THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING
Department of Chemical and Metallurgical Engineering

Technical Report

THE DETERMINATION OF ELECTRICAL MOBILITIES
IN MOLTEN ALLOYS

J. D. Verhoeven
J. C. Angus
W. D. Bouwsma
E. E. Hucke

UMRI Project 2917

TABLE OF CONTENTS

ABSTRACT

A method of determining the electric mobility in molten metals
is presented. The partial differential equation describing the process
of electrodiffusion is rigorously integrated for the case of a diffusion
channel of finite length with the concentration at one end held constant.
The solution may also be used to interpret thermal diffusion and sedi-
mentation experiments. Tables of the roots of the eigenfunctions and a
discussion of errors are included.

INTRODUCTION

In recent years interest in the experimental measurement of transport properties in liquids has increased. Thermal and electrodiffusion coefficients have been measured in a variety of ways. For the past two years the authors have used a particularly simple method for determining electric mobilities in molten alloys. During the investigation it was necessary to solve the partial differential equation describing the process and to investigate the errors inherent in the method. Since this solution has utility in other areas, for example, thermal diffusion and sedimentation, it is presented as the basis of this report. The details of the experimental procedure and the results will be discussed fully in a subsequent report. They will be used here only to illustrate the method. In addition to the formal solution of the equation, tables of the roots of the eigenfunctions are included.

The experimental method involves the passage of D.C. current through a thin capillary of molten metal of uniform concentration. One end of the capillary is maintained at constant concentration by keeping it in contact with a reservoir of the molten alloy (fig. 1). To end the experiment the tube is separated from the reservoir and chemically analyzed. The resistivity of the melt, the current, the time, and the increase (or decrease) of solute in the tube are known. From these one can calculate the electrical mobility, u, of the solute atoms from the flux equation (1) by making a mass balance of solute across the mouth of the tube.

$$(1) \quad \bar{J} = uN\bar{E} \quad *$$

------------- ---

* Equation 1 is the defining relation for u. For this treatment the reference frame is the electrodes. This corresponds to the reference frame defined by zero volume flux only when the partial molar volumes of the two species are not functions of concentration.

It is sometimes possible to determine the concentration directly by measuring the resistivity change between probes spaced along the diffusion channel (1,2). This method is suitable for binary systems in which the resistivity changes markedly with concentration. For multi-component systems and alloy pairs without large resistivity changes the chemical technique may be necessary. In addition, it is not easy to design and build a suitable cell for the resistivity method at high temperatures. So far we have found it necessary to use the chemical technique in the range from 300 to 800°C. The solution to the partial differential equation will be of value in interpreting both types of experiments however.

Since one is simply determining the amount of solute that crosses the boundary between the tube and the reservoir, the mobility obtained is for the conditions prevailing at the mouth of the tube. In other words, no matter what form the concentration distribution takes inside the tube, all of the solute that enters (or leaves) the tube must cross the boundary at the entrance to the reservoir.

At the start of the experiment the first change takes place at the electrode end of the tube. If the polarity is such that the solute enters the tube, the concentration will increase at the electrode first. As the experiment proceeds, the concentration will gradually increase back down the tube towards the reservoir. If the polarity is reversed, the concentration first decreases at the electrode end of the tube. A concentration "wave" moves down the tube towards the reservoir, broadening as it goes from ordinary diffusion.

One can approximate this behavior with the solution to the diffusion equation for the initial condition

$$C = 1 \quad X > 0$$

$$C = 0 \quad X < 0$$

for the boundary conditions of a tube of infinite length in the + X and - X directions. This solution is well known. By transforming to a coordinate system that moves with a velocity of $u\bar{E}$ cm/sec (the average velocity of the solute atoms) one obtains an approximate solution to the equation. This solution is best for high solute velocities. For lower velocities the end effect at the electrode becomes appreciable.

When using equation 1 to calculate the mobility one must be certain that the experiment has not proceeded to the point where there is a concentration gradient at the mouth of the tube. If there is, solute will be transported across the boundary between the tube and the reservoir by ordinary diffusion. This ordinary diffusion flux will always oppose the flux due to the electric field. The calculated electrical mobilities will therefore be too low. If the experiment is continued for a very long time the steady state condition is approached. At steady state the concentration gradient at the mouth has increased to the point where the flux caused by electrodiffusion is exactly offset by the ordinary diffusion flux in the reverse direction.

By running experiments under exactly similar conditions but for different lengths of time one can test whether back diffusion is introducing errors. If there is no back diffusion, the mobilities will be the same. If an experiment has been run too long, the result will be lower than the others. This effect has been observed by the authors.

The formal solution will aid in determining optimum experimental times and in designing experiments. By applying the results of the solution to experiments in which back diffusion has taken place it is possible to estimate the ordinary diffusion coefficient.

FORMAL SOLUTION

The one dimensional flux equation including ordinary diffusion is

$$(2) \quad \bar{J} = uN\bar{E} - D \left(\frac{\partial N}{\partial Z}\right) \quad *$$

Differentiating once with respect to distance the partial differential equation is obtained

$$(3) \quad \frac{\partial N}{\partial \theta} = D \left(\frac{\partial^2 N}{\partial Z^2}\right) - \left(\frac{uV}{a}\right) \left(\frac{\partial N}{\partial Z}\right)$$

Here we have introduced the assumption that the electric field strength $\bar{E}$ throughout the tube may be approximated by the total voltage drop, V, divided by the length of the tube a.

Furth (3,4) and DeGroot (5) integrated equation (3) for the boundary conditions corresponding to a tube closed at both ends i.e. zero solute flux at each end of the tube. The equation has not been solved for the case of constant composition at one end and zero flux at the other. Since the solution is unusual in some respects it is presented in detail.

Make the following substitutions **✱**

$$X = \frac{Z}{a} \ , \quad S = \frac{uV}{D} \ , \quad C = \frac{N}{N_o} \ , \quad t = \frac{D\theta}{a^2}$$

----

* The corresponding flux equations for thermal diffusion and sedimentation are respectively

$$\bar{J} = D' N \text{ grad } T - D \left(\frac{\partial N}{\partial Z}\right)$$

$$\bar{J} = v N - D \left(\frac{\partial N}{\partial Z}\right)$$

✱* For thermal diffusion $S = \frac{D'T}{D}$ and for sedimentation $S = \frac{va}{D}$

Equation (3) becomes

$$(4) \quad \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - s \left(\frac{\partial c}{\partial x} \right)$$

Equation (4) is first solved for the homogeneous boundary conditions.

$$(5) \quad C = 0, \text{ for } x = 0, \quad t > 0$$

$$(6) \quad \frac{\partial c}{\partial x} - SC = 0, \quad \text{for } x = 1, \quad t > 0$$

We let $x = 0$ at the reservoir end of the tube and $x = 1$ at the electrode. These boundary conditions do not correspond to the real situation, but they allow the problem to be solved. The solution is then made to fit the real boundary conditions. The familiar separation of variables technique is used.

$$(7) \quad C_{(x,t)} = X_{(x)} \, T_{(t)}$$

After separating and equating to λ one obtains the two ordinary differential equations

$$(8) \quad T' - \lambda T = 0$$

$$(9) \quad X'' - SX' - \lambda X = 0$$

The solution to (8) is simply

$$(10) \quad T = Ae^{\lambda t}$$

From (10) it is apparent that $\lambda < 0$ if the time solution is to remain finite. For (9) the solution of the auxiliary equation is

$$(11) \quad m = \frac{S}{2} \pm \sqrt{\frac{S^2}{4} + \lambda}$$

There are therefore three solutions to (9) depending on whether

$$(12) \quad \lambda + \frac{S^2}{4} = 0$$

$$(13) \quad \lambda + \frac{S^2}{4} > 0$$

$$(14) \quad \lambda + \frac{S^2}{4} < 0$$

From (12) the solution of (9) is

$$X = A e^{\frac{S}{2} x} + Bxe^{\frac{S}{2} x}$$

Applying the boundary conditions (5) and (6) one obtains

$$(15) \quad A = 0$$

$$(16) \quad (1 - \frac{S}{2}) B = 0$$

Since if B = 0 this solution vanishes, one must have S = 2. Therefore for the case where S = 2 one term of the solution is

$$(17) \quad (\text{const.}) \; xe^{x} e^{-t}$$

Now consider the second case i.e. equation (13). First define α by the relation

$$(18) \quad \alpha^2 = \lambda + \frac{S^2}{4}$$

One immediately finds the solution

$$(19) \quad X = \left(A e^{\alpha x} + Be^{-\alpha x} \right) e^{\frac{S}{2} x}$$

Applying the first boundary condition one finds that A = -B. One term of the solution them must be of the form

(20) (const.) (sinh αx) e $e^{\frac{S}{2}x \left(\alpha^2 - \frac{S^2}{4}\right)t}$

Applying the second boundary condition one finds

(21) $\alpha \coth \alpha = \dfrac{S}{2}$

This equation has a single root for every S>2. For S = 2 the root is zero. For S<2 there are no roots. In appendix VIII it is proved that $\alpha^2 - \frac{S^2}{4} < 0$.

Next consider the third case (equation 14). Define β by the relation

(22) $-\beta^2 = \lambda + \dfrac{S^2}{4}$

The corresponding solution is

(23) $X = \left(A \cos\beta x + B \sin \beta x\right) e^{\frac{S}{2}x}$

Applying the boundary conditions one obtains

(24) $A = 0$

(25) $\beta \cot \beta = \dfrac{S}{2}$

Equation 25 has an infinite number of roots for any S. One now has

(26) (const.)(sin$\beta_n x$) $e^{\frac{S}{2}x}$

Before these solutions are tested against the real boundary conditions
it is necessary to consider the special case where $\lambda = 0$. The solution is
simply

$$(27) \quad C_{(x)} = Ke^{Sx} + D$$

This is the "steady state" solution since time does not appear. A trial
solution for the real boundary conditions will be constructed for each of
three cases by adding equation 27 to the solution already obtained.

$$(28) \quad S = 2$$
$$C(x,t) = (const.)xe^{x}e^{-t} + (const.)(\sin\beta x)e^{(S/2)x}e^{\lambda t}$$
$$+ Ke^{Sx} + D$$

$$(29) \quad S > 2$$
$$C(x,t) = (const.)(\sinh\alpha x)e^{(S/2)x}e^{(\alpha^2 - S^2/4)t}$$
$$+ (const.)(\sin\beta x)e^{(S/2)x} e^{\lambda t} + Ke^{Sx} + D$$

$$(30) \quad S < 2$$
$$C(x,t) = (const.)(\sin\beta x)e^{(S/2)x} e^{\lambda t} + Ke^{Sx} + D$$

