y_r = mole fraction of adsorbate in bulk stream if radial gradient exists (See Figure 1)
z = axial position along bed, ft.
z_E = length of bed, ft.

Greek Letters

α = intraparticle void fraction, cu.ft./cu.ft. of bed
β = coefficient in loading function, 1/lb./sq.in.abs.
γ = coefficient in loading function, $1/(\text{lb./sq.in.abs.})^2$
ϵ = external void fraction, cu.ft./cu.ft. of bed
ρ_a = bulk density of adsorbent, lb./cu.ft. of bed
ρ_p = gas density in pores, lb.-mole/cu.ft.
ρ = gas density in bulk stream, lb.-mole/cu.ft.
ρ_F = density of feed gas, lb.-mole/cu.ft.
σ = solid fraction of bed, cu.ft./cu.ft. of bed

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Frequency Response of Gas Mixing in a Fluidized-Bed Reactor

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Frequency response methods were used to compare dynamic models for gas mixing and first-order reaction in a fluidized-bed reactor and for the experimental determination of interphase transfer characteristics. Theoretical predictions of frequency response characteristics were derived for two models based on the two-phase theory of fluidization. Experimental frequency response for a 1-ft. high bed were correlated better by a model based on perfect mixing in the dense phase than by a model based on plug flow in the dense phase. Excellent correlation was also obtained by a simple empirical model.

In recent years, there have been significant advances in understanding the nature of the fluidized state which have resulted in a plausible physical picture of fluidization embodied by the two-phase theory of fluidization. An excellent treatment of this theory and the experiments in support of it has been presented in a recent book by Davidson and Harrison (*2*). Several two-phase models have been presented in the literature to explain gas mixing and reaction kinetics in fluidized beds (*6* to *9*, *11*, *13*). In these models, mass transfer between the bubble and dense phases was accounted for in terms of an empirical interchange coefficient. The models differ mainly in the degree of mixing that is attributed to the dense phase; however, the two extremes of plug flow and complete mixing in the dense phase have not as yet been experimentally distinguishable.

It has not been possible to place great confidence on empirical correlations of interchange coefficients. Davidson and Harrison have developed a theory that can be used to predict interchange coefficients from bubble size, but this theory is presently of limited usefulness due to a lack of an empirical or theoretical method for predicting bubble size (*2*). Interchange coefficients have been determined experimentally from steady state measurements of a first-order reactions (*6* to *8*, *10* to *12*) and from step response mixing experiments with a tracer gas (*3*, *5*, *9*).

A more demanding test of the two-phase mixing models is to use them to predict the frequency response over a wide range of frequencies. The distinguishing features of such predictions can then be used for comparison of mod-

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els and determination of interchange coefficients.

UNSTEADY STATE MATERIAL BALANCES AND TRANSFER FUNCTIONS

The mixing models presented here are substantially the same as those of Orcutt et al. *(10)* but are extended to include the unsteady state response. The bubble phase material balance per unit volume of bed is written for a differential slice of cross section.

$$V_b \frac{\partial C_b}{\partial t} = q_b\,(C_d - C_b) - V_b u_b \frac{\partial C_b}{\partial z} \qquad (1)$$

This material balance does not account for catalyst within the bubbles, possibly due to fingering, which would be important in the kinetic analysis at high conversions.

MODEL I: PERFECT MIXING IN THE DENSE PHASE

With perfect mixing, the concentration of the dense phase is uniform, and the interchange of gas between bubbles and dense phase is an integrated term in the material balance. It is also assumed that an irreversible first-order reaction takes place in the dense phase

$$V_d \frac{dC_d}{dt} = \frac{u_o}{Z}\,(C_f - C_d) + \frac{1}{Z}\int_0^Z q_b\,(C_b - C_d)\,dz - k_w\,\rho_B\,C_d \qquad (2)$$

In the case of nonporous particles, the dense phase volume per unit volume of bed would simply be $\epsilon_0 Z_0/Z$, the void volume at incipient fluidization adjusted for bed expansion. With porous particles, the question arises if the internal voidage should be included in V_d. It can be shown that the time constant for the lag between the responses of the internal and external concentration is of the order of a few milliseconds for conditions commonly found in fluidized beds *(1)*, and under these conditions, V_d should include both internal and external voidage. Gas absorbed on the catalyst surface is not included in V_d, but could be if adsorption is linear.

The transfer function for model I can be derived from Equations (1) and (2) and the relation for the exit concentration of the bed.

$$C(s) = (1-\beta)C_d(s) + \beta C_b(s) \qquad (3)$$

where $\beta = 1 - u_o/u$. Equations (1) and (2) are combined with (3) after they have been Laplace transformed with respect to time and integrated along the height of the bed. The resulting transfer function is given in terms of the following parameters: $T_{vd} = V_d Z/u$, $T_{vb} = V_b Z/u$, $L_b = Z/u_b$, $\beta = 1 - u_o/u$, $N = (q_b Z/V_b u_b)$, $K = k_w \rho_B Z/u$, and $T_b = V_b/q_b = L_b/N$.

$$\frac{C(s)}{C_f(s)} = \beta H(s) + \frac{[1 - \beta H(s) + (1-\beta)T_b s]^2}{(T_b s + 1)^2\left[\left(T_{vd} + \dfrac{T_{vb}}{T_b s + 1}\right)s + \dfrac{\beta(T_b s + 2)\,T_b s}{(T_b s + 1)^2} + 1 + K - \beta H(s)\right]} \qquad (4)$$

where

$$H(s) = \exp -\,(N + L_b s)$$

This derivation is an extension of an earlier derivation given in detail elsewhere (1).

