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THE ELECTRICAL AND THERMAL CONDUCTIVITY OF TWO-PHASE SYSTEMS

BY

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13 ABSTRACT

Equations from the theory of the elastic moduli of composite materials are used to calculate transport properties, such as electrical and thermal conductivities, of two-phase systems. The nature of the packing of the dispersed particles and their shape are important factors. The effect of particle shape can be incorporated into the theory as a generalized Einstein coefficient, which has been published for many shapes. The effect of particle packing can be taken care of by the maximum packing fraction, which can be experimentally measured in many cases and calculated in other cases. The theory appears to agree well with experimental results.

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FOREWORD

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The Electrical and Thermal Conductivity of Two-Phase Systems

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ABSTRACT

Equations from the theory of the elastic moduli of composite materials are used to calculate transport properties, such as electrical and thermal conductivities, of two-phase systems. The nature of the packing of the dispersed particles and their shape are important factors. The effect of particle shape can be incorporated into the theory as a generalized Einstein coefficient, which has been published for many shapes. The effect of particle packing can be taken care of by the maximum packing fraction, which can be experimentally measured in many cases and calculated in other cases. The theory appears to agree well with experimental results.

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Introduction

The estimation of the electrical and thermal conductivity of many kinds of two-phase systems is a problem often encountered in chemical engineering and other engineering sciences. The types of systems vary from the electrical conductivity of metal-filled plastics to the thermal conductivity of packed beads, porous materials and foams.

Many equations have been proposed for the transport properties, such as electrical and thermal conductivity, of two-phase systems (Ashton, et al., 1969, Behrens 1968, Cheng and Vachon 1969, Hamilton and Crosser 1962, Kerner 1956, Springer and Tsai 1967, Sundstrom and Chen 1970, Tsao 1961, and Zinsmeister and Purohit 1970). Nearly all of these theories and equations neglect one very important factor, however. The conductivity should change rapidly in the concentration range near the maximum packing fraction of the dispersed phase since in this concentration range the large number of particle-particle contacts provides a through-going path for the flow of heat or electricity. Most of the equations assume uniform changes up to the point where the dispersed phase makes up the complete system.

During the past few years, the theory of the elastic moduli of composite materials has developed to the extent that one can predict these moduli with a high degree of confidence. (Ashton, et al., 1969, Halpin 1969, Hashin and Shtrikman 1963, Hashin and Rosen 1964, Kerner 1956, Lewis and Nielsen 1970,

Nielsen 1969, Nielsen 1970, Rosen 1970, Tsai 1968, and Whitney and Riley 1966). These equations also may be used to calculate electrical and thermal conductivities (Ashton, et al., 1969, Kerner 1956). Comparison of the equations with experiments indicates good agreement if the nature of the packing of the particles is taken into account.

Theory

Of the numerous equations proposed for calculating the elastic moduli of all kinds of composite materials, the best and most versatile are the so-called Halpin-Tsai equations (Ashton, et al., 1969, Halpin 1969, Tsai 1968) as modified by Nielsen (1969, 1970) and Lewis (1970). These equations are really mixture equations of the type which are constantly being used by engineers to calculate many kinds of properties when two materials are mixed. The Halpin-Tsai equations are capable of covering the entire range of possibilities from the highest upper bound to the lowest lower bound. In addition, these equations have the advantage that the constants which go into the equations are known theoretically or are easily obtained experimentally for many kinds of two-phase systems covering the range from dispersions of rigid spheres or rods in a matrix material to foams.

The modified equations for two-phase systems are (Lewis and Nielsen 1970, Nielsen 1970):

$$\frac{K}{K_1} = \frac{1 + AB\,\phi_2}{1 - B\psi\,\phi_2} \qquad (1)$$

$$A = k_E - 1 \tag{2}$$

$$B = \frac{K_2/K_1 - 1}{K_2/K_1 + A} \tag{3}$$

$$\psi \doteq 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right)\phi_2 \tag{4}$$