The real boundary conditions are

$$(31) \quad C = 1, \quad \text{for } x = 0, \quad t > 0$$

$$(32) \quad \frac{\partial C}{\partial x} - SC = 0, \text{ for } x = 1, \quad t > 0$$

In addition one has the final or steady state condition

$$(33) \quad C = e^{Sx}, \quad \text{for } x = x, \quad t = \infty$$

It is easily shown that for $K = 1$ and $D = 0$ these conditions are met. The
initial condition is

$$(34) \quad C = 1, \quad \text{for } x = x, \quad t = 0$$

This is satisfied by forming the sum of all the solutions given by equations 25 and 26. The proof of orthogonality and the calculation of the coefficients is given in the appendix. The final results are

(35) $S = 2$
$$C(x,t) = e^{Sx} + A_0 x e^x e^{-t} + \sum_{n=1}^{\infty} C_n (\sin\beta_n x) e^{\frac{S}{2}x} e^{\lambda t}$$

(36) $S > 2$
$$C(x,t) = e^{Sx} + B_0 (\sinh \alpha x) e^{\frac{S}{2}x} e^{(\alpha^2 - \frac{S^2}{4})t} + \sum_{n=1}^{\infty} Cn(\sin\beta_n x) e^{\frac{S}{2}x} e^{\lambda t}$$

(37) $S < 2$
$$C(x,t) = e^{Sx} + \sum_{n=1}^{\infty} C_n (\sin\beta_n x) e^{\frac{S}{2}x} e^{\lambda t}$$

where

$$A_0 = -\frac{6}{e}$$

$$B_0 = \frac{16\alpha S (\cosh \alpha) e^{-\frac{S}{2}}}{(S^2 - 4\alpha^2)(S - 2 \cosh^2 \alpha)}$$

$$C_n = -\frac{16\beta_n S (\cos \beta_n) e^{-\frac{S}{2}}}{(S^2 + 4\beta_n^2)(S - 2 \cos^2 \beta_n)}$$

and

$$\alpha (\coth \alpha) = \frac{S}{2}$$

$$\beta_n (\cot \beta_n) = \frac{S}{2}$$

$$\lambda = -(\beta_n^2 + \frac{S^2}{4})$$

The solutions were tested by calculating the concentration at $t = 0$. Figure 2 shows the series converging to $C = 1$. For 10 terms the sum is correct within 1.0% for X from 0.0 to 0.9. For $X = 1.0$ $C_0 = .919$.*

----

* For all subsequent calculations the first ten terms were used. Ten significant figures were carried during the computations. All computations were carried out on a Bendix G-15 computer.

DISCUSSION AND APPLICATION OF THE SOLUTION

In order to illustrate the diffusional processes taking place in the tube the changing concentration profile in the tube was plotted for various values of S. These plots are shown in figures 3, 4, and 5. For $S > 0$ the solute enters the tube, for $S < 0$ it leaves the tube. In both cases the first change occurs at X = 1. For S = -20 one can easily see the concentration "wave" move towards the mouth of the tube. This behavior has been observed by Schwarz (1), Mangelsdorf (2), and one of the authors. The experimental conditions of figure 5 are easily obtainable in practice.

In order to determine the error caused by back diffusion it is necessary to calculate the mean concentration in the tube as a function of time. This is done by integrating equations 35, 36 and 37 over the length of the tube. The integrals may be found in any standard table. The results are given below.

$$(38) \quad S = 2 \qquad C_m = \frac{1}{S}\left[e^{S}-1\right] + A_o e^{-t} + \sum_{n=1}^{\infty} \frac{4\beta n}{(S^2+4\beta_n^2)} C_n e^{\lambda t}$$

$$(39) \quad S > 2 \qquad C_m = \frac{1}{S}\left[e^{S}-1\right] + \frac{4\alpha}{(S^2-4\alpha^2)} B_o e^{(\alpha^2 - \frac{S^2}{4})t} + \sum_{n=1}^{\infty} \frac{4\beta n}{(S^2+4\beta_n^2)} C_n e^{\lambda t}$$

$$(40) \quad S < 2 \qquad C_m = \frac{1}{S}\left[e^{S}-1\right] + \sum_{n=1}^{\infty} \frac{4\beta_n}{(S^2+4\beta_n^2)} C_n e^{\lambda t}$$

Plots of the mean concentration versus time are given in figures 6 and 7. The curves all have an initial slope of S. The effect of back diffusion is apparent in the departure of the curves from linearity. From these

curves it is easy to construct plots of the error caused by back diffusion versus the percent change of concentration in the tube. These are shown in figures 8 and 9. It can be seen that one radically decreases the error by running the solute into the tube. For even moderate values of S one can theoretically increase the concentration at the electrode end to extremely high values. In general, solid phases will precipitate out before this happens.

In addition, the errors caused by the chemical analysis of the tube must be considered. One uses the difference in the tube and reservoir compositions to calculate the total solute flux. Therefore, if there is not a large change in concentration, one must subtract two numbers of the same magnitude. For small changes this magnifies the analytical errors considerably. Figure 10 is a plot showing this (see appendix VIII for details of this calculation). By using figures 8, 9, and 10 it is possible to design experiments to minimize the analytical and diffusion errors. These are the two largest sources of error in this technique.

The final application considered is the calculation of ordinary diffusion coefficients. As the solution now stands D appears in both dimensionless constants, i.e. uV/D and $D\Theta/a^2$. By choosing the dimensionless time as uV/a^2 one can construct plots equivalent to figures 6 and 7. These are shown in figures 11 and 12. This leaves the diffusion coefficient in only one of the constants, and eliminates the necessity of a trial and error solution. In order to estimate the diffusion coefficient one makes a series of experiments at progressively longer times. The runs at shorter times should give a constant value for u. This is the true value of the electric mobility. Since

one now knows u, V, a, and the results of an experiment that has gone to the point where back diffusion takes place, one has both the coordinates of figure 11 (or 12) specified. This then determines the value of S from which the diffusion coefficient is calculated. The results of our preliminary experiments are given in table 1 for the Cu-Bi and Ni-Bi systems. The diffusion coefficients show considerable scatter and are approximately an order of magnitude larger than what one would expect. This is undoubtedly due to convection. It is possible the convection is caused by thermal gradients associated with the transfer of the I^2R heat from the tube. All other sources of convection have presumably been eliminated. The diffusion channels were 0.5 and 1.0 mm I.D. thin walled pyrex tubes. The tops of the tubes were kept several degrees hotter than the bottoms. It should be emphasized that convection does not affect the determination of u as long as the experiment is ended before a concentration gradient forms at the mouth of the tube.

At any time during the experiment the change of the mean concentration in the tube is caused only by the sum of the two diffusion fluxes at the mouth of the tube. For this reason the diffusion coefficient calculated by this method is for the reservoir concentration. This method is analogous to the technique described by De Groot (6) for thermal diffusion.

TABLE 1

Observed Diffusion Coefficients in Molten Bismuth*

Cu	τ	Cm	S	$D \times 10^5$ cm^2/sec
	0.48	0.77	0.60	22
	0.44	0.76	0.75	17
	0.53	0.73	0.75	19
Ni	0.47	0.77	0.64	13
	0.61	1.48	1.15	28
	0.99	1.62	1.13	30
Pb				6.2 reference 8
Sn				4.6 reference 8

* All runs made at 500°C and with 0.5 weight percent solute.

CALCULATION OF THE ROOTS OF THE EIGENFUNCTIONS

The roots of the two eigenfunctions (equations 21 and 25) were obtained on the Bendix G-15 digital computer. The half-interval method was used. The first ten roots of equation 25 are given in tables 2 and 3 for various values of S. Equation 21 has just one root for each value of $S > 2$; it has no roots for $S < 2$. The value of this root rapidly approaches $S/2$ as S becomes large. The roots of equation 21 are given in table 4. Tables 2, 3, and 4 are photoduplicates of the original computer output. There has been no intermediate copying of the numbers. Only the first seven of ten decimal places carried in the computer were typed out. The number in the seventh place was not rounded off, so it may be 1×10^{-7} too low in some cases.

Some of these roots are given by Carslaw and Jaeger to four decimal places. A spot comparison showed a few cases of disagreement of one unit in the fourth place. For these cases the function $\beta \cot \beta - S/2$ was calculated for their values and ours. The results were much closer to zero using our roots. For these the function was also calculated using our roots plus and minus 2×10^{-7}. In all cases the function changed sign. We therefore believe our roots to be correct.

TABLE 2

ROOTS OF THE EQUATION   TAN[X] – [2/S]X = 0

	S	1	2	3	4	5
+	100.00	3.2056172	6.4107036	9.6147541	12.8173131	16.0179926
+	50.00	3.2717219	6.5390146	9.6211306	13.0473806	16.2853314
+	20.00	3.4761403	6.8862352	10.2211104	13.4996040	16.7402823
+	15.00	3.5877884	7.0367250	10.3693928	13.6342584	16.8602097
+	10.00	3.7902224	7.2502483	10.5531104	13.7893118	16.9925900
+	9.00	3.8492006	7.3016646	10.5938960	13.8224306	17.0202835
+	8.00	3.9164354	7.3559270	10.6358514	13.8561267	17.0483005
+	7.00	3.9926471	7.4128592	10.6788567	13.8903313	17.0766005
+	6.00	4.0781497	7.4721926	10.7227710	13.9249699	17.1051395
+	5.00	4.1725967	7.5335684	10.7674349	13.9599617	17.1338722
+	4.00	4.2747822	7.5965460	10.8126733	13.9952220	17.1627513
+	3.00	4.3826255	7.6606214	10.8582999	14.0306627	17.1917287
+	2.00	4.4934094	7.7252518	10.9041216	14.0661939	17.2207552
+	1.00	1.1655611	4.6042167	7.7898837	10.9499436	14.1017251
+	0.50	1.3932490	4.6587782	7.8220315	10.9727946	14.1194627
+	0.10	1.5383044	4.7017550	7.8476103	10.9910251	14.1336292
+	0.05	1.5547176	4.7070778	7.8507972	10.9933001	14.1353983
+	0.01	1.5676067	4.7113277	7.8533449	10.9951195	14.1368132
–	0.01	1.5739729	4.7134497	7.8546182	10.9960289	14.1375206
–	0.05	1.5865524	4.7176881	7.8571634	10.9978474	14.1389351
–	0.10	1.6019972	4.7229751	7.8603425	11.0001196	14.1407028
–	0.50	1.7155071	4.7648089	7.8856740	11.0182600	14.1548269
–	1.00	1.8365972	4.8158423	7.9170526	11.0408298	14.1724320
–	2.00	2.0287578	4.9131804	7.9786657	11.0855384	14.2074367
–	3.00	2.1746260	5.0036452	8.0384627	11.1295434	14.2421016
–	4.00	2.2889297	5.0869850	8.0961635	11.1727058	14.2763529
–	5.00	2.3806444	5.1633054	8.1515643	11.2149058	14.3101229
–	6.00	2.4556438	5.2329384	8.2045313	11.2560430	14.3433507
–	7.00	2.5179545	5.2963423	8.2549929	11.2960368	14.3759824
–	8.00	2.5704315	5.3540318	8.3029291	11.3348255	14.4079711
–	9.00	2.6151525	5.4065327	8.3483619	11.3723648	14.4392772
–	10.00	2.6536624	5.4543537	8.3913455	11.4086265	14.4698680
–	15.00	2.7859313	5.6385305	8.5727360	11.5706762	14.6113962
–	20.00	2.8627725	5.7605579	8.7083138	11.7026780	14.7334723
–	50.00	3.0213230	6.0459048	9.0765155	12.1151150	15.1627701
–	100.00	3.0800690	6.1605913	9.2420008	12.3246945	15.4090185

