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STUDIES ON THE CONDUCTIVITIES OF DISPERSIONS

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UNIVERSITY OF CALIFORNIA

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STUDIES ON THE CONDUCTIVITIES
OF DISPERSIONS

Robert Eugene Meredith

(Thesis)

July 1959

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STUDIES ON THE CONDUCTIVITIES OF DISPERSIONS

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STUDIES ON THE CONDUCTIVITIES OF DISPERSIONS

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(Thesis)

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University of California, Berkeley, California

July 1959

ABSTRACT

The conductivities of dispersions are studied theoretically and experimentally. Data on foams, emulsions, and mixtures of solids in liquids indicate that the dilute suspension relations are not obeyed above a dispersed-phase volume fraction of about 0.2. A review of previous attempts at predicting the behavior of the data at higher concentrations reveals need for improvement both in regards to experimental accuracy and theory.

Electrical-conductivity data on emulsions are presented where the conductivities of the two phases vary over a wide range and where the volume fraction of the dispersed phase extends up to 0.6. In addition, measurements are made on dispersions of ordered arrangements of spheres and cylinders.

Theoretical developments are presented following three different methods of attack: (a) the mathematical technique used by Bruggeman for dispersions of spheres is employed to develop an expression that is valid for dispersions of spheroidal particles. (b) A new approximation (distribution model) is proposed for treating a concentrated dispersion of spherical and nonspherical particles. The resulting expression is in good agreement with measurements on spheroidal particles over the entire range of concentrations. (c) The Rayleigh equation for the conductivity of a cubical lattice of spheres is re-developed by using a different potential function and considering higher terms.

STUDIES ON THE CONDUCTIVITIES OF DISPERSION

I. INTRODUCTION

Statement of the Problem

In this dissertation we deal with the problem of predicting the conductivities of two-phase mixtures in terms of a few common and usually known parameters. Primarily we are concerned with mixtures or dispersions such as foams, emulsions, packed beds, etc., and specifically we are interested in evaluating the effective thermal or electrical conductivities of these dispersions, knowing the individual conductivities of the phases involved as well as their relative amounts.

The solution for a problem of this nature is not, in general, restricted to the concept of thermal or electrical conductivity, but it is applicable with equal validity for such properties as dielectric constants, magnetic permeability, diffusion coefficients, refractive indices, etc. of mixtures when the appropriate variables are known. These phenomena are related inasmuch as the potentials involved in these cases all obey the Laplace equation and the concepts differ only in the name given to the constant of proportionality that applies at the boundary conditions. In making this generalization, we ask only that the model and the basic assumptions that are inherent in the solution be approximately obeyed in the application of the results.

Application

In addition to the obvious applications of work of this type, it is worth noting that studies of this nature can be used in the determination of the character of emulsions, the porosity of ground strata, the dielectric constants of pure crystals from measurements on powders, the effective shape of particles in a dispersion, and the volume concentration of certain biological material such as red blood cells.

The Model, Assumptions and Variables

In reviewing the previous work on this subject, one finds that in many cases experimental data has been unknowingly mismatched to perfectly rigorous theories that were never meant to apply to the data in question. Combinations of this type, which sometimes exhibit a high degree of fortuitous agreement, have, more often than not, succeeded in confusing successive generations as to the true limits on the theories that were presented. Unless otherwise mentioned, we are operating with the following model and assumptions and recognize the following variables. The dispersions that will be treated shall consist of a dispersed phase surrounded by a second medium that we shall call the continuous phase. The properties of these phases are assumed to be isotropic and not a function of field strength or position. In addition to the conductivities of the two phases, the other variables normally associated with this problem are primarily factors associated with the dispersed phase. These parameters include the volume fraction, surface resistance, shape, orientation, and size distribution of the dispersed particles.

Many authors in the past have chosen to ignore the effects of concentration, particle shape, and size distribution with statements to the effect that they considered their systems to be approximated by a dilute dispersion of spherical particles. While very dilute dispersions of nearly spherical shapes may indeed be well represented by making such approximations, at higher concentrations the use of the relations that are valid for dilute systems lead to very serious errors.

The Scope of this Work

In this work we strive to control the variables that have been mentioned above. Data on emulsions are presented with conductivity ratios varying from 0.006 to 137.0 and with a dispersed-phase volume fraction ranging up to 0.6. Studies are presented in which ordered arrangements of spheres and cylinders constitute the dispersed phase.

Accurate data are presented on these models, thus allowing one to evaluate the difference between an ordered arrangement of particles and a random dispersion. Theoretical models are proposed that consider the effects of concentrated volume fraction and the shape of the dispersed particle. The results of these theories appear in good agreement with conductivity data on dispersions of spheroidal particles up to volume fractions of 0.6.

Nomenclature

To simplify our presentation, we have chosen to use the word "conductivity" at times to also refer to the allied phenomena that have been mentioned above. In the past, studies of this type have been presented with various Greek symbols being used to denote the parameters that are equivalent to a conductivity. In place of these symbols we have chosen to use the letter k to expedite the typing, and the subscripts c , d , and m have been reserved to represent the continuous phase, the dispersed phase, and the mixture respectively. As much as possible, the relations that will be presented in this thesis have been made dimensionless by use of the symbols K_d and K_m . These upper case letters denote the conductivities of the dispersed phase and mixture respectively when the conductivity of the continuous phase is unity (i.e. $K_d = k_d/k_c$ and $K_m = k_m/k_c$). The reciprocal of K_m is equivalent to the "tortuosity" or "resistance factor" terms that have been used by some of the previous authors. The symbol f will be used to denote the volume fraction of the dispersed phase.

II. PREVIOUS WORK

The literature contains many papers concerning this subject. Some of the work on the conductivity of dispersions dated back over a hundred years and is colored with many well-known and important names. Most of the important publications are reviewed below and are classified according to the type or object of the study. The original symbols used in the equations by these authors have been changed here when possible to conform to the nomenclature of this thesis.

Studies on Electrical Conductivity

Theoretical Treatments

The work of Maxwell. The classical work on the theory of conduction through heterogeneous media was developed independently by H. A. Lorentz,¹ L. Lorenz,² and J. C. Maxwell³ during the years 1880 and 1881. These authors applied potential theory to the case of a single sphere in a continuum, both phases being isotropic and homogeneous. By using boundary conditions that imply that the current and potential are continuous at the interface and that the field is uniform at large distances from the sphere, they obtained the following relation between the conductivity of the resulting mixture (k_m) and the conductivity of the continuous (k_c) and dispersed (k_d) medium:

$$\frac{k_m - k_c}{k_m + 2k_c} = \frac{(k_d - k_c)f}{k_d + 2k_c} \quad (1)$$

In this relation and in all of the following equations, f represents the volume fraction of the dispersed phase. This expression may be put in a more convenient form by dividing out k_c and substituting K_m and K_d respectively for k_m/k_c and k_d/k_c . Upon rearrangement we have

$$K_m = \frac{K_d + 2 - 2f(1 - K_d)}{K_d + 2 + f(1 - K_d)} \quad (2)$$

The limitations associated with this relation and comparison with data are given in other sections of this thesis. It will suffice to say here that excellent agreement with experimental results is obtained for f less than 0.1 as long as the dispersed particle is spherical and has negligible surface resistance.

The work of Rayleigh. Lord Rayleigh has studied the limiting assumptions involved in the derivation of Maxwell's equation.⁴ By removing the boundary condition that the field be uniform at large distances from the sphere, Rayleigh has taken a first step toward extending the Maxwell relation and model into a region where the distances between particles are no longer large. In essence, Rayleigh has examined the effect of neighboring particles on each other and has to some extent allowed for the interaction of fields that are not considered in the Maxwell model. For the two-dimensional case, the element of the Rayleigh model consists of a circle of the dispersed phase surrounded by a rectangle of continuous phase. Rayleigh applied the principle of superposition and expressed the conductivity of the dispersed and continuous phases in the form of two series expansions with interdependent coefficients. Green's theorem was then applied to find the relationship between the constant terms of the two expansions. For an ordered conductivity of the mixture in a direction normal to the sides of the cylinders becomes

$$K_m = 1 - \frac{2f}{\frac{1 + K_d}{1 - K_d} + f - 0.3058 \frac{1 - K_d}{1 + K_d} f^4}, \quad (3)$$

and for the case of spheres he obtains

$$K_m = 1 - \frac{3f}{\frac{2 + K_d}{1 - K_d} + f + 1.65 \frac{K_d - 1}{K_d + 4/3} f^{10/3}}. \quad (4)$$

This latter expression reduces to Maxwell's equation as the volume fraction of the dispersed phase approaches zero.

The work of Runge. Runge has reviewed the work of Rayleigh and redeveloped his expressions for ordered cylinders and spheres.⁵ Runge correctly stated that the coefficient of 1.65 in Rayleigh's equation for spheres is in error by a factor of π . That is, the coefficient 1.65 should be replaced by $1.65/\pi$ or 0.525. In the same expression Runge has replaced $(K_d + 4/3)$ by $(K_d - 4/3)$ but makes no mention of this in the text of his article, indicating that it is a typographical error. In addition, Runge has derived an expression for the conductivity normal to the sides of an ordered arrangement of cylindrical shells. The resulting equation is

$$K_m = 1 - \frac{1}{K_{d1} + 0.5 - 0.01911 (1/K_{d3}) - 5.22 (10^{-5})(1/K_{d7})}, \quad (5)$$

where

$$K_{dn} = \frac{(1 + K_d) - (1 - f)^{2n} (1 - K_d)}{(1 - K_d) - (1 - f)^{2n} (1 - K_d)}. \quad (6)$$

This expression is subject to the same types of limitation that restricted the Rayleigh equation for solid cylinders.

The work of Bruggeman. In 1935 Bruggeman⁶ expanded the Maxwell equation in a Taylor's series and treated the first two terms by an integral technique which led to

$$1 - f = \frac{K_m - K_d}{K_m^{1/3} (1 - K_d)}. \quad (7)$$

A subsequent interpretation of the mathematical steps used by Bruggeman indicate that a special type of model was being proposed. In this model each of the dispersed spherical particles was considered as being very different in size from its nearest neighbors. This size difference was to be such that the distortion of the field due to a particle's smaller neighbors was negligible. Under these conditions, Maxwell's

equation is valid in the neighborhood of each particle, and thus this latter relation may be applied to calculate the change in conductivity that arises after the addition of each particle. In the limit, one obtains Eq. (7). This relation has received wide acceptance for a number of reasons. First, it makes an attempt at pointing out the correction necessary for concentration effects, although in reality a practical mixture never meets the conditions on which the theory is based. Second, it shows that for two cases of equal volume fraction, a difference in conductivity would be obtained depending upon the size distribution of the particles in a random mixture. Third, this equation and the Maxwell equation appear to form boundaries on most of the data that have been obtained on dispersions of spherical particles. Finally, the Bruggeman equation reduces to a very simple form for two of the common cases, i.e., for $K_d \longrightarrow 0$,

$$K_m = (1 - f)^{3/2}, \quad (8)$$

and, for $K_d \longrightarrow \infty$,

$$K_m = (1 - f)^{-3}. \quad (9)$$

The work of Burger and Fricke. Burger,⁷ and later Fricke,⁸⁻¹² presented studies on the theory of the shape effect of the dispersed particle in a two-phase mixture. These studies were analogous to Maxwell's work, but instead of solving the potential problem for a sphere, the authors considered the more general case of a dispersed spheroid and mathematically worked in confocal ellipsoidal coordinates. The validity and limitations of the results are in a like manner also similar to those in the Maxwell treatment. The detailed derivations are discussed in the chapter on The Shape Effect.

Other Treatments

The work of Wiener. Wiener^{13,14} recognized that conduction through a mixture of lamina-shaped particles was bounded by the values obtained when the lamina were all aligned parallel or perpendicular to the electrodes.^{13,14} The equations for these two limiting cases are respectively

$$k_m = f k_d + (1 - f) k_c \quad (10)$$

and

$$1/k_m = f/k_d + (1 - f)/k_c \quad (11)$$

Wiener also recognized that dispersions of other shapes would lie between these latter two models and proposed that for such mixtures a linear combination be used such as

$$k_m/(k_m + u) = f k_d/(k_d + u) + (1 - f)/(k_c + u) \quad (12)$$

where u , a "form number", was to be experimentally determined for each mixture.

The work of Lichtenecker. Lichtenecker, in a series of papers proposed that a logarithmic equation of the following form would fit most of the data:¹⁵⁻¹⁸

$$\ln(k_m) = f [1 + u(1 - f)] \ln(k_d) + (1 - f)(1 - uf) \ln(k_c). \quad (13)$$

Here u was also an unknown function or "form number". This work and the work of Wiener were attempts at obtaining simple correlations by using nothing more complicated than the rules for adding resistances and ideas on how to best fit the data.

The work of Mashovets. Mashovets has studied the electrical conductivity of nonconducting cylindrical and spherical particles arranged in an ordered manner in a conducting fluid.¹⁹ This author found

that the conductivity of the system was apparently independent of the arrangement of the dispersed spheres as long as the volume fraction remained constant. Mashovets obtained, by means of curve fitting, the following empirical equation for dispersions of nonconducting spheres with volume fractions up to $f = 0.4$:

$$K_m = 1 - 1.78 f + f^2 . \quad (14)$$

The work of Eucken. Eucken²⁰ has presented a few conductivity measurements on benzene-water and phenol-water emulsions. Measurements are given where potassium iodide was used to make both phases conducting, but because of the poor distribution of this electrolyte the data are essentially for the case where $K_d = 0$. The data by Eucken are bounded by the Maxwell and Bruggeman curves.

The work of Clark. Clark has made electrical-conductivity measurements on various types of foams and presents excellent data for the case where the volume fraction is large and the K_d value is zero.²¹

The work of Frey. Some data on dispersions of nonconducting particles have been presented by Frey.²² A volume fraction range of 0.1 to 0.8 was covered by mixing such particles as long, thin glass rods, spheres, and fine sand. Runs on duplicate volume fractions obtained by different combinations of the above particles were not taken, and therefore Frey did not recognize a shape effect.

The work of Pearce. Pearce has made some measurements on formal arrangements of brass balls in a conducting bath.²³ Although the conductivities obtained were greater than what the Maxwell equation would predict, it is interesting to note that the actual conductivities should be even higher because no evidence is given by Pearce that polarization was negligible. Polarization effects could be significant when the frequency is as low as 400 cps and the system is brass in tap water.

The presence of polarization would cause the apparent conductivity to decrease as the surface area per unit volume increases, and Pearce did find that, for a given volume fraction, small brass spheres gave a lower apparent conductivity than the larger spheres.

The work of Cornell and Katz. Cornell and Katz in a study of flow through porous media have presented conductivity data on various types of sandstone.²⁴ The volume-fraction range investigated extends only from $f = 0.8$ to 0.98 . Measurements of this type do not relate directly to the present study. Materials such as sandstone cannot be approximated in general by a simple geometric model. Conductance takes place through long winding channels or slits, and conductivity measurements are thus not only a function of porosity but also of permeability. Studies of this kind have sometimes been correlated by using the parallel resistor analogy where the net length of the conducting path has been modified with a tortuosity factor. These authors give references to similar investigations.

The work of Slawinski. Slawinski has conducted experiments on two-phase mixtures where the dispersed phase was nonconducting.²⁵ These studies were made on systems where the dispersed particles were all spherical in shape. The author finds that the relation that fits his data is

$$K_m = \frac{1}{1 + (f/p) (1 + 0.321 p)^2 / (1 - p) - (f/p)}, \quad (15)$$

$$\begin{array}{ll} \text{where for } 0.15 > f & p = 0.806 (f)^{2/3}, \\ \text{for } 0.15 < f < 0.60 & p = (0.806 + 0.133 f) (f)^{2/3}, \\ \text{and for } 0.60 < f & p = 0.904 (f)^{2/3}. \end{array}$$

This equation was derived by calculating integral mean path lengths and correcting for certain spheres in certain lattice positions.

The work of De La Rue and Tobias. De La Rue and Tobias have studied the electrical conductivity of dispersions of various types of nonconducting particles.²⁶ Measurements were made on systems consisting separately of sand, cylinders, and spheres of one size and of mixed sizes. These authors found that the conductivity data obtained on a large size range of glass spheres lay closely to the curves represented by

$$K_m = (1 - f)^Y, \quad (16)$$

where

$$1.43 < Y < 1.51. \quad (17)$$

The large number of measurements made in this study, and the reproducibility of the data presented indicate with little doubt that randomly distributed spherical nonconductors give a lower conductivity than that predicted by the Maxwell equation.