The property of interest, such as the thermal or electrical conductivity of the two-phase material, is K. Subscripts 1 and 2 refer to the continuous and dispersed phases, respectively. The constant A depends primarily upon the shape of the dispersed particles and how they are oriented with respect to the direction of flow of thermal or electrical currents; the constant A is related to the generalized Einstein coefficient k_E (Einstein 1905, 1906). The factor B is a constant which takes into account the relative conductivity of the two components. The factor ψ is determined by the maximum packing fraction ϕ_m of the dispersed particles. The volume fraction of the dispersed phase is ϕ_2. The maximum packing fraction ϕ_m is defined as the true volume of the particles divided by the volume they appear to occupy when packed to their maximum extent. Thus, $\psi\phi_2$ can be considered as a reduced concentration which approaches 1.0 when $\phi_2 = \phi_m$ rather than at $\phi_2 = 1$. Table 1 lists the value of A for various kinds of composites. Some of these values have been calculated for

the viscosity of suspensions. For instance, the Einstein coefficient for a suspension of rigid spheres is 2.5, so A = 1.5 (Einstein 1905, 1906). Table 2 lists typical maximum packing fractions for spheres and rods packed in various ways. Equation 4 is not exact, but for composite systems it has been found to be a very good approximation in most cases. Equations 1 to 4 predict values of conductivity which are somewhat too high when $\phi_2 = \phi_m$ if the discontinuous dispersed phase is the more conducting of the two phases. However, at lower concentrations, theory and experiment generally agree very well.

An example of the agreement between theory and experiment is shown in Figure 1 for the thermal conductivity of aluminum spheres and rods embedded in rubber (Hamilton and Crosser 1962). Random close packing ($\phi_m = 0.64$) was assumed for the spheres; and for the randomly oriented rods, it was assumed that $\phi_m = 0.52$. From Table 1, the values of A are 1.5 for spheres and 4.93 for rods with an aspect ratio of 10 to 1 (Burgers 1938). Since aluminum has much greater conductivity than rubber, $B \doteq 1$. The experimental results are fitted much more closely by the modified equations using a reduced concentration $\psi\phi_2$ than by the original Kerner or Halpin-Tsai equations, which are shown by the dotted lines.

A second example is the thermal conductivity of a graphite-epoxy composite in the direction perpendicular to the graphite fiber axis (Ashton et al., 1969). Table 1 gives A = 0.5 for dispersed aligned fibers. However, the fibers used in composites are generally yarns made up of many fibers in a bundle, so the

yarns are analogous to the case of aggregated spheres in which the generalized Einstein coefficient is (Lewis and Nielsen 1968)

$$k_E = \frac{A + 1}{\phi_a} = \frac{1.5}{0.82} \doteq 1.84, \qquad (5)$$

so the proper value of A is approximately 0.84. The value of ϕ_a (the packing fraction in the agglomerate) is 0.82 for random packing of aligned fibers according to Table 2. The experimental values are compared with the theoretical predictions for A = 0.5 and for A = 1.0 in Figure 2. The agreement is quite satisfactory if the maximum packing fraction is taken into account. The agreement is much worse if ϕ_m is not considered.

Equations 1 to 4 include an infinite number of mixture laws. When $A \to \infty$, the equations become the ordinary "rule of mixtures" if $\phi_m = 1$, that is,

$$K = K_1\phi_1 + K_2\phi_2 \ . \qquad (6)$$

When $A \to 0$, the equations become the inverse rule of mixtures

$$\frac{1}{K} = \frac{\phi_1}{K_1} + \frac{\phi_2}{K_2} \qquad (7)$$

Intermediate values of A give mixture rules which are between these upper and lower bounds. If both phases are continuous in the direction of thermal or electrical flow, equation 6 is roughly valid. Equation 7 is approximated if the more conducting component is a dispersed phase.

Equations 1 to 4 also are applicable to foams. The use of these equations for foams and other inverted systems has been discussed by Nielsen (1969).

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Table 1

Value of A for Various Two-Phase Systems

Type of Dispersed Phase	Direction of Heat Flow	A
Spheres	Any	1.50
Aggregates of spheres	Any	$\frac{2.50}{\phi_a} - 1$*
Randomly oriented rods Aspect ratio = 2**	Any	1.58
Randomly oriented rods Aspect ratio = 4	Any	2.08
Randomly oriented rods Aspect ratio = 6	Any	2.8
Randomly oriented rods Aspect ratio = 10	Any	4.93
Randomly oriented rods Aspect ratio = 15	Any	8.38
Uniaxially oriented fibers	Parallel to fibers	2L/D
Uniaxially oriented fibers	Perpendicular to fibers	0.5

*ϕ_a = Maximum packing fraction of the spheres in the aggregates.