TABLE 3

ROOTS OF THE EQUATION   Tan[X] − [2/S]X = 0

S	±	6	7	8	9	10
100.00	+	19.2164807	22.4125469	25.6060382	28.7968724	31.9850272
50.00	+	19.5122876	22.7290015	25.9365234	29.1359838	32.3284680
20.00	+	19.9558194	23.1542562	26.3407046	29.5184941	32.6898572
15.00	+	20.0626079	23.2499016	26.4270081	29.5969499	32.7616747
10.00	+	20.1774438	23.3510065	26.5171686	29.6782238	32.8356100
9.00	+	20.2011714	23.3717323	26.5355518	29.6947324	32.8505862
8.00	+	20.2250979	23.3925884	26.5540253	29.7113060	32.8656107
7.00	+	20.2491969	23.4135576	26.5725767	29.7279352	32.8806767
6.00	+	20.2734415	23.4346216	26.5911932	29.7446115	32.8957773
5.00	+	20.2978034	23.4557621	26.6098623	29.7613253	32.9109058
4.00	+	20.3222538	23.4769601	26.6285710	29.7780673	32.9260552
3.00	+	20.3467635	23.4981967	26.6473060	29.7948283	32.9412186
2.00	+	20.3713029	23.5194525	26.6660542	29.8115987	32.9563890
1.00	+	17.2497818	20.3958423	23.5407082	26.6848024	29.8283692
0.50	+	17.2642798	20.4081028	23.5513301	26.6941724	29.8367514
0.10	+	17.2758653	20.4179034	23.5598226	26.7016650	29.8434548
0.05	+	17.2773126	20.4191279	23.5608838	26.7026013	29.8442925
0.01	+	17.2784702	20.4201073	23.5617326	26.7033503	29.8449626
0.01	−	17.2790489	20.4205970	23.5621571	26.7037248	29.8452977
0.05	−	17.2802063	20.4215764	23.5630058	26.7044737	29.8459678
0.10	−	17.2816528	20.4228004	23.5640667	26.7054098	29.8468054
0.50	−	17.2932151	20.4325870	23.5725500	26.7128960	29.8535042
1.00	−	17.3076405	20.4448034	23.5831433	26.7222463	29.8618724
2.00	−	17.3363779	20.4691674	23.6042847	26.7409160	29.8785865
3.00	−	17.3649267	20.4934161	23.6253509	26.7595337	29.8952633
4.00	−	17.3932439	20.5175229	23.6463238	26.7780870	29.9118938
5.00	−	17.4212891	20.5414616	23.6671861	26.7965638	29.9284692
6.00	−	17.4490243	20.5652079	23.6879210	26.8149521	29.9449807
7.00	−	17.4764146	20.5887383	23.7085125	26.8332405	29.9614200
8.00	−	17.5034282	20.6120311	23.7289453	26.8514179	29.9777788
9.00	−	17.5300362	20.6350660	23.7492049	26.8694738	29.9940492
10.00	−	17.5562132	20.6578243	23.7692776	26.8873980	30.0102236
15.00	−	17.6799601	20.7669265	23.8664224	26.9747260	30.0894095
20.00	−	17.7908353	20.8672381	23.9573676	27.0575502	30.1652365
50.00	−	18.2197675	21.2858232	24.3603021	27.4423964	30.5312497
100.00	−	18.4952593	21.5836396	24.6743180	27.7673940	30.8629136

TABLE 4

ROOTS OF THE EQUATION   TANH[X] - [2/S]X = 0

S	ROOT
+ 3.0	1.2878394
+ 4.0	1.9150080
+ 5.0	2.4640596
+ 6.0	2.9847045
+ 7.0	3.4935397
+ 8.0	3.9568430
+ 9.0	4.4988869
+ 10.0	4.9995456
+ 15.0	7.4999954
+ 20.0	9.9999999

LIST OF SYMBOLS

a   Length of diffusion tube   cm

α Defined by the relation $\alpha^2 = \lambda + S^2/4$ $(S > 2)$

β Defined by the relation $-\beta^2 = \lambda + S^2/4$

C   Dimensionless concentration N/N_o

D   Ordinary diffusion coefficient cm^2/sec

D'   Thermal diffusion coefficient $cm^2/sec \; ^oC$

$\overline{E}$ Elastic field strength vector   volts/cm

$\overline{J}$ Mass flux vector $grams/cm^2 sec$

λ Separation of variables constant

N   Concentration $grams/cm^3$

N_o Initial concentration $grams/cm^3$

S   Dimensionless solute velocity uV/D

Θ Time   sec.

T   Temperature ^oC

t   Dimensionless time $D\Theta/a^2$

τ Dimensionless time $uV\Theta/a^2$

u   Electrical mobility $cm^2/sec \; volt$

v   Sedimentation velocity   cm/sec

V   Voltage drop across tube   volts

X   Dimensionless distance Z/a

Z   Distance   cm

LITERATURE

1. Schwarz, K., Elektrolytische Wanderung in flussigen und festen Metallen. J. A. Barth, Leipzig, 1940.

2. Mangelsdorf, P., J. Chem. Phys. 30, 1170 (1959).

3. Furth, R., Z. Physik. 40, 351 (1926).

4. Furth, R., Z. Physik. 45, 83 (1927).

5. De Groot, S. R., Physica, 9, 699 (1942).

6. De Groot, S. R., L'effect Soret, Thesis, Amsterdam, (1945).

7. Carslaw, H. S., and J. C. Jaeger, Conduction of Heat in Solids, Oxford University Press, (1959).

8. Niwa, K. et. al., J. Metals, 9, 96 (1957).

DIFFUSION TUBE CAN BE
LIFTED FROM RESERVOIR.