Studies on Dielectric Constants

Theoretical Treatment

The work of Clausius and Mosotti. The counterpart to the Maxwell equation in the field of dielectric behavior was first treated by Mosotti (1850)²⁷ and Clausius (1867).^{28,29}

The work of Wagner. Wagner has proposed the use of the following equation for evaluating the dielectric constants of dispersion:³⁰

$$K_m = 1 - 3f (1 - K_d) / (2 + K_d). \quad (18)$$

This expression may be recognized as being identical to the first two terms of Maxwell's equation after the latter is expanded in a Taylor's series about $f = 0$. Such an equation is therefore valid only for dilute dispersions.

The work of Bottcher. Bottcher has derived the following formula for predicting the dielectric constants of irregular distributed particles:³¹

$$\frac{K_m - 1}{3K_m} = \frac{f (K_d - 1)}{K_d + 2K_m} \quad (19)$$

By comparing this expression with the Maxwell equation, it can be seen that the net results appear to replace the 2's in the latter expression by $2K_m$. For $K_d = 0$ we obtain the same result as if we had used the Wagner relation (see above), and so in this case, the validity of the above expression must be restricted to dilute dispersions. For the case where the K_d value approaches infinity, Eq. (19) gives a conductivity value which greatly exceeds the value predicted by both the Maxwell and Bruggeman relations.

The work of de Loor and Poley. In a study of the effective field about a dispersed particle, de Loor^{32,33} and Poley³⁴ have pointed out that as the volume fraction of the dispersed phase increases, the effects as far as the dielectric constant of the mixture is concerned is as if the dielectric constant of the continuous phase had changed.

The work of Polder and Van Santen. Polder and Van Santen have derived an expression for the dielectric constant of mixtures, giving a special emphasis to the shape of the dispersed particle.³⁵ The technique used by these authors was a combination of that employed by Fricke and Bottcher (see above). The relations obtained in this study are discussed in a later chapter on The Shape Effect.

The work of Frenkel and Fradkina. Frenkel and Fradkina in a series of papers have discussed the electrical parameters and theories that one should consider in dispersed systems.³⁶⁻³⁸ The authors remind us that emulsions of water in oil or systems of living tissues (e.g. blood cells) have a surface film or membrane about the

dispersed particle which plays the role of an insulating medium. Such insulated particles have very high capacity and ohmic resistance in low-frequency alternating fields. On the other hand, at high frequencies the capacity and resistance of the particles correspond to the properties of the dispersed media, and contact effects between phases cease to play an essential role. In other words, the effective film resistance has been removed when measurements are conducted in high-frequency fields. Fradkina has measured the dielectric constants of water in oil emulsions. This study extends to a volume fraction of 0.3 and is for a K_d value of 35. Fradkina found that the following expression adequately fits his data:

$$K_m = (1 + f)/(1 - 2f) . \quad (20)$$

This expression may be compared to the Maxwell equation where K_d becomes very large, i.e.

$$K_m = (1 + 2f)/(1 - f) . \quad (21)$$

The former relation, of course, would indicate that Maxwell's equation underestimates the K_m values even at very low volume fractions.

Studies on Dielectric Constants

Other Treatments

The work of Millikan. Millikan in 1897 made some measurements on the dielectric constants of water in oil emulsions where the K_d value was probably between 20 and 40.³⁹ The author compared the four low volume-fraction readings with the Maxwell equation in its limiting form where K_d becomes very large. His data were slightly larger than values predicted from this latter equation.

The work of Piekara. Piekara has reviewed some of the work of the early authors and has made measurements on the dielectric constants of mercury in vaseline mixtures.⁴⁰⁻⁴² Piekara's measurements correspond to the case where the K_d value is very large. Like Millikan, Piekara

found that his measurements were greater than would be predicted by the Maxwell relation.

The work of Voet. Voet has measured the dielectric constants of mixtures obtained by dispersing iron filings in linseed oil.^{43,44} Measurements were made when the mixture was subjected to shear and when the suspension was at rest. Voet found that a difference in the dielectric constant is obtained in the two cases and attributes this difference to an "agglomeration factor".

The work of Kamiyoshi. In a study of the dielectric constants of various powders (e.g. KI, NaCl, etc.) Kamiyoshi has empirically deduced the relation^{45,46}

$$K_m = 1 + (0.900 f - 0.139) (K_d - 1) . \quad (22)$$

The volume-fraction range was from 0.34 to 0.61 while K_d values varied from 3.3 to 8.5. In all cases one phase of the mixture was air.

The work of Smith. By packing powders into a coaxial line and measuring the impedance of the line, Smith has in turn obtained the dielectric constants of air mixed with silica, magnesia, polystyrene, and zinc oxide.⁴⁷

Studies on Thermal Conductivity

Significant Treatments

The work of Schumann and Voss. Schumann and Voss, in a study of heat flow through granulated material, have derived an expression for the thermal conductivity of a granular bed in terms of the usual parameters.⁴⁸ Their resulting expression is quite long and involved and is based on the dispersed particle having the shape of a long "hyperbolic" cylinder with its long axis perpendicular to the field. Although the results were meant to be employed for concentrated dispersions, other

authors have often extrapolated the expressions to dilute volume fractions. Schumann and Voss have neglected field distortions, thus assuming that the field was linear up to and through the dispersed phase. The most serious error in this work was made, however, when it was found necessary to add on a term in the expression for K_m which gave some reasonable value for the conductivity of the mixture when K_d was equal to zero. For this condition the authors chose to write

$$K_m = (1 - f)^3, \quad (23)$$

although it is known from the work of Bruggeman that a better expression would have been obtained if the exponent has been $3/2$ instead of 3 . The net effect of this is to give a lower conductivity over the entire range of K_d and f than one might otherwise obtain. This probably accounts for the fact that in 12 out of 13 comparisons with experimental results which were made by the authors, the expression gave a conductivity that was too low.

The work of Wang and Knudsen. Wang and Knudsen have experimentally measured thermal conductivities of oil-in-water and water-in-oil emulsions.⁴⁹ Considerable scatter of data about Maxwell's equation was obtained. Such scatter is, as one would expect, somewhat inherent in thermal conductivity measurements of this type where the K_d value is not very far from one and in addition is a function of the potential gradient between the measuring electrodes.

The work of Deissler and Eian. In an investigation of the effective thermal conductivities of powders, Deissler and Eian propose that all data may be represented by a series of curves which are individually based upon four points.⁵⁰ Two of these points are the obvious conductivity values that result when the volume fraction is zero and one respectively. The other two points are evaluated for cubical-packed spheres and square-packed cylinders by neglecting the bending of lines of constant potential and by neglecting shape effects.

The work of Wilhelm, Johnson, Wynkoop, and Collier. In a study of heat transfer in fixed beds, Wilhelm et al. have summarized data from several other sources and have evaluated the mean deviation from the curves of Schumann and Voss (see above).⁵¹

The work of Topper. Topper, as late as 1955, claims a first in deriving an expression that would predict the conductivity of a mixture in terms of the component properties.⁵² By neglecting potential theory and assuming that all porous material may be approximated by a cubical arrangement of spheres, he derives,

$$K_m = \frac{Z}{XZ + Y} , \quad (24)$$

where

$$X = 1 - 2 (3f/4\pi)^{1/3} , \quad (24a)$$

$$Y = 2 \tan^{-1} \left\{ \frac{(3 f/4\pi)^{1/3}}{[1/\pi (1 - K_d) - (3 f/4\pi)^{2/3}]^{1/2}} \right\} . \quad (24b)$$

and

$$Z = \pi (1 - K_d) [1/\pi (1 - K_d) - (3 f/4\pi)^{2/3}]^{1/2} . \quad (24c)$$

No data is offered in support of this expression and it is difficult to decide over what volume-fraction range the equation should apply. The physical model breaks down for $f > 0.525$ and a spot calculation shows that for $K_d = 0$ in the low-volume-fraction range, the conductivity obtained with this expression is greater than that given by the Maxwell equation.

The work of deVries. The thermal conductivity of granular material, with special reference to soils, has been studied by deVries.⁵³ In other articles, deVries has pointed out a number of errors made by authors who have used the simplified approach.⁵⁴⁻⁵⁶

Summary of the Previous Work

From the preceding reviews it can be seen that the problem of evaluating the effective conductivities of dispersions has received considerable attention both from the point of theoretical development and obtaining experimental data. It is unfortunate however, that these two types of studies do not appear to compliment each other — for most of the rigorous theoretical studies apply to models that are usually not approximated by experiment. The theoretical work of Maxwell, Burger, Fricke, etc. has been restricted to dilute suspensions of spheres or spheroids, but most of the data demand treatments that are valid into the more concentrated regions. The studies by Lord Rayleigh and Runge offer the only rigorous treatments at extending theory into the realm of concentrated dispersions, but these works are restricted to ordered arrangements of spheres or cylinders which represent models that are not approximated by most of the data. Bruggeman, Bottcher, Polder, and van Santen have presented various relations which are based on uncertain models and which, for the most part, tend to overcompensate for the concentration effect.

From a sampling of the reviews on the preceding pages, it is noticeable that the workers in the fields of electrical conductivity and dielectric constants have tended towards a more theoretical approach than the authors in the field of thermal conductivity. In this latter field most of the workers have not considered the problem as subject to the rules of potential theory and have been much less than rigorous, probably because of the difficulty and scatter inherent in thermal conductivity measurements.

Regardless of the field of application, it is also apparent that authors seldom make real efforts to properly define the exact models and restrictions under which their proposed theory can be expected to be valid. Some have made a few measurements and have then indulged in broad generalizations on the basis of such restricted experience. It is of course true, that in some regions of the key variables, it really

does not make a great deal of difference which approximations one chooses. In the sensitive regions on concentration, shape, orientation, and size distribution, many of these relations lose their validity to such an extent that one should not even consider them as good for rough approximations.

III. EXPERIMENTAL PROCEDURES AND DATA ON EMULSIONS

The Emulsion Study

The Need for the Study

One of the convenient ways for obtaining data on dispersions of spherical particles is to examine the electrical conductivity of suitable emulsions. Relatively few data on emulsions have been published by earlier investigators. Fradkina,³⁸ Eucken,²⁰ and Knudsen⁴⁹ have respectively presented some data on the dielectric constant, electric conductivity, and thermal conductivity of certain types of oil and water mixtures. (See the section on Previous Work.) In general their investigations were restricted in scope, covering only certain ranges of variables. In addition, experimental procedures employed by the various authors do not provide adequate confidence in the data to enable one to satisfactorily compare values predicted by various theories.

Selection of the Liquid-Liquid System

The study planned required two immiscible liquid phases in which one could vary the electrical-conductivity ratio of the two phases over a very wide range by dissolution of a suitable electrolyte. The system was further restricted by requiring that the solvents be chemically safe, stable, and pleasant to use at room temperature, because a great deal of handling was anticipated. Furthermore, it was desired that over most of the conductivity range the two phases would individually have specific conductances of rather large values. These latter two specifications seemed to eliminate about 90% of the possible combinations and made it more apparent that water should probably constitute one of the solvents. After a preliminary study regarding such factors as immiscibility, dielectric constants, and electrolyte solubility, some tests were made on the systems tabulated in Table I. The samples were prepared as follows. The two solvents were mixed in such proportions that the result gave two phases of nearly equal volume. A "reasonable" amount of

Table I

Qualitative conductance data on emulsions			
1st solvent	2nd solvent	Electrolyte	Conductivity ratio ^a
n-amyl alcohol	water	CaI ₂	11.2
n-amyl alcohol	water	LiI	84
n-amyl alcohol	water	(C ₂ H ₅) ₄ NI	3,100
chloroform	water	(n-C ₃ H ₇) ₄ NI	12.7
propylene carbonate	water	(C ₂ H ₅) ₄ NI	2.80
propylene carbonate	water	(n-C ₃ H ₇) ₄ NI	0.93

^aThe conductivity ratio tabulated in this column is found by dividing the conductivity of the aqueous phase by the conductivity of the organic phase.

electrolyte was then added, and the mixture was emulsified. After the phases separated, a sample from each was drawn off, and the conductivities of the two phases were measured. No quantitative data on concentrations were taken, as this study was designed to give only a qualitative indication of a suitable system.

The Emulsion System To Be Used

As can be seen from Table I, the systems that seem to offer the greatest possibilities are the last two entries. We make this statement because it appears that it is possible with these systems to obtain an organic phase that is more conducting than the aqueous phase. Thus we have a chance of covering a wide range of K_d values, i.e., ratio of the conductivity of the dispersed phase to the continuous phase. We can, for example, obtain a K_d value of unity by adding the proper amounts of sodium chloride and ternary ammonium iodide salts to the water and propylene carbonate. The addition of simple salts like sodium or potassium chloride to a pure water and propylene carbonate mixture gives a very much better conducting aqueous phase than organic phase, and thus it is possible to obtain data on high or low K_d mixtures by making water-in-oil or oil-in-water emulsions, respectively.

A Note On Propylene Carbonate

Because propylene carbonate is a common but not very widely known chemical, we shall say a few words about its character before proceeding with a description of the method of obtaining data. Propylene carbonate is an odorless, colorless, mobile liquid. In natural medium it is stable, it is not hygroscopic, and it is not corrosive. With respect to water, it has a lower freezing point (-49°C) and a higher boiling point (242°C). At 20°C it has a specific gravity of about 1.20 and it is only partially miscible with water. At 25°C a two-phase mixture of water and propylene carbonate has the following composition: in the aqueous phase there are 17.5 grams of propylene carbonate for every 100 grams of water, and in the organic phase there are 8.3 grams

of water for every 100 grams of propylene carbonate.* The solubility of certain salts in propylene carbonate have recently been studied by Harris.⁵⁷

Method of Obtaining Data on Emulsions

Technique and Design Factors

The equipment and procedure that was used in obtaining data on emulsions was designed with the following points in mind. We were not studying emulsions per se, that is, emulsions were used only to study a dispersion of spherical particles in a continuous media. Because of this it was necessary to take care in forming the emulsion; only one phase at a time was to constitute the dispersed region. Since we were also interested in obtaining data under conditions where the dispersed phase was essentially free of interfacial surface resistance, the addition of any emulsifying agent or surface-active material had to be avoided. Although in the absence of surface resistance, the results obtained would be independent of the actual size of the dispersed particle, it would still be desirable to have an order of magnitude of the size of the droplets to insure that we were always making a conductivity measurement across a large number of particles regardless of the volume fraction. With these factors in mind, the following equipment was assembled.

Equipment

The cell and emulsifying equipment required for this study are shown in Fig. 1. The apparatus depicted consisted of the following parts:

- (1) A 5-liter round-bottom flask which was modified and designed to act as a cell and a mixing chamber. The components included in this flask were:

*The propylene carbonate used for this study was a commercial grade obtained from the Jefferson Chemical Company of Houston, Texas.

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Fig. 1. Chemical schematic drawing of the equipment used in the emulsion study.

- (a) two pairs of bright platinum electrodes made from 20-mil platinum sheet. One pair of these electrodes had surfaces which were circular in shape with a diameter of 2 cm. The separation between these electrodes was approximately 3 cm. The other pair of electrodes was located on the opposite side of the flask and had surfaces in the shape of small squares with a dimension of 0.5 cm on a side. The separation between conducting surfaces for this pair was about 8 cm.
- (b) a differential thermometer which read in units of $1/100^{\circ}\text{C}$ and which was fitted with a tapered joint.*
- (c) a photocell[†] and light source which were placed in the cell opposite the large electrodes described above. The gap that could be occupied by liquid between the light source and the photocell was approximately 1 cm.
- (d) a stirring unit that consisted of a sector of a Teflon disk which sat in the bottom of the flask. The disk was driven by a glass rod that was attached to a magnetic coupling unit at the top of the flask.[‡] This unit, in turn, was driven by a small universal motor that was mounted vertically above the cell.
- (e) outlets near the top and bottom of the flask for circulating liquid.

* Beckman Instruments Inc., Pasadena, California

[†] RCA 1P41.

[‡] Scientific Glass Apparatus Company, Bloomfield, New Jersey.

- (2) A small pump with a Teflon rotary seal and a universal motor.*
This pump was used to both circulate the liquid under study and to keep the phases emulsified.
- (3) A 100-cc automatic buret.[†]
- (4) A fixed-contact mercury thermostat set at 25°C.[‡]
- (5) A mercury plunger electronic relay.[§]
- (6) A 115-volt solenoid valve.^{||}
- (7) A small, metal heat exchanger controlled by the thermostat, relay, and solenoid valve mentioned above. The purpose of this heat exchanger was to remove the heat that the liquid picked up in passing through the circulating pump.
- (8) Tygon tubing and glass tees, stopcocks, and ground joints used to connect the various parts of the system.

