

¹⁷ Wittliff, C. E. and Wilson, M. R., "Heat Transfer to Slender Cones in Hypersonic Air Flow, Including Effects of Yaw and Nose Bluntness," *Journal of the Aerospace Sciences*, Vol. 29, No. 7, July 1962, pp. 761-774.

¹⁸ Wilkinson, D. B. and Harrington, S. A., "Hypersonic Force, Pressure, and Heat Transfer Investigations of Sharp and Blunt Slender Cones," AEDC-TDR-63-177, Aug. 1963, Arnold Engineering Development Center, Arnold Air Force Station, Tenn.

¹⁹ Van Dyke, M., *Perturbation Methods in Fluid Dynamics*, Academic Press, New York, 1964.

²⁰ Beckwith, I. E., "Similar Solutions for the Compressible Boundary Layer on a Yawed Cylinder With Transpiration Cooling," TN 4345, 1958, NACA.

²¹ DeJarnette, R. F. and Davis, R. M., "A Simplified Method for Calculating Laminar Heat Transfer Over Bodies at an Angle of Attack," TN D-4720, 1968, NASA.

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Reaction Product Fluctuations in a Sphere Wake

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Fluctuations of chemical reaction product were detected in the reacting and nonreacting wake of a sphere. Using the principle of conductometric titration, a single electrode microprobe was used to detect the local concentration of ammonium acetate produced when acetic acid and ammonium hydroxide solutions were injected into the wake of a sphere suspended in the test section of a water tunnel. Reacting and nonreacting wakes were produced when the reactants were injected separately or premixed, respectively. Measurements were taken in the reacting wake with a micro-pH probe in order to have an estimate of the extent of reaction. Data reduction was accomplished using digital techniques. Preliminary results have been obtained that indicate that the distribution of the salt concentration is nongaussian for both reacting and nonreacting wakes. Spectra have been calculated at two wake positions and have similar forms for reacting and non-reacting wakes except at low wavenumber. Inflections from inertial-convective $k^{-5/3}$ subranges to viscous-convective k^{-1} subranges were observed at about $\frac{1}{30}$ of the Kolmogoroff wavenumber.

I. Introduction

UNDERSTANDING the distribution of a product of a chemical reaction in turbulent flow has considerable practical importance in problems such as electromagnetic wave scattering from meteor or missile wakes as well as fundamental importance as a basic unsolved problem of turbulent mixing theory. It is not only unsolved; it is nearly untouched, either theoretically or experimentally.

The simplest nontrivial form of the problem is probably for high Reynolds number flow of constant viscosity and density fluid with infinitely fast (compared to the time of mixing) irreversible reactions of the form $A + B \rightarrow C$. The conservation equations assumed are as follows:

$$d\mathbf{v}/dt = -\text{grad}p/\rho + \nu \Delta \mathbf{v} \quad (1)$$

$$\text{div} \mathbf{v} = 0 \quad (2)$$

$$dC/dt = D\Delta C + S \quad (3)$$

where D is the molecular diffusivity of the product of a chemical reaction C . The problem would be the same as passive scalar mixing of C except for the production term S . For the assumed case of very rapid chemical reaction $S = 0$ except for a vanishingly small volume of fluid representing the reaction

surfaces separating regions containing reactants A and B . Consequently, we might expect a number of similarities between the dynamically passive scalar mixing distribution and the reaction product distribution.

The fact that S is not everywhere zero couples Eq. (3) to similar species conservation equations for the reactants A and B , and introduces to the problem additional dimensional parameters describing the reaction order and rate. The assumption of very rapid homogeneous reaction rate permits some simplification of the problem, but it is not clear how S will be distributed, or how its distribution will affect that of C .