RESERVOIR
ELECTRODE

ELECTRODE SEALED INTO
DIFFUSION TUBE

RESERVOIR OF LIQUID METAL

GLASS DIFFUSION TUBE
FILLED WITH LIQUID METAL
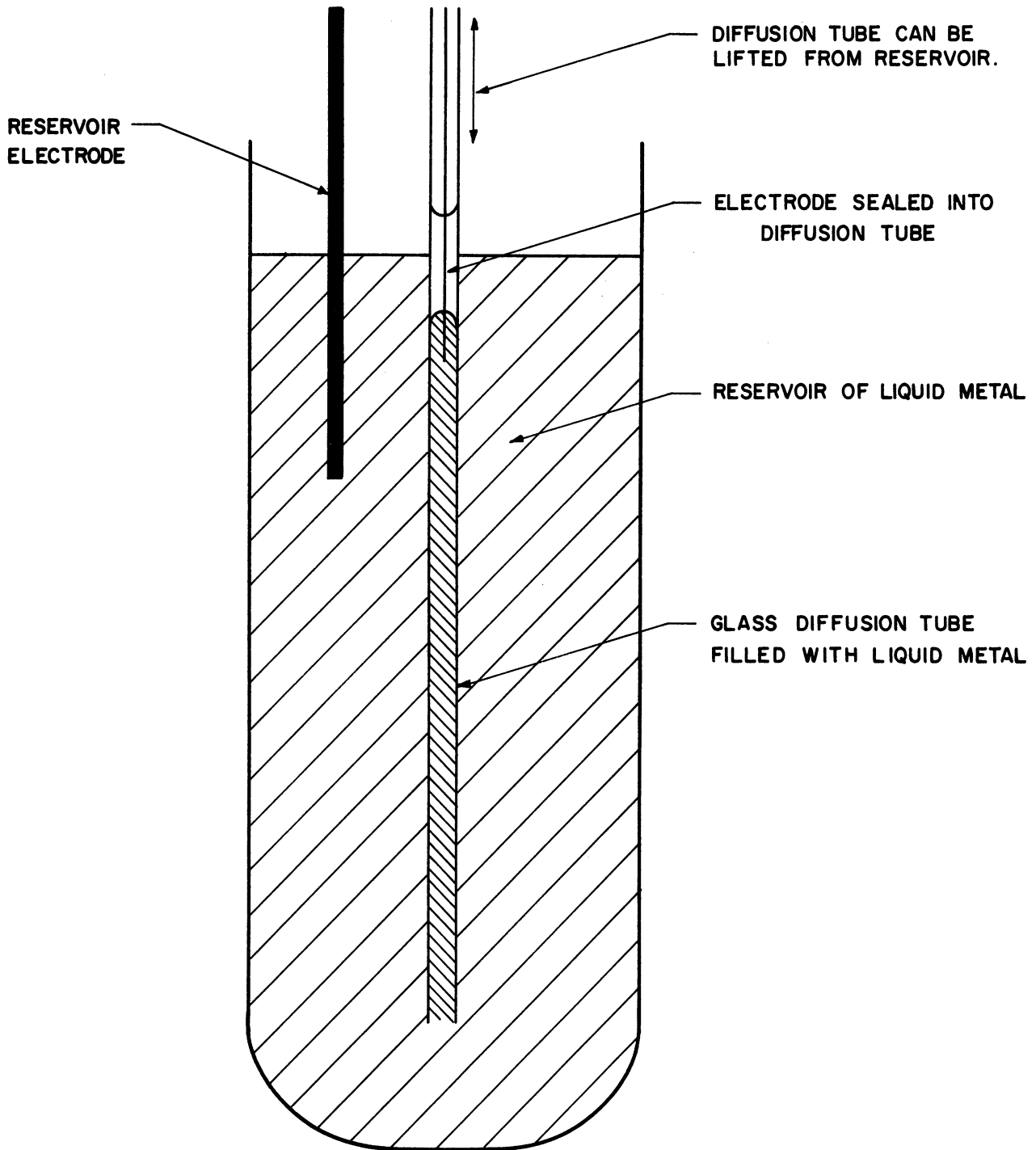
Fig. 1. Cell for electrodiffusion experiments.
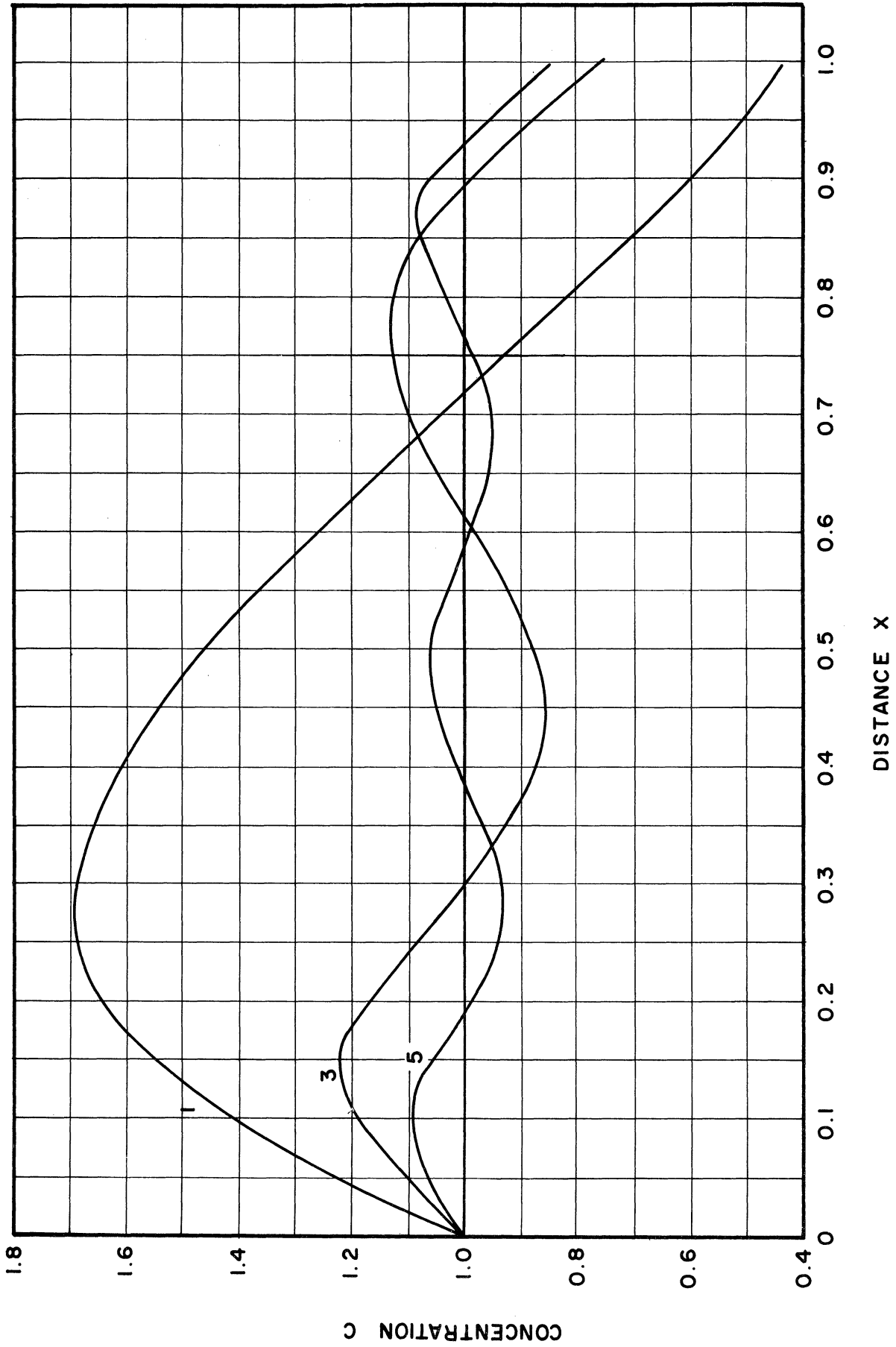
Fig. 2. Convergence to initial condition for S = .4 using 1,3,5 terms of the series.
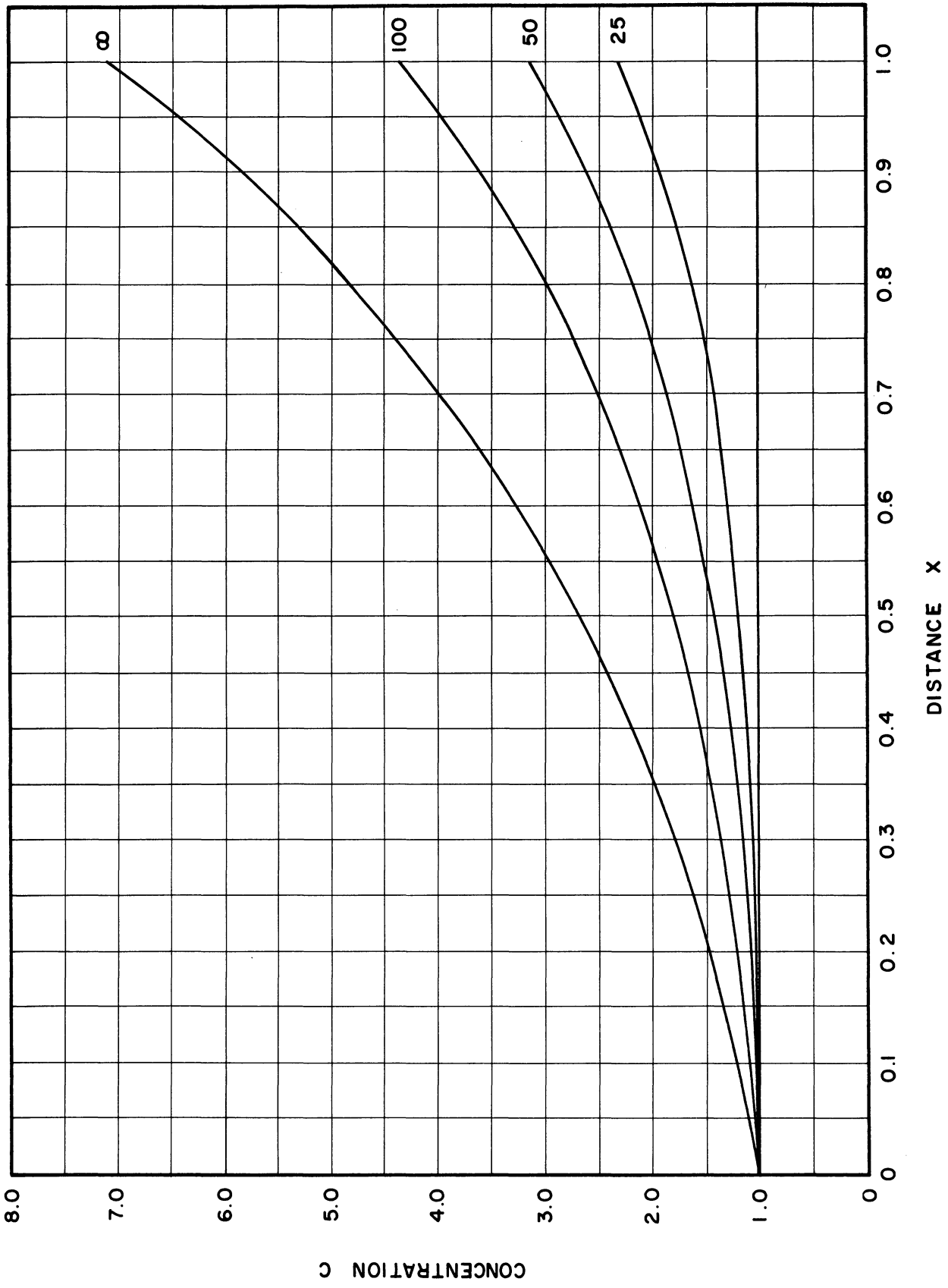