In addition to this equipment, approximately seven small conductivity cells of various geometries and cell constants were used in determining K_d values.

All measurements were made at 25°C unless otherwise noted. This isothermal condition was obtained by using a 50-gallon water bath that was kept at 25 ± 0.02 °C.

*Model E-7, Eastern Engineering Co., New Haven, Conn.

†Scientific Glass Apparatus Company, Bloomfield, New Jersey.

‡Model T-151, Precision Thermometer and Instrument Co., Philadelphia, Pa.

§Model T-672, Precision Thermometer and Instrument Co., Philadelphia, Pa.

||Skinner Electric Valves, New Britain, Conn.

The commercial grade of propylene carbonate that was obtained for this experiment contained a few impurities that seemed to accelerate its hydrolysis. In order to remove these impurities and thus obtain a solution that would give a stable conductivity ratio, it was necessary to vacuum distill the starting material. The column that was used for this operation is similar to a common small-scale commercial unit. It consisted of a 5-liter kettle with an upper and lower heating mantel, a 1.5-inch i.d. vacuum-jacketed column packed with "Heli-pak",^{*} a vacuum-jacketed still head equipped with a reflux condenser,[†] and a reflux-ratio controller.[‡] The propylene carbonate was distilled at a pressure of 40 mm of Hg where the boiling point was 40°C. A reflux of 5:1 was used in this distillation, and the middle 80% was taken off as product.

The Photocell Instrumentation

The purpose of this equipment was to enable us to obtain an estimate of the dispersed particle size by use of the Langlois, Gullberg, and Vermeulen correlation.⁵⁸ A schematic diagram of the circuit is shown in Fig. 2. The components shown are as follows:

- (a) an RCA-1P41 photocell, mounted as described above
- (b) a penlight flashlight bulb
- (c) a switch for the light source
- (d) a 1.5-v dry-cell battery
- (e) a 2.2-megohm resistor
- (f) a 50,000-ohm variable resistor

* No. 3013 Podbielniak, Inc., Chicago, Ill.

†,‡ Glass Engineering Laboratories, Belmont, California, Models D-6, D-25, and D-40.

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Fig. 2. Schematic diagram of the photocell circuit.

- (g) a recorder^{*}
- (h) a 90-v B battery
- (i) a switch for the photocell circuit.

The Conductivity Bridge

The ac conductivity bridge that was used to make the measurements associated with this experiment is depicted schematically in Fig. 3. The components shown are as follows:

- (A) an oscillator with a variable-frequency output.[†]
- (B) a cathode-ray oscillograph that was used as a null detector.[‡]
- (C) a linear amplifier with a gain of 1000
- (D) the conductivity cell
- (E) a variable decade resistance box[§]
- (F) a capacitance arrangement that consisted of both a variable precision condenser and a decade capacitor^{||}
- (G) a switch that allowed the above capacitance to shunt either the decade resistance box or the cell
- (H) and
- (I) fixed deposited carbon resistors of 1000 ohms each
- (J) a shielded transformer.[|]

^{*} Leeds and Northrup Co., Philadelphia, Pa., type G.

[†] Hewlett-Packard, Palo Alto, California, model 605A.

[‡] Dumont Lab. Inc., Passiac, New Jersey, model 304 H.

[§] General Radio Corp., Cambridge, Mass., type 1432-M.

^{||} General Radio Corp., Cambridge, Mass., types 722-N and 219-M.

[|] General Radio Corp., Cambridge, Mass., type 578

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Fig. 3. Schematic diagram of the conductivity bridge.

Experimental Procedure

Approximately 6 liters each of propylene carbonate and distilled water were equilibrated in a 12-liter flask at 25°C with the proper amount and kind of electrolyte to give the desired conductivity ratio. The K_d value for the mixture was determined by making measurements in one of the cells described above. The phase that was to constitute the continuous media was then separated from the mixture, and a known amount -- approximately 5400 cc -- was added to the system depicted in Fig. 1. Initial readings on both the photocell and the conductivity were taken and the circulation pump was started. In finite steps, small amounts of the second phase were buretted into the system. After about five minutes, or when the system had come to equilibrium, a conductivity reading and a photocell recording were made. An amount of mixture, equal in volume to the amount of the second phase that was added, was then drawn off and the above steps repeated. The amount of the dispersed phase that was present in the liquid that was drawn off was taken into account in calculating the volume fractions. Data were taken in this manner until the volume fraction of the dispersed phase approached 0.5. Above this value there was a possibility that phase inversion would take place in localized regions of the system and thus cause us to record results that were misleading.

The character of the emulsion was observed through a section of glass tubing as it passed to the suction side of the centrifugal pump. If the phases seemed to have had any tendency to separate at this point, the pump, which acted as the primary mixer, was increased in speed. In most cases, the addition of the electrolyte gave added stability to the emulsion, and because the propylene carbonate-water emulsion always seemed to have had some stability of its own, phase separation in the mixing flask never became a problem.

One technique that was considered for the determination of volume fractions was to draw off a sample of the mixture, centrifuge a portion of it, and ascertain the relative volume of the two phases. This method was

rejected, however, because the centrifuge heated the sample, causing the phases to separate at a temperature other than that which existed in the cell. The determination of the interface of the two phases was also difficult and the over-all procedure was quite slow. Spot checks were made, however, by using this method, and the results agreed with the values that were tabulated for these experiments.

In order to aid in obtaining a desired conductivity ratio, some sample runs were made on a small scale with two ternary ammonium salts. The results for these measurements are given in Table II.

Evaluation of the Data on Emulsions

A Note Regarding Accuracy

The random error introduced in the measurements of the volume fraction and conductivity ratio is a variable during any one run. The least error is made in both of these measurements at the beginning of a run or when the volume fraction is low. As the volume fraction builds up the residual errors in this measurement may tend to accumulate in one direction or another, however it is felt that all of the data tabulated for the volume fractions are within $\pm 1\%$ of the true value and this limit must be considered to be very generous over most of the range. Concerning the conductivity measurements, in some of the tables four significant figures are given; for these values the error of ± 3 units in the last figure is allowed. The figure covers both the 0.1% error allowance in the decade box and the inability in some cases to decide on the last figure in this measurement. In the cases where only three significant figures are given for the conductivity ratio, the error may be considered to be ± 1 unit in the third figure. The fourth figure in this latter case is omitted either because of the type of decade box used or the difficulty involved in obtaining a null at the higher volume fractions.

Every attempt was made of course, to eliminate systematic error. It was not possible to make exact runs to check the reproducibility of the data because the necessary handling of the system between runs always

Table II

Equilibrium data on a mixture of propylene carbonate and water (equal volume of the two phases)			
Grams of electrolyte per 1000 cc of total solution	Specific conductivity of organic phase (mho/cm x 10 ⁴)	Specific conductivity of aqueous phase (mho/cm x 10 ⁴)	Ratio of the conductivity of the aqueous phase to the organic phase
<u>Electrolyte: tetra ethyl ammonium iodide</u>			
0.7308	0.909	2.81	3.09
1.781	2.12	5.89	2.78
3.727	4.25	11.6	2.73
10.68	11.0	29.1	2.65
15.50	15.3	39.3	2.57
<u>Electrolyte: tetra-n-propyl ammonium iodide</u>			
0.3280	0.531	0.619	1.16
0.6240	0.981	0.957	0.975
1.216	1.86	1.66	0.892
1.540	2.33	2.02	0.867
4.030	5.76	4.73	0.821

resulted in a slight contamination which changed the conductivity ratio for the next series of measurements. For this sort of test however, the difference between the K_d values in Tables VI, VII, and VIII may be considered negligible, and thus in comparing these tables we see that the apparent reproducibility is very good.

Evidence of Surface Resistance

When the data that are presented in Tables XII, XIII, and XIV are plotted and compared to the values calculated from the Maxwell and Bruggeman relations, we see that the experimental points lie below both of these relations in the dilute regions, and then gradually rise to take on their expected value between the two curves. At first this behavior appears to be quite anomalous. It is, for instance, in this concentration range that one would expect almost perfect agreement with the Maxwell equation. The experimental conditions in this region are almost identical with the model suggested by Maxwell and yet, contrary to expectation, the percent deviation between the data and theory seems to become larger as we go to smaller volume fractions. Thought on this subject was not made any easier when it was found that our data was also in agreement with some experimental work published by Fradkina.³⁸ Fradkina, in a study of the dielectric constant of some water-in-oil mixtures, gave a set of data for the conditions where $K_d = 35.4$ and which also closely resembled the values tabulated in Table XIV.

Slowly the following clues were collected which indicated where the difficulty laid. First of all, it was noted that such abnormal phenomena were observed only when the dispersed phase was more conducting than the continuous media. Secondly, under these conditions it was found that the shunt capacity required across the resistance decade box in the bridge was greater for the mixtures than the value required for either of the phases alone. Thirdly, the phenomenon was most noticeable at very low volume fractions and this coincided with the zone where the interfacial surface area per unit volume of dispersed phase was the largest. (See Fig. 4 and Table III.) Finally, it was discovered that the discrepancy gradually disappeared as the ac bridge frequency was increased above the normal 1,000 cps value.

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Fig. 4. An example of surface resistance

Legend: Data points from Table XIV ○

Data points of Fradkina ●

Maxwell's equation for $K_d = 137$ —

Table III

Typical size of the particles in the emulsion studies		
Volume fraction of dispersed phase	Surface area per unit vol. of dispersed phase (cm^{-1})	Diameter of the dispersed droplet (microns)
<u>Emulsion type: oil in water</u>		
.00397	869	69.0
.00794	851	70.5
.01191	733	81.9
.01588	630	95.3
.0238	492	122
.0316	397	151
.0394	337	178
.0471	291	206
<u>Emulsion type: water in oil</u>		
.0048	5,309	11.3
.00797	3,896	15.4
.0159	2,083	28.8
.02315	1,438	41.7
.0315	1,107	54.2
.0392	902	66.5

Taken as a whole, these facts could only indicate that we were dealing with a type of surface resistance. More specifically, this resistance would have to be viewed as a capacitive resistance which existed at the interface of the dispersed and continuous media. The mode of conduction through the interface would therefore have to be primarily due to a capacitive effect, thereby destroying the idea that the cell was electrically represented by a simple RC shunt arrangement. To correct this data to the case of zero surface resistance requires a more elaborate bridge study. That is, the reading on the decade box in the leg opposite the cell no longer gives the pure resistive component of the solution. Such a reading must be corrected as indicated in Appendix I.

Fortunately there exists a simple experimental technique that easily overcomes this problem, and that is to increase the ac frequency of the bridge until no further change in the conductivity ratio of the emulsion is noted. To vary this frequency, we had to redesign the bridge in order to obtain the accuracy desired. First of all, the amplifier and oscillograph shown in Fig. 3 were replaced with a unit null detector,* and then all leads were symmetrically layed out and shielded. Every attempt was made to keep stray capacity to a minimum. The resulting changes in the frequency characteristics of the bridge are shown in Table IV.

In practice it was found that it was not necessary to increase the frequency very much in order to eliminate the effect of surface reactance. No significant changes were noted in going above 10 kc, and so the remainder of the data on emulsions were obtained at this frequency. As can be seen by comparing the graphs that follow, all data collected under these conditions now gave expected agreement with the Maxwell relation at the dilute volume fractions, and the data seemed to be bound by the Maxwell and Bruggeman curves over most of the range.

*General Radio Co., type No. 1212-A.

Table IV

Bridge calibration		
Frequency (kc)	Before ^a (ohms)	After ^a (ohms)
1	1,000	1,000
5	1,000	1,000
10	1,001	1,000
50	1,017	1,001
100	1,075	1,001
150	1,188	1,002
200	1,385	1,002
250	1,805	1,001

^aThe terms "Before and "After" refer to measurements that were made on the ac conductivity bridge before and after the high-frequency modifications were made. The data in these two columns indicate the design errors in the bridge by showing how the apparent resistance of a 1,000-ohm deposited-carbon resistor changes with frequency.

In order to further test for the presence of a surface resistance, one run was made at a K_d ratio very close to unity. With this type of measurement, where the conductances of the two phases are very nearly equal, the presence of any surface resistance will be accentuated and very easily detected. The results of this test is given in Table V. Surface resistance is clearly present in the data taken at 1 kc, for under these conditions the K_m values have begun to fall below the mixture's K_d value around a volume fraction of 0.25. The measurements taken at 10 kc are free from this anomaly. The data collected in this study are presented in Tables V through XIV on the following pages and in subsequent graphs.

Table V

Data on emulsions for $K_d = 0.980$ and a comparison of measurements at 1 and 10 kc		
Conditions: O/W emulsion		
Frequency: 1 and 10 kc		
Electrolyte: tetra n-propyl ammonium iodide		
f	K_m at 1 kc	K_m at 10 kc
0.000	1.000	1.000
0.017	0.999	0.999
0.035	0.998	0.999
0.053	0.996	0.998
0.069	0.994	0.998
0.103	0.992	0.997
0.135	0.989	0.997
0.166	0.986	0.993
0.196	0.983	0.991
0.224	0.981	0.990
0.252	0.978	0.989
0.279	0.976	0.988
0.305	0.974	0.987
0.329	0.973	0.986
0.353	0.972	0.985
0.376	0.971	0.985
0.399	0.970	0.984
0.420	0.969	0.984

Table VI

Data on emulsions for $K_d = 0.006$		
Conditions: O/W emulsion		
Frequency: 1000 cps		
Electrolyte: sodium chloride		
f	ohms	K_m
0.000	217	1.000
0.0185	225	0.964
0.0360	231	0.939
0.0535	237	0.916
0.0708	244	0.889
0.0876	250	0.868
0.104	257	0.844
0.136	270	0.804
0.168	285	0.761
0.198	300	0.723
0.226	316	0.687
0.254	332	0.654
0.281	349	0.622
0.307	367	0.592
0.332	384	0.561
0.387	424	0.512

Table VII

Data on emulsions for $K_d = 0.009$		
Conditions: O/W emulsion		
Frequency: 10,000 cps		
Electrolyte: sodium chloride		
f	ohms	K_m
0.000	215	1.000
0.0185	222	0.968
0.0360	228	0.943
0.0535	234	0.919
0.0708	240	0.896
0.0876	246.5	0.872
0.104	253	0.850
0.136	267	0.805
0.168	281	0.765
0.198	296	0.726
0.226	312	0.689
0.254	328	0.6555
0.281	344	0.625
0.307	362	0.594
0.332	379.5	0.5565
0.387	420	0.512

Table VIII

Data on emulsions for $K_d = 0.011$		
Conditions: O/W emulsion		
Frequency: 10,000 cps		
Electrolyte: sodium chloride		
f	ohms	K_m
0.000	213.0	1.000
0.0046	214.8	0.9916
0.0092	216.0	0.9861
0.0137	217.5	0.9793
0.0182	219.0	0.9726
0.0360	225.0	0.947
0.0535	231	0.922
0.0708	237.5	0.897
0.0876	243	0.876
0.120	256.4	0.831
0.152	270	0.788
0.183	284.5	0.7486
0.212	299.5	0.7112
0.241	315.6	0.675
0.268	332	0.642
0.307	357.6	0.596
0.353	384.5	0.554
0.387	413	0.516
0.420	444	0.480
0.451	477	0.446
0.480	515	0.414
0.508	552	0.386

Table IX

Data on emulsions for $K_d = 0.172$

Conditions: O/W emulsion

Frequency: 1000 cps

Electrolyte: tetra ethyl ammonium iodide

f	ohms	K_m	f	ohms	K_m
0.00	270.4	1.000	0.195	341.2	0.7925
0.00397	271.8	0.9948	0.208	347.0	0.7792
0.00794	272.9	0.9908	0.221	352.6	0.7669
0.01190	274.1	0.9865	0.233	358.7	0.7538
0.0159	275.4	0.9818	0.245	364.9	0.7410
0.0238	278.0	0.9727	0.257	370.7	0.7294
0.0316	280.5	0.9640	0.269	376.8	0.7176
0.0394	283.0	0.9555	0.281	382.1	0.7077
0.0471	285.5	0.9471	0.292	388.3	0.6964
0.0548	288.0	0.9389	0.304	395.0	0.6845
0.0623	290.7	0.9302	0.315	401.1	0.6741
0.0699	293.6	0.9210	0.326	407.3	0.6639
0.0774	296.4	0.9123	0.337	413.3	0.6542
0.0848	298.8	0.9049	0.347	418.5	0.6461
0.0921	301.2	0.8977	0.358	425.0	0.6362
0.0994	303.7	0.8903	0.368	431.5	0.6266
0.107	306.3	0.8828	0.378	437.9	0.6175
0.114	309.0	0.8751	0.388	444.9	0.6077
0.121	311.7	0.8675	0.398	451.8	0.5985
0.128	314.5	0.8598	0.407	459.1	0.5889
0.135	317.2	0.8525	0.417	466.2	0.5800
0.144	318.9	0.8479	0.426	473.4	0.5712
0.149	321.6	0.8408	0.435	480.5	0.5627
0.156	324.1	0.8343	0.444	486.5	0.5558
0.169	329.7	0.8201	0.453	493.3	0.5481
0.182	335.5	0.8060			

