indicated that it would provide considerably
more variation of the constants than did temperature variation of aqueous solutions. Furthermore, temperature variation for other solvents seems to give greater relative differences between electrolytes than is obtained in water. For
the solution of the three-component systems being considered,
a minimum of three solvents would be necessary in the absence

of temperature variation. Fewer could be used if temperature variation would suffice to supply one or more equations.

The feature which most drastically limits the applicability of solvent variation is the generally low solubility of electrolytes in solvents other than water.

APPENDIX

TABLE I

CELL CONSTANTS FOR LOW-PREQUENCY CONDUCTANCE AT

VARIOUS TEMPERATURES

10° C	25° C	35° C	450 C	65° C
0.1045	0.1062	0.1079	0.1093	1.1119

TABLE II

LOW-FREQUENCY CONDUCTANCE* OF POTASSIUM CHLORIDE
AT VARIOUS TEMPERATURES AND CONCENTRATIONS**

			andre de la companya			
Conc.	o° c	15.5° C	25° C	35° C	50° C	65° C
500	31480	45545	54750	65400	80950	*
125	8310	12280	14825	17812	22387	• •
62.5	4275	6343	7681	9231	• •	• •
31.2	2196	3252	3930	4728	5976	7315
7.8	570	853	1032	1247	1593	1927
1.95	145	218	264.2	317.8	407.7	498.8
0.97	73.4	109.5	132.8	160.4	205.3	252.1

^{*}Conductance in ohm-1 cm-1

^{**}Concentration in milli-equivalents per liter

TABLE III

LOW-FREQUENCY CONDUCTANCE* OF SODIUM CHLORIDE IN WATER
AT VARIOUS TEMPERATURES AND CONCENTRATIONS**

Conc.	O° C	12.5° C	25° C	35° C	50° C
62.5	3593	5037	6675	8094	10268
31.2	1872	2631	3490	4225	5437
7.8	485.0	684.8	907	1101	1412
1.95	121.5	171.2	226	275	353
0.97	60.1	84.8	112.6	136.6	178.8

^{*}Conductance in ohm-1 $cm^{-1} \times 106$

TABLE IV

LOW FREQUENCY CONDUCTANCE* OF BARIUM NITRATE IN WATER AT VARIOUS TEMPERATURES AND CONCENTRATIONS**

Conc.	o° c	10° C	25° C	35° C	50° C	65° C
0.97	120.5	158.8	222.3	266.9	349.9	427.5
3.9	446	588	819	982	1269	1552
15.6	1523	2025	2858	3429	4299	5214
31.2	2759	3675	5162	6253	• •	
62.5	4773	6437.5	9150	11081	14131	17262

 $^{^*}$ Conductance in ohm⁻¹ cm⁻¹ x 10⁶

^{**}Concentration in milli-equivalents per liter

^{**}Concentration in milli-equivalents per liter

TABLE V

LOW-FREQUENCY CONDUCTANCE* OF CUPRIC CHLORIDE IN WATER AT VARIOUS TEMPERATURES AND CONCENTRATIONS**

Conc.	00 C	10° C	25° C	35° C
0.97	114.8	170.0	217.3	265.2
3.9	434.9	641.5	819.4	996.8
15.6	1580	2295	2925	3529
31.2	2958	4275	5413	7057
62.5	5473	7937	9893	11868

^{*}Conductance in ohm^{-1} cm⁻¹ x 10⁶

TABLE VI

LOW-FREQUENCY CONDUCTANCE* OF POTASSIUM CHLORIDE IN EIGHTY
PER CENT DIMETHYL FORMAMIDE SOLUTION AT VARIOUS
TEMPERATURES AND CONCENTRATIONS**

	10° C	25° C	35° C	45° C	65° C
Conc.	TO- C	25- 6		AND THE REAL PROPERTY AND ADDRESS OF THE PROPERTY ADDRESS OF THE PROPERTY AND ADDRESS OF THE PROPERTY AND ADDRESS OF THE PROPERTY	
100	2100	3034	3853	4750	6359
50	1166	1344	2158	2632	3669
10	283.8	418.1	513.8	638.8	892.5
1	34.1	50,8	64.2	78.0	102.7
0.5	22.2	31.2	37.2	46.3	62.2
0.1	11.9	*•	15.1	20.9	23.8

