An Interpretation of Experimental Results on Sonic Chemical Analysis

I. R. A. GURA and D. D. PERLMUTTER

University of Illinois, Urbana, Illinois

The work of Crowthamel and Diehl (*1*) several years ago established a method of gas analysis which utilizes indirect measurements of the velocity of sound. Because it is continuous and nondestructive, this method has particular interest for experimentors who are involved in studies of chemical kinetics or reactor dynamics. Analytical results obtained are independent of flow rate and flow-rate fluctuations and vary only slightly with temperature.

In an experimental apparatus the gas to be analyzed is passed through a metal tube so that it fills the space between a speaker and a microphone mounted in opposite ends of the tube. A sound of constant frequency is generated by the speaker, passes through the gas, and is picked up by the microphone. The output of the microphone may be calibrated against composition. The measurements of Crowthamel and Diehl and those of the present writers yield calibration curves which agree in form (see Figure 1). Curves of this general form are also known to describe the microphone output if frequency or tube length are varied (*1, 3, 6*). Although these findings are in the literature, there does not appear to be an analytic interpretation available. In the equations that follow, a result is derived that explains the experimental findings.

The wave equation for sound propagation in one dimension is

$$\frac{\partial^2 \Phi}{\partial t^2} = a^2 \frac{\partial^2 \Phi}{\partial x^2} \tag{1}$$

where $\Phi\ (x, t)$ is the velocity potential, defined by Rayleigh (*5*) in terms of the particle velocity in the tube:

$$\frac{\partial \Phi}{\partial x} = u = \frac{\partial \theta}{\partial t} \tag{2}$$

The constant a is the velocity of sound; that is, the velocity of propagation of the wave, as distinct from the particle velocity u, or the velocity of flow of gas through the tube.

Initially, there is no disturbance in the tube. This may be expressed by the boundary condition

$$\Phi = 0,\ t = 0 \tag{3}$$

At the microphone end of the tube, there must be a node in particle displacement, since no motion can occur at a closed end. This is expressed by

$$\theta = 0,\ x = d \tag{4}$$

or

$$\frac{\partial \theta}{\partial t} = \frac{\partial \Phi}{\partial x} = 0,\ x = d$$

At the speaker position ($x = 0$) the system is forced by the periodic motion related to the sound-generating coil. In general, a sinusoidal voltage fluctuation will produce a sinusoidal response in the particle velocity (*7*). Thus from Equation (2)

$$\frac{\partial \Phi}{\partial x} = A \sin \omega t,\ x = 0 \tag{5}$$

Solution of Equation (1) with boundary conditions (3), (4), and (5) gives

$$\Phi(x, t) = \left(\frac{aA}{\omega}\right) \csc\left(\frac{\omega d}{a}\right) \sin \omega t \cos \frac{\omega}{a}(d - x) \tag{6}$$

$$\Phi(d, t) = \frac{a}{\omega} A \csc \left(\frac{\omega d}{a}\right) \sin \omega t \tag{7}$$

Microphones are sensitive to the pressure fluctuations which propagate as sound waves. To express the above result in terms of pressure, it is necessary to use the following relation of Rayleigh's (*5*)

$$-\rho \frac{\partial \Phi}{\partial t} = p \tag{8}$$

Combining this equation with (7)

$$p(d, t) = -\rho A a \csc\left(\frac{\omega d}{a}\right) \cos \omega t \tag{9}$$

A microphone output (voltage or current) is generally a linear function of the input pressure (*7*). Thus

$$i(d, t) = \beta p(d, t) \tag{10}$$

If, as is common, the output is measured as a root-mean-square value, the result is

$$i_{RMS} = \frac{\sqrt{2}\beta}{2} \rho A a \left| \csc \frac{\omega d}{a} \right| \tag{11}$$

The speed of sound in a gas is a function of its molecular weight and ratio of specific heats (*1*)

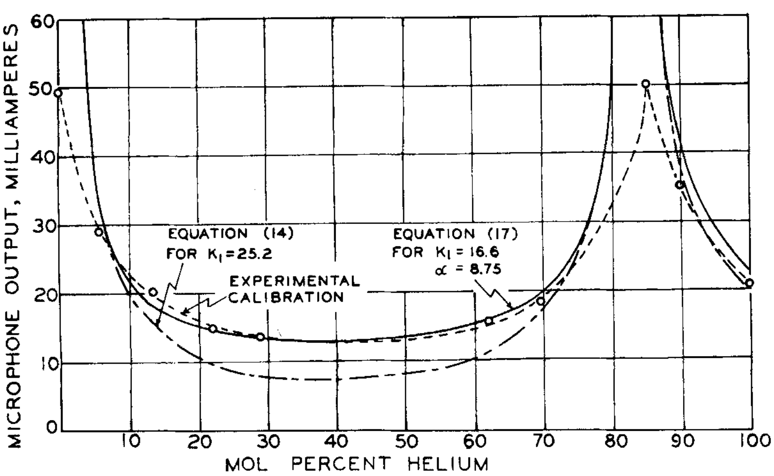

Fig. 1. Microphone output vs. gas composition.