** Aspect ratio = $\frac{\text{Length L}}{\text{Diameter D}}$.

Table 2

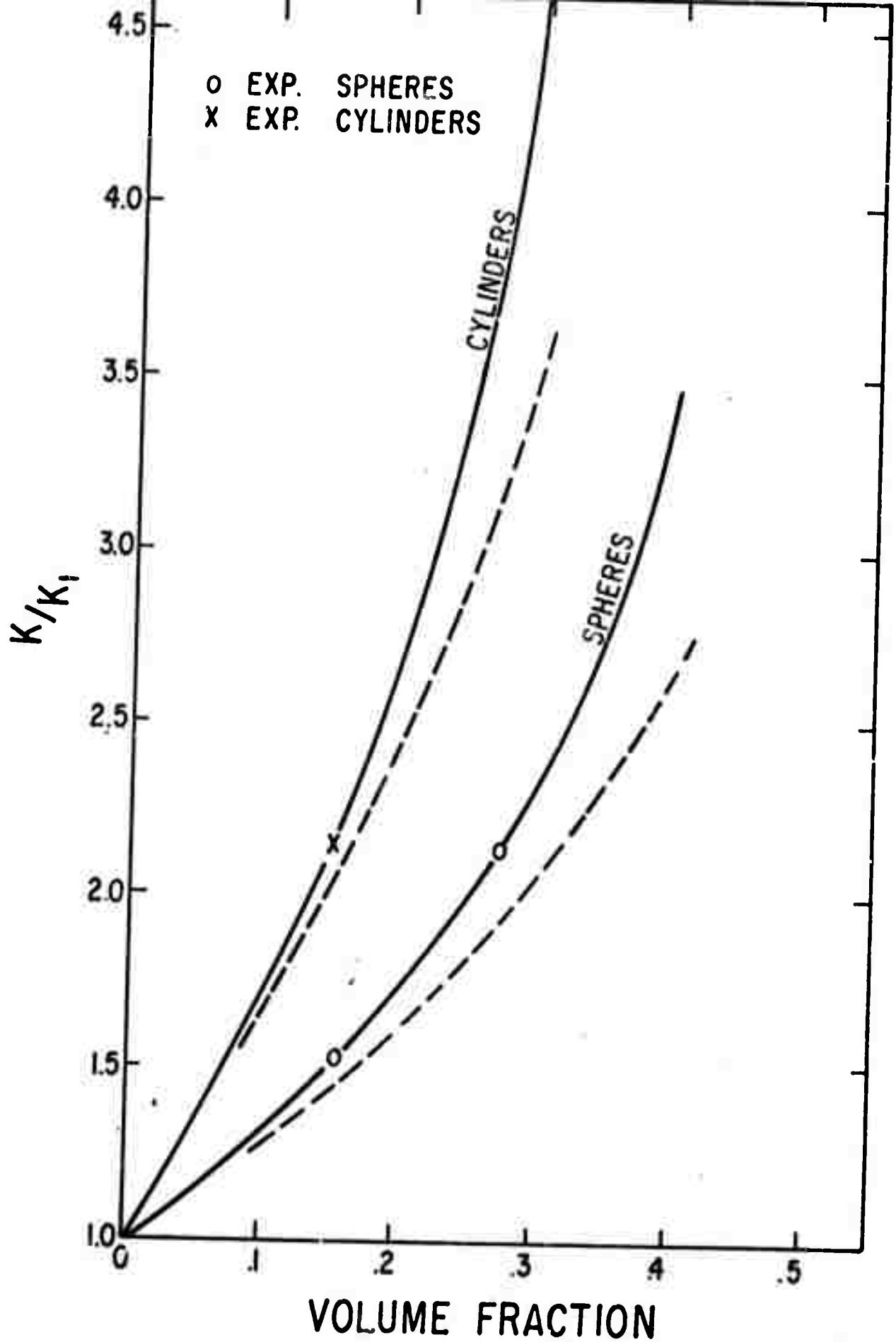
Maximum Packing Fractions ϕ_m

Shape of Particle	Type of Packing	ϕ_m
Spheres	Hexagonal close	0.7405
Spheres	Face centered cubic	.7405
Spheres	Body centered cubic	.60
Spheres	Simple cubic	.524
Spheres	Random close	.637
Spheres	Random loose	.601
Rods or fibers	Uniaxial hexagonal close	.907
Rods or fibers	Uniaxial simple cubic	.785
Rods or fibers	Uniaxial random	.82
Rods or fibers	Three dimensional random	.52 (?)

List of Figures

1. Thermal conductivity of composites consisting of aluminum spheres and aluminum cylinders (aspect ratio 10:1) in rubber. Solid lines are theoretical predictions using equations 1 to 4. Dotted lines are predictions of the original Halpin-Tsai equations. O, experimental values for spheres, X, experimental value for cylinders.