Fig. 3. Concentration distribution. Parameters of time in hours. $S = +1.96$, $D/a^2 = 0.0072$ sec^{-1}.
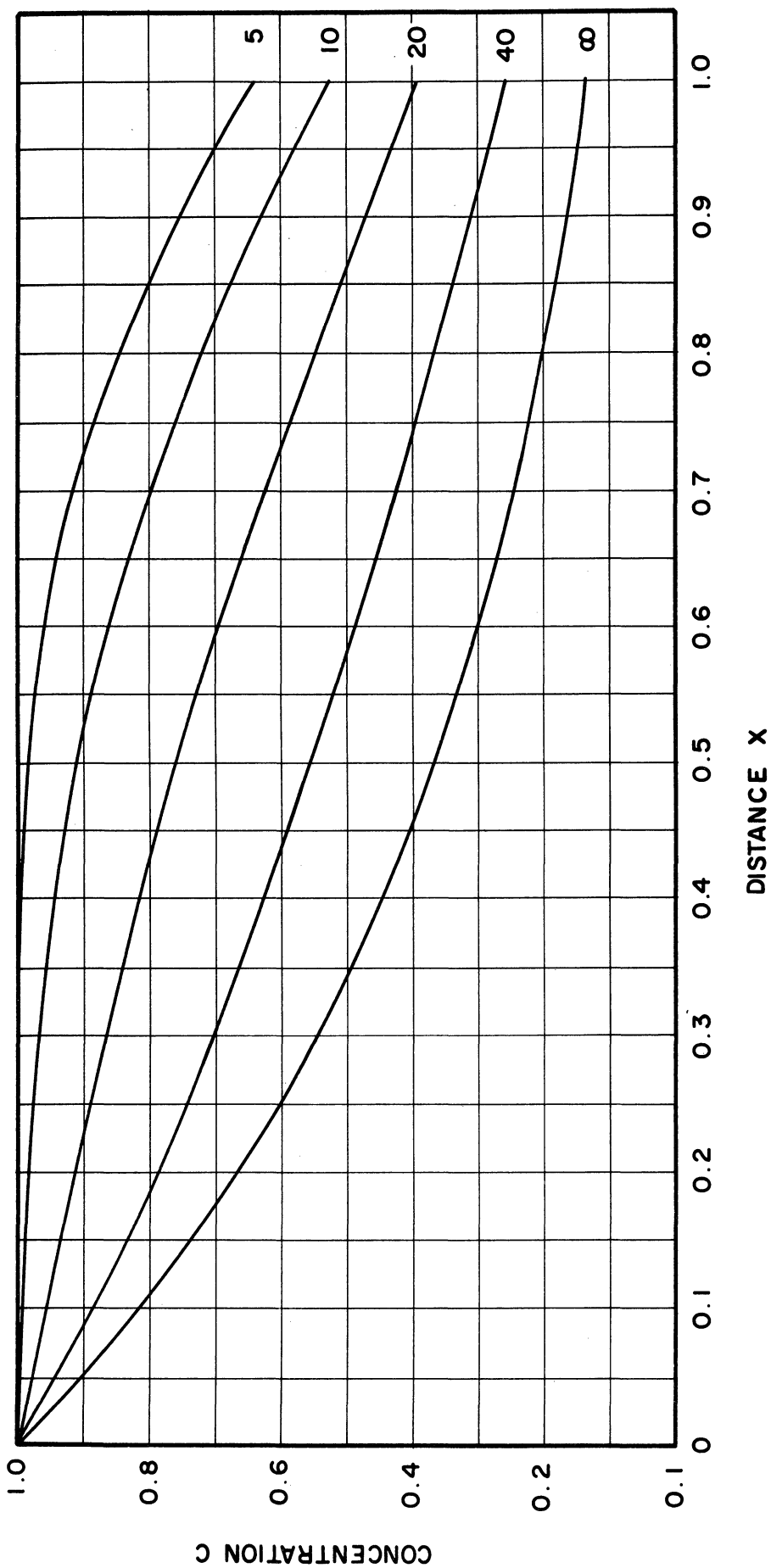
Fig. 4. Concentration distribution. Parameters of time in hours. S = -2.00, $D/a^2 = 0.0072$ sec^{-1}
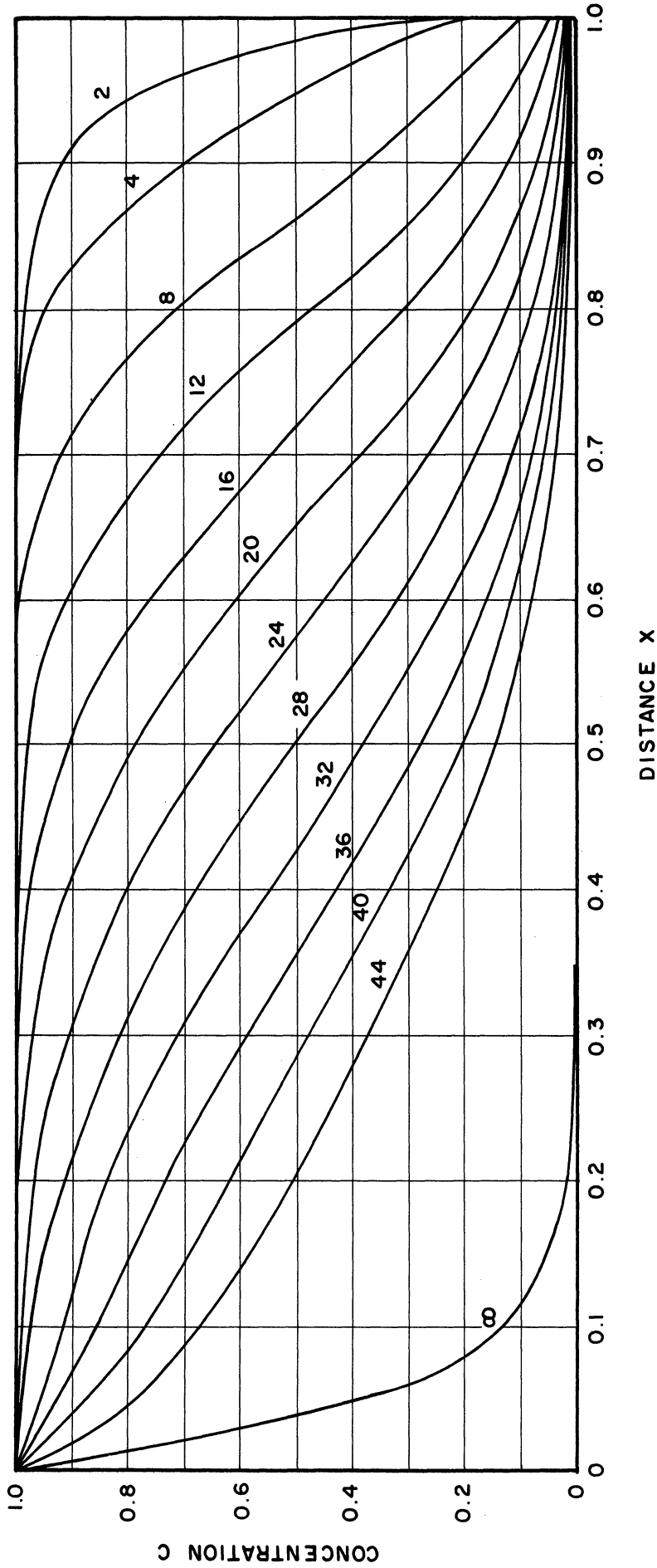
Fig. 5. Concentration distribution. Parameters of time in hours. $S = -20$, $D/a^2 = 9 \times 10^{-4}$ sec^{-1}. Corresponds to the following:

$u = 5 \times 10^{-4}$ cm^2/sec-volt $a = 10$ cm

$D = 2.5 \times 10^{-5}$ cm^2/sec $E = 0.1$ volt/cm
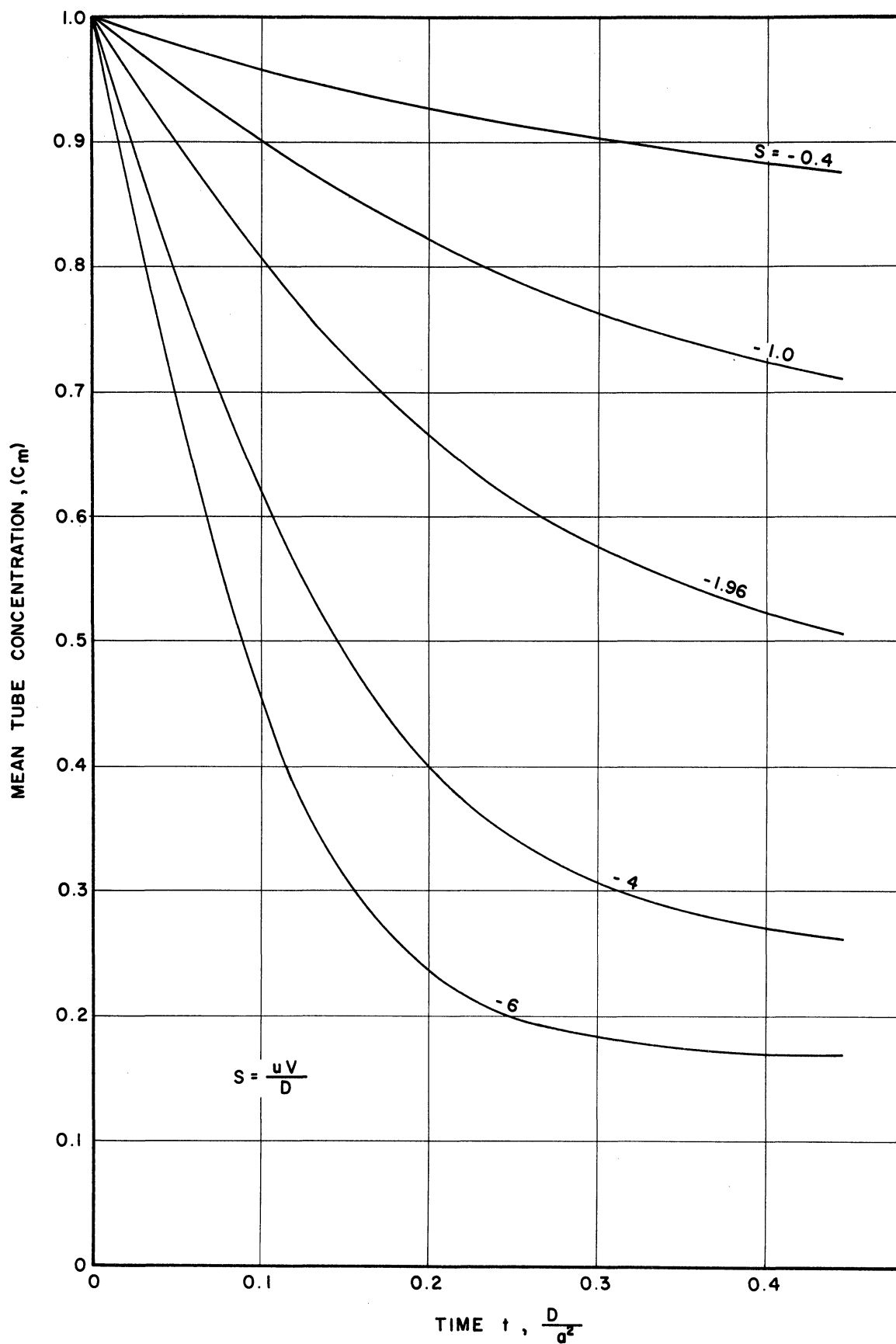
Fig. 6. Mean tube concentration versus dimensionless time. Parameters of S.
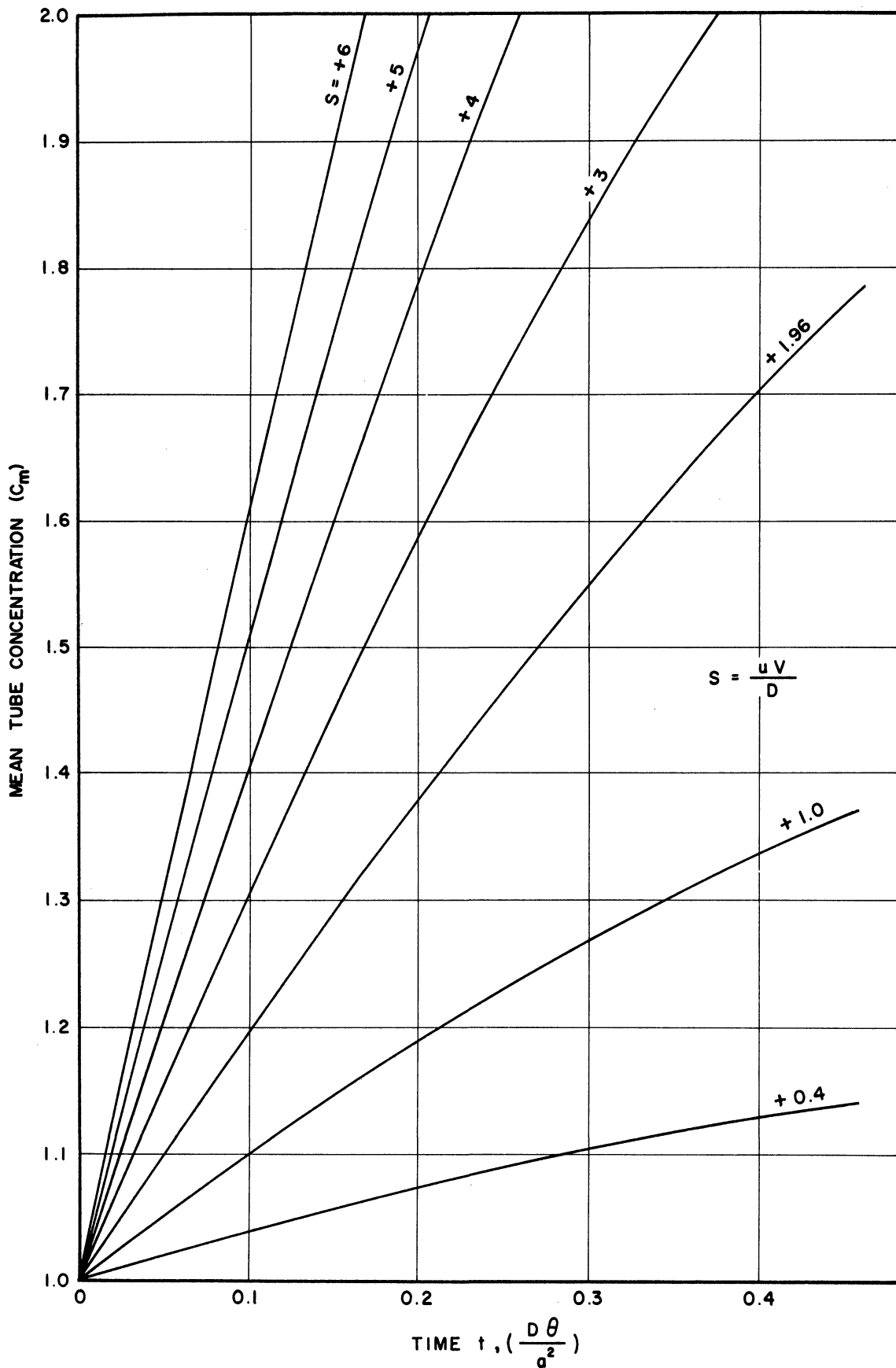
Fig. 7. Mean tube concentration versus dimensionless time. Parameters of S.
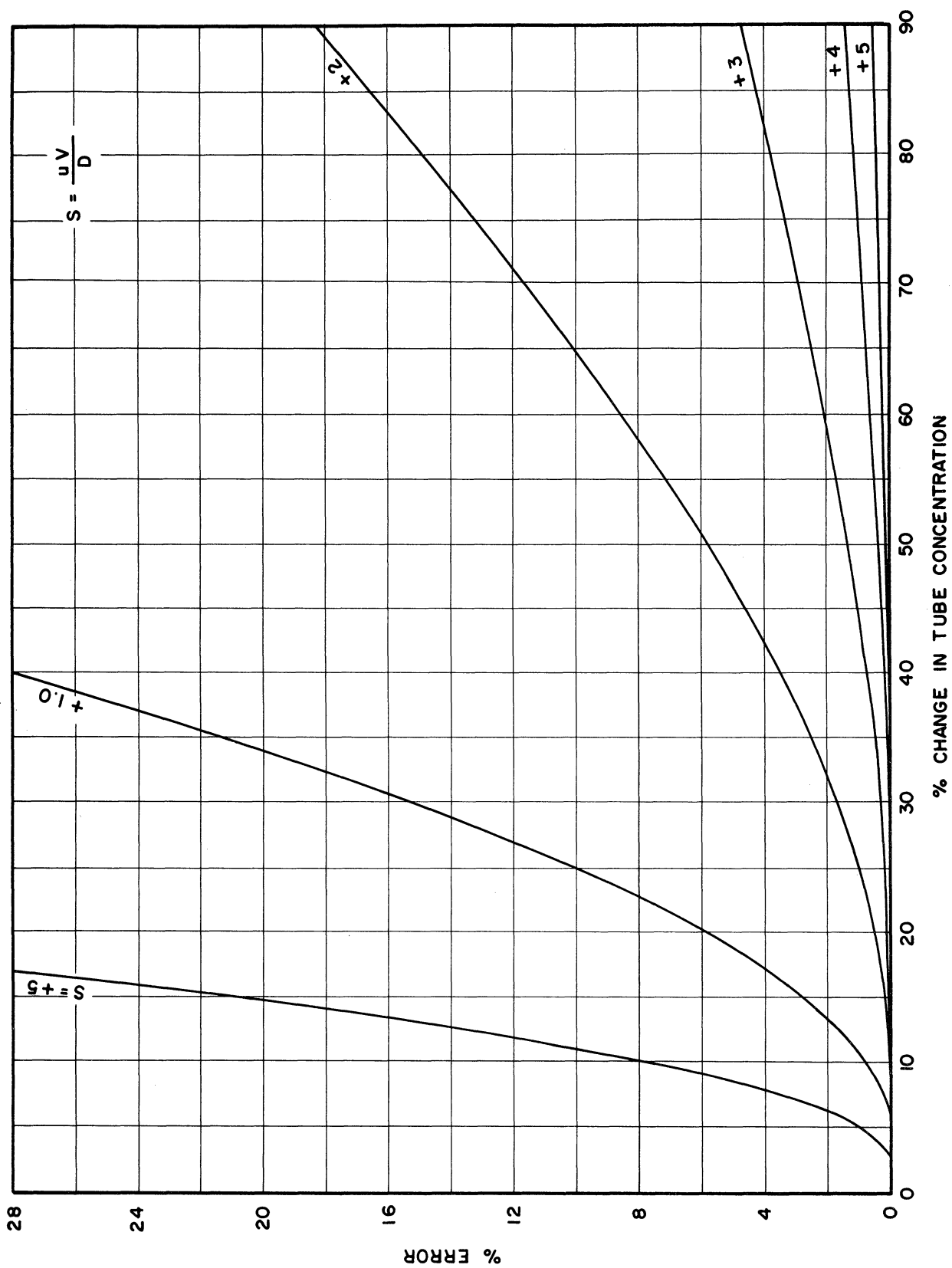
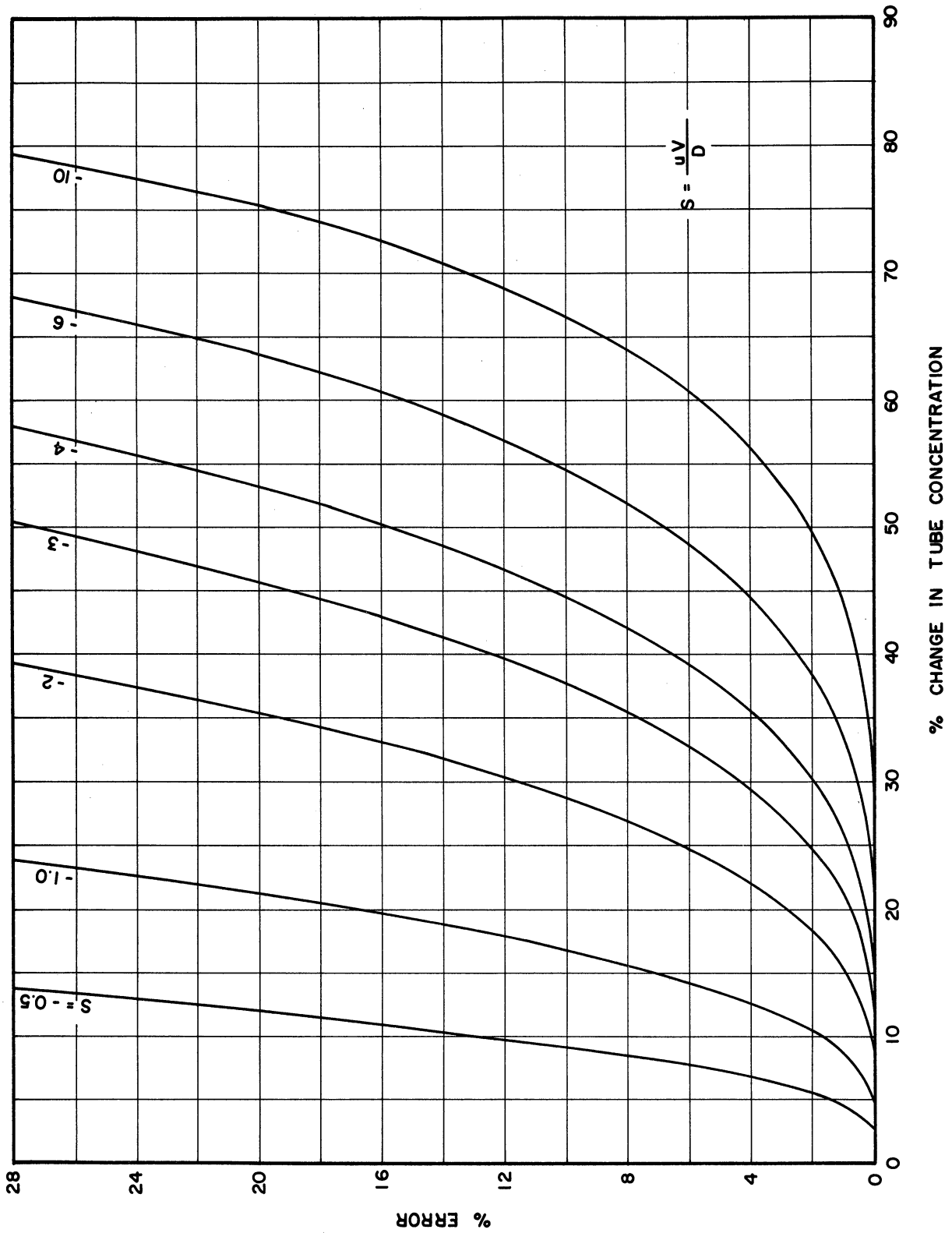Fig. 8. Percent error in mobility versus percent change in tube concentration.