$$a = \sqrt{\frac{g_c \gamma RT}{M}} \qquad (12)$$

Then

$$i_{RMS} = \frac{\sqrt{2}\beta}{2} \rho A \sqrt{\frac{g_c \gamma RT}{M}} \left| \csc \frac{\omega d \sqrt{M}}{\sqrt{g_c \gamma RT}} \right| \qquad (13)$$

In a typical experimental analytical application, only (M/γ) is variable. The separate constants may then be accumulated in the form

$$i_{RMS} = \frac{K_1}{\sqrt{M/\gamma}} \left| \csc K_2 \sqrt{M/\gamma} \right| \qquad (14)$$

The constant K_1 depends on the equipment used and on the properties of the gases under study. It is, in effect, a scale factor and can most conveniently be determined by comparison of theoretical and experimental results. The constant K_2 depends on the physical properties of the system considered. For example, it is known that at 70°F. pure nitrogen has a 20.2 cm. wavelength at 1,720 cycles/sec. (ω = 10,820 radians/sec.). In a tube of that length, resonance at the receiver can be expected. From Equation (14):

$$\csc (K_2 \sqrt{28/1.4}) \rightarrow \infty \qquad (15)$$

and

$$K_2 = \frac{2\pi}{\sqrt{20}} = 1.4 \text{ (lb. moles)}^{1/2} \text{ (lb.)}^{-1/2} \qquad (16)$$

Experimental results for the system nitrogen-helium are given in Figure 1. A theoretical curve based on Equation (14) is shown, where the constant K_1 = 25.2 (ma.) (lb.)$^{1/2}$(lb. mole)$^{-1/2}$. Since this equation was derived using idealized boundary conditions and is based on the assumption of unidirectional propagation of waves of infinitesimal amplitudes, the agreement of theory and experiment must be considered quite satisfactory.

The gap between the two curves where the microphone output is low suggests the use of a semiempirical expression of the form

$$i_{RMS} = \alpha + \frac{K_1}{\sqrt{M/\gamma}} \left| \csc K_2 \sqrt{M/\gamma} \right| \qquad (17)$$

The constant α can be considered a correction factor for the nonideal behavior of the system. A fit of Equation (17) to the experimental data is shown in Figure 1, by α = 8.75 ma., K_1 = 16.6 (ma.) (lb.)$^{1/2}$ (lb. mole)$^{-1/2}$. This curve agrees remarkably well with the measurements. Exact agreement at very high microphone outputs is im-

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INFORMATION RETRIEVAL

Transport characteristics of suspensions VII. relation of hindered-settling floc characteristics to rheological parameters, Thomas, David G., **A.I.Ch.E. Journal, 9,** No. 3, p. 310 (May, 1963).

Key Words: Thorium Oxide-1, Titania-1, Kaolin-1, Alumina-1, Graphite-1, Suspension-2, Water-5, Methanol-5, Concentration-6, Particle Size-6, Electrolyte Atmosphere-6, Immobilized Water-6, Settling Rate-7, Rheological Parameters-7, Non-Newtonian Characteristics-7, 8, Flocculated Suspensions-8, Particle Interactions-9, Hindered-Settling Rate-8, 10, Rheological Measurements-10.

Abstract: Both the rheological and the hindered-settling characteristics of small particle size suspensions (0.4 to 17 μ) were shown to be proportional to the value of α determined from the hindered-settling measurements (α is defined as the ratio of the volume of fluid immobilized by the floc structure to the volume of solids in the floc structure). The materials studied included suspensions of thorium oxide in water and methanol and of titania, kaolin, alumina, and graphite in water. Values of the attractive force between particles calculated from the rheological and hindered-settling data were in good agreement with each other and with the theoretical values calculated from the Derjaguin-Verwey-Overbeek theory of colloid stability.

Semifluidization in solid-gas systems, Wen, Chin-Yung, Shih-Chung Wang, and Liang-Tseng Fan, **A.I.Ch.E. Journal, 9,** No. 3, p. 316 (May, 1963).

Key Words: Gas-1, Air-1, Flow Rate-6, Particle Size-6, Particle Density-6, Height of Fluidized Bed-7, Height of Packed Bed-7, Semifluidization-8, Fluidization-8, Height of Packed Section-9, Glass Bead-10, Polyethylene Particle-10, Solid Particles-10.

Abstract: The mechanical characteristics of semifluidized beds of solid-air systems were investigated. Glass beads and two shapes of high-density polyethylene particles were used. The formation of the packed bed above the fluidized bed was studied and the results were successfully correlated in terms of the velocity required to balance a particle within the upflowing fluid instead of the free fall terminal velocity. Two dimensionless groups, $(h-h_0)/(h-h_{pa})$ and $(G-G_{mf})/(G_t''-G_{mf})$, were used for the correlation, and a unique relation was found to exist between these two dimensionless groups for both solid-gas and solid-liquid systems of semifluidization.