The steady state solution of Equation (4) is found by setting $s = 0$ with $H(0) = e^{-N}$

$$\frac{C}{C_f} = \beta e^{-N} + \frac{(1-\beta e^{-N})^2}{K + 1 - \beta e^{-N}} = 1 - x \qquad (5)$$

When the interchange transfer rate is much greater than the flow rate of the bubbles (that is, $q_b Z >> V_b u_b$; $N \to \infty$), the conversion approaches that of a continuous stirred-tank reactor. For fast reaction (that is, $K \to \infty$), the conversion is limited by interphase transfer, and the fraction of unconverted reactant is equal to the fraction of the gas bypassed as bubbles. The dynamic behavior also approaches that of a continuous stirred-tank reactor when the interchange transfer coefficient q_b is large.

$$\lim_{q_b \to \infty} \frac{C(s)}{C_f(s)} = \frac{1}{(T_{vd} + T_{vb})\,s + 1 + K} = \frac{\dfrac{1}{1+K}}{\dfrac{V/F\,s}{1+K} + 1} \qquad (6)$$

The initial response is found from the initial value theorem and is dominated by the time delay of the bubble phase.

$$\lim_{s\to\infty} \frac{C(s)}{C_f(s)} = \beta e^{-N} \lim_{s\to\infty} e^{-L_b s} \qquad (7)$$

The equations that have been developed for model I can also be used to describe gas mixing without reaction. The transfer function for gas mixing is obtained from Equation (4) by setting K equal to zero. This case was independently treated in a recent paper by Heimlich and Gruet (5) under the assumption that no gas enters or leaves the bed through the dense phase. The transfer function they presented is similar to Equation (4) with $K = 0$. As $q_b \to \infty$, the mixing dynamics of Equation (4) approaches the first-order behavior of a stirred tank with a time constant equal to the holdup time.

MODEL II: PLUG FLOW IN THE DENSE PHASE

In this model, the dense phase is assumed to be in plug flow, and the bulk flow through the dense phase is neglected, that is, $u_o = 0$. This second assumption greatly simplifies the mathematics for model II and does not appreciably affect the results for $u/u_o \geqq 10$, which is common for industrial and laboratory fluidized beds. The dense phase material balance for a differential slice of bed is

$$V_d \frac{dC_d}{dt} = q_b\,(C_b - C_d) - k_w\,\rho_B C_d \qquad (8)$$

The transfer function for model II is found by Laplace transforming Equations (1) and (8), combining and integrating to give

$$\frac{C(s)}{C_f(s)} = \exp\left(-N - L_b s + \frac{N^2}{T_{vd}s + N + K}\right) \qquad (9)$$

Note that when $u_o = 0$, Equation (3) gives $C(s) = C_b(s)$ and $N = q_b Z/u$.

The steady state conversion is again found by setting $s = 0$:

$$\frac{C}{C_f} = (1-x) = \exp -N\left(1 - \frac{N}{N+K}\right)$$

$$= \exp -N\left(\frac{N}{N+K}\right) \qquad (10)$$

The conversion approaches that of a plug flow reactor for large N and is limited by gas bypassing for fast reaction.

Models I and II give the same limits for fast reactions and initial response, except that $\beta = 1.0$ in model II. The gas mixing transfer function for model II is obtained by setting $K = 0$ in Equation (9).

FREQUENCY RESPONSE OF MODELS I AND II

The frequency response is found by the substitution of $s = j\omega$ in the transfer functions and resolving the resulting complex numbers into a magnitude (amplitude ratio) and phase angle. The calculations for model I are quite tedious and were therefore carried out with the aid of a digital computer. The results of these calculations, presented in Figure 1, use $\omega V/F = \omega(T_{vd} + T_{vb})$ as a dimensionless frequency. The curves were calculated for the experimental conditions listed in Table 1 at 0.1 ft./sec.

The frequency response for $K = 0$ (gas mixing without reaction) is given in Figure 1[*] for model I and Figure 2 for model II. The frequency response of model I shows several unique features. At high frequencies, the amplitude ratio approaches a limiting value equal to βe^{-N}, and the phase lag is approximately equal to ωL_b. Both of these limits are given by Equation (7) with $s = j\omega$. At high frequencies, the oscillations in the dense phase are damped out, and the response is dominated by bubble phase dynamics. At large values of N, the frequency response is the same as the first-order response of a stirred tank, except at very high frequencies. For values of N greater than 3, the amplitude ratio shows large oscillations in a transition region as shown in Figure 1. This type of behavior is not uncommon in lumped-distributed systems and has been predicted and observed in some heat exchangers (*4*).

The frequency response for model II is easily obtained from Equation (9).

$$\text{Amplitude ratio} = \exp\left\{-N + \frac{N^2(N+K)}{(N+K)^2 + (\omega T_{vd})^2}\right\} \tag{11}$$

$$\text{Phase lag} = \omega L_b + \frac{N^2(\omega T_{vd})}{(N+K)^2 + (\omega T_{vd})^2} \tag{12}$$

At high frequencies, the amplitude ratio approaches e^{-N} and the phase lag approaches ωL_b, which is equivalent to the behavior of model I with $u_o = 0$. The Bode plot for model II with $K = 0$ is shown in Figure 2. For small N the phase lag is approximately equal to ωL_b, while at large N it is approximately equal to $(\omega T_{vd} + \omega L_b)$.

A comparison of the frequency responses of model I and II for $K = 0$ is shown in Figure 3. Models I and II give substantially the same response except at large values of N. In this region, there is a wide divergence between the responses of models I and II, over most of the frequency range of practical interest, and it may be possible to distinguish experimentally an intermediate degree of dense phase mixing under these conditions. Intermediate mixing could be described by a model that accounts for diffusional mixing in the dense phase, similar to the model presented by May (9). May's model used both an interchange parameter and a diffusion parameter. The interchange parameter was expressed as a crossflow ratio, which is the same as the number of transfer units N in this paper. In his model, the diffusion coefficient of the gas in the dense phase was tacitly assumed to be equal to the diffusion coefficients of the solid particles which was measured experimentally. This questionable assumption would not be necessary with the frequency response method.