Table X

Data on emulsions for $K_d = 15.7$					
Conditions: W/O emulsion					
Frequency: 10,000 cps					
Electrolyte: tetra ethyl ammonium iodide and sodium chloride					
f	ohms	K_m	f	ohms	K_m
0.000	7,770	1.00	0.431	2,510	3.09
0.0175	7,455	1.04	0.441	2,430	3.20
0.0354	7,180	1.08	0.451	2,370	3.28
0.0526	6,910	1.12	0.461	2,300	3.38
0.0695	6,670	1.16	0.472	2,240	3.47
0.103	6,185	1.26	0.482	2,170	3.58
0.135	5,755	1.35	0.495	2,120	3.66
0.166	5,350	1.45	0.508	2,060	3.77
0.196	4,975	1.56	0.517	2,010	3.87
0.224	4,635	1.68	0.525	1,960	3.96
0.252	4,320	1.80	0.534	1,900	4.09
0.279	4,030	1.93	0.542	1,850	4.20
0.292	3,890	1.20	0.550	1,800	4.32
0.305	3,770	2.06	0.559	1,750	4.44
0.317	3,640	2.13	0.566	1,715	4.53
0.329	3,410	2.28	0.574	1,670	4.65
0.341	3,380	2.30	0.582	1,630	4.77
0.353	3,200	2.43	0.590	1,600	4.86
0.365	3,100	2.51	0.597	1,560	4.98
0.376	2,950	2.63	0.604	1,525	5.09
0.387	2,775	2.80	0.611	1,490	5.21
0.409	2,660	2.92	0.618	1,460	5.32
0.420	2,590	3.00			

Table XI

Data on emulsions for $K_d = 101$

Conditions: W/O emulsion

Frequency: 10,000 cps

Electrolyte: sodium chloride

f	ohms	K_m
0.000	21,300	1.000
0.0092	20,820	1.023
0.0137	20,500	1.040
0.0182	19,930	1.068
0.0360	18,900	1.126
0.0535	18,000	1.183
0.0708	17,130	1.243
0.0877	16,340	1.303
0.104	15,580	1.367
0.120	14,860	1.433
0.152	13,540	1.573
0.183	12,350	1.728
0.212	11,300	1.885
0.241	10,340	2.060
0.268	9,400	2.26
0.307	8,250	2.58
0.353	7,210	2.95
0.388	6,570	3.24
0.420	5,940	3.58
0.451	5,460	3.90
0.480	4,730	4.50
0.508	4,120	5.17

Table XII

Data on emulsions for $K_d = 4.86$
and evidence of surface resistance

Conditions: W/O emulsion

Frequency: 1000 cps

Electrolyte: tetra ethyl ammonium iodide

f	ohms	K_m	f	ohms	K_m
0.000	1,055	1.000	0.191	796.7	1.325
0.00480	1,052.7	1.002	0.197	788.6	1.339
0.00797	1,049.2	1.005	0.204	780.4	1.353
0.0159	1,040	1.014	0.210	772.3	1.367
0.0237	1,029	1.025	0.217	764.1	1.382
0.0315	1,018	1.036	0.223	756.4	1.396
0.0408	1,007	1.048	0.229	749.0	1.410
0.0484	996.1	1.060	0.235	741.4	1.424
0.0560	985.8	1.071	0.242	734.2	1.438
0.0635	974.5	1.084	0.248	727.2	1.452
0.0710	964.5	1.095	0.254	719.8	1.467
0.0784	954.5	1.106	0.260	712.8	1.481
0.0858	943.0	1.120	0.266	706.9	1.494
0.0931	931.0	1.134	0.272	700.0	1.503
0.100	921.0	1.147	0.278	693.5	1.523
0.108	916.3	1.152	0.284	686.9	1.537
0.115	904.6	1.167	0.289	674.3	1.566
0.122	895.6	1.179	0.295	668.1	1.581
0.129	888.8	1.188	0.301	662.4	1.594
0.136	879.0	1.201	0.307	656.5	1.609
0.143	868.0	1.217	0.312	650.5	1.623
0.150	858.5	1.230	0.318	644.6	1.638
0.157	849.3	1.243	0.323	639.2	1.652
0.164	837.0	1.262	0.329	633.8	1.666
0.171	825.0	1.280	0.334	627.9	1.682
0.177	814.0	1.297	0.340	622.9	1.695
0.184	805.0	1.312	0.345	618.3	1.708

Table XIII

Data on emulsions for $K_d = 14.95$ and evidence of surface resistance		
Conditions: W/O emulsion		
Frequency: 1,000 cps		
Electrolyte: tetra ethyl ammonium iodide		
f	ohms	K_m
0.000	6,311	1.000
0.0014	6,298	1.002
0.00951	6,233	1.012
0.0175	6,147	1.027
0.0255	6,053	1.043
0.0335	5,950	1.061
0.0413	5,849	1.079
0.0491	5,749	1.098
0.0568	5,652	1.116
0.0645	5,552	1.137
0.0721	5,455	1.157
0.0797	5,359	1.178
0.0871	5,263	1.199
0.0946	5,170	1.221
0.102	5,077	1.243
0.109	4,988	1.265
0.116	4,903	1.287
0.123	4,818	1.310
0.131	4,738	1.332
0.138	4,657	1.355
0.145	4,573	1.380
0.152	4,497	1.403
0.159	4,420	1.428
0.166	4,344	1.453
0.172	4,273	1.477
0.179	4,204	1.501
0.186	4,134	1.527
0.192	4,069	1.551
0.199	4,005	1.576
0.212	3,878	1.627
0.225	3,753	1.681

Table XIV

Data on emulsions for $K_d = 137$
and evidence of surface resistance

Conditions: W/O emulsion
Frequency: 1,000 cps
Electrolyte: sodium chloride

f	ohms	K_m
0.000	28,770	1.000
0.0362	27,010	1.065
0.0710	24,180	1.19
0.1045	21,700	1.32
0.137	19,400	1.48
0.168	17,300	1.66
0.198	15,500	1.86
0.2265	13,700	2.10

IV. EXPERIMENTS ON ORDERED ARRANGEMENTS OF SPHERES AND CYLINDERS

A series of experiments on ordered arrangements of spheres and cylinders was undertaken for the following reasons: First, it was desirable to obtain conductivity data on cubical arrays of spheres and cylinders to compare experimental results with the Rayleigh equation, the Rayleigh extension, and the distribution model that are presented in the section on the Concentration Effect (Chapter VIII). Second, it would be interesting to observe the differences in conductivities incurred in the cases where the cylinders were parallel and where they were crossed at right angles. These latter experiments could also be used to compare with data on materials that resemble cylinders arranged in two dimensions. Third, a comparison of the study of cubical arrays of spheres with the study of emulsions would indicate the difference in conductivity involved between a random dispersion and an ordered arrangement of particles.

Some work of this nature has previously been performed by Pearce²³ and Mashovets¹⁹ (See the section on Previous Work). The findings of these authors on similar models and in similar concentration ranges are not in agreement. The experimental techniques employed and the analysis of data in both cases point to questions unresolved by the authors.

The Equipment Used

The Conductivity Cells

The cells used for this study consisted of units of rectangular geometry with lucite walls and silver-plated copper electrodes. One of the cells was designed to act as a reference unit and to give a measurement of the continuous phase or electrolyte. The other cell, which may be called the working cell, contained a unit cell of the geometry that was to be studied. (See Fig. 5.) The overflow outlets were arranged in such a manner that the electrode surfaces were each covered to a depth of

ZN-2183

Fig. 5. A view of the cells used in measurements on the ordered arrangements of spheres and cylinders.

5.00 in. The width of the electrodes in both cells was also 5.00 in. The distance between the electrodes in the reference cell was fixed at this same value, but in the case of the working cell this distance was adjustable in steps up to 5.00 in. by using different lucite spacers.

The Spheres and Cylinders

For a study of spheres in cubic packing there are several possible ways in which one may isolate a unit cell. Thus the sectioning used in these measurements is not unique, although it is one that invites the least amount of geometrical error. Figure 6 illustrates some of the basic sectioning patterns that may be used. With the idea in mind that the cell would also be used to obtain data on crossed cylinders, we decided to use the third pattern in this figure. Thus by working with hemispheres and half cylinders, we could obtain data on spheres and cylinders in cubic and square arrays respectively. Furthermore, if the electrodes formed the dividing plane for the half cylinders, we could obtain a basic cell for crossed cylinders by rotating one of the half cylinders 90 degrees with respect to the other.

Two carefully machined hemispheres and half cylinders were constructed for each run. For the case of a nonconducting dispersed phase these objects were made of lucite, and for the case of an infinitely conducting dispersed phase the material of construction was brass. The machining was such that the difference between the volumes of any two objects that formed a pair was less than 0.1%. Furthermore, the volume of any hemisphere or half cylinder as calculated from its measured radius was in agreement with its volume as calculated from its measured diameter to within 0.1%. Thus the hemispheres or half cylinders that formed a pair were not only equal in size but were also true in shape for all practical purposes.

Threaded screw holes were placed in the center of the flat sides of the hemispheres and half cylinders and were matched with holes in the center of the electrode surfaces. The objects to be studied were locked flush against the electrodes by means of a locking screw.

MU-17382

Fig. 6. Examples of unit cells in cubic or square packing.

The length of the half cylinders exactly matched the width of the cell; so when a half cylinder was turned crossways in the cell, no conduction could occur between the walls of the cell and the end of the half cylinder. A view showing the arrangement of the cylinders in the cell is given in Fig. 7.

The Conductivity Bridge

The bridge used in this study was identical to that described in the study of emulsions. Measurements were made at 50 kc to minimize chemical polarization at the surface of the brass hemispheres.

Experimental Procedure

The electrodes of the working cell were combined with the various lucite spacers or walls that were to be used in this study and were calibrated against the reference cell. This operation took place before the holes were placed in the electrodes to hold the hemispheres and half cylinders.

Tap water was used as the electrolyte in this study, and prior to making any measurements, the water was circulated between the working cell and the reference cell and allowed to come to equilibrium at room temperature. The liquid level in both cells was carefully brought up to a standard reference mark by using a hypodermic syringe.

At least four measurements were made for every run or data point that appears in the following tables. The typical standard deviation for these runs was less than 1%.

Results and Conclusions

A study of one set of brass hemispheres as a function of bridge frequency is given in Table XV. From these data it is evident that, for studies involving clean brass and tap water, polarization can continue to be a source of error up to relatively high frequencies. Pearce's data,²³ in a similar study of this kind at 400 cps, can consequently be seen to be in error by as much as 25% when it is assigned to the model in question.

ZN-2184

Fig. 7. An exploded cell showing two cases of cylinder geometry.

Table XV

Data on the 4.976" dia. brass hemi-
spheres as a function of frequency

Freq. in kc	K _m
0.40	5.7
1.00	6.9
10.00	7.5
50.00	7.6
90.00	7.6

The data obtained for spheres in cubical arrays are given in Table XVI. These measurements are also plotted in Figs. 8 and 9 where comparison is made with the Rayleigh equation and the Rayleigh extension.

Some of the data on cylinders are given in Table XVII. These values refer to measurements that were made in the cubic cell and have thus been designated as "square arrays". The remainder of the measurements on cylinders appears in Table XVIII. This latter table contains data for the condition where the distance between the electrodes was equal to the diameter of the cylinder being studied. Therefore this final model was for the case where the parallel or crossed cylinders were always touching or in contact.

All of the data on cylinders are compared in Fig. 10. Qualitatively the following facts are clear. There is very little difference between the results obtained for the parallel cylinders and the crossed cylinders in square arrays. The crosses, however, do give a slightly lower conductivity than their parallel counterparts. For the measurements on cylinders in contact, the parallel units act very much like lamina, and the data points for this arrangement are close to the line obtained by volume fraction averaging. The crossed cylinders in contact act intermediate between lamina and true dispersions, which agrees with expectation because the section of the cylinders at the cross would act as a pure lamina, while the portion of the cylinders which was some distance away from the cross would act as a dispersion.

Table XVI

Conductivity data on dispersions of spheres
arranged in cubic arrays

$K_d = 0$

Dia. in inches	Vol. fract.	K_m
1.993	0.0332	0.9609
3.468	0.1747	0.7649
3.959	0.2600	0.6510
4.976	0.5161	0.3520

$K_d = \infty$

Dia. in inches	Vol. fract.	K_m
1.993	0.0332	1.114
3.468	0.1747	1.659
3.957	0.2595	2.141
4.487	0.3785	3.008
4.726	0.4421	3.905
4.976	0.5161	7.570

MU-17163

Fig. 8. Conductivity measurements on a dispersion of spheres in cubical arrays ($K_d = 0$).

Legend: Data points of this work o
 Bruggeman's equation - - - - -
 Rayleigh extension _____
 Rayleigh's equation _____
 Maxwell's equation _____

MU-17164

Fig. 9. Conductivity measurements on a dispersion of spheres in cubical arrays ($K_d = \infty$).

Legend: Data points of this work o
 Bruggeman's equation - - - - -
 Rayleigh extension _____
 Rayleigh's equation _____
 Maxwell's equation _____

Table XVII

Conductivity data on dispersions of nonconducting
cylinders arranged in square arrays

Volume fraction f	Parallel cylinders K_m	Crossed cylinders K_m
0.0314	0.9473	0.9471
0.1226	0.7896	0.7756
0.2827	0.5653	0.5543
0.5026	0.3242	0.3253
0.7088	0.1235	0.1224

Table XVIII

Conductivity data on dispersions of nonconducting cylinders arranged with sides in contact		
Volume fraction f	Parallel cylinders K_m	Crossed cylinders K_m
0.0745	0.9218	0.8867
0.1570	0.8330	0.7677
0.3066	0.6495	0.5719
0.4712	0.4661	0.4144
0.6283	0.2872	0.2637
0.7461	0.1209	0.1145

MU-17161

Fig. 10. Conductivity measurements on dispersions of solid cylinders.

Legend: Parallel cylinders in contact $\bullet$
 Cross cylinders in contact $\times$
 Parallel cylinders in square arrays $\circ$
 Crossed cylinders in square arrays Δ
 Volume fraction average —————
 Runge's extension to Rayleigh's cylinder equation - - - - -
 Distribution model — · — · —

V. MISCELLANEOUS EXPERIMENTS

Data on Materials that Resemble Cylinders

Arranged in Two Dimensions

The Object of the Study

Because data have been obtained on studies of cylinders arranged in two dimensions, it should be interesting to compare the results of these measurements with data taken on material such as cloth or sheet asbestos and thus ascertain if materials of this type could be approximated by our ordered arrangements of cylinders.

The Experimental Technique and Equipment

A rectangular lucite cell with copper electrodes was designed for this study. This cell resembled the units shown in Fig. 5 except that it was much smaller in size and closed. The internal dimensions of the cell were 0.5 by 0.5 in. with 1.0 in. between electrodes. The sample was prepared by cutting the material into 0.5-in. squares and saturating it with an electrolyte consisting of tap water. After the sample had been pre-equilibrated with electrolyte, the squares were carefully laid on top of one another within the cell until the distance between the electrodes was fully occupied. All entrained air was displaced with electrolyte, and a conductivity reading was obtained. The conductivity of the clear phase or the electrolyte was also determined in the same cell. Conductivity measurements were made at 1 kc. The volume fraction of the samples were determined in a Cassia flask. The materials studied include: cotton cloth, thin sheet asbestos, and pads of spun glass. The data are given in Table XIX and presented in Fig. 11.

Conclusions on the Experiment

As can be seen in Fig. 11 the agreement of data of this type with measurements on crossed cylinders in square arrays is rather good. A priori, one might have expected that the results would match fairly

Table XIX

Conductivity data on materials that resemble
cylinders arranged in two dimensions

Material	f	K_m
Pads of spun glass in layers	0.037	0.950
Cotton cloth in layers	0.212	0.645
Cotton cloth in layers	0.258	0.590
Sheet asbestos in layers	0.42	0.427

MU-17162

Fig. 11. A comparison of materials which resemble a mixture of solid cylinders arranged in two dimensions.