^{*}Conductance in $ohm^{-1} cm^{-1} x 10^6$

^{**}Concentration in milli-equivalents per liter

^{**}Concentration in milli-equivalents per liter

TABLE VII

LOW-FREQUENCY CONDUCTANCE* OF BARIUM NITRATE IN EIGHTY
PER CENT DIMETHYL FORMAMIDE SOLUTION AT VARIOUS
TEMPERATURES AND CONCENTRATIONS**

Conc.	10° C	25° C	35° C	45° C	65° C
100	2839	3933	4795	5602	7462
50	1741	2308	2677	3479	4550
10	454.3	624.7	793.3	966.8	1316
1	57.2	86.6	116.0	134.8	177.6
0.5	31.8	43.5	58.0	71.6	94.0
0.1	11.6	15.1	18.6	25.2	31.2

 $^{^*}$ Conductance in ohm $^{-1}$ cm $^{-1}$ x 10^6

^{**}Concentration in milli-equivalents per liter

TABLE VIII

LOW-FREQUENCY CONDUCTANCE* OF CUPRIC CHLORIDE IN EIGHTY PER CENT DINETHYL FORMAMIDE SOLUTION, AT VARIOUS TEMPERATURES AND CONCENTRATIONS

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Conc.	10° G	25° C	35° C	45° C	65° C
100	1105	1464	1768	2146	2331
50	724	948	1172	1332	1356
10	190.9	327.7	399.6	466.8	586.0
5.	140.0	196.6	239.7	284.5	327.2
1.	38.9	58.2	67.2	86,7	124.3
0.5	22.8	30.8	44.0	54.6	79.9
0.1	11.6	22.5		24.1	34.9

^{*}Conductance in ohm-1 cm-1 x 106

^{**}Concentration in milli-equivalents per liter

TABLE IX

HIGH-FREQUENCY CAPACITANCE* FOR POTASSIUM CHLORIDE
IN WATER SOLUTION AT VARIOUS TEMPERATURES
AND CONCENTRATIONS**

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Conc.	10 ° C	15° C	20° C	25° C
1000	28883	28919	28976	29066
100	23784	28837	28894	28965
80	28751	288 08	288 68	28936
60	28731	28772	28833	28905
40	28687	28746	28807	28874
20	28414	28484	28568	28666
10	27808	27921	28119	28263
8	27560	27699	27869	28066
6	27140	27265	27505	27718
4	26114	26325	26646	26941
2	23798	24067	24424	24758
1	22363	22428	22560	22726

^{*}Capacitance in instrument divisions

^{**}Concentration in milli-equivalents per liter

TABLE X

HIGH-FREQUENCY CAPACITANCE* OF SODIUM CHLORIDE IN WATER SOLUTION AT VARIOUS TEMPERATURES

AND CONCENTRATIONS**

	an a constitutação pra resista com materia sona do meso de constituto de constituto de constituto de constitu	participate conference processors and commentary acting a commentary planting according or acting the second reservoir.		
Conc.	10° C	15° C	20° C	25° C
1000	28809	28852	28893	28952
100	2 8702	287 33	28794	288 56
80	28668	28717	28778	28832
60	28624	28676	28747	28803
40	28524	28587	28654	28717
20	28079	28176	28300	28417
10	27628	27754	27914	28122
8	27272	27426	27557	27729
6	26720	26940	27179	27425
4	25519	25825	26234	26506
2	23389	23594	23890	24235
1	22227	22297	22391	22540
0.1	21913	21873	21777	21691

^{*}Capacitance in instrument divisions

^{**}Concentration in milli-equivalents per liter

TABLE XI

HIGH-FREQUENCY CAPACITANCE* OF SODIUM CHLORIDE
AND POTASSIUM CHLORIDE MIXTURE IN WATER
SOLUTION AT VARIOUS TEMPERATURES AND
CONCENTRATIONS**

					
Conc. KC1	Conc. NaCl	10° C	15° C	20° C	25° C
250	7 50	28867	28919	28960	29045
25	75	28789	28837	28888	28939
20	60	28748	28794	28850	28924
15	45	28710	28767	28829	28891
10	30	28605	28643	28709	28785
5	15	28326	28401	28496	28595
2.5	7.5	27755	27876	28062	28184
2.0	6.0	27513	27618	27800	27959
1.5	4.5	2 6990	27198	27428	27606
1.0	3.0	25969	26255	26584	26898
0.5	1.5	23886	24145	24493	24844
0.25	0,75	22338	22405	22546	22711