The apparent chemical kinetics of surface reactions in external flow systems; diffusional falsification of activation energy and reaction order, Rosner, Daniel E., **A.I.Ch.E. Journal, 9,** No. 3, p. 321 (May, 1963).

Key Words: Diffusion-6, Heterogeneous Catalysis-8, Surface Reaction-8, Forced Convection-6, Boundary Layer Theory-10, Mass Transfer-6, Apparent Activation Energy-9, Apparent Reaction Order-9, Flat Plate-9, Effectiveness Factor-9, Transport Control-9, Laminar Flow- , Frank-Kamenetskii- , Quasistationary Method- .

Abstract: For catalytic solids immersed in a reactant-containing fluid stream general expressions are derived relating overall effectiveness factor to diffusional falsification of activation energy and reaction order. Approximate solutions are given for the thin nonturbulent diffusion layer which develops along an impermeable catalytic flat plate for arbitrary values of the true reaction order and Schmidt number. Comparisons with exact solutions to the laminar boundary layer equations and alternate approximate methods are given for the special case of first-order surface reactions. The physico-chemical conditions under which quasistationary approximations are likely to be unacceptable are discussed and kinetic applications are given.

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possible, since real physical systems saturate under conditions of resonance.

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NOTATION

A = amplitude of sinusoidal speaker input
a = velocity of propagation of sound
d = length of sound tube
g_c = gravitational constant
i = output of microphone (current or voltage)
i_{RMS} = root mean square value of i
K_1 = $\frac{\sqrt{2}\beta}{2} \rho A \sqrt{g_c RT}$
K_2 = $(\omega d)/\sqrt{g_c RT}$
M = molecular weight of gas in sound tube
p = excess pressure due to sonic vibrations
R = gas constant
t = time
T = absolute temperature
u = velocity of gas particles due to sonic vibrations
x = axial coordinate in sound tube

Greek Letters

α = constant as defined in Equation (17)
β = constant as defined in Equation (10)
γ = ratio of specific heats
θ = displacement of gas particles due to sonic vibrations
ρ = density of gas under conditions at which a is measured
Φ = velocity potential as defined in Equation (3)
ω = angular frequency

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The Maximum Velocity Locus for Axial Turbulent Flow in an Eccentric Annulus

R. A. WOLFFE and C. W. CLUMP

Lehigh University, Bethlehem, Penna.

Deissler and Taylor (*1*) and Heyda (*3*) present analytical solutions for the turbulent flow of incompressible fluids in plain annuli containing eccentrically positioned cores. Comparison of these solutions with experimental observations is not offered by these authors. It is the purpose of this note to compare the results of a recent experimental study (*8*) of flow in annuli containing a fixed eccentric core with the calculated solutions of the above mentioned authors.

Deissler and Taylor devised an interative procedure in which the locus of maximum velocity and the velocity gradient lines are assumed such that they satisfy force balances calculated employing the equations of Eckert (*2*) for velocity distribution in turbulent flow. Heyda solved the Navier-Stokes equations for laminar flow and used the resulting laminar maximum velocity locus as the basis for his iterative nongeometric procedure for the description of turbulent flow. Heyda's assumption that the laminar and turbulent loci of maxima are identical has support in the results of studies of flow in concentric annuli. These studies (*4, 5, 6, 7*) indicate that the radius of maximum velocity for Reynolds numbers somewhat less than 10,000, based on the hydraulic radius, is identical to the radius of maximum velocity for laminar flow, and that the maximum velocity radius moves slightly toward the inner wall as the Reynolds number increases.

In a recent experimental study isovelocity lines and the locus of maximum velocity were determined for the turbulent flow of air (Reynolds number 20,000, maximum velocity 40 ft./sec.). Impact tube measurements were used to determine point velocities in an annular system consisting of a 3.00 in. I.D. smooth aluminum tube with a 2.00 in. O.D. eccentric aluminum core (ϵ = 0.25). Calming lengths of 15 ft. upstream and 6 ft. downstream from the test section were employed. Point velocity data was reproducible within 1%.

In Figure 1 the experimentally determined maximum velocity points are plotted along with points of maximum velocity predicted by the solution of the Navier-Stokes equation for laminar flow. Also presented is the locus of maximum velocity predicted by a simple approximate solution of the Navier-Stokes equation suggested by Noyes (*3*) in conjunction with the work of Heyda. A comparison between experimentally determined maximum points

TABLE 1.

	Angle θ						
	10	40	80	120	180	200	240
	% difference						
Navier-Stokes	2.4	1.8	11.4	6.7	7.2	10.0	14.3
Noyes approximation	0.0	0.0	0.0	0.0	7.2	10.0	6.6