Toor¹ has considered the rapid reaction problem and has related the extent of reaction to the degree of mixing in a similar passive scalar mixing system by assuming quantities mixed by turbulence are normally distributed. Keeler's² measurements of extent of reaction and mean square passive scalar fluctuations were consistent with Toor's theory although no measurements of the smaller scale distribution of reaction product were predicted or measured. Consequently, two of the goals of the present experiments were to test the assumption that scalar fluctuations mixed by turbulence are gaussian and also to measure the product "fine structure." Because of the localization to reaction surfaces of the production rate, the fine structure is of fundamental importance to the problem.

A further goal of the experiment was the development of techniques for digital data acquisition and computer processing of the turbulent mixing signals. The results of this effort have proved quite encouraging. It is clear that in terms of speed, flexibility, and efficiency, digital techniques open up a new dimension in experimental turbulence research.

Finally, one intention of the measurements was to investigate the spectral form of a scalar mixed by a turbulent wake, not only for comparison with the spectrum of the reacting scalar, but also for its own sake since few such measurements exist for any turbulent flow, and apparently none for sphere wakes.

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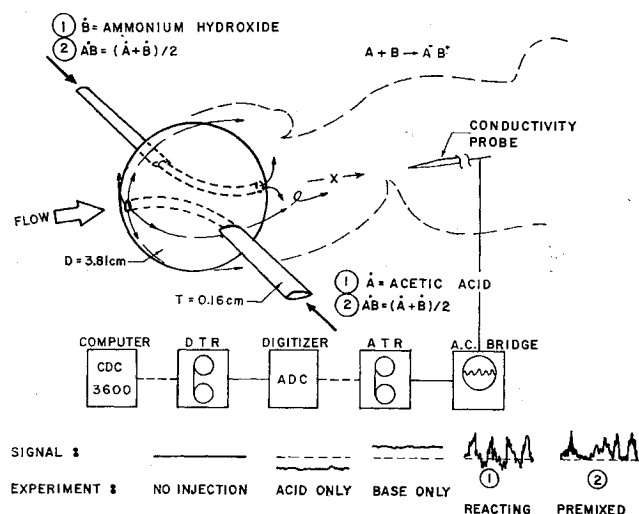


Fig. 1 Schematic of experimental arrangement.

II. Experimental Arrangement

A schematic diagram of the experimental arrangement is shown in Fig. 1. Turbulent mixing with and without chemical reaction was studied in the turbulent wake of a sphere. About 1% by weight acetic acid and ammonium hydroxide solutions were injected in stoichiometric ratio at upstream and downstream stagnation points of the 3.81-cm-diam sphere through the two 0.16-cm streamlined supports. The rate constant of the neutralization reaction is very fast, probably of order 10^{11} liters/mole sec.

Because both the acid and base used are weakly ionized, they do not affect the conductivity of the 0.1% background tunnel water until after the reaction had taken place. Consequently, any fluctuations of conductivity in the solution swept by the tip of the conductivity probe should only be due to the presence of the ionized chemical reaction product ammonium acetate. With an ideal probe that responds only to the conductivity changes, these reaction product fluctuations could be observed in the reacting wake. This is the principle of the conductometric titration of weak acid by weak base, except that the spatial resolution of the conductivity probe is very fine (about $10^4 \mu^3$) in order to approximate a point measurement of the product concentration.

One advantage of this particular flowfield was that a series of measurements had recently been completed of velocity and temperature fluctuations in the wake of the same sphere in a water tunnel so that the characteristics of the turbulent wake were already well known. For more details of the equipment and measurement techniques, see Ref. 3.

Representative signals from the a.c. bridge are shown schematically in Fig. 1. With no injection, only low-level background conductivity fluctuations are present. When the tunnel water is adjusted to pH = 7, neither acid nor base injected alone should be detected by the conductivity probe if it re-

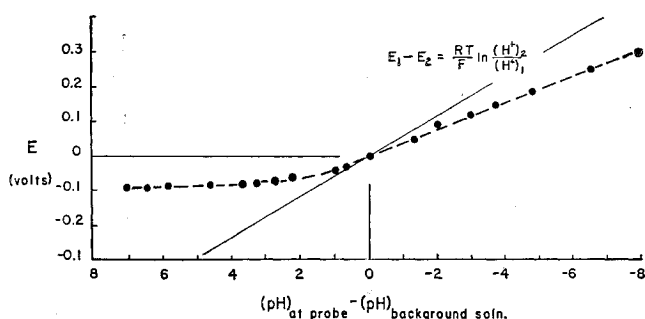


Fig. 2 Calibration of probe used as a micro-pH meter.