^{*}Capacitance in instrument divisions

^{**}Concentrations in milli-equivalents per liter

TABLE XII

HIGH-FREQUENCY CAPACITANCE* OF SODIUM CHOLRIDE
AND POTASSIUM CHLORIDE MIXTURE IN WATER
SOLUTION AT VARIOUS TEMPERATURES AND
CONCENTRATIONS**

Conc. KCl	Conc. NaCl	10° C	15° C	20° C	25° C
750	250	28867	28919	28960	29045
7 5	25	28789	28837	28888	28 9 39
60	20	28748	28794	28850	28924
45	15	28710	28767	28829	28891
3 0	10	28605	28643	28709	28785
15	5	28326	28401	28496	28595
7.5	2.5	27755	27876	28062	28184
6.0	2.0	27513	27618	27800	27959
4.5	1.5	26990	27196	27428	27606
3.0	1.0	25969	26255	26584	26898
1.5	0.5	23886	24145	24493	24844
0.75	0.25	22338	22405	22546	22711

^{*}Capacitance in instrument divisions

^{**}Concentration in milli-equivalents per liter

TABLE XIII

COMPARISON OF CALCULATED CONDUCTANCE* WITH CON-VERTED HIGH-FREQUENCY MEASUREMENTS FOR MIXTURES OF SODIUM CHLORIDE AND POTASSIUM CHLORIDE AT 25 DEGREES CENTIGRADE

Conc**	Conc ^{**} KC1	Calculated conductance	Measured conductance
1.5	0.5	257	260
0.5	1.5	283	280
4.5	1.5	761	765

^{*}Conductance in ohm-1 $cm^{-1} \times 10^6$

TABLE XIV

CONSTANTS FOR EQUATION (9) FOR SODIUM CHLORIDE
AND POTASSIUM CHLORIDE AT VARIOUS
TEMPERATURES

Constants	10° C	15° C	20° ¢	25° C
A (NaCl)	0.0915	0.1012	0.1140	0.1264
B (NaCl)	0.06087	0.06898	0.07868	0.08865
D (KCl)	0.1115	0.1211	0.1350	0.1498
E (KCl)	0.06531	0.07343	0.08342	0.09300

^{**}Concentration in milli-equivalents per liter

TABLE XV CONSTANTS FOR EQUATION (9) FOR POTASSIUM CHLORIDE AND BARIUM NITRATE IN AQUEOUS SOLUTION AT VARIOUS TEMPERATURES

	25° C	30° G	35° C	40° C	45° C
A Ba(NO ₃) ₂	0.13508	0.15020	0.16581	0.18194	0.19857
B Ba(NO ₃) ₂	0.26350	0.29299	0.32345	0.35490	0.38725
D KCl	0.14986	0.16623	0.18338	0.1994	0.21742
E KCl	0.09398	0.10424	0.11500	0.12505	0.13635

TABLE XVI HIGH-FREQUENCY CAPACITANCE MEASUREMENTS ON MIXTURES OF BARIUM NITRATE AND POTASSIUM CHLORIDE IN AQUEOUS SOLUTION AT 25 DEGREES CENTIGRADE.
AT VARIOUS TEMPERATURES

	25 ⁰ C	30° C	35° C	40° C	45° C
Sol #1	24775	24970	25300	25568	25980
Sol #2	26059	26270	26500	26733	27150
Sol #3	25377	25626	25915	26217	26625

The composition of the mixtures are:

Sol #1 - 1 mew/l Ba(NO₃)₂ -l mew/l KCl Sol #2 - 2 mew/l Ba(NO₃)₂ -l mew/l KCl Sol #3 - 2 mew/l Ba(NO₃)₂ -0.5 mew/l KCl

TABLE XVII

COMPARISON OF CALCULATED CONDUCTANCE* WITH CONVERTED EXPERIMENTAL HIGH-FREQUENCY MEASUREMENTS FOR MIXTURES OF BARIUM NITRATE AND POTASSIUM CHLORIDE IN AQUEOUS SOLUTION AT

VARIOUS TEMPERATURES

Measured Theoretical Temperature conductance conductance Solution # 1 25° C 280 273 30° C 290 303 35° C 340 335 40° C 357 365 45° C 382 399 Solution # 2 25° C 415 393 30° C 445 436 35° C 496 482 40° C 527 520 450 C 580 575 Solution # 3 25° C 323 320 30° C 355 344 35° C 375 393 40° C 412 430 45° C 467 470

^{*}Conductance in ohm-1 cm-1 x 106

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