Legend:

Cotton cloth in layers	x
Sheet asbestos in layers	o
Pads of spun glass in layers	Δ
Cylinders crossed at right angles in square arrays	o
Volume fraction average	—————
Runge's extension to Rayleigh's cylinder equation	- - - - -
Distribution model	—————

well the data on cylinders in contact. Although some of the points deviate in the direction of this type of geometry, it is apparent that most of the rods or cylindrical bodies in the materials studied are not in tight contact, although the cell was firmly packed when the measurements were made. A few point contacts between the sheets of the samples studied have obviously determined the tightness of the packing and at the same time the number of these contacts are so few that the bulk of the sample must resemble a loose arrangement of rods causing the conductivity measurements to more closely agree with the square array than with cylinders in contact.

Data on Packed Beds of Spherical Particles

The Object of the Study

The study of emulsions has given data up to a volume fraction of 0.5. It was evident that this range could be extended, at least for the case of nonconducting particles, by making studies on packed beds. It was with this object in mind that the following study was made.

Experimental Technique and Equipment

The conductivity cell used in this study was similar to the cell described in the preceding experiment; this cell however, was much larger. The distance between electrodes was about 13.5 cm and the internal cross-section of the cell was a circle with a diameter of 2 cm. The dispersions studied consisted of nearly spherical particles of sand and round beads ranging in diameter from 6 mm to 0.02 mm. As in the preceding study, the particles were pre-equilibrated with the electrolyte before conductivity readings were obtained. The volume fraction was obtained by the displacement of liquid in the cell.

Conclusions on the Experiment

The results of the packed bed experiments are given in Table XX and are presented in Fig. 12 where a comparison is made with the Bruggeman and Maxwell relations. A comparison is also made to the

Table XX

Data on packed beds of spherical particles ($K_d = 0$)		
Description of packing	f	K_m
Glass beads diameter = 6 mm	0.572	0.325
Glass beads diameter = 3 mm	0.592	0.303
Glass beads diameter = 0.02 mm	0.629	0.268
Sand (nearly spherical particles)	0.654	0.232
Glass beads (a mixture of 6 mm and 0.75 mm)	0.716	0.162

Fig. 12. Data on packed beds consisting of spherical particles.

Legend: Data points of this work o
Maxwell's equation ————
Distribution model - - - - -
Bruggeman's equation — · — · —

distribution model that is developed in the section on The Concentration Effect. It can be noticed that the trend that was present in the emulsion data is still with us in these measurements. That is, the data continue to lie between the Maxwell and Bruggeman curves.

VI. THE SIZE EFFECT

Restrictions on Particle Size

A question that often arises in employing the relations discussed in this paper is, "What is the effect of the dispersed particle size?" In answering this question, one would be tempted to think that there should be no effect. This, however, is true only if the following conditions are fulfilled:

(a) The dispersed particles are small compared with the sensing element or electrodes measuring the conductivity of the mixture. This restriction forces one to deal with a representative sample of the mixture.

(b) The particles are large compared with the molecules of the medium that constitute the continuous phase and are small compared with the wavelength of the examining radiation. It is under these conditions that the potential satisfies Laplace's equation.

(c) The dispersed particles do not have a film or surface resistance that would normally cause the conductivity of the mixture to drop as the particles decreased in size or the surface area per unit volume increased in magnitude.

(d) All of the particles constituting the dispersed phase are of the same order of magnitude. The reason for this restriction becomes clear in the following section.

A Dispersion of Two Different Size Particles

In the last paragraph in the preceding restrictions it was implied that the conductivity of a mixture consisting of dispersed particles of different sizes would differ from the conductivity obtained with identical particles. The reason for this can best be shown by considering the following example.

Let us visualize a system consisting of a continuous phase of conductivity k_c and immerse nonconducting spherical particles

homogeneously throughout the system. If the dispersed particles are of the same size and constitute a small volume fraction compared to the total system, then Maxwell's equation should hold, and we can write

$$k_m = k_c (2 - 2f_1)/(2 + f_1), \quad (25)$$

where k_m is the resulting conductivity of the mixture. Suppose we were now to be told that the phase that we thought was continuous actually was a mixture consisting of microscopically small particles immersed in a continuous phase of conductivity k_c' . If these small particles are also spherical and nonconducting and constitute a volume fraction f' with reference to our original continuous phase, then we can write as before

$$k_c = k_c' (2 - 2f')/(2 + f'). \quad (26)$$

The substitution of Eq. (26) into Eq. (25) gives an expression for the conductivity of the entire mixture as a function of the volume fractions of the dispersed particles and the clear-phase conductivity:

$$k_m = 4 \frac{(1 - f_1)(1 - f')}{(2 + f_1)(2 + f')} k_c'. \quad (27)$$

The volume fractions in the above expression are not additive in the usual way because f_1 is based on the total volume of the system and f' is based on the volume that remains after the larger dispersed particles have been removed. In terms of the total volume, we may denote f' by the symbol f_2 and write

$$f_2 = f' (1 - f_1). \quad (28)$$

The latter two relations yield

$$k_m = 4 \frac{(1 - f_1)(1 - f_1 - f_2)}{(2 + f_1)(2 - 2f_1 + f_2)} k_c', \quad (29)$$

where the volume fractions are now additive. We now have an expression that depends not only on the total amount of the dispersed phase, but also on the relative amounts of the different size particles. It is

possible of course to continue this treatment until all of the dispersed particle fractions are different in size by an order of magnitude. Such a treatment yields Bruggeman's equation for nonconducting spherical particles, i.e.,

$$k_m = k_c' (1 - f_t)^{3/2} . \quad (30)$$

Here f_t denotes the total volume fraction of the dispersed particles, or for the case being considered,

$$f_t = f_1 + f_2 . \quad (31)$$

it is well to note that Eq. (29) differs by a significant amount from the expression that one would use knowing only that the mixture had a dispersed phase with a volume fraction f_t . In this latter case one would write

$$k_m = 2 \frac{(1 - f_1 - f_2)}{(2 + f_1 + f_2)} k_c' . \quad (32)$$

The validity of Eq. (32) is of course very questionable, for it neglects the requirement in Maxwell's derivation that the distance between all particles be large. Equation (29) is also to be preferred to Bruggeman's relation since the particular problem at hand has particles of only two different sizes and does not form an infinite continuum. Equations (29), (30), and (32) permit K_m values to be formed and the results are compared in Table XXI.

Table XXI

A comparison of K_m values from Eqs. (29), (30), and (32)					
f_1	f_2	f_t	K_m Eq. 32	K_m Eq. 29	K_m Eq. 30
0.01	0.09	0.1	0.8571	0.8566	0.8535
0.02	0.08	0.1	0.8571	0.8560	0.8535
0.03	0.07	0.1	0.8571	0.8558	0.8535
0.04	0.06	0.1	0.8571	0.8556	0.8535
0.05	0.05	0.1	0.8571	0.8555	0.8535
0.06	0.04	0.1	0.8571	0.8556	0.8535
0.07	0.03	0.1	0.8571	0.8558	0.8535
0.08	0.02	0.1	0.8571	0.8560	0.8535
0.09	0.01	0.1	0.8571	0.8566	0.8535
0.2	0.2	0.4	0.5000	0.4701	0.4650
0.3	0.3	0.6	0.3077	0.2864	0.2530
0.4	0.4	0.8	0.1428	0.1250	0.0891

VII. THE SHAPE EFFECT

General

The theories treated in the preceding sections have dealt with dispersions of spherical particles. The repeated use, by many authors, of this particular three-dimensional form did not happen by accident; nor did the spherical form occur again and again because the investigators were ignorant of shape effects. The cause may be blamed on the nature of mathematics. It simply turned out that the solution of the Laplace equation for the potential resulting inside the dispersed body was most easily obtained if the body had the shape of a sphere.

Orientation and Average Field

When the unit of dispersion assumes a shape other than that of a sphere, it is easy for one to realize that the orientation of the particle also becomes important. A nonconducting circular disk, for instance, would cause the lowest conductivity of the system when the plane of the disk was aligned parallel to the electrodes measuring the conductivity. On the other hand, the highest conductivity would be obtained when the plane of the disk was perpendicular to the electrode surfaces. If the body were allowed to take on a random position, the conductivity would fall between the above limits, and consequently, if the dispersion consisted of only one particle, we would obviously have to know its orientation with respect to the field before we could say anything more about the conductivity of the system. When we have a large number of particles in the system (but not so many that we have field disturbances between any two bodies) then statistics may be used and, contrary to the case of one particle, we need to know nothing regarding the individual orientation of the bodies. The inherent assumptions required for this last statement are of course that the particles are in a completely random state, taking on all possible positions and orientations, and naturally, as previously states, that the dispersion concentration must be such that any one particle is

unaware that neighboring particles exist. Under these conditions it can be shown that the average field within an average particle is the same as the time average field that one would obtain in a single particle if that body had moved through all possible positions with equal periodicity. This point has been investigated in detail by Kirkwood.⁵⁹ In other words, for a coordinate system fixed within the dispersed body, the average field must have equal x, y, and z components. This same result holds for the average field when the entire dispersion is considered and the coordinate system is fixed between the electrodes. This conclusion should be kept in mind throughout the following paragraphs when we discuss the potential within a spheroidal particle.

Previous Work and Theories

Several authors have developed expressions relating the conductivity of mixtures with non-spherical dispersed particles to the usual parameters of the system (see references 7, 8, and 35). Using a rigorous approach, the problem essentially boils down to finding the solution to the Laplace equation in ellipsoidal coordinates for the potential inside and outside of the dispersed particle. These solutions are well known and can be found in many texts on electrical or electromagnetic theory.*

For the "x component" of the potential within the dispersed particle when the original field was E, we have the following expression:

$$V_{x \text{ int}} = - E_x \frac{x}{1 - (1 - K_d) L_x} \quad (33)$$

where

$$L_x = (abc/2) \int_0^\infty \frac{d\eta}{(\eta + a^2) R_\eta} \quad (34)$$

* For example see Smythe,⁶⁰ Stratton,⁶¹ Maxwell,⁶² or Kellogg.⁶³

$$R_{\eta} = [(\eta + a^2)(\eta + b^2)(\eta + c^2)]^{1/2} \quad (35)$$

The terms a, b, c designate the length of the semi-principal axes of the ellipsoid, and the parameter η gives a family of ellipsoids all confocal with the surface of the body where $\eta = 0$. The expression for L_x involves an elliptic integral of the second kind and has a solution in closed form only for spheroids (i.e., $b = c$). Values of L , however, have been tabulated for the general integral.* The y and z components for the potential are obtained by cyclic permutations of x, y, z and a, b, c in the above equations, and the total potential, is of course, the sum of these components.

If we utilize the conclusion, that we have already drawn regarding the average field, the preceding reduces to the following simple form:

$$V_{\text{avg.int.}} = - (Ex/3) \sum_i \frac{1}{1 - (1 - K_d) L_i} \quad (36)$$

The x is retained because we assume this to be the direction perpendicular to the electrode surfaces, and the sum is extended over $i = (x, y, z)$. In a similar manner the average external potential is found to be

$$V_{\text{avg.ext.}} = - (Ex/3) \sum_i \frac{1 - (1 - K_d) I_i}{1 - (1 - K_d) L_i}, \quad (37)$$

where I is similar to L except the limits of integration are from zero to η instead of from zero to infinity.

Fricke has made use of Eq. (36) and by a technique of "volume averaging", arrived at the following expression:⁸

* For these terms, see for example the work of Osborn.⁶⁴

$$K_m = 1 - \frac{f (K_m - K_d)}{3 (1 - f)} \sum_i \frac{1}{1 - (1 - K_d) L_i} \quad (38)$$

In a similar manner Burger has derived⁷

$$K_m = 1 - \frac{f (1 - K_d)}{3} \sum_i \frac{1}{1 - (1 - K_d) L_i} \quad (39)$$

and Polder and van Santen have developed

$$K_m = 1 - \frac{f (1 - K_d)}{3} \sum_i \frac{K_m}{K_m - (K_m - K_d) L_i} \quad (40)$$

These relations all appear quite similar but give varied results when applied to specific cases. For example, for the case of spherical particles each of the L values equals one-third and Eq. (38) reduces to Maxwell's equation; Eq. (39) reduces to Wagner's equation; and Eq. (40) reduces to Bottcher's equation (see section on Previous Work). It may be further noted that the net effect of Eq. (38) is to change the "2" in Maxwell's equation to another value when the dispersed particle has a shape other than that of a sphere. This value depends only on the axial ratios and the conductivity of the dispersed particle, it would thus appear that we have a method of evaluating Wiener's "form number" (see page 11). Because of the assumption of noninteraction among the particles. Equations (36) to (40) have validity only for low concentrations and therefore any agreement with high volume-fraction data can only be fortuitous.

Experimental Verification

Fricke tested Eq. (38) on Stewart's data⁶⁵ for the blood of a dog where the dispersed phase consists of nonconducting red cells

which resemble the shape of oblate spheroids. Fricke assumed an axial ratio of 4.25 for the dispersed particle and showed that his relation agrees nicely with Stewart's measurements over the moderately concentrated region. The greatest disagreement between the data and the equation occurs, however, at the lower volume fractions, and this is where one would expect the deviation to be the least. It would have been more in line with expectation if Fricke had assumed an axial ratio that gave the best agreement with the least concentrated dispersion and forgot about using a value that secures the best agreement over the entire range of Stewart's data (volume fraction range of 0.1 to 0.9). Fricke's value of 4.25 gives a 6% deviation for a volume fraction of 0.1 and no deviation for a volume fraction of 0.6, whereas the true value of the axial ratio is likely to cause this behavior to be reversed. The true effective axial ratio can easily be evaluated from the slope of the data in the dilute region, and this value is found to be closer to 3 than 4.25. The authors of Eqs. (39) and (40) have offered no experimental justification for their results, however they may be tested equally well on Stewart's data. These latter two relations become identical when the dispersed phase is nonconducting. With respect to the Fricke relation, these two expressions exhibit the same type of behavior as do the Wagner and Bottcher relations when these latter two relations are compared to the Maxwell equation. That is, the Burger expression and the Polder and van Santen expression cannot be counted on to agree with data except in the very dilute region.

The conductivity values obtained for nonspherical particles are always lower than the values obtained with dispersions of spheres for $K_d < 1$. The reverse is true for $K_d > 1$. A comparison is given in Fig. 13 along with a relation that is developed in the following section on The Concentration Effect.

The applications of the preceding equations are considerably simplified if the dispersed particle is a spheroid (i.e. $b = c$). In this case we need to determine only one L value because

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Fig. 13. An illustration of the shape effect.

Legend: Data points on emulsions o
Stewart's data on blood x
Distribution model —

$$L_1 + L_2 + L_3 = 1, \quad (41)$$

and

$$L_2 = L_3. \quad (42)$$

(Note: subscripts 1, 2, and 3 are now used in place of x, y, and z.)

Also for this case, the elliptic integral of Eq. (34) may be evaluated.

If we set $e = (b/a)^2$, we have for prolate spheroids ($a > b$):

$$L_1 = \frac{e}{(e - 1)} \left[1 - \frac{1}{2(1 - e)^{1/2}} \ln \frac{1 + (1 - e)^{1/2}}{1 - (1 - e)^{1/2}} \right], \quad (43)$$

for oblate spheroids ($a < b$):

$$L_1 = \frac{e}{(e - 1)} \left[1 - \frac{1}{(e - 1)^{1/2}} \arctan (e - 1)^{1/2} \right], \quad (44)$$

and for oblate or prolate spheroids if a approximately equals b :

$$L_1 = 1/3 + (4/15) (b - a)/(a). \quad (45)$$

From these expressions, some representative values of L_3 are given in Table XXII for prolate and oblate spheroids.