sponds only to conductivity changes. In fact, it was found that the actual probe response was a slowly fluctuating offset signal in the direction of increasing conductivity when base only was injected with neutral background, and in the direction of decreasing conductivity for acid. This probe response has yet to be satisfactorily explained. Clearly the probe is sensitive to acid and base concentration when used in an a.c. bridge, but with very poor frequency response. Assuming the response to acid, base and salt concentrations are independent of each other, we might still be able to measure small-scale features of the salt (reaction product) distribution in the presence of the reactants because the probe appears to be insensitive to small-scale fluctuations of acid and base. Since for rapid reactions the source distribution of reaction product is probably confined to very thin "reacting surfaces," the small-scale features of the reaction product field might be expected to exhibit differences with and without reaction which would still be detectable with the present detector.

In order to test for such differences in the small-scale distributions of reaction product with and without reaction, the comparison experiments 1 and 2 indicated by Fig. 1 were carried out. In experiment 1, a reacting wake is generated by injecting acid at the upstream stagnation point of the sphere at molal flow rate \dot{A} and injecting base at the downstream point at approximately the same flow rate \dot{B} . In experiment 2, a nonreacting wake is generated by injecting premixed reactants at rates $(\dot{A} + \dot{B})/2$ through upstream and downstream ports of the sphere under identical flow conditions, where exactly the same ratio of A and B solutions used in experiment 1 are added to a mixing tank where they form the injected salt solution.

In the following, two sets of measurements of the reacting and premixed wake at stations 2.17 diam and 7.5 diam along the wake axis are described. The wake has been described as "reacting." It is quite certain that some reaction was present at the points of measurement, but it is possible that the reaction was nearly completed even at the 2.17 diam station. For example, if we assume (arbitrarily) an e -folding distance of 1 diam, the reaction would have been 90% completed at 2 diam.

An attempt was made to measure the extent of reaction in the reacting wake by using the conductivity probe as a micro-pH meter. Using an oscilloscope, it was found that voltage fluctuations exist between the probe tip and the grounded metal tunnel walls in the reacting wake, or when acid or base are injected alone. The voltage fluctuations for weak acid or weak base in the presence of their salt are small because of the buffering action of the salt. The voltage fluctuations are also at low frequencies, less than 3 Hz or so, because the high resistance of the probe (50–200 kohm) causes capacitive shunt-

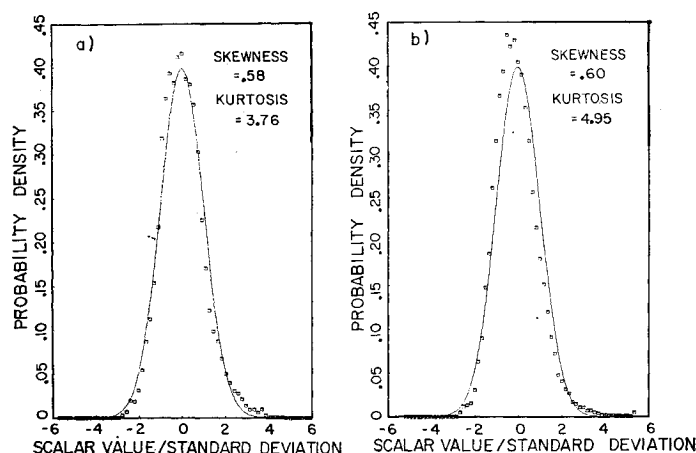


Fig. 3 Probability density function at 2.17 diam compared with gaussian, 8×10^4 samples, wake axis: a) reacting wake, b) premixed wake.

ing of higher frequencies due to cable capacitance and the finite input impedance of the oscilloscope amplifier. The sign of the probe voltage was found to be consistent with the Nernst electrode equation $E_2 - E_1 = -(RT/F)\ln(H_2^+/H_1^+)$ for injection of strong acid and base solutions of known pH with the probe in the injection port of the sphere, where R = gas constant, F = Faraday's constant, T = temperature, H^+ = hydrogen ion concentration, E_1 and E_2 are voltages.⁴ The measured voltage of the probe at various pH values is shown in Fig. 2, compared to the Nernst equation.