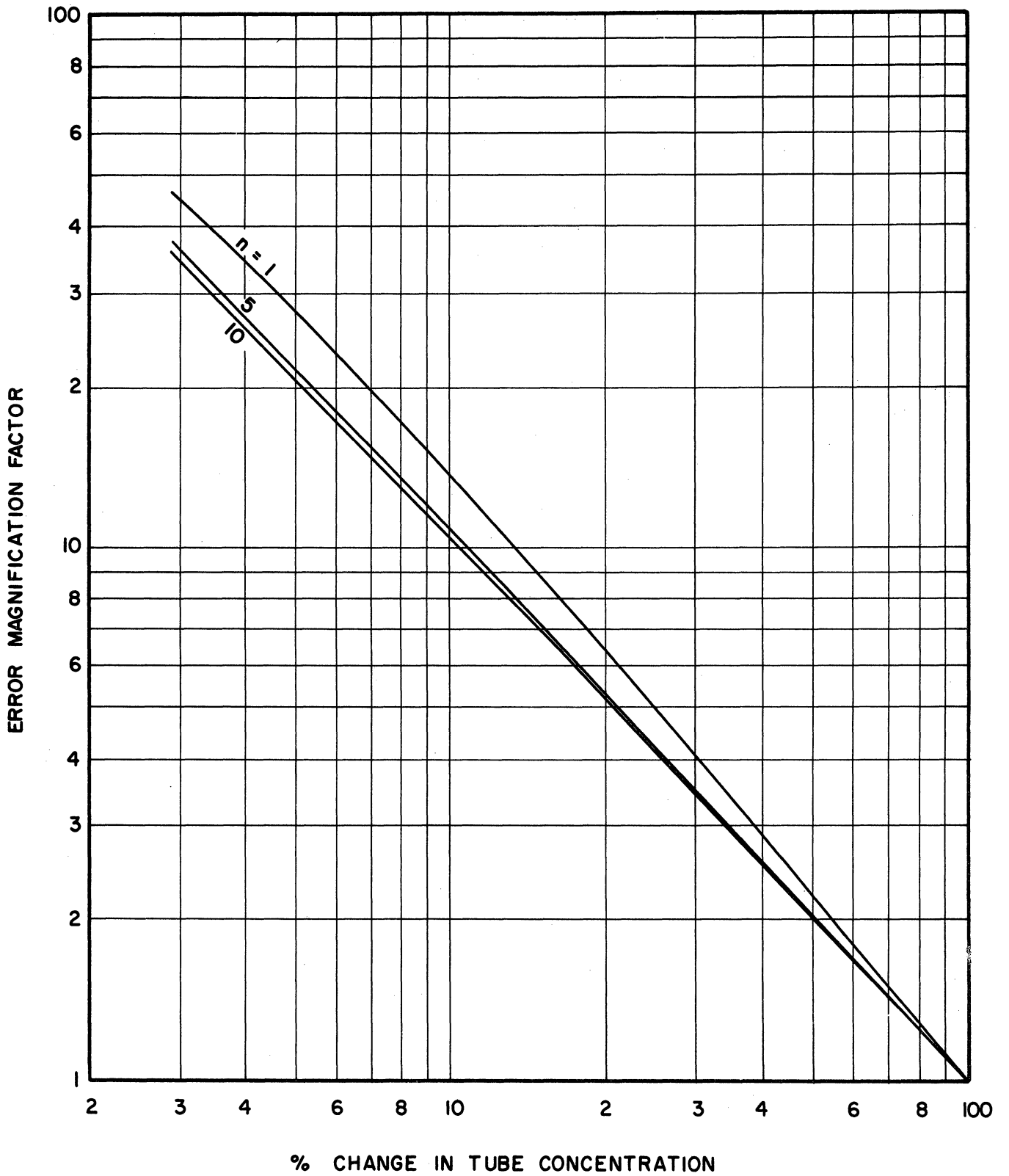Fig. 9. Percent error in mobility versus percent change in tube concentration.
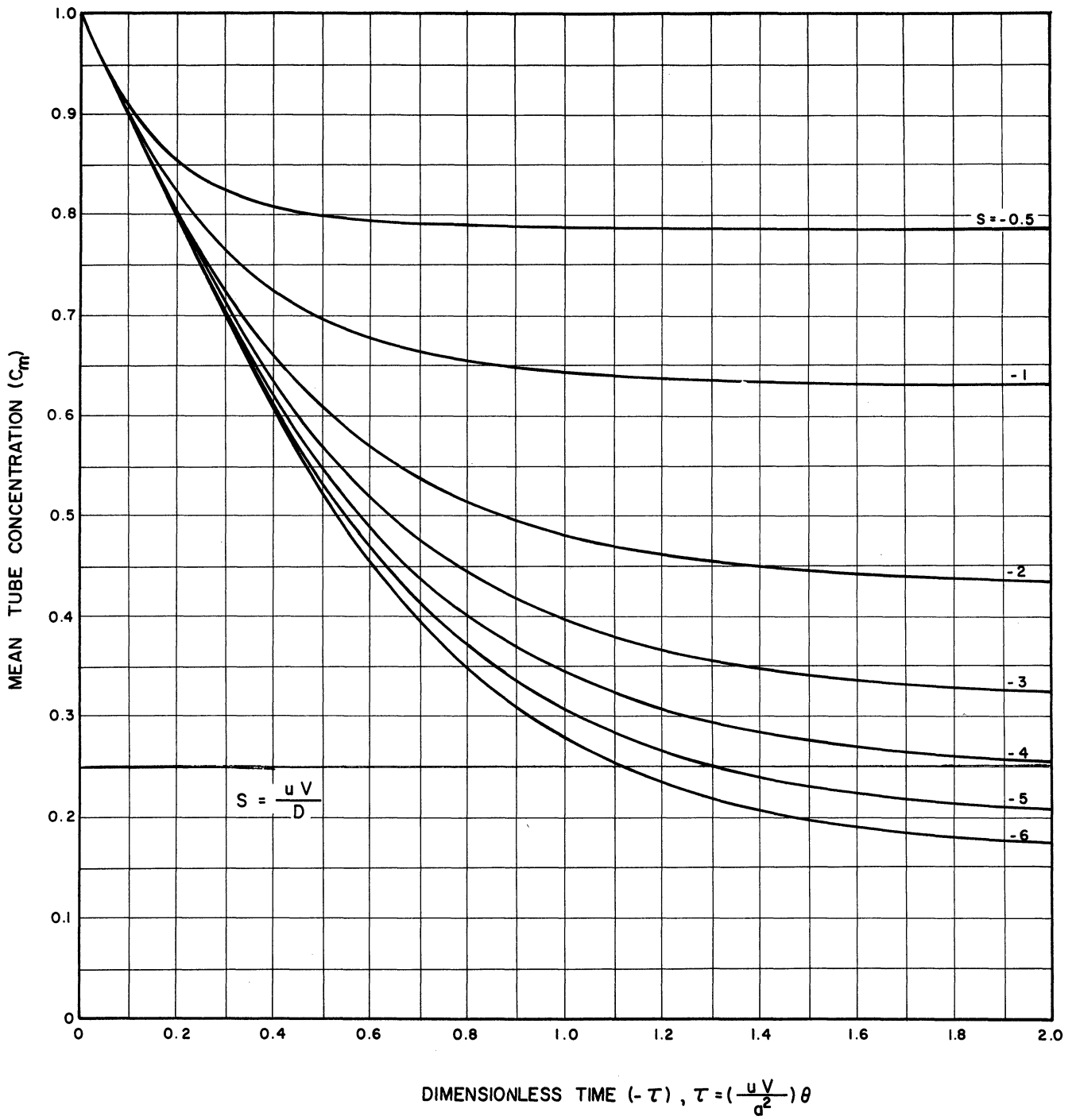
Fig. 10. Error magnification in mobility calculation.

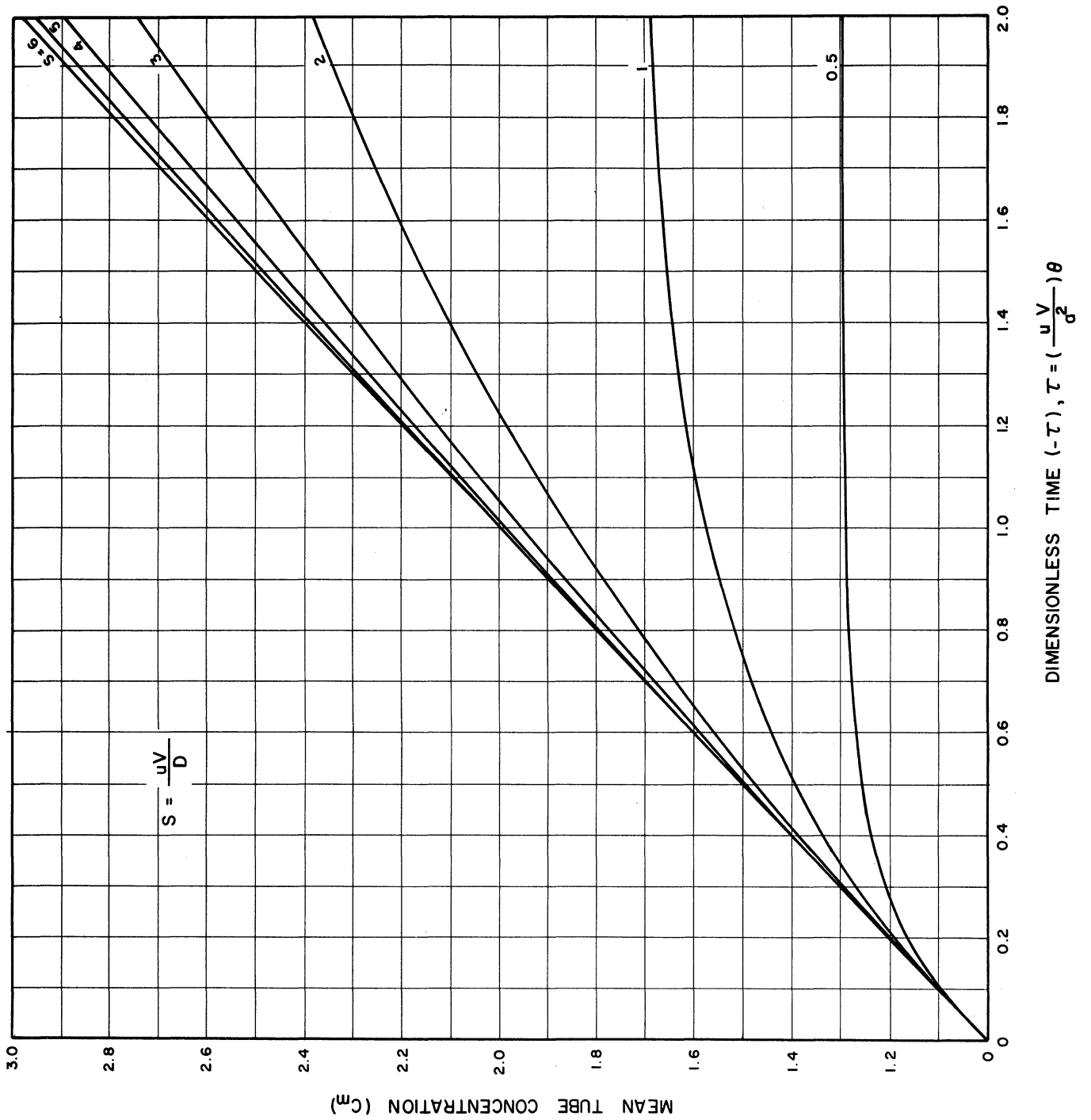Fig. 11. Mean tube concentration versus dimensionless time.
Parameters of S.

Fig. 12. Mean tube concentration versus dimensionless time.
Parameters of S.