The effects of reaction in the dense phase with $N = 4.0$ are shown in Figure 4 for model I and Figure 5 for model II. The main effects of reaction are to change the zero frequency amplitude ratio to the values given by Equations (5) and (10), and to shift the corner frequency to higher frequencies as indicated by Equation (6). Reaction in the dense phase has a negligible effect on the high frequency portion of the response. For fast reactions, the amplitude ratio has the same limit at high and low frequencies in either model I or model II. For slow reactions, the response approaches that given in Figures 1 and 2. Similar behavior was found for other values of N.

From the preceding analysis, it can be concluded that the unique features of the frequency response of models I and II occur mainly in the high frequency regions where reaction has little effect and that these features can be investigated by gas mixing tests.

EXPERIMENTAL STUDIES

Figure 6 is a diagram of the apparatus used in the frequency response tests. Care was taken to ensure equal sampling gas flow rates and lengths of the sampling lines so that the time delays in the inlet and exit lines would be the same. This apparatus was capable of producing measurable variations in the inlet concentration at frequencies as high as 10 cycles/sec.

The tests were conducted at gas velocities of 0.1 and 0.2 ft./sec. in a 3-in. I.D. bed with a bed height of about 1 ft. The details of the experimental conditions are given in Table 1 along with the bed properties calculated from the expansion data. The highest frequency that yielded useful data was about 0.7 cycles/sec. This frequency corresponded to an amplitude ratio of about 0.05. At higher frequencies, there was a random drift in the average concentration of the bed that

Table 1. Bed Properties

Catalyst: Grade 902 Fluid Vanadia Oxidation Catalyst,
W. R. Grace & Co.

Catalyst volume-surface mean diameter:		0.0030 in.
Bed diameter:	$D =$	3.01 in. I.D.
Bed height at incipient fluidization:	$Z_o =$	0.875 ft.
Bulk density at incipient fluidization:	$\rho_B =$	45.7 lb./cu. ft.
Voidage at incipient fluidization:	$\epsilon_o =$	0.65
Minimum fluidization velocity:	$u_o =$	0.01 ft./sec.

u, ft./sec.	Z, ft.	V_b, cu. ft./cu. ft.	u_b, ft./sec.	L_b, sec.	V/F, sec.
0.1	0.980	0.107	0.842	1.165	6.75
0.2	1.050	0.237	1.12	0.940	3.74

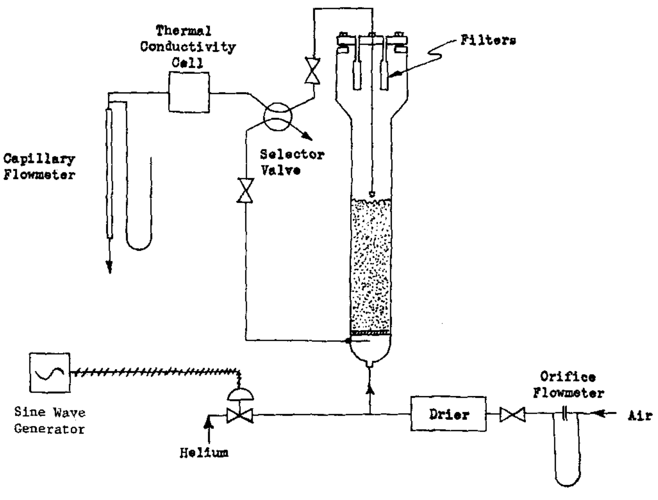

Fig. 6. Flow diagram for mixing studies.

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[*] See pages 468 to 474 for Figures 1 to 5 and 7 and 8.