To reduce capacitive shunting a Tektronic PG045 Field Effect Transistor (FET) probe was immersed in the test section with less than 2 in. of conductor between its input and the platinum electrode. This improved the frequency response of the "micro-pH probe" by over a factor of ten. HNO_3 and $NaOH$ solutions were injected at approximately the sample flow conditions as used in the previous experiments and the concentration of reactants remaining were estimated from the measured voltage fluctuations and integrated. Because the frequency response of the pH probe is still limited, and because the voltage-concentration relation is so nonlinear, it was difficult to obtain precise estimates of the amount of remaining reactants. The values indicated by the preceding method were that at least 5% of the reactants initially injected are still unreacted at 2.17 diam downstream, and that at least 2% remain at 7.5 diam.

Bridge signals proportional to salt concentration fluctuations at the probe tip were recorded with an FM analog tape recorder. Later this tape was played back, usually at reduced speed, and the output signal sampled, held, converted to a 6 bit digital number and recorded on computer compatible tape on an incremental tape recorder.

The tape was rerecorded under computer control as records of 2048 samples each separated by record gaps, and the time series analysis was performed on the "gapped" data using the CDC 3600 computer.

III. Results and Conclusions

As previously indicated, reacting and premixed wake concentration fluctuations were detected on the wake axis at $x = 2.17$ and 7.5 diam. All measurements were made during a period of less than 1 hr using the same conductivity probe, injected solutions, tunnel pump setting, and probe position at each x station. The Reynolds number based on the upstream velocity and the sphere diameter was 17,400.

Using the gapped digital time series, the record mean, the second, third, and fourth moments about the mean and the histogram of the distribution of samples about the mean were calculated and averaged for various numbers of 2048 sample records. For comparison with the gaussian distribution the

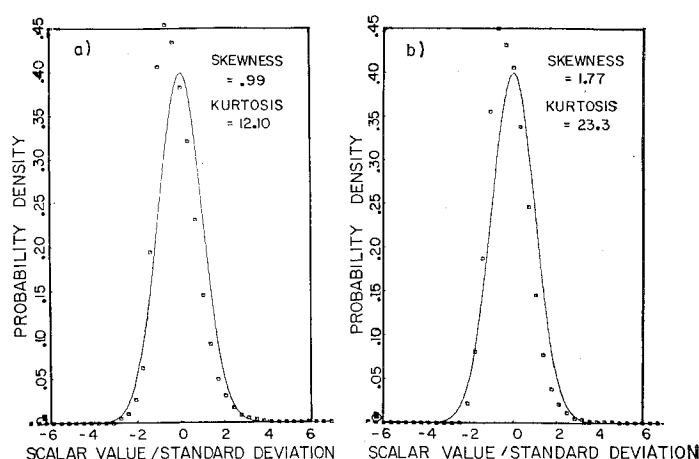


Fig. 4 Probability density function at 7.5 diam compared with gaussian, 8×10^4 samples, wake axis: a) Reacting wake, b) Premixed wake.

skewness, defined as the third moment divided by the $\frac{3}{2}$ power of the second moment, and the kurtosis, defined as the fourth moment over the square of the second moment (all moments are taken about the record mean), were computed and the results listed along with the plot of the histogram on the graph generated by the computer plotter.