2. Thermal conductivity of uniaxially oriented graphite fibers in epoxy resin measured perpendicular to the direction of fiber alignment. Curve A: Theoretical prediction using $A = 1$, $\phi_m = 0.82$. Curve B: Theoretical curve using $A = 0.5$, $\phi_m = 0.82$. Curve C: Original Halpin-Tsai equations using $A = 0.5$. X = experimental values.


o EXP. SPHERES
x EXP. CYLINDERS
CYLINDERS
SPHERES
K/K1
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
.1
.2
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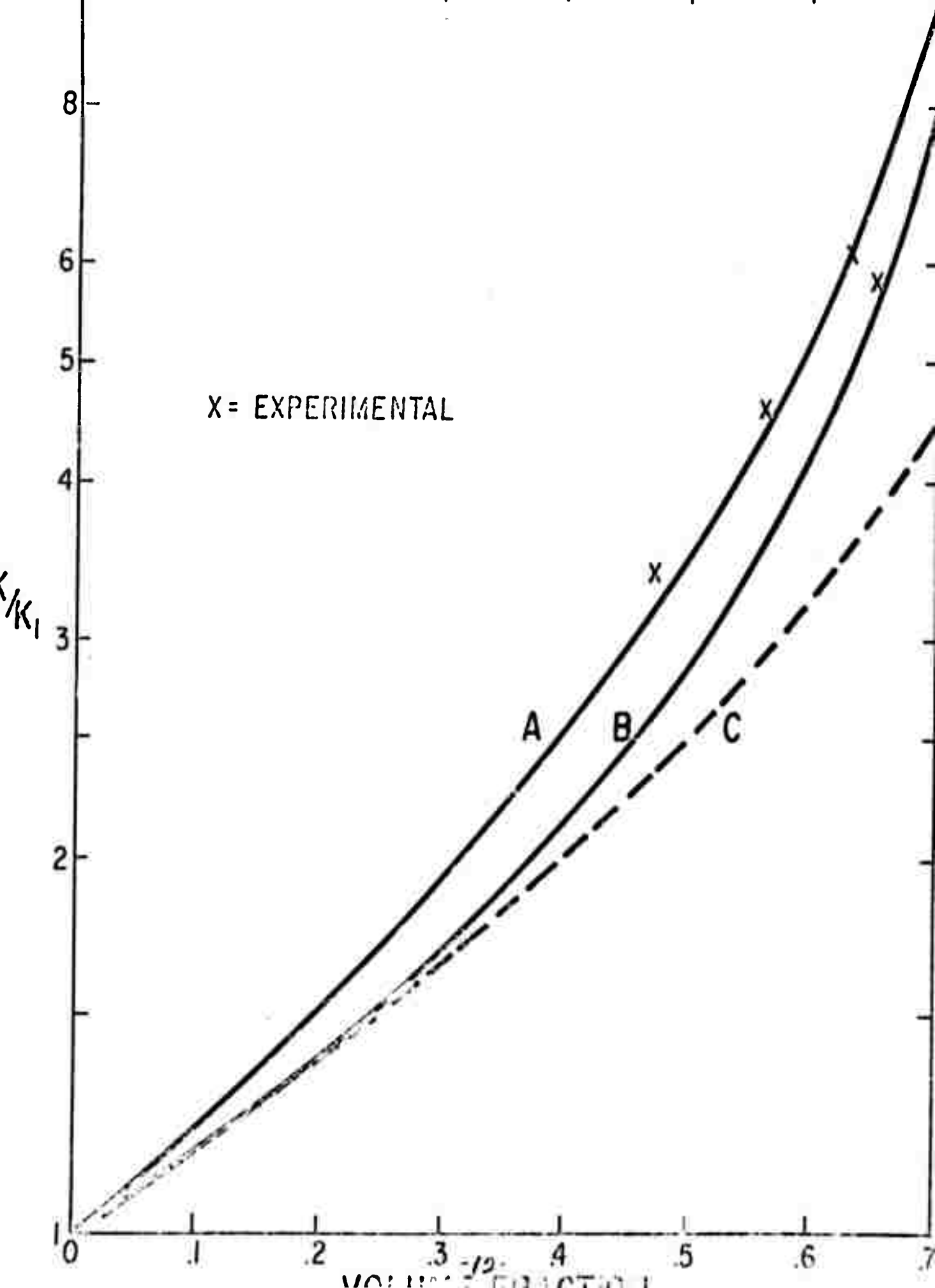
.4
.5
VOLUME FRACTION


X = EXPERIMENTAL
A
B
C
8
6
5
4
3
2
1
0
.1
.2
.3
.4
.5
.6
.7