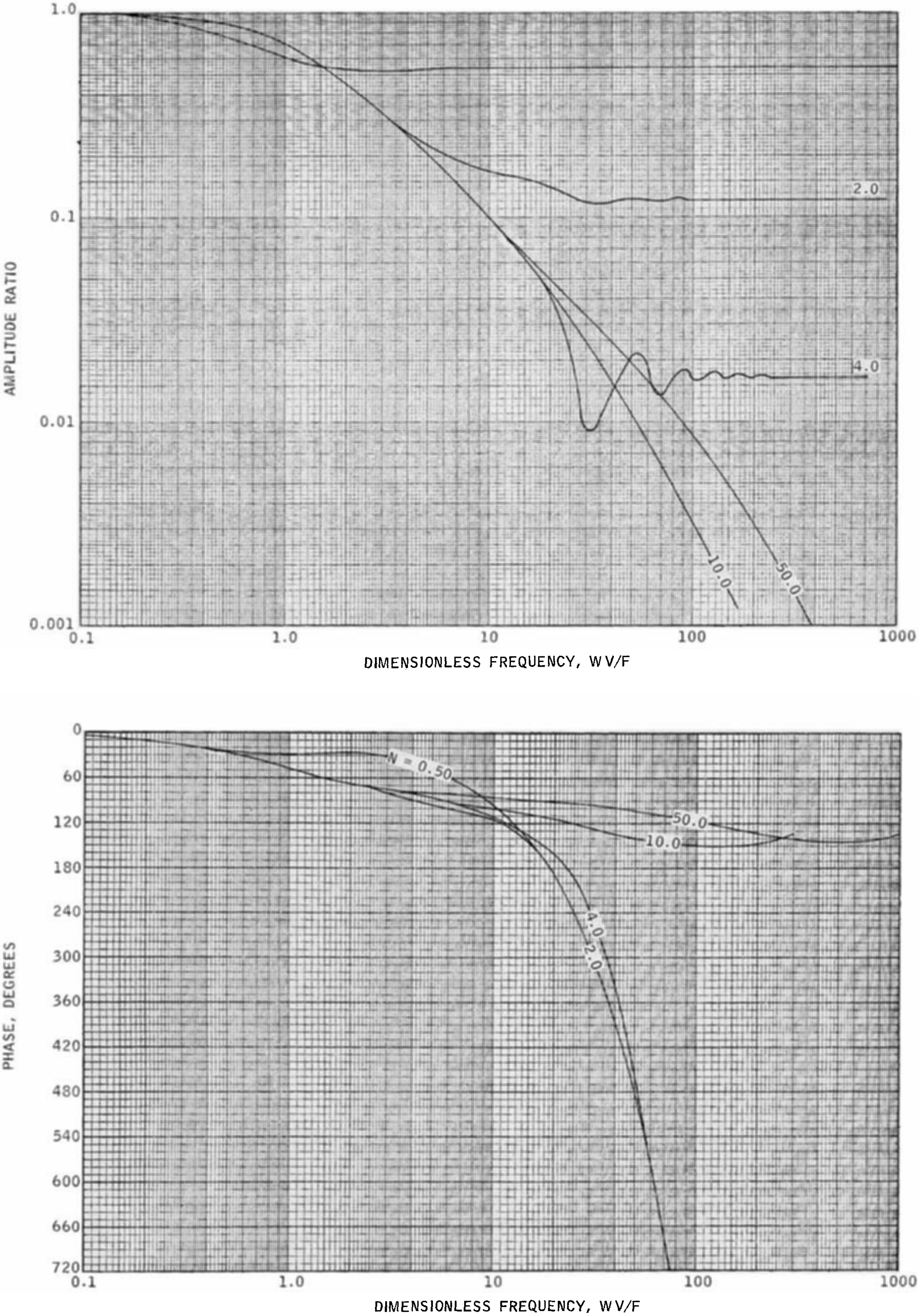

Fig. 1. Frequency response of model I with $K = 0$ at 0.1 ft./sec.

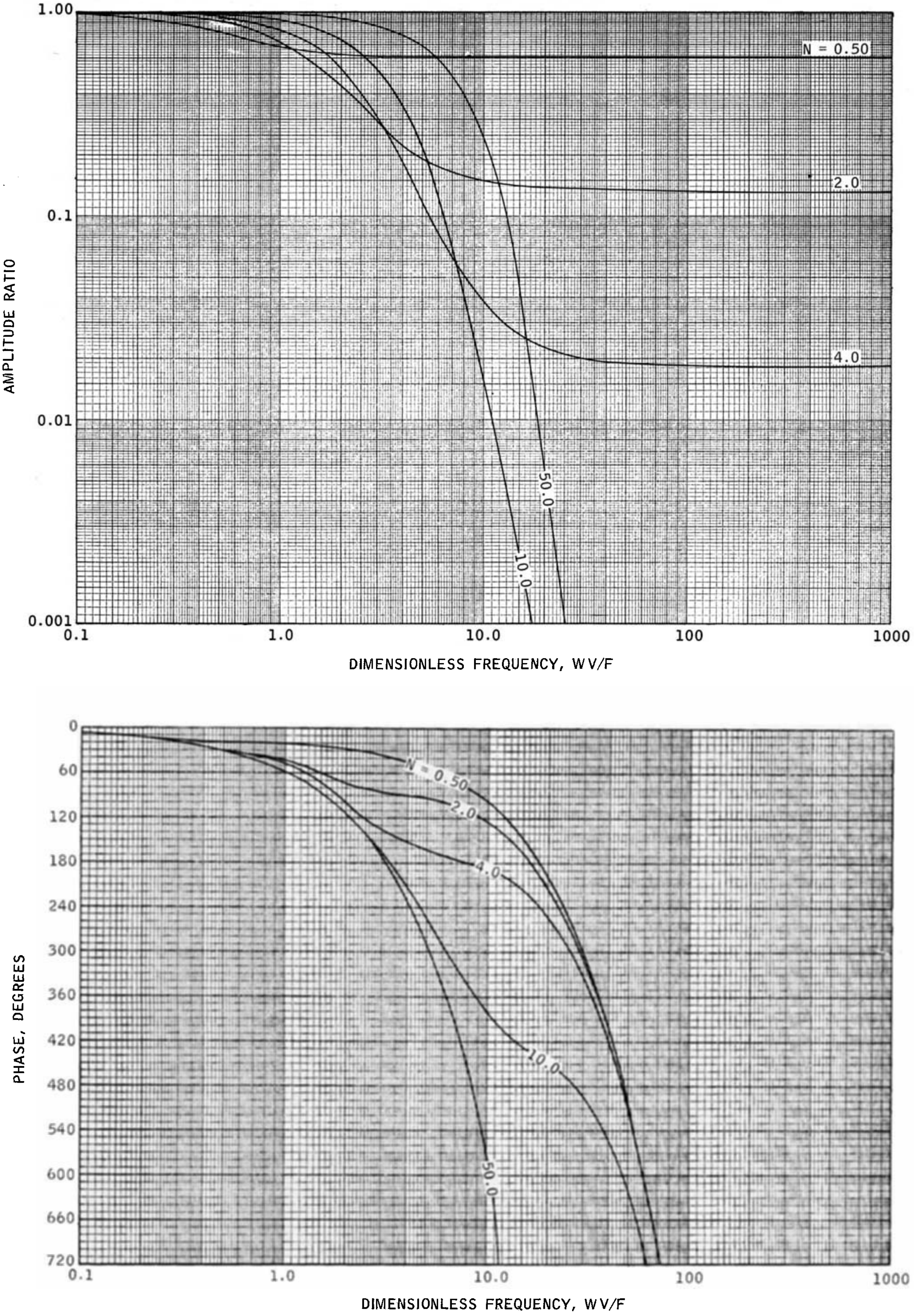

Fig. 2. Frequency response of model II with $K = 0$ at 0.1 ft./sec.