The Generalized Bruggeman Equation

The Bruggeman equation (see the section on Previous Work) was developed for a dispersion made up of a continuous distribution of spheres. This expression is restricted to spherical particles because Maxwell's equation was incorporated in its development. It is possible however, to use an expression such as Eq. (39) as the starting point and generate an equation analogous to the Bruggeman equation which can be used to treat the more general case of dispersions of spheroids. Such a development is given in Appendix II and the results are summarized in the expression

Table XXII

Values of L_3 for spheroids, $b = c$		
Shape	b/a	L_3
Rods	0	0.500
Prolate spheroids	1/5	0.472
	1/4	0.463
	1/3	0.447
	1/2	0.414
Spheres	1	0.333
Oblate spheroids	2	0.238
	3	0.182
	4	0.148
	5	0.125
Disks	∞	0.000

$$(1 - f) = \left(\frac{K_m - K_d}{1 - K_d} \right) \left(\frac{K_m + \alpha K_d}{1 + \alpha K_d} \right)^{\gamma} (K_m)^{\beta} \quad (46)$$

where

$$\alpha = (2 - 3L_3)/(3L_3 + 1), \quad (47)$$

$$\beta = 3L_3 (1 - 2L_3)/(3L_3 - 2), \quad (48)$$

and

$$\gamma = 2 (3L_3 - 1)^2 / [(3L_3 - 2) (3L_3 + 1)]. \quad (49)$$

For spheres where the value of L_3 is $1/3$, the above results agree with Eq. (2). For a random mixture of cylinders or rods, where L_3 is $1/2$, the following relation is obtained:

$$(1 - f) = \left(\frac{K_m - K_d}{1 - K_d} \right) \left(\frac{5K_m + K_d}{5 + K_d} \right)^{-2/5}, \quad (50)$$

and, if in addition the rods are nonconductors we have

$$K_m = (1 - f)^{5/3}. \quad (51)$$

In a similar manner, we obtain the following for the case where the dispersed phase is made up of a random mixture of disks:

$$(1 - f) = \left(\frac{K_m - K_d}{1 - K_d} \right) \left(\frac{K_m + 2K_d}{1 + 2K_d} \right)^{-1}. \quad (52)$$

This latter expression breaks down, however, when one tries to also impose the condition that the disks are nonconductors. This apparent anomaly is not due to any fault in the development of Eq. (52) but originates in the Burger relation [Eq. (39)].

The constants α , β , and γ which appear in Eq. (46) are a function of L_3 alone, and this variable is in turn a function of only the axial ratio of the spheroidal particle that constitutes the dispersed phase. Thus it is possible to tabulate the values that appear in Table XXIII and greatly simplify the use of the generalized relation.

Table XXIII

Values of the constants for the generalized Bruggeman relation (Eq. 46)				
Shape	b/a	α	β	r
Rods	0	0.200	0.000	-0.400
Prolate spheroids	1/5	0.242	-0.136	-0.245
	1/4	0.256	-0.168	-0.207
	1/3	0.282	-0.216	-0.151
	1/2	0.338	-0.282	-0.069
Spheres	1	0.500	-0.333	0.000
Oblate spheroids	2	0.750	-0.291	-0.074
	3	0.940	-0.239	-0.183
	4	1.077	-0.201	-0.275
	5	1.182	-0.173	-0.350
Disks	∞	2.000	0.000	-1.000

Summary on the Shape Effect

In accurate conductivity work the effect of the shape of the dispersed particle cannot be ignored. As an illustration of the amount of error that one can make, we refer to Fig. 13 where data on the spherical and oblate-spheroidal particles are compared. It can be seen that the differences between the conductivities of suspensions containing spheres and disks may be as high as 10 to 20% in the moderate concentration range.

VIII. THE CONCENTRATION EFFECT

Unquestionably one of the most important and yet one of the most difficult problems in this field of study is that concerned with theoretically evaluating the effect of concentration on the conductivity of dispersions. As the volume fraction of the dispersed phase becomes large the ratio of the diameter of the dispersed particle to the distance between particles is no longer small, and relations such as Maxwell's equation, which give excellent agreement with data in the dilute range, begin to break down.

The Rayleigh Equations

The first classical work on extending the dilute-suspension relations into a region of higher concentration was carried out by Lord Rayleigh in 1892.⁴ Rayleigh examined the conductivity of a cubical arrangement of cylinders or spheres where the distance between particles was not large compared to their radii. In the two-dimensional case where the field is perpendicular to the long axes of the cylinders, Rayleigh obtained the following expression:

$$K_m = 1 - \frac{2f}{\frac{1 + K_d}{1 - K_d} + f - 0.3058 (f^4) \frac{1 - K_d}{1 + K_d} + \dots}, \quad (53)$$

and for the cubical array of spheres where the field is perpendicular to one of the sides of the cube, the conductivity including the correction of Runge is given by

$$K_m = 1 - \frac{3f}{\frac{2 + K_d}{1 - K_d} + f + 0.525 \frac{K_d - 1}{K_d + 4/3} (f)^{10/3} + \dots}. \quad (54)$$

These expressions, of course, are valid only for cubical packing. Consequently they have no meaning and begin to break down when a volume fraction is employed that is greater than the value that corresponds to the most

dense packing for this geometry. For cylinders and spheres, these upper volume fraction limits are $\pi/4$ and $\pi/6$, respectively. Since Eqs. (53) and (54) correct the dilute-suspension relations by only one term, the question often arises as to whether or not another term might yield a significant change in the conductivity as the limiting volume fractions are approached. The answer to this question may be obtained by noting the difference between the Rayleigh equations and the dilute-suspension relations. For example, in the case of infinitely conducting cylinders or spheres, the Rayleigh equations predict that the dilute-suspension relations are in error by 45% and 9% respectively at the highest volume fractions. Such relatively large corrections indicate that perhaps the next term in each equation might indeed be of some significance and thus warrant the work involved in its calculation.

In 1925 Runge evaluated the next term involved in the Rayleigh expression for dispersed cylinders,⁵ and thus Eq. (53) is extended to the following form:

$$K_m = 1 - \frac{2f}{\frac{1 + K_d}{1 - K_d} + f - 0.3058 \frac{1 - K_d}{1 + K_d} f^4 - 0.1334 \frac{1 - K_d}{1 + K_d} f^8} \quad (55)$$

The difference between values of K_m calculated using this latter expression and those from Eq. (53) is less than 1% under all conditions, indicating that higher-order terms need not be considered.

No work is known to date on evaluating the next term in the expression for the conductivity of spherical dispersed particles, and therefore such an extension has been undertaken as part of this dissertation.

An Extension of Rayleigh's Equation for Spheres

In Appendix III of this work a technique similar to that used by Lord Rayleigh is presented. The resulting expression which may be called an extension of Rayleigh's equation for conduction through a cubical array of spheres is

$$K_m = \frac{\frac{2 + K_d}{1 - K_d} - 2f + 0.409 \frac{6 + 3K_d}{4 + 3K_d} f^{7/3} - 2.133 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}}{\frac{2 + K_d}{1 - K_d} + f + 0.409 \frac{6 + 3K_d}{4 + 3K_d} f^{7/3} - 0.906 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}} \quad (56)$$

As indicated above, it was originally thought that such a treatment would only yield a term of a higher power in the volume fraction, but upon comparing the above expression with Eq. (54) we see that we have instead created a lower-power term and have obtained a different coefficient on the higher-power terms compared to the one given by Rayleigh. As pointed out in Appendix III, this latter discrepancy is a consequence of using a different type of expansion in the expression for the potential -- but one which is nonetheless accurate. The coefficients on the terms involving $f^{7/3}$ and $f^{10/3}$ in Eq. (56) are such that these terms are of the same order of magnitude over the valid range of f , and thus if one is used, they both must be used. As can be seen in Figs. 8 and 9, this extension offers a fair improvement over Rayleigh's equation; especially so for the case where K_d is large.

The Formation of Doublets

Some of the concentration effects observed in dispersions or emulsions, where the dispersed phase undergoes random motion, can be attributed to agglomeration of particles. If, for example, two particles with negligible surface resistance were to come into contact during a finite period of time, they could be considered to act as a unit as far as potential was concerned. The net effect would be that of a particle with a volume equal to the sum of the volumes of the two particles and a shape dependent upon the individual particles and how they came together. In a like manner it is possible to form multiple units of higher order which become increasingly predominate as the volume fraction of the dispersed phase continues to increase. Of the many combinations that might arise, the only case that lends itself to simple mathematical treatment is that of spherical particles and the formation of doublets.

Vand⁶⁶ and others have shown that the time-average volume concentration of two-unit inelastic collisions (doublets) in a suspension of spherical particles is equal to four times the square of the concentration of single units. Armed with this knowledge, and recognizing that a doublet of spheres would have roughly the character of a prolate spheroid with a 2:1 axial ratio, it is possible to derive an appropriate expression for the conductivity of such a mixture.

Imagine that we have a suspension of spherical particles with the dispersed-phase volume fraction in a range where the probability of three-body and higher-order collisions are small compared to the probability of forming doublets. If we denote the fraction of particles existing as separate units with a subscript I, and the fraction involved in the doublet state with a subscript II, we may write

$$f_{II} = 4f_I^2 \quad (57)$$

and

$$f = f_I + f_{II} \quad (58)$$

or

$$f_I = (1/8) [(1 + 16f)^{1/2} - 1] \quad (59)$$

and

$$f_{II} = (1/8) [1 - (1 + 16f)^{1/2}] + f \quad (60)$$

Associated with each of the above fractions, we can say that there exists a shape factor, X , which allows us to write the following expression:

$$K_m = \frac{2 + K_d - 2(1 - K_d) \sum f_i X_i}{2 + K_d - (1 - K_d) \sum f_i X_i} \quad (61)$$

The sum, of course, extends over the product of each volume fraction, and the appropriate shape factor that goes with each type of dispersed particle. This expression can be derived in a manner similar to the derivation of Eq. (2). For the equation to have meaning, clearly the

values of X must be chosen so that the expression reduces to Wagner's equation (See page 14) and to Burger's equation (See page 80) for dilute suspensions of spheres and spheroids respectively. Thus X may be found by forcing the following two expressions to agree:

$$K_m = 1 - \frac{3(1 - K_d) fX}{(2 + K_d)} \quad (62)$$

$$K_m = 1 - \frac{(1 - K_d)}{3} \left[\frac{2}{1 - (1 - K_d) L_3} + \frac{1}{1 - (1 - K_d)(1 - 2L_3)} \right] \quad (63)$$

In doing so, we obtain

$$X = \frac{(2 + K_d)}{9} \left[\frac{2}{1 - (1 - K_d) L_3} + \frac{1}{1 - (1 - K_d)(1 - 2L_3)} \right] \quad (64)$$

For spheres, where $L_3 = 1/3$ (See Table XXII), the equation for X reduces to

$$X_I = 1, \quad (65)$$

and for prolate spheroids with a 2:1 axial ratio, where $L_3 = 0.414$, we have

$$X_{II} = 1.18 \frac{(K_d + 2.00)(K_d + 2.96)}{(K_d + 4.81)(K_d + 1.41)} \quad (66)$$

Thus, the above relation with the combination of Eqs. (59), (60), (61), and (65) give the desired expression for the conductivity of the mixture of singlets and doublets, i.e.,

$$K_m = \frac{6(3 + K_d) - 2(1 - K_d) \left[(1+16f)^{1/2}(1 - X_{II}) + (1+8f) X_{II} \right]}{3(5 + 3K_d) + (1 - K_d) \left[(1+16f)^{1/2}(1 - X_{II}) + (1+8f) X_{II} \right]} \quad (67)$$

Although this relation appears quite involved, it is to be noted that the equation is explicit in K_m and is a function of f and K_d only. Thus it lends itself to easy tabulation or plotting. For this purpose the equation may be reduced to the form

$$K_m = \frac{1 - 2(f_I Y_I + f_{II} Y_{II})}{1 + (f_I Y_I + f_{II} Y_{II})}, \quad (68)$$

where the values of f_i and Y_i are given in Table XXIV and XXV as functions of f and K_d respectively. A comparison with Eq. (61) shows

$$Y_i = \frac{1 - K_d}{2 + K_d} X_i. \quad (69)$$

The results of this section will henceforth be referred to as the "doublet model". As can be seen in the plots that follow, the doublet model gives good agreement with the observed values of the conductivity. It can be seen that a disagreement continues to exist between the theory and the data at the higher volume fractions, but this is as it should be, because higher-order collisions are becoming important in this region.

The Distribution Model

The primary reason that the dilute-suspension relations are no longer valid at the higher concentrations is that the region in the neighborhood of any one particular particle can no longer be characterized by the properties of the continuous phase, but rather taken on the nature of the mixture as a whole. That is, the effective conductivity of the continuous medium in the neighborhood of a particle is better represented by the conductivity of the surrounding mixture than by the conductivity of the continuous medium alone. Polder and Van Santen³⁵ and also Bottcher³¹ have realized that this kind of correction is necessary and have modified the Fricke and Maxwell relations, respectively. The net changes that were made by these authors, however, were to replace some of the k_c terms in the Fricke and Maxwell relations with k_m terms. The resulting relations (See the section on Previous Work) have in effect shifted the Fricke and Maxwell curves in the right direction with respect to the experimental data, but the

Table XXIV

Parameters for the doublet model
(Eq. 68)

f	f_I	f_{II}
0.1	0.0765	0.0235
0.2	0.1312	0.0688
0.3	0.1760	0.1240
0.4	0.2150	0.1850
0.5	0.2500	0.2500
0.6	0.2820	0.3180
0.7	0.3116	0.3884

Table XXV

Parameters for the doublet model (Eq. 68)		
K_d	Y_I	Y_{II}
0	0.500	0.515
0.01	0.493	0.507
0.1	0.429	0.438
1	0	0
10	-0.750	-0.815
100	-0.971	-1.13
1000	-0.997	-1.17
∞	-1.000	-1.18

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Fig. 14. Conductivity measurements on emulsions
($K_d = 0.172$).

Legend: Data points of this work $\circ$
 Bruggeman's equation — — — — —
 Doublet model —————
 Maxwell's equation - - - - -

net shift is too great. Thus the effective conductivity in the neighborhood of a dispersed particle cannot be represented by the conductivity of the mixture as a whole, but lies somewhat intermediate between this latter value and the conductivity of the continuous phase, depending upon the volume fraction and the conductivity of the dispersed phase.

A consideration of these ideas is utilized in the following proposed model. Consider a dispersion of equal size particles with a volume fraction such that we are in the concentrated range as far as the dispersed phase is concerned. Let us now focus our attention on one particular particle of the mixture. Clearly, in the absence of all other particles, the disturbance of the field in the continuous phase about this particle is due to its presence alone and such a disturbance may be rigorously evaluated and used to develop the Maxwell or Fricke relations. Since our particle is not alone however, the field of the region in question is also disturbed to a certain extent by all of the other particles in the mixture. Thus the presence and the position of all of the neighboring particles must be taken into account in the rigorous treatment of the problem in question. To put the problem on a workable basis let us assume that the disturbance due to the presence of neighbors is due mostly to the neighboring particles which happens to be closest to the particle and region of interest and thus assign a secondary effect to all of the remaining particles. This closest neighbor, in a random mixture, will on the average take on positions that are spherically symmetrical about our primary particle. Thus it would appear in time that this neighboring particle was everywhere at once and its approximate effect would be no different than it if had been subdivided into many smaller pieces and scattered uniformly about the region in question.

The technique of deriving a conductivity expression will thus be somewhat similar to the approach used by Bruggeman, but instead of assuming an infinite continuum of particles, our mixture of identical particles will act rather as if it consisted of particles of two different orders of size. For what follows, and for simplicity, let us

denote the particle whose surrounding conductivity is in question as a particle of the first kind, and let us also call its closest neighbor (the particle which disturbs its field the most) a particle of the second kind. In a random mixture, we shall observe that there exists a particle of the second kind for every particle that we have of the first kind, and in general for any instant of time, we can assign one half of the total particles to each of these two categories. Thus we may write

$$f = f_1 + f_2 \quad (70)$$

and

$$f_1 = f_2, \quad (71)$$

where the subscripts refer to the particles of the two types.

In order to keep the results as general as possible, we shall use the Fricke relation as the starting point instead of Maxwell's equation. This expression has been discussed in the section on the Shape Effect, and for the fraction of the particles that act as particles of the first kind we may write this relation as

$$k_m = \frac{1 + (WK_d - 1) f_1}{1 + (W - 1) f_1} (k'_c), \quad (72)$$

where

$$W = 1/3 \sum_i \frac{1}{1 - (1 - K_d) L_i} \quad (73)$$

for $i = 1, 2, 3$.

The L terms in Eq. (73) have previously been discussed in the section on the Shape Effect and may easily be evaluated by use of Table XXII in conjunction with Eqs. (41) and (42). The prime superscript appears in Eq. (72) to remind us that this conductivity symbol is not to be confused with the conductivity of the continuous media, but represents instead the conductivity of the "surrounding media".