Appendix I

Prove the orthogonality of the xe^x term. The weight function for this Sturm Lioville system is e^{-Sx}. The following integral must therefore vanish.

$$I = \int_0^1 e^{-2x}(xe^x)(\sin\beta x)e^x dx$$

$$I = \frac{1}{\beta^2}\left[\sin\beta x - \beta x \cos\beta x\right]_0^1$$

$$I = \frac{1}{\beta^2}\left[\sin\beta - \beta\cos\beta\right]$$

but for $S = 2$ $\sin\beta = \beta\cos\beta$.

$$I = 0$$

Q.E.D.

Appendix II

Prove the orthogonality of $(\sinh \alpha x)e^{(S/2)x}$

$$I = \int_0^1 e^{-Sx}(\sinh\alpha x)e^{(S/2)x}(\sin \beta x)e^{(S/2)x}dx$$

$$I = \frac{1}{2}\int_0^1 e^{\alpha x}\sin\beta x\,dx - \frac{1}{2}\int_0^1 e^{-\alpha x}\sin\beta x\,dx$$

$$I = \frac{\beta}{2}\left\{\left[\frac{e^{\alpha x}}{\alpha^2+\beta^2}\right]\left[\frac{\alpha}{\beta}\sin \beta x - \cos\beta x\right]_0^1 - \left[\frac{e^{-\alpha x}}{\alpha^2+\beta^2}\right]\left[\frac{\alpha}{\beta}\sin\beta x - \cos\beta x\right]_0^1\right\}$$

$$I = \left[\frac{\beta}{\alpha^2+\beta^2}\right]\left[\frac{\alpha}{\beta}\sin \beta \cosh \alpha - \cos \beta \sinh \alpha\right]$$

substituting

$$\beta \cos \beta = (S/2)(\sin \beta)$$

$$\alpha \cosh \alpha = (S/2)(\sinh \alpha)$$

$$I = 0$$

Q.E.D.

Appendix III

Prove the orthogonality of the $(\sin \beta x)\, e^{(S/2)x}$ terms.

$$I = \int_0^1 e^{-Sx}(\sin \beta_m x)e^{(S/2)x}(\sin \beta_n x)e^{(S/2)x}\,dx$$

$$I = \int_0^1 \sin \beta_m x \sin \beta_n x \, dx$$

$$I = \left[\frac{\sin(\beta_m-\beta_n)x}{2(\beta_m - \beta_n)} - \frac{\sin(\beta_m + \beta_n)x}{2(\beta_m + \beta_n)}\right]_0^1$$

$$I = \frac{\sin \beta_m \cos \beta_n - \cos \beta_m \sin \beta_n}{2(\beta_m - \beta_n)} - \frac{\sin \beta_m \cos \beta_n + \sin \beta_n \cos \beta_m}{2(\beta_m + \beta_n)}$$

$$I = \frac{1}{(\beta_m - \beta_n)^2}\left[\beta_n \sin \beta_m \cos \beta_n - \beta_m \sin \beta_n \cos \beta_m\right]$$

but $\beta \cos \beta = \left(S/2\right)\sin \beta$

$$I = 0$$

Q.E.D.

Appendix IV

Calculate the coefficient for the term xe^x. Denote the coefficient by A_0

$$A_0 = \frac{\int_0^1 e^{-2x}(xe^x)(1-e^{2x})\, dx}{\int_0^1 e^{-2x}(xe^x)^2\, dx}$$

$$A_0 = \frac{\int_0^1 xe^{-x}dx - \int_0^1 xe^x dx}{\int_0^1 x^2 dx}$$

$$A_0 = \left[\frac{-e^{-x}(x+1)-e^x(x-1)}{\dfrac{x^3}{3}} \right]_0^1$$

$$A_0 = -6/e$$

Appendix V

Calculate the coefficient of the $(\sinh \alpha x)e^{(S/2)x}$ term. Denote the coefficient by B_O

$$B_O = \frac{\int_0^1 e^{-Sx}(\sinh \alpha x)e^{(S/2)x}(1-e^{Sx})\ dx}{\int_0^1 e^{-Sx}(\sinh^2 \alpha x)e^{Sx}\ dx}$$

First evaluate the numerator, N.

$$N = \int_0^1 e^{-(S/2)x} \sinh \alpha x\ dx - \int_0^1 e^{(S/2)x} \sinh \alpha x\ dx$$

$$N = -2 \int_0^1 (\sinh \alpha\ x)(\sinh S/2\ x)\ dx$$

$$N = -\left[\frac{\sinh (\alpha + S/2)x}{(\alpha + S/2)} - \frac{\sinh (\alpha - S/2)x}{(\alpha - S/2)}\right]_0^1$$

$$N = \left(\frac{8\ \alpha\ \cosh \alpha}{4\ \alpha^2 - S^2}\right) e^{-S/2}$$

Now evaluate the denominator, D.

$$D = \int_0^1 \sinh^2 \alpha x\ dx$$

$$= \frac{1}{\alpha}\left[\frac{\sinh 2\alpha x}{4} - \frac{\alpha x}{2}\right]_0^1$$

$$D = \frac{1}{\alpha}\left[\frac{\sinh 2\alpha}{4} - \frac{\alpha}{2}\right]$$

Combining N and D and simplifying one has

$$B_o = \frac{16\,\alpha\,S(\cosh\alpha)\,e^{-S/2}}{(S^2-4\alpha^2)(S - 2\cosh^2\alpha)}$$

Appendix VI

Calculate the coefficients of the $(\sin \beta x)e^{(S/2)x}$ terms.

$$Cn = \frac{\int_{o}^{1} e^{-Sx}(\sin \beta n x)e^{(S/2)x}(1-e^{Sx})dx}{\int_{o}^{1} e^{-Sx}(\sin^2 \beta n x)e^{Sx} dx}$$

$$Cn = \frac{\int_{o}^{1}(\sin \beta n x)e^{-(S/2)x}dx - \int_{o}^{1}(\sin \beta n x)e^{(S/2)x}dx}{\int_{o}^{1}\sin^2 \beta n \, x \, dx}$$

Evaluate the first integral in the numerator, N_1.

$$N_1 = \int_{o}^{1}(\sin \beta n \, x)e^{-(S/2)x} \, dx$$

$$N_1 = -\frac{\beta n \, e^{-(S/2)x}}{\frac{S^2}{4} + \beta n^2}\left[\frac{S}{2\beta n}\sin \beta n \, x + \cos \beta n \, x\right]_{o}^{1}$$

$$N_1 = -\frac{\beta n}{\frac{S^2}{4} + \beta n^2}\left[e^{-S/2}(\frac{S}{2\beta n}\sin \beta n + \cos \beta n) - 1\right]$$

Evaluate the second integral in the numerator, N_2.

$$N_2 = -\int_{o}^{1}(\sin \beta n \, x) \, e^{(S/2)x} \, dx$$

$$= -\left[\frac{\beta n}{\frac{S^2}{4} + \beta n^2}\right]e^{(S/2)x}\left[\frac{S}{2\beta n}\sin \beta n \, x - \cos \beta n \, x\right]_{o}^{1}$$

Using the relation $\beta n \cos \beta n = \dfrac{S}{2} \sin \beta n$

$$N_2 = -\frac{\beta n}{\dfrac{S^2}{4} + \beta n^2}$$

Evaluate the denominator, D.

$$D = \int_0^1 \sin^2 \beta n \, x \, dx$$

$$D = \frac{1}{\beta n} \left[\frac{\beta n \, x}{2} \qquad \frac{\sin \beta n \, x \cos \beta n \, x}{2} \right]_0^1$$

$$D = \frac{\beta n - \sin \beta n \cos \beta n}{2 \, \beta n}$$

Combine N_1, N_2, and D and simplify

$$Cn = \frac{-16S \, \beta n \cos \beta n \, e^{-(S/2)}}{(S-2 \cos^2 \beta n)(S^2 + 4 \, \beta n^2)}$$

Appendix VII

Show that for $\lambda + \frac{s^2}{4} > 0$ the condition $\lambda < 0$ is fulfilled. Suppose that $\lambda > 0$. Then one has

$$\alpha^2 = \lambda + \frac{s^2}{4}$$

$$\lambda = \alpha^2 - s^2/4$$

so $\alpha > s/2$

However for $\alpha > 0$ one has

$$\coth \alpha > 1$$

Therefore

$$\alpha \coth \alpha > s/2$$

This is a contradiction so therefore $\lambda < 0$.

Appendix VIII

In this method the mobility is determined by an equation of the form,

$$u = -k \left[\frac{m_o - m_f}{m_o} \right] = -k \left[1 - \frac{m_f}{m_o} \right]$$

where m_f = final mass of solute in tube
m_o = original mass of solute in tube
k = constant

Normally one makes several determinations of m_o and only one of m_f. Since the dependent errors in m_o and m_f tend to cancel each other they are ignored. The relation between the standard deviations of m_o, m_f, and u is given by

$$s_u{}^2 = \frac{s_{m_o}{}^2}{n} \left(\frac{\partial u}{\partial m_o} \right)^2 + s_{m_f}{}^2 \left(\frac{\partial u}{\partial m_f} \right)^2$$

where n = no. of determinations of m_o.

Assuming $s_{m_o} = s_{m_f}$,

$$s_u{}^2 = s_m{}^2 \left[\frac{1}{n} \left(\frac{\partial u}{\partial m_o} \right)^2 + \left(\frac{\partial u}{\partial m_f} \right)^2 \right]$$

$$\frac{\partial u}{\partial m_f} = k \left(\frac{1}{m_o} \right)$$

$$\frac{\partial u}{\partial m_o} = -k \left(\frac{m_f}{m_o{}^2} \right)$$

$$s_u^2 = s_m^2 k^2 \left[\frac{1}{n}\left(\frac{m_f}{m_o^2}\right)^2 + \frac{1}{m_o^2} \right]$$

$$S_u = S_m\left(\frac{k}{m_o}\right)\left[1 + \frac{1}{n}\left(\frac{m_f}{m_o}\right)^2\right]^{\frac{1}{2}}$$

Let $\mathcal{E}_m$ equal the fractional error of the chemical analysis. Then $N S_m = \mathcal{E}_m m_o$, where N is the number of standard deviations corresponding to the chosen confidence level. The fractional error in the mobility $(\mathcal{E}_u)$ at the confidence level of the chemical analysis is then,

$$\mathcal{E}_u = \frac{Ns_u}{u} = \frac{\mathcal{E}_m m_o \left(\frac{k}{m_o}\right)\left[1 + \frac{1}{n}\left(\frac{m_f}{m_o}\right)^2\right]^{\frac{1}{2}}}{k\left[\frac{m_f}{m_o} - 1\right]}$$

$$\mathcal{E}_u = \mathcal{E}_m \frac{\left[1 + \frac{1}{n}\left(\frac{m_f}{m_o}\right)^2\right]^{\frac{1}{2}}}{\left[\frac{m_f}{m_o} - 1\right]}$$

The coefficient of $\mathcal{E}_m$ is the factor of error magnification introduced in the calculation of the mobility.