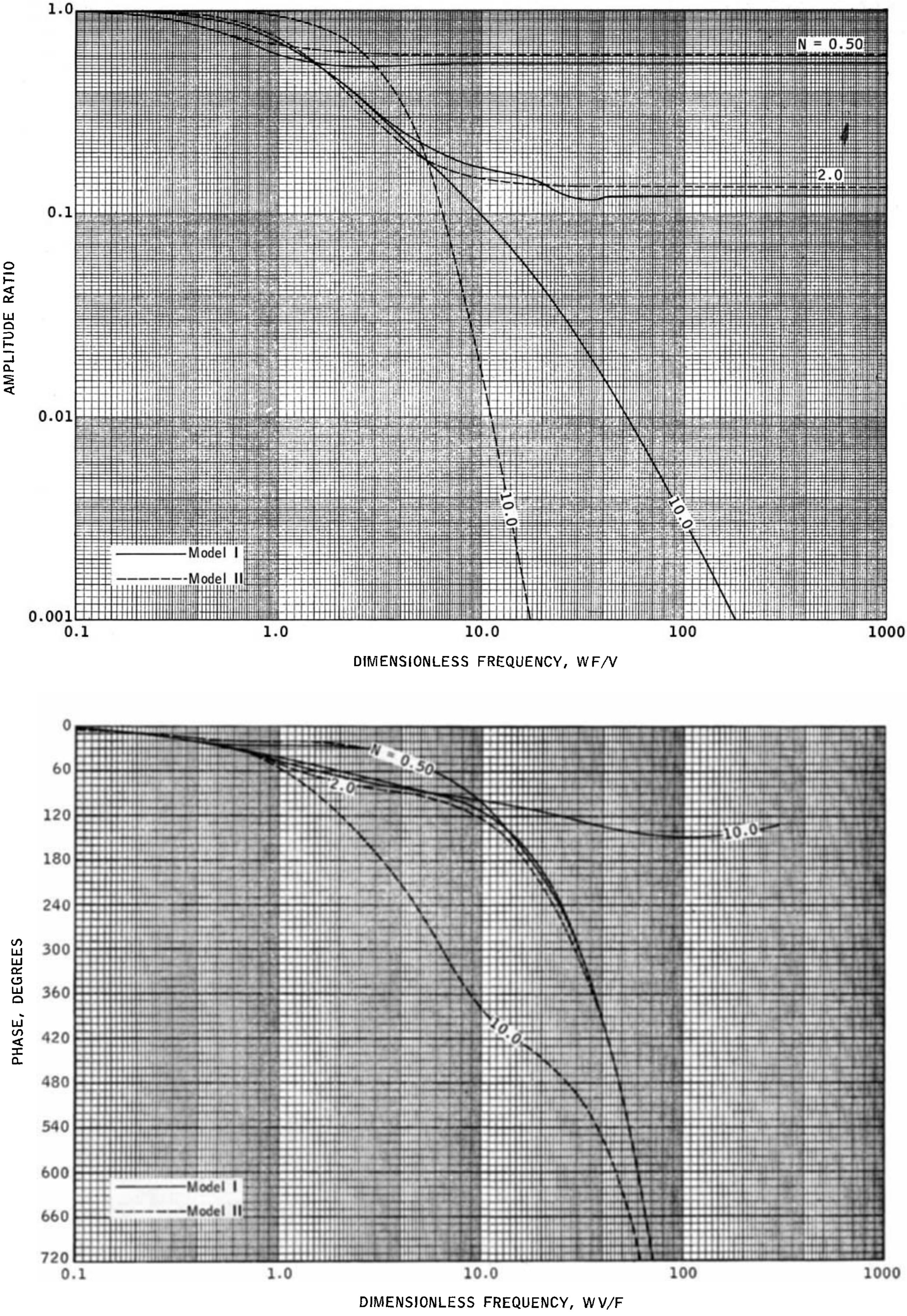

Fig. 3. Comparison of models I and II with $K = 0$ at 0.1 ft./sec.