Figure 3a shows a plot of the mean histogram of 40 records (81,920 samples) of the reacting wake at 2.17 diam normalized by the standard deviation and compared to a gaussian probability density function normalized in the same way. It is clear that the fit is far from perfect, and the skewness, which is zero for a gaussian, is +0.58 for the reacting wake. The mean kurtosis of 3.76 is also somewhat larger than 3.0 expected for a gaussian distribution. For the nonreacting "premixed" wake at the same position the fit is even worse, with skewness = 0.60 and kurtosis = 4.95 as shown by Fig. 3b. The estimated rms concentration fluctuation for the premixed wake is 15 ppm, although an absolute calibration was not determined. All distribution plots are on the same relative scale of "scalar value."

For 7.5 diam downstream on the wake axis similar 40 record histograms for the reacting and premixed wakes are shown in Figs. 4a and 4b, respectively. It is clear that both distributions are distinctly nongaussian, with the premixed wake having the greatest departure.

Part of the explanation for the very large values of kurtosis observed may be found by examining "local" histograms calculated from fewer records. Skewness and kurtosis values calculated for only 5 records (containing only 1024 samples each) are shown in Table 1 for reacting the premixed wakes at the two axial positions 2.17 and 7.5 sphere diameters. Extreme variation is indicated, especially for the kurtosis, which ranged from 2.7 to 36.5 for "local" samples shown in Table 1. Examination of the individual histograms shown in Figs. 5a and 5b for 2.17 diam and Figs. 6a and 6b for 7.5 diam reveals that associated with most very large kurtosis values are a cluster of large positive points corresponding to the maximum measurable scalar value; namely $2^6 = 32$ (see Fig. 6b). These "spikes" are also evident from observation of the oscilloscope records, and are much more frequent and pronounced for the "premixed" salt injection and occur most frequently if the injection is upstream and quite smooth. Any jetting of the upstream injection, or injecting downstream, causes them to decrease in both amplitude and frequency. The spikes are thought to be due to fragments of the high salt concentration injection fluid which by some unknown mechanism manages to become part of the irrotational flow and ride for long distances just outside the "superlayer" separating the rotational wake fluid and the essentially irrotational external flow. Because of the very small molecular diffusivity of the salt, the

Table 1 Skewness and kurtosis values for "local" histograms, 10^4 data samples

Reacting wake		Premixed wake	
S	K	S	K
2.17 sphere diameters, wake axis			
0.34	3.6	0.40	3.8
0.72	3.7	0.80	5.3
0.70	3.0	0.69	6.4
7.5 sphere diameters, wake axis			
1.1	10.9	3.3	36.5
3.1	31.1	-0.1	3.2
-0.1	2.7	0.7	10.4

Definition of skewness S and kurtosis K :

$$S(x) \equiv \langle x^3 \rangle / \langle x^2 \rangle^{3/2}$$

$$K(x) \equiv \langle x^4 \rangle / \langle x^2 \rangle^2$$

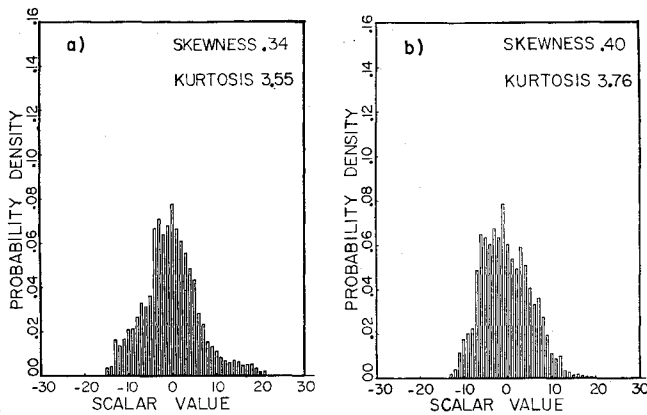


Fig. 5 Probability density function at 2.17 diam, 10^4 samples, wake axis: a) Reacting wake, b) Premixed wake.

particle retains its initial high conductivity and will produce a spike if it encounters the conductivity probe tip. Observation of simultaneous velocity and conductivity signals with hot-film anemometer and conductivity probe tips less than 2 mm apart showed frequent coincidence of the spikes and the superlayer.