This consists of the suspending media plus the other half of the dispersed phase or the particles of the second kind. If we were to imagine that the particles of this first kind were momentarily removed from the dispersion, then k'_c could be evaluated in a manner similar to Eq. (72). That is, we would obtain

$$k'_c = \frac{1 + (WK_d - 1) f'_2}{1 + (W - 1) f'_2} (k_c), \quad (74)$$

where k_c is now the conductivity of the continuous phase. The prime superscript on f'_2 denotes that this volume fraction is the fraction of the particles of the second kind in the surrounding media in the absence of any particles of the first kind, and thus it is not based upon the total volume of the system. To convert f'_2 to a volume fraction on this latter basis, we must use

$$f_2 = f'_2 (1 - f_1). \quad (75)$$

Remembering that we have

$$K_m = k_m / k_c \quad (76)$$

and combining Eqs. (70), (71), (72), (74), (75), and (76), we obtain

$$K_m = \left[\frac{2 + (WK_d - 1) f}{2 + (W - 1) f} \right] \left[\frac{2 (1 - f) + WK_d f}{2 (1 - f) + Wf} \right]. \quad (77)$$

Equation (77) in conjunction with the expression for W will now be designated the "distribution model" and the following particular cases can be considered:

(1) A Dispersion of Spheres

For this case, we have

$$W = 3/(K_d + 2) \quad (78)$$

and

$$K_m = \left[\frac{2(K_d + 2) + 2(K_d - 1) f}{2(K_d + 2) - (K_d - 1) f} \right] \left[\frac{(2 - f)(K_d + 2) + 2(K_d - 1) f}{(2 - f)(K_d + 2) - (K_d - 1) f} \right]. \quad (79).$$

If the spheres are also nonconducting, the above reduces to

$$K_m = \frac{8 (2 - f) (1 - f)}{(4 + f) (4 - f)}. \quad (80)$$

If the spheres are infinitely conducting, we use

$$K_m = \frac{(1 + f) (2 + f)}{(1 - f) (2 - f)}. \quad (81)$$

(2) A Dispersion of Rods Randomly Oriented in Three Dimensions

Here we have

$$W = \frac{(K_d + 5)}{3(K_d + 1)} \quad (82)$$

$$K_m = \left[\frac{6(K_d + 1) + (K_d^2 + 2K_d - 3) f}{6(K_d + 1) - 2(K_d - 1) f} \right] \left[\frac{6(K_d + 1 - f) + (K_d^2 - K_d) f}{6(K_d + 1) - (5K_d + 1) f} \right]. \quad (83)$$

If the rods are also nonconducting the above reduces to

$$K_m = \frac{9 (2 - f) (1 - f)}{(3 + f) (6 - f)}. \quad (84)$$

(3) A Dispersion of Rods Randomly Oriented in Two Dimensions with the Long Axis Perpendicular to the Field

For this case we have

$$W = 2/(K_d + 1). \quad (85)$$

(Note: for the two-dimensional case the expression for W becomes

$$W = \frac{1}{2} \sum_i \frac{1}{1 - (1 - K_d) L_i}, \quad (86)$$

where i now takes on the values of only 1 and 2).

With this value of W the distribution model yields:

$$K_m = \left[\frac{2(K_d + 1) + (K_d - 1)f}{2(K_d + 1) - (K_d - 1)f} \right] \left[\frac{(2 - f)(K_d + 1) + (K_d - 1)f}{(2 - f)(K_d + 1) - (K_d - 1)f} \right] \quad (87)$$

If the rods are also nonconducting the above reduces to

$$K_m = (2 - f)(1 + f)/(2 + f) \quad (88)$$

These are a few of the particular cases of general interest.

The distribution model has been presented in various figures in this thesis, and its agreement with data looks satisfactory. It would be desirable, however, to have additional data on spheroidal particles to give this model a more critical test.

Fig. 15. Conductivity measurements on emulsions
($K_d = 15.7$).

Legend: Data points of this work o
 Bruggeman's equation -----
 Distribution model - . - . - . - . - . - . - . - . - .
 Doublet model —————
 Maxwell's equation - - - - -

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Fig. 16. Conductivity measurements on emulsions ($K_d = 101$).

Legend: Data points of this work o
Bruggeman's equation - - - - -
Distribution model - - - - -
Doublet model _____
Maxwell's equation - . - . -

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Fig. 17. Conductivity measurements on foam ($K_d = 0$).

Legend: Data points of Clark ○
Maxwell's equation -----
Doublet model
Distribution model —————
Bruggeman's equation - - - - -

IX. CONCLUSIONS

Comments on Previous Work

The results of this study indicate that the dilute-suspension relations that have been developed in the past by authors such as Maxwell and Fricke do not represent experimental data above a volume fraction of about 0.2. The concentration corrections employed by Bruggeman, Bottcher, Polder, and van Santen also appear ineffective in representing the data, because these authors have overcompensated for the concentration effect in their work.

A Consideration of Variables

A rigorous study of the conductivity of dispersions cannot ignore the effects of surface resistance, shape, orientation, and particle size distribution associated with the dispersed phase. In this study we have seen that these variables, in addition to the usual conductivities and the volume fraction, can measurably change the effective conductivity of a dispersion.

Orientation of the Particles.

Among these variables, the effect of particle arrangement, at least for dispersions of spheres, seems to be of the least importance in practical cases compared to the effects of surface resistance or shape of the dispersed particle. In extreme cases such as comparing the cubic packing of spheres to random arrangements at high volume fractions and large K_d values, the effect may be considerable (Compare Figs. 9 and 16). Orientation is always a variable of the first magnitude when the dispersed particles are nonspherical.

Size Distribution

The size distribution of the dispersed particles causes only a slight effect as long as one is dealing with particles of roughly the same size. That is, the effect of dispersed particles different in size

by two or three diameters is going to be fairly negligible. By comparing Table XX and Fig. 12, one can see that even for a mixture which contains particles that differ in size by ten diameters the deviation from data on particles of uniform size is small.

Shape

In Fig. 13 one can see the effect of the shape of the dispersed particle. In the example given, one can make an error of about 20% in conductivity near a volume fraction of 0.5 if the effect of shape is neglected. Much greater errors will correspondingly be made as the conductivity of the dispersed phase becomes appreciable.

Surface Resistance

This effect has been demonstrated in Fig. 4 and of course is of no importance if the dispersed phase is nonconducting.

Concentration

A simple conclusion may be reached on the effect of increasing concentration. On the basis of the foregoing study on dispersions where f is greater than 0.1, the following relations represent data best: For spheres arranged in a cubical lattice, the Rayleigh extension or Eq. (56) is recommended. For other geometries and arrangements the distribution model or Eq. (77) represents the data very well.

Applications

The studies on cylinders in parallel and crossed arrangements indicate that materials that represent two-dimensional arrays of cylinders are closely approximated by parallel cylinders in a square array and tests conducted on cloth and sheet asbestos show that data of this type are also represented by the distribution model that has been mentioned above.

Future Work

Although even the formulation of the mathematical problem corresponding to the case of a random dispersion appears to be prohibitive, there is some hope that this problem may yet be treated in a rigorous manner by using a statistical method to obtain the solution to the potential distribution within a cluster of spheres.

Future work should include studies of the following kind:

- (a) Experiments should be devised to obtain accurate data on dispersions of various types of spheroidal particles over broad ranges of f and K_d to further critically test the models proposed in this dissertation.
- (b) Systematic experimental work on the role of interfacial surface resistance could be performed by studying a single laminated sphere. For this latter study, carbon or a tellurium alloy could be used to give an electrical conductivity intermediate between the conductivity of the pure metal and the electrolytic solution.

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APPENDIX I

"Bridge Balancing Calculations"

As indicated in Chapter III, the presence of a surface reactance at the interface between the dispersed and continuous phases forces one to abandon the simple RC shunt analogy for the conductivity cell if one is to obtain the electrolytic resistance from a direct measurement. Under these circumstances the more correct analogy would be the circuit shown in Fig. 18A. The cell is now represented by the series parallel arrangement on the left of this figure and, as usual, the bridge balance is obtained by the RC shunt arrangement on the right. The equation of balance for this combination is

$$\frac{(R_s j/\omega C) + (1/\omega^2 C C_s)}{R_s - j[(1/\omega C_s) + (1/\omega C)]} = \frac{(R_1 j/\omega C_1)}{R_1 - (j/\omega C_1)}, \quad (89)$$

where $j = (-1)^{1/2},$ (90)

$$\omega = 2\pi\nu, \quad (91)$$

and ν is the frequency in cps.

Rearranging Eq. (89) and separating the real and imaginary parts, we obtain

$$C_s = \frac{R_1 (C - C_1)}{(R_s - R_1)} \quad (92)$$

and

$$R_s = \frac{1}{R_1 (C_1 - C)\omega^2 C_s}, \quad (93)$$

Combining these latter two equations and eliminating C_s , we have

$$R_s = \frac{R_1}{1 + [R_1 \omega (C - C_1)]^2}. \quad (94)$$

All terms on the right-hand side of Eq. (94) can now be directly measured except the variable C and a good estimate for this term would probably be the volumetric average of the cell capacity obtained for the pure phases

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Fig. 18. Bridge balancing circuits.

alone. Equation (94) is essentially correct only for a case in which the mixture in the cell is made up of stratified series lamina, and gives only a rough correction in the right direction for emulsions.

Also, the results mentioned above hold only when the interfacial resistance is purely reactive, with negligible electrolytic conductance. When the latter restriction is not applicable we must solve the more complicated bridge shown in Fig. 18B. The equation for the balance condition of this combination is

$$\frac{\frac{j}{\omega C} \left\{ R_s - \frac{R_p j}{R_p \omega C_p - j} \right\}}{\left\{ R_s - \frac{R_p j}{R_p \omega C_p - j} - \frac{j}{\omega C} \right\}} = \frac{R_1 j}{R_1 \omega C_1 - j} ; \quad (95)$$

equating the real and imaginary parts of this expression we obtain

$$R_1(R_p + R_s)(C_1 - C) = R_p C_p(R_1 + R_s) , \quad (96)$$

$$R_p R_s R_1 \omega^2 C_p (C_1 + C) = R_p + R_s - R_1 . \quad (97)$$

Eliminating C_p from this combination gives

$$R_p = \frac{R_1^2 - R_s^2}{R_1 + R_s} \frac{\left\{ 1 - R_1^2 \omega^2 (C_1^2 - C^2) \right\}}{\left\{ 1 - R_1^2 \omega^2 (C_1^2 - C^2) \right\}} , \quad (98)$$

where the unknowns are now R_p , R_s , and C .

APPENDIX II

An Application of the "Bruggeman Technique" to Burger's Generalized Equation

The Bruggeman equation for dispersions which consist of spherical shaped particles, i.e.,

$$1 - f = \frac{(K_m - K_d)}{K_m^{1/3} (1 - K_d)} \quad (99)$$

was developed from Maxwell's equation after the latter was expanded in a Taylor's series about $f = 0$, and higher order terms dropped. Although it is valid only for a mixture of spheres, one can ask if it were not possible to start with Burger's equation which is not restricted to spheres, i.e.

$$k_m = k_c \left\{ 1 - (f/3)(k_c - k_d) \sum_{i=1}^3 \frac{1}{k_c - (k_c - k_d)L_i} \right\}, \quad i = 1, 2, 3 \quad (100)$$

and develop an expression analogous to Eq. (99) which would be of use in treating dispersions which are made up of nonspherical particles. In general we can do this only if we restrict ourselves to spheroids where we can write

$$L_1 + L_2 + L_3 = 1 \quad (101)$$

and

$$L_2 = L_3 \quad (102)$$

Using these latter two relations, we may express all of the L values in terms of L_3 . Doing this and rearranging Eq. (100) we obtain

$$k_m - k_c = \frac{(f/3)(k_c)(k_d - k_c)(2k_d + 3k_c L_3 - 3k_d L_3 + k_c)}{[k_c - (k_c - k_d)L_3] [k_c - (k_c - k_d)(1 - 2L_3)]} \quad (103)$$

Mechanically, the Bruggeman treatment consists in setting the left hand side of the above equation equal to dk , then f is replaced by $df/(1 - f)$ and k is substituted for k_c . The variables f and k are then separated and the former is integrated from 0 to f while the latter is integrated from k_c to k_m . In doing this, we obtain from Eq. (103)

$$- (1/3) \int_0^f \frac{df}{(1 - f)} = \int_{k_c}^{k_m} \frac{2L_3(1 - L_3)k^2 + (1 - 3L_3 + 4L_3^2)k_d k + L_3(1 - 2L_3)k_d^2}{k(k - k_d) [(2 - 3L_3)k_d + (3L_3 + 1)k]} dk. \quad (104)$$

The left hand side of Eq. (104) may be integrated at once to give

$$(1/3)\ln(1 - f) = g(k). \quad (105)$$

In order to deal with the remainder of the equation we may set

$$\alpha = (2 - 3L_3)/(3L_3 + 1) \quad (106)$$

and break the integral under consideration up as follows

$$\begin{aligned} g(k) = & \frac{2L_3(1 - L_3)}{3L_3 + 1} \int_{k_c}^{k_m} \frac{(k)dk}{(k - k_d)(k + \alpha k_d)} \\ & + \frac{(1 - 3L_3 + 4L_3^2)k_d}{3L_3 + 1} \int_{k_c}^{k_m} \frac{dk}{(k - k_d)(k + \alpha k_d)} \\ & + \frac{L_3(1 - 2L_3)k_d^2}{3L_3 + 1} \int_{k_c}^{k_m} \frac{dk}{(k)(k - k_d)(k + \alpha k_d)}. \quad (107) \end{aligned}$$

For further simplification, the coefficients of the above integrals may be set equal to C_1 , C_2 , and C_3 respectively.

In treating the last integral of the above we obtain

$$C_3 \int_{k_c}^{k_m} \frac{dk}{k(k - k_d)(k + \alpha k_d)} = (C_3/2k_d^2 \alpha) \ln \frac{(k_m - k_d)(k_m + \alpha k_d)k_c^2}{(k_c - k_d)(k_c + \alpha k_d)k_m^2} \\ + \frac{C_3 (\alpha - 1)}{2k_d \alpha} \int_{k_c}^{k_m} \frac{dk}{(k - k_d)(k + \alpha k_d)}, \quad (108)$$

and the second integral that results can be combined with the second integral of Eq. (107) to give

$$[C_2 + C_3 (\alpha - 1)/(2k_d \alpha)] \int_{k_c}^{k_m} \frac{dk}{(k - k_d)(k + \alpha k_d)} = \\ [C_2 + C_3 (\alpha - 1)/(2k_d \alpha)] [1/k_d (1 + \alpha)] \ln \frac{(k_m - k_d)(k_c + \alpha k_d)}{(k_c - k_d)(k_m + \alpha k_d)}. \quad (109)$$

Finally the first integral of Eq. (107) can be written

$$C_1 \int_{k_c}^{k_m} \frac{(k)dk}{(k - k_d)(k + \alpha k_d)} = [(C_1)/(1 + \alpha)] \ln \frac{k_m - k_d}{k_c - k_d} \\ + [(\alpha C_1)/(1 + \alpha)] \ln \frac{k_m + \alpha k_d}{k_c + \alpha k_d}, \quad (110)$$

We can now combine the significant parts of expressions (105), (107), (108), (109), and (110) after making the substitutions

$$K_m = (k_m/k_c) \quad (111)$$

and

$$K_d = (k_d/k_c) \quad (112)$$

to obtain

$$\begin{aligned} (1/3) \ln (1 - f) = & - (C_3/k_d^2 \alpha) \ln K_m \\ & + [1/(\alpha + 1)] [(C_3/k_d^2) + (C_2/k_d) + C_1] \ln (K_m - K_d)/(1 - K_d) \\ & + [1/(\alpha + 1)] [(C_3/k_d^2 \alpha) - (C_2/k_d) + \alpha C_1] \ln (K_m + \alpha K_d)/(1 + \alpha K_d) \end{aligned} \quad (113)$$

Upon substituting the coefficients into the above relation and rearranging terms, we have the desired expression, i.e.,

$$(1 - f) = \left(\frac{K_m - K_d}{1 - K_d} \right) \left(\frac{K_m + \alpha K_d}{1 + \alpha K_d} \right)^r (K_m)^\beta \quad (114)$$

where

$$\alpha = (2 - 3L_3)/(3L_3 + 1) \quad (115)$$

$$\beta = 3L_3(1 - 2L_3)/(3L_3 - 2) \quad (116)$$

$$r = 2(3L_3 - 1)^2/(3L_3 - 2)(3L_3 + 1) \quad (117)$$

For spheres where the value of L_3 is $1/3$, the above results agree with Eq. (7). For a random mixture of cylinders or rods, where L_3 is $1/2$, we obtain

$$(1 - f) = \left(\frac{K_m - K_d}{1 - K_d} \right) \left(\frac{5K_m + K_d}{5 + K_d} \right)^{-2/5}, \quad (118)$$

and when the dispersed phase is made up of a random mixture of disks, we have

$$(1 - f) = \left(\frac{K_m - K_d}{1 - K_d} \right) \left(\frac{K_m + 2K_d}{1 + 2K_d} \right)^{-1} \quad (119)$$

In addition to the common shapes that have been enumerated, Eq. (114) may be used with the L_3 values of Table XXII to obtain expressions for the conductivity of mixtures of other spheroidal shaped particles.