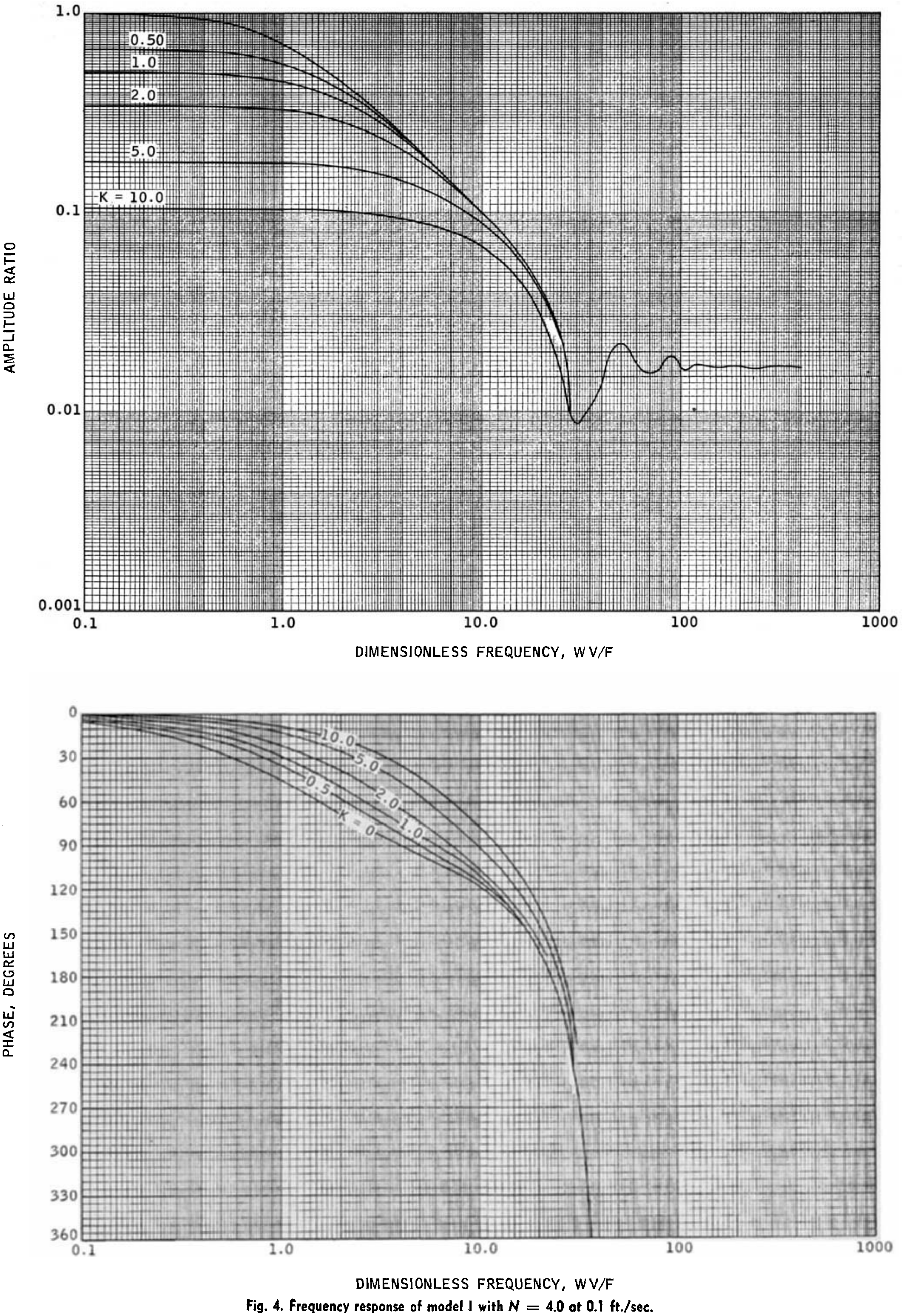

Fig. 4. Frequency response of model I with $N = 4.0$ at 0.1 ft./sec.

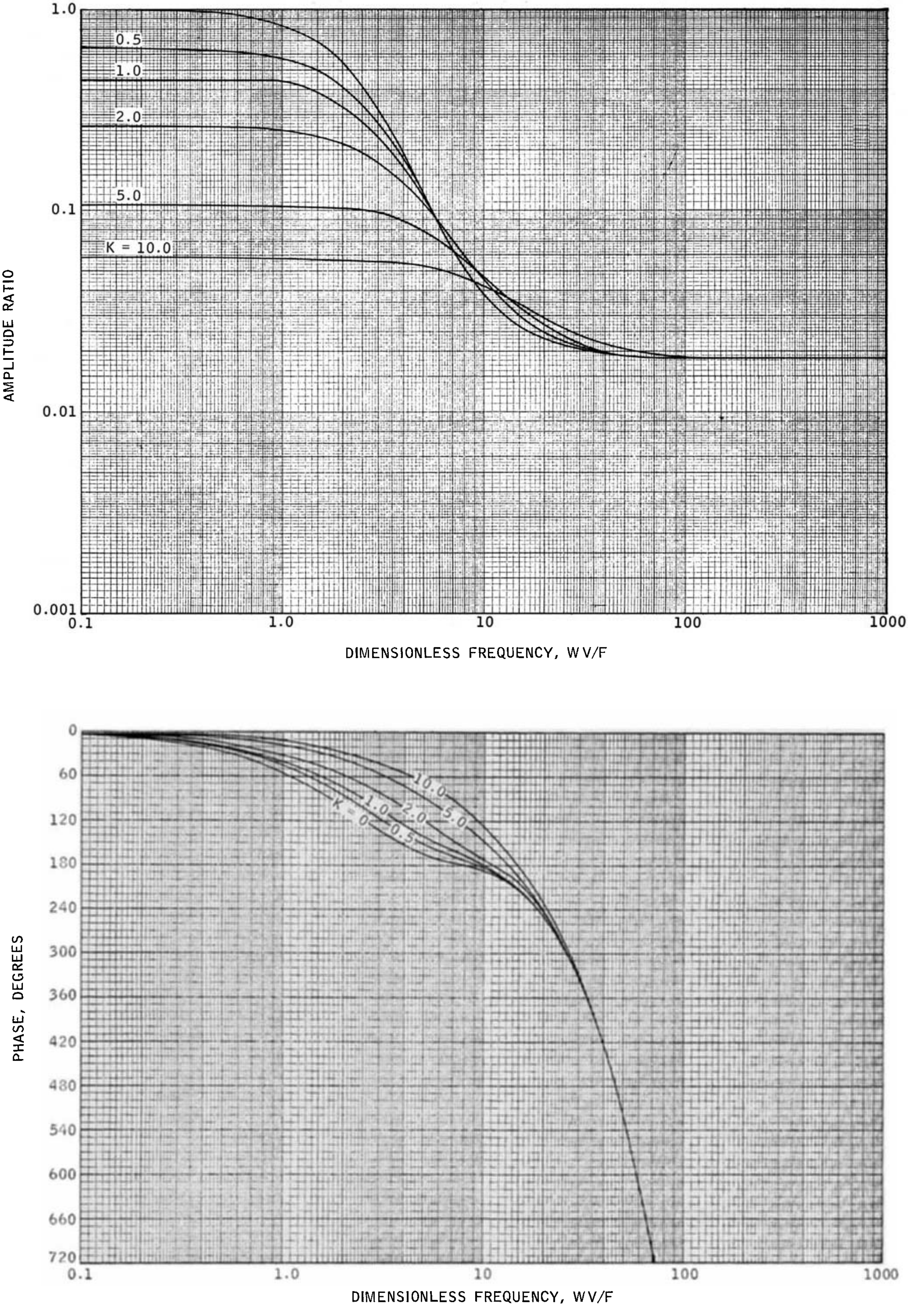

Fig. 5. Frequency response of model II with $N = 4.0$ at 0.1 ft./sec.