Presumably the same thing could happen to an acid fluid particle injected upstream in the "reacting" wake experiments, but if the conductivity of the acid solution and background solutions are closely matched then the acid blob would not be able to produce a spike because the unreacted acid is nonconducting.

It is interesting to observe that a form of spike phenomena was rather expected, but it was expected to occur in the reacting wake because of the presence of reacting surfaces and not in the premixed wake. So far no observation has been made of a phenomenon which can be attributed to the presence of reacting surfaces, but these are merely preliminary observations in an exploratory study, and all possibilities have not been exhausted. It may well be that the extent of reaction is too large for any "reacting" effects to be observable, even at 2 diam.

Figure 7 shows mean power spectra computed for the reacting and premixed wakes at the 2.17 diam station. Each data record was Fourier transformed using the Cooley-Tukey Fast Fourier transform algorithm, the power spectrum found from the sum of the squares of the real and imaginary coefficients, smoothed over $\frac{1}{10}$ decade wavenumber increments, and the average power for each increment found for 100 records (making 204,800 samples per spectrum shown in Fig. 7). The computation time plus plotting took a little over three minutes per spectrum, which is less than the real time elapsed in accumulating the hundred data records. This implies that it

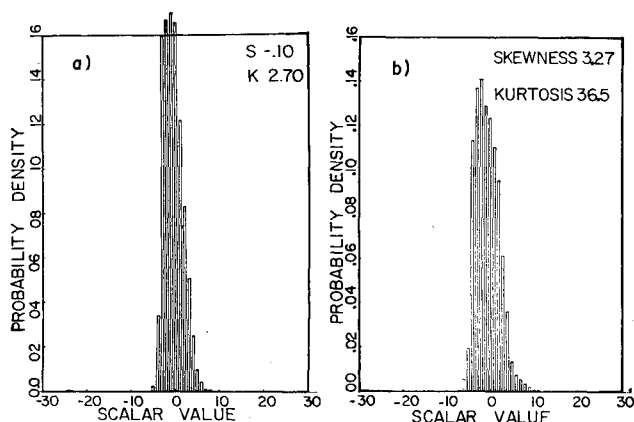


Fig. 6 Probability density function at 7.5 diam, 10^4 samples, wake axis: a) Reacting wake, b) premixed wake.

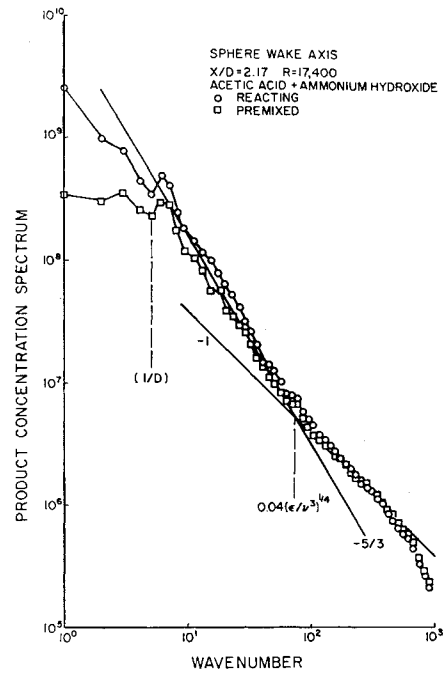


Fig. 7 Power spectra at 2.17 diam, wake axis.

would be possible to acquire and reduce the data to average power spectra in real time with no loss of information if this were desired.

Both reacting and premixed spectra in Fig. 7 are nearly identical both in absolute value and shape except for the smaller wavenumbers, where the reacting spectrum is at a higher level. Both show similar bumps at $k = 1/D$ and larger, with an inertial $-\frac{5}{3}$ subrange as expected from theories of Obukhoff⁵ and Corrsin⁶ for $1/D < k < 0.04 (\epsilon/\nu^3)^{1/4}$, where $(\epsilon/\nu^3)^{1/4}$ is the Kolmogoroff wavenumber based on the kinematic viscosity ν and the mean viscous dissipation rate per unit mass ϵ . For this calculation, ϵ was estimated from the empirical formula determined in Ref. 3.