The main value of Eq. (114) is that it may be used with the Fricke equation (see the section on "The Shape Effect") to form a boundary on the data obtained from dispersions of nonspherical particles, just as the Bruggeman and Maxwell equations form boundaries on the data obtained from dispersions of spheres.

Since the Fricke equation reminds one of a generalized Maxwell relation; Eq. (114), in a like manner, resembles a generalized Bruggeman equation. For lack of a better expression, we shall thus use this latter connotation in further discussions on the relation that we have just developed.

APPENDIX III

On the Resistance to Potential Flow Through a Cubical Array of Spheres

In this appendix we shall examine the Rayleigh equation for conduction through a cubical lattice of spheres. The object of this examination shall be to extend the Rayleigh equation by determining the next significant term in the series expression for the conductivity. The treatment or procedure that appears in the following pages is closely identical to that used by Lord Rayleigh.

Consider a cubical lattice of spheres with a conductivity of K_d when the conductivity of the continuous medium is unity. If the spheres are aligned with respect to the original field E_0 as shown in Fig. 19, then a unit cell consists of a cube α units on a side, with a sphere of radius a in the center. Let the center of a sphere at point P be chosen as the origin for rectangular coordinates and let θ be an angle in the xy plane, as shown in Fig. 19. Symmetry considerations require that the potential be reversed when $(\pi - \theta)$ is substituted for θ , and requires also that the results be independent of angle in the yz plane. The expressions for the potential in the continuous phase around P and in the dispersed phase which includes P are thus expansions in odd Legendre polynomials and may be obtained from any advanced treatise on electricity and magnetism:^a

$$V_c = A_0 + \sum_{n=1}^{\infty} (A_{2n-1} r^{2n-1} + B_{2n-1} r^{-2n}) P_{2n-1}, \quad (120)$$

$$V_d = \sum_{n=1}^{\infty} (C_{2n-1} r^{-2n}) P_{2n-1}. \quad (121)$$

^aThe expressions for the potential given in Eqs. (120) and (121) are of a different form from the relations used by Lord Rayleigh. In his work he chose to extract a term from the above expressions which results in changing the P_{2n-1} term to a Y_{2n-1} , where

$$P_n = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{n!} Y_n \quad (122)$$

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Fig. 19. The model used in the Rayleigh Extension.

At the interface between the dispersed and continuous phases, the potential and current must be continuous. Using these boundary conditions, one may obtain, for the constants in Eq. (120),

$$A_n = \frac{K_d + (n+1)/n}{1 - K_d} a^{-(2n+1)} B_n \quad (123)$$

An expression for the conductivity of the mixture may be obtained by applying Green's Theorem to the boundary of the continuous medium in the unit cell. If U and V are harmonic functions, we may write

$$\int_S \left(U \frac{\partial V}{\partial n} - V \frac{\partial U}{\partial n} \right) dS = 0. \quad (124)$$

More specifically, set $V = V_c$ and $U = r \cos(\theta) = x$. The above integral now has no contribution from the sides of the cube parallel to the field. Along the faces normal to the direction of the field, the terms in the above integral have the values of $I \alpha$ and $V' \alpha^2$ respectively. Here I is the total current crossing the unit cell and V' is the potential drop through the unit cell. Along the spherical boundary, the direction of the normal is negative to the radius vector and Eq. (124) becomes

$$2\pi a^2 \int_0^\pi [V_c - a(\partial V_c / \partial r)_{r=a}] \cos(\theta) \sin(\theta) d\theta. \quad (125)$$

When Eq. (120) is substituted into this expression and the integral is evaluated term by term, it is found that the only nonzero value is $4\pi B_1$. The Green's Theorem thus yields

$$I \alpha - V' \alpha^2 + 4\pi B_1 = 0. \quad (126)$$

The above equation may be rearranged to give the specific conductivity of the mixture, i.e.

$$K_m = I/V' \alpha = (1 - 4\pi B_1/E_0 \alpha^3). \quad (127)$$

Here V' has been replaced by $E_0 \alpha$ in the latter part of the expression. This identity is valid because the drop in potential across the cell is equal to the line integral of the field between the faces of the cube.

In order to use Eq. (127) one must obtain a value for $B_1/E_0 \alpha^3$. An approximate value for this term may be had in the following manner.

Note that the potential around P , when P is not included, is given by Eq. (120) with terms in B omitted, i.e.,

$$V_c = A_0 + \sum_{n=1}^{n=\infty} (A_{2n-1} r^{2n-1}) P_{2n-1} \quad (128)$$

This same potential, however, may be regarded as due to the original field plus sources of potential on each of the neighboring spheres (P not included), i.e.,

$$V_c = E_0 x + \sum_{n=1}^{n=\infty} \sum_{i=1}^{i=\infty} B_{2n-1} r_i^{-2n} P_{2n-1,i} \quad (129)$$

In this latter expression, the summation in i extends over all spheres in the mixture except the sphere P which is located at the center of the coordinate system. The radius vector and the Legendre Polynomials that appear in this relation are understood to be evaluated with an origin at the i th sphere. That is, if r is a radius vector with respect to the center of the sphere at P and ξ_i , η_i , and ζ_i are the coordinates of the i th sphere with respect to P , then we have

$$x_i = x - \xi_i, y_i = y - \eta_i, z_i = z - \zeta_i \quad (130)$$

and

$$r_i^2 = (x - \xi_i)^2 + (y - \eta_i)^2 + (z - \zeta_i)^2 \quad (131)$$

For convenience let us also set

$$\rho^2 = \xi^2 + \eta^2 + \zeta^2, \quad (132)$$

so that where r is zero we have

$$r_i = \rho_i \quad (133)$$

with respect to the origin centered at P .

Let us now equate Eqs. (128) and (129) and obtain

$$\begin{aligned} A_0 + \sum_{n=1}^{n=\infty} (A_{2n-1} r^{2n-1}) P_{2n-1} \\ = E_0 x + \sum_{n=1}^{n=\infty} \sum_{i=1}^{i=\infty} (B_{2n-1} r_i^{-2n}) P_{2n-1,i} \end{aligned} \quad (134)$$

The next step in evaluating $B_i/E_0 \alpha^3$ is to take successive derivatives of Eq. (134) with respect to x and evaluate the results at the point P . In performing this latter operation we note that the point (x_i, y_i, z_i) becomes the point (ξ_i, η_i, ζ_i) and r_i is replaced by ρ_i . The Legendre polynomials, e.g., $P_{2n-1,i}$ become functions of ξ_i/ρ_i . Noting also

$$\frac{\partial}{\partial x} (r^{2n-1} P_{2n-1}) = (2n-1)r^{2n-2} P_{2n-2} \quad (135)$$

and

$$\frac{\partial}{\partial x} (r^{-2n} P_{2n-1}) = -(2n)r^{-2n-1} P_{2n} \quad (136)$$

we find that the first five derivatives yield

$$A_1 - E_0 = -(2n)B_{2n-1} \rho_i^{-2n-1} P_{2n,i}, \quad (137)$$

$$6A_3 = -(2n)(2n+1)(2n+2)B_{2n-1} \rho_i^{-2n-3} P_{2n+2,i},$$

$$120A_5 = -(2n)(2n+1)(2n+2)(2n+3)(2n+4)B_{2n-1} \rho_i^{-2n-5} P_{2n+4,i},$$

where summations in n and i from 1 to ∞ are understood. Since the

A's may be expressed in terms of B's by use of Eq. (123), we may generate an n-by-n matrix in terms of calculable values and the unknown B's, but since we are interested in only a few of the more important terms, we may proceed as follows:

Rewrite Eq. (123) to obtain

$$B_n = K'_n a^{(2n+1)} A_n, \quad (138)$$

where

$$K'_n = \frac{1 - K_d}{K_d + (n+1)/n}. \quad (139)$$

Note, in addition, that the coordinates of all other spheres with respect to the sphere at P are of the form $l\alpha, m\alpha, n\alpha$, where l, m , and n are integers. If α is chosen as a unit distance then we may write

$$\sum_{n=1}^{n=\infty} \rho_i^{-2n-1} P_{2n,i} = \alpha^{-2n-1} S_{2n}, \quad (140)$$

where S_{2n} is now purely numerical and represents a sum over all spheres except the one at P, e.g.,

$$S_2 = \sum_{i=1}^{i=\infty} \frac{2 \xi_i^2 - \eta_i^2 - \zeta_i^2}{2 \rho_i^5}. \quad (141)$$

Let us use Eq. (140) and consider only the following terms in the relations given by Eq. (137):

$$A_1 - E_0 = -2B_1 S_2 \alpha^{-3} - 4B_3 S_4 \alpha^{-5} - 6B_5 S_6 \alpha^{-7}, \quad (142)$$

$$A_3 = -4B_1 S_4 \alpha^{-5} - 20B_3 S_6 \alpha^{-7}, \quad (143)$$

$$A_5 = -6B_1 S_6 \alpha^{-7}. \quad (144)$$

If we use Eq. (138) and combine the above so as to eliminate all the B's other than B_1 , we can rearrange the results to obtain

$$B_1/E_0 \alpha^3 = (a/\alpha)^3 \left[\frac{1}{K_1} + 2S_2(a/\alpha)^3 - \frac{16K_3'S_4^2(a/\alpha)^{10}}{1 + 20K_3'S_6(a/\alpha)^7} - 36K_5'S_6^2(a/\alpha)^{14} \right]^{-1} \quad (145)$$

Note that the volume fraction of the dispersed phase is given by

$$f = (4\pi/3)(a/\alpha)^3, \quad (146)$$

and thus, upon substituting Eqs. (145), (139), and (146) into Eq. (127), we have the desired expression for the conductivity of the mixture in terms of (K_d, f, S_2, S_4, S_6) . Lord Rayleigh has evaluated S_2 and S_4 for a medium which is infinitely more extended in the direction of the field. His results are:

$$S_2 = 2\pi/3 \quad (147)$$

and

$$S_4 = 3.11. \quad (148)$$

It thus remains for us to evaluate S_6 , where

$$S_6 = \sum_{i=1}^{i=\infty} \frac{231 \xi_1^6 - 315 \xi_1^4 \rho_1^2 + 105 \xi_1^2 \rho_1^4 - 5 \rho_1^6}{16 \rho_1^{13}} \quad (149)$$

The numerical evaluation is presented in Table XXVI. The left column in this table gives the absolute value of the coordinate numbers of the spheres adjacent to P. In general there are up to eight spheres which have a position that can be generated by permutating the numbers in this column. The second column gives the square of the corresponding radius vector and the calculation leading to the contribution of S_6 by

Table XXVI

Evaluation of S_6				
Order	ρ^2	ρ^7	Calculation	$S_{6,i}$
0 0 1	1	1	2 [2(-0.315) + 1]	0.7500
0 1 1	2	11.3	4 [2(-0.1484) - 0.315] (1/11.3)	-0.216
1 1 1	3	47	8 [(0.223)] (1/47)	0.0380
0 0 2	4	128	2 [2(-0.3125) + 1] (1/128)	0.00585
0 1 2	5	280	4 [-0.3125 + 0.327 - 0.2675] (1/280)	-0.00362
1 1 2	6	540	8 [2(0.3024) - 0.411] (1/540)	0.00287
0 2 2	8	1450	4 [2(-0.1484) - 0.3125] (1/1450)	-0.00168
1 2 2	9	2200	8 [2(-0.018) + 0.194] (1/2200)	0.000574
0 0 3	9	2200	2 [2(-0.3125) + 1] (1/2200)	0.00034
0 1 3	10	3200	4 [-0.3125 + 0.163 + 0.168] (1/3200)	0.00002

$$S_6 = 0.576$$

each sphere is shown in the next two columns. To three figures, we thus find

$$S_6 = 0.576 \quad (150)$$

Combining Eqs. (127), (139), (145), (146), (147), (148), and (150), we now have the desired expression for the conductivity of the mixture, i.e.,

$$K_m = 1 - \frac{3f}{\frac{2 + K_d}{1 - K_d} + f - \frac{1.315f^{10/3}}{\frac{(4/3) + K_d}{1 + K_d} + 0.409f^{7/3}} - \frac{0.016(1 - K_d)}{(6/5) + K_d} f^{14/3}} \quad (151)$$

The above expression is of course restricted to smaller volume fractions of the dispersed phase than the maximum value that can be obtained in the cubic packing of identical spheres, i.e.,

$$f = \pi/6 = 0.5236. \quad (152)$$

With this in mind, it may be shown that the last term in the denominator of Eq. (151) is always negligible for all values of K_d , and for $f < 0.52$, and, can therefore be neglected. Doing this and rearranging Eq. (151), we obtain

$$K_m = \frac{\frac{2 + K_d}{1 - K_d} - 2f + 0.409 \frac{6 + 3K_d}{4 + 3K_d} f^{7/3} - 2.133 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}}{\frac{2 + K_d}{1 - K_d} + f + 0.409 \frac{6 + 3K_d}{4 + 3K_d} f^{7/3} - 0.906 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}} \quad (153)$$

For the case of a nonconducting dispersed phase, the above expression reduces to

$$K_m = \frac{2 - 2f + 0.6135f^{7/3} - 1.600f^{10/3}}{2 + f + 0.6135 f^{7/3} - 0.6795f^{10/3}}, \quad (154)$$

and for the case in which the conductivity of the dispersed phase is very much larger than the conductivity of the continuous phase, we have

$$K_m = \frac{1 + 2f - 0.409f^{7/3} - 2.133f^{10/3}}{1 - f - 0.409f^{7/3} - 0.906f^{10/3}} \quad (155)$$

In comparing Eq. (153) with the Rayleigh equation, i.e.,

$$K_m = \frac{\frac{2 + K_d}{1 - K_d} - 2f - 0.525 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}}{\frac{2 + K_d}{1 - K_d} + f - 0.525 \frac{3 - 3K_d}{4 + 3K_d} f^{10/3}} \quad (156)$$

we see that the additional consideration of the term involving S_6 given in this section has actually introduced a lower order term in the volume fraction than the one given by Rayleigh. The coefficients are such, however, that both the terms in $f^{7/3}$ and $f^{10/3}$ are of the same order of magnitude, and thus if one is used, both must be used. It must further be noted that the simple elimination of the term in $f^{7/3}$ from Eq. (153) does not cause the relation to reduce to Rayleigh's equation. This is a consequence both of the steps involved in rearranging Eq. (151), and of the manner in which an expression for the potential was obtained.

LIST OF IMPORTANT EQUATIONS

<u>Equation number</u>	<u>Name</u>	<u>Page</u>
2	Maxwell's equation for spheres.	7
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38	Fricke's equation for spheroids	79
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NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>
<u>English letters</u>	
a, b, c	Semiprinciple axes of an ellipsoid
f	Volume fraction of the dispersed phase
k	Conductivity
u	Wiener "form number"
x, y, z	Components of rectangular coordinates
C	Capacitance
E	Electric field
I	An elliptic integral defined on page 78
K	A conductivity ratio with respect to the continuous media
L	An elliptical integral as defined on page 77
P	A symbol used in Appendix III to represent a point or a Legendre polynomial
R	Resistance
V	Potential
W	A summation defined on pages 98 and 100
X	A shape factor defined on page 92
O/W	Oil-in-water emulsion
W/O	Water-in-oil emulsion

<u>Symbol</u>	<u>Definition</u>
<u>Greek letters</u>	
ϵ	Dielectric constant
η	A parameter in ellipsoidal coordinates
ν	Frequency
χ	Electric susceptibility
ω	Circular frequency
<u>Roman numerals</u>	
I	Designating singlet spheres
II	Designating doublet spheres
<u>Subscripts and superscripts</u>	
avg.	Average
c	Continuous phase
d	Dispersed phase
ext.	External
i	An index
int.	Internal
m	Mixture
t	Total
1, 2	Fractions of the total
'	A change in system

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