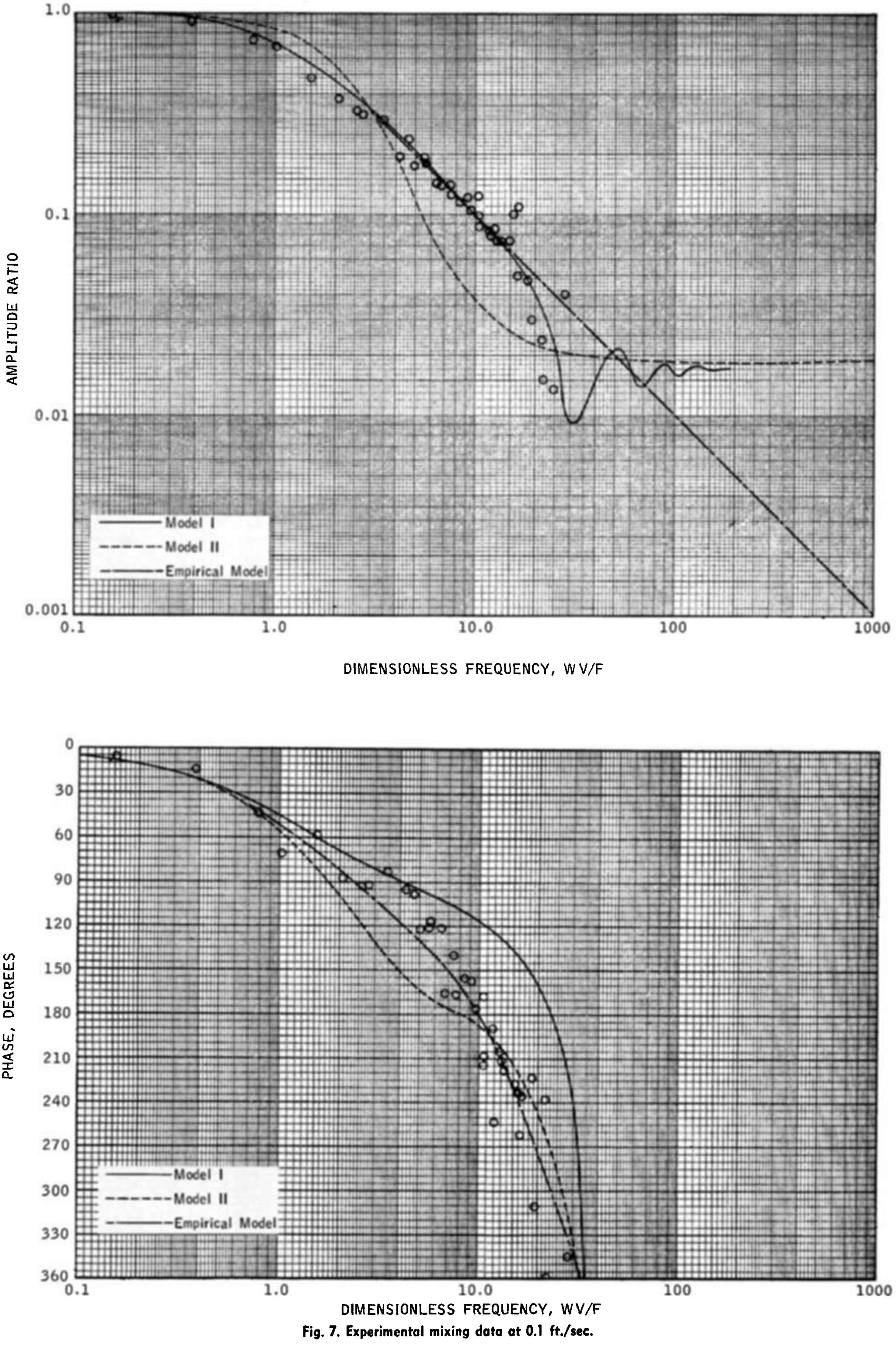

Fig. 7. Experimental mixing data at 0.1 ft./sec.