At about $0.04 (\epsilon/\nu^3)^{1/4}$ both spectra exhibit a distinct upward inflection to a slope very close to the value of -1 predicted by Batchelor⁷ before cutting off at a frequency set on a

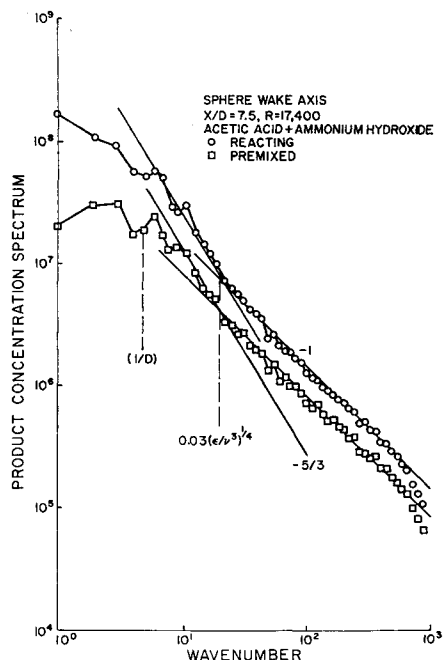


Fig. 8 Power spectra at 7.5 diam, wake axis.

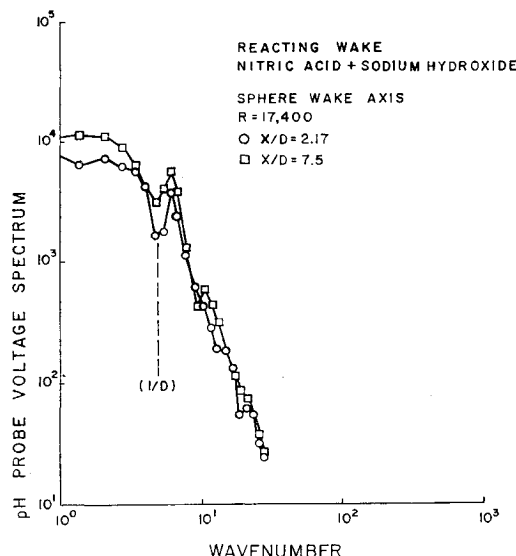


Fig. 9 Power spectra of pH probe voltage in reacting wake, wake axis.

low pass analog filter, which was used to prevent high-frequency aliasing.

Figure 8 is an equivalent pair of reacting and premixed scalar spectra, this time detected on the wake axis at 7.5 diam downstream. Again the shapes are more similar than at 2 diam. The absolute value of the reacting spectra was at a distinctly higher level. It is not clear at this time whether this result is reproducible or not, and if it is, how it can be explained.

Both spectra again exhibit low-frequency bumps apparently related to the wake diameter and an upward inflection at nearly the same fraction of the Kolmogoroff wavenumber, this time 0.03 rather than 0.04, to much more extensive and precise viscous convective minus one subranges than it has ever been possible to measure previously⁸⁻¹⁰ because of the limitations of analog techniques. The value of the inflection from the inertial to viscous-convective subranges of 0.035 ± 0.005 indicated by these spectra are consistent with the inflection values measured by Gibson and Schwarz⁸ and are also in good agreement with the value reported recently by Grant et al.¹⁰ of 0.024 ± 0.008 .