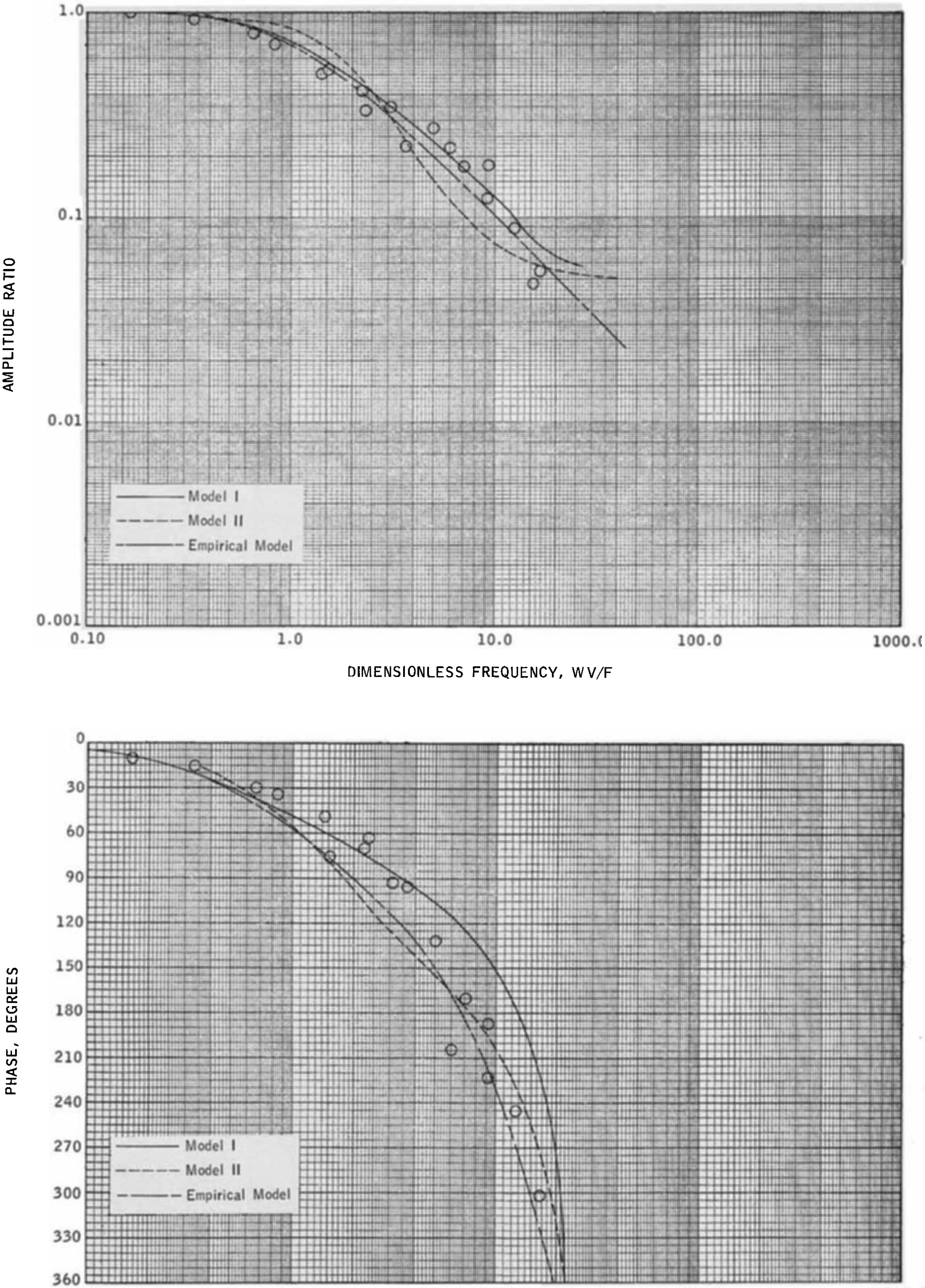

Fig. 8. Experimental mixing data at 0.2 ft./sec.

obscured the frequency response measurements. This low frequency noise is thought to be due to the variability of gas bubbles and interphase transfer. Data at higher frequencies could probably have been obtained with the aid of correlation techniques.

RESULTS AND DISCUSSION

The frequency response data are presented in Figure 7 for a fluidizing gas velocity of 0.1 ft./sec. and in Figure 8 for 0.2 ft./sec. In both cases three different models were used to correlate the experimental data: model I, model II, and an empirical model with fluidization parameters. The parameters used to correlate all three models were computed from the expansion data listed in Table 1. For models I and II, a value of interchange coefficient q_b was selected to give the best fit (by eye) to the experimental data. In finding q_b, both amplitude ratio and phase lag curves were considered over the range of frequencies investigated. A poorer fit was obtained at both higher and lower values of q_b. The response of the empirical model consisted of the superposition of two parts: a distance-velocity time delay equal to L_b, the time it takes for a bubble to rise from the bottom to the surface of the bed, and first-order response with a time constant equal to the holdup time of the bed; it is expressed by the transfer function:

$$G(s) = \frac{e^{-Lbs}}{\left(\frac{V}{F}S + 1\right)} \qquad (13)$$

The Bode plots show that the amplitude ratio decreased with increasing frequency in a manner similar to a stirred tank and did not reach the high frequency leveling off predicted by models I and II at small N. At high frequencies, the phase lag was appreciably greater than the 90-deg. maximum of a stirred-tank model, and the phase lag increased in a manner similar to that of a time delay. At both 0.1 and 0.2 ft./sec., the amplitude ratio and phase lag curves were fit remarkably well by the empirical function based on the bed holdup and bubble time delay.

The same value of N gave the best fit for both models I and II: at 0.1 ft./sec., $N = 4.0$ was used corresponding to $q_b = 0.367$; and at 0.2 ft./sec., $N = 3.0$ was used corresponding to $q_b = 0.543$. Model I gives a better fit of the amplitude ratio data. Over a range of frequencies of $\omega V/F$ between 4 and 8, for the test at 0.1 ft./sec., the measured amplitude ratios were as much as twice those predicted by model II. It is felt that over this range, the amplitude ratio measurements were accurate enough to distinguish such a large difference, and the correlation with model I is therefore preferred.

The values of N found from the frequency response test can be compared with the value for N of 3.2 found by Orcutt (*9*) in his studies of the conversion of ozone to oxygen in an air-fluidized bed. This single value of N represented all his data and was insensitive to variations in Z_o, u, D.

Heimlich and Gruet (*5*) found that the transient data from their gas mixing tests in a 10-ft. high, 4-ft., 11-in. diameter bed at 3 ft./sec. could be correlated well with a two-phase mixing model with a value of N of 3.0.

Frequency response methods have been found to be useful in the theoretical and experimental analysis of gas mixing in fluidized beds and offer a definitive means for relating experiments and theory.

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NOTATION

C = concentration of exit gas stream, lb.-moles/cu.ft.
C_b = bubble phase concentration, lb.-moles/cu.ft.
C_d = dense phase concentration, lb.-moles/cu.ft.
C_f = feed concentration, lb.-moles/cu.ft.
D = bed diameter
F = volumetric flow rate, cu.ft./sec.
$G(s)$ = empirical transfer function
$H(s) = e^{-(N+L_b s)}$
$j = \sqrt{-1}$
k_w = rate constant per unit weight of catalyst, moles/(sec.)(lb.) of catalyst (mole/cu.ft.)
$K = k_w \rho_B Z/u$
$L_b = Z/u_b$ = bubble time delay, sec.
$N = q_b Z/V_b u_b$ = number of transfer units
q_b = interchange coefficient, cu.ft./(sec.)(cu.ft.) of bed
$s = \sigma + j\omega$ = Laplace transform variable
t = time
$T_b = V_b/u_b$
$T_{vb} = V_b Z/u$
$T_{vd} = V_d Z/u$
u = superficial gas velocity, ft./sec.
u_b = bubble velocity, ft./sec.
u_o = superficial velocity at incipient fluidization, ft./sec.
V = total void volume, cu.ft.
V_b = $(Z - Z_o/Z)$ = volume of bubbles per unit volume of bed, cu.ft./cu.ft.
$V_b U_b = u - u_o$
V_d = volume of dense phase per unit volume of bed, cu.ft./cu.ft.
$V/F = T_{vd} + T_{vb} = \frac{Z - (1 - \epsilon_o) Z_o}{u}$ = holdup time, sec.
x = conversion
z = height above bottom of bed, ft.
Z = total height of expanded bed, ft.
Z_o = bed height at incipient fluidization, ft.

Greek Letters

$\beta = 1 - u_o/u$
ϵ = voidage at incipient fluidization
ρ_B = bulk density of catalyst bed, lb./cu.ft.
ω = frequency, rad./sec.

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