Figure 9 shows two power spectra (with shifted ordinates for comparison) of the FET probe amplified conductivity probe voltage in a reacting wake with nitric acid and sodium hydroxide injection. A platinum probe was used nearly identical to the probe used previously for the data of Figs. 7 and 9. Mean velocity and probe positions were also the same. In view of the voltage versus pH calibration of Fig. 2 we might also consider Fig. 9 as roughly the spectrum of the logarithm of the acid concentration in the reacting wake. It also probably represents the source of low-frequency "noise" affecting the reacting spectra in Figs. 7 and 8. Without the FET probe the spectra would fall off even more steeply than those of Fig. 9, which are steeper than $-\frac{5}{3}$ for all wavenumbers beyond the energy scale. Peaks occur in the voltage spectra of Fig. 9 at wavelengths about 3 times the sphere diameter, just

as they did for the reacting and nonreacting wakes of Figs. 7 and 8. At present no attempt has been made to invert the voltage signal to recover reactant concentration using the calibration curve of Fig. 2, but this procedure is clearly feasible using digital techniques, and offers exciting possibilities for future study.

IV. Summary

Measurements of chemical reaction product distribution in the reacting and nonreacting turbulent wake of a sphere have been described along with some promising techniques for digital data acquisition and reduction. It was discovered that conductivity probes can be used to measure pH fluctuations less than 7. Long and short time average distribution functions were determined for the reacting and premixed wake signals and were found to be quite nongaussian even after ignoring the effect of an interesting but somewhat spurious spike generation phenomena associated with the injection technique. Spectral shapes for reaction product fluctuations for the reacting and nonreacting wakes were found to be nearly identical except for low wavenumbers where the reacting spectrum is apparently distorted by the pH signal. The larger wavenumber subrange slopes and intersection points were quite consistent with theoretical predictions and previous measurements for locally isotropic turbulent mixing of weakly diffusive scalar fluid properties. A precise determination of the inflection point from the inertial to viscous convective subrange of the scalar spectrum was achieved using digital harmonic analysis techniques. The point occurs at $\frac{1}{30}$ the Kolmogoroff wavenumber.

References

- ¹ Toor, H. L., "Mass Transfer in Dilute Turbulent and Non-Turbulent Systems with Rapid Irreversible Reactions and Equal Diffusivities," *AIChE Journal*, Vol. 8, No. 1, March 1962, pp. 70-78.
- ² Keeler, R. N., "Mixing and Chemical Reactions in Turbulent Flow Reactors," thesis UCRL-7852, 1964, Univ. of California, Berkeley.
- ³ Gibson, C. H., Chen, C. C., and Lin, S. C., "Measurements of Turbulent Velocity and Temperature Fluctuations in the Wake of a Sphere," *AIAA Journal*, Vol. 6, No. 4, April 1968, pp. 642-649.
- ⁴ Bates, R. G., *Determination of pH; Theory and Practice*, Wiley, New York, 1964, Chap. 2, p. 21.
- ⁵ Obukhoff, A. M., *Izvestiya Akademii Nauk, SSSR, Seriya Geograficheskaya i Geofizicheskaya*, Vol. 13, No. 58, 1949.
- ⁶ Corrsin, S., *Journal of Applied Physics*, Vol. 22, No. 4, April 1951, pp. 469-473.
- ⁷ Batchelor, G. K., "Small Scale Variation of Convected Quantities Like Temperature in Turbulent Fluid. Part I: General Discussion and the Case of Small Conductivity," *Journal of Fluid Mechanics*, Vol. 5, Pt. 1, Jan. 1959, pp. 113-133.
- ⁸ Gibson, C. H. and Schwarz, W. H., "The Universal Equilibrium Spectra of Turbulent Velocity and Scalar Fields," *Journal of Fluid Mechanics*, Vol. 16, Pt. 3, July 1963, pp. 365-384.
- ⁹ Nye, J. O. and Brodkey, R. S., "The Scalar Spectrum in the Viscous Convective Subrange," *Journal of Fluid Mechanics*, Vol. 29, Pt. 1, July 1967, pp. 151-163.
- ¹⁰ Grant, H. L., et al., "The Spectrum of Temperature Fluctuations in Turbulent Flow," *Journal of Fluid Mechanics*, Vol. 34, Pt. 3, 1968, pp. 423-442.