Thermal Method of Measuring Concentration During Turbulent Reactive Mixing

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When the total reactant diffusivities are equal, the time-average concentration fields which result from turbulently mixing reactants can be measured thermally if the temperature difference between the feed streams is suitably chosen. Each reactant profile is obtained from measurements of the temperature profile in an experiment in which the inlet temperature of that reactant is less than that of the other reactant by an amount equal to the adiabatic reaction temperature change of the measured reactant. The method is demonstrated in a liquid phase confined jet reactor.

The thermal method of measuring conversion derives from a simple steady-state energy balance on a dilute adiabatic reactor without axial dispersion (Roughton and Chance, 1963; Vassilatos and Toor, 1965).

$$\rho C_p(\overline{T}-\overline{T}_O)=\lambda(\overline{C}_{AO}-\overline{C}_A)=\lambda\overline{C}_{AO}(1-F) \qquad (1)$$

This balance states that all the heat absorbed or released by the reaction has gone into changing the temperature of the fluid passing through the reactor. It is true (if axial dispersion is negligible) when the inlet and exit concentration and temperature are constants. It is also true when concentration and/or temperature are not constants—functions of tube radius, for example—if concentration and temperature are bulk averages. Measurement of the average temperature change then determines the average concentration change and hence the average concentration crossing a downstream plane, but gives no information about any local concentrations. In this situation, in which the concentration and temperature fields inside the reactor are multidimensional, all parts of the system are interconnected by molecular and turbulent diffusion. Thus the development of a multidimensional analog of Eq. 1 must start with the detailed transport equations.

We start with the averaged equations for a turbulent, dilute reacting system:

$$\frac{DC_i}{Dt}=\frac{\partial C_i}{\partial t}+\underline{V}\cdot\nabla C_i=\nabla\cdot(D_i+\epsilon_{\mathrm{mi}})\nabla C_i-r_i \qquad (2)$$

$$\frac{DT}{Dt}=\frac{\partial T}{\partial t}+\underline{V}\cdot\nabla T=\nabla\cdot(\alpha+\epsilon_h)\nabla T+\frac{\lambda r_i}{\rho C_p} \qquad (3)$$

All quantities are time-averaged. The eddy diffusivity formalism has been used to partially close the equations—there is no need to close the averaged reaction term since it will be eliminated. The eddy diffusivities are position, geometry and flow dependent (Hinz, 1959). They are also generally tensorial in nature, but are basically scalar in situations where turbulent diffusion is effectively unidirectional.

We now wish to carry out transformations of Eqs. 2 and 3 which require equality among the total diffusivities:

$$D_A+\epsilon_{mA}=D_B+\epsilon_{mB}=\alpha+\epsilon_\alpha\equiv D_t \qquad (4)$$

These conditions are satisfied if

$$\epsilon_{mA}=\epsilon_{mB}=\epsilon_h \qquad (5)$$

and either $D_A=D_B=\alpha$ or (6)

$$\epsilon_{mA}\gg D_A,\quad \epsilon_{mB}\gg D_B,\quad \epsilon_h\gg\alpha \qquad (7)$$

Equation 6 is approximately true in some gaseous systems, but since we are mixing miscible fluids, not transferring heat or mass across interfaces, Eq. 7 will hold in liquids as well as gases with only moderate amounts of mixing.

The weight of evidence in *nonreacting* systems (Reynolds, 1975; Launder, 1978) indicates that, except for extreme cases like liquid metals, or H_2 in air (Kerstein and Dibble, 1989), eddy diffusivities are independent of molecular diffusivities and Eq. 5 is satisfied. The data are primarily from experiments

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in which the turbulent diffusion was effectively unidirectional, but there is little reason not to expect the equality to hold otherwise.

There is more uncertainty about applying Eq. 5 to reacting systems since Bilger et al. (1991) report on effect of reaction on eddy diffusivities in an isothermal, nonpremixed reacting system of gases. Since the effect is different for each reactant it must be small if Eq. 5 is to hold. We will tentatively assume that Eq. 5 is valid and that the turbulence level is high enough for Eq. 7 to hold so that Eq. 4 is satisfied. The consequences will be tested with liquid phase reactions.

For concreteness and also because we will present data for this situation we consider a coaxial turbulent jet of fluid mixing with a second stream of the same fluid. The jet leaves the nozzle with dilute reactant A at the concentration C_{AO} and A reacts with reactant B which enters at the dilute concentration C_{BO}. The single reaction is $A + nB \leftrightarrow$ products and the enthalpy change on reaction is $-\lambda$. The heat released (or absorbed) by the reaction affects a temperature field which fluctuates but whose time-average value is stationary and easily measured.

The boundary conditions on Eqs. 2 and 3 are:

$$A \text{ inlet}, \quad C_A = C_{AO}, \quad C_B = 0, \quad T = T_A \tag{8a}$$

$$B \text{ inlet}, \quad C_B = C_{BO}, \quad C_A = 0, \quad T = T_B \tag{8b}$$

$$\text{tube walls}, \quad \frac{\partial C_A}{\partial n} = \frac{\partial C_B}{\partial n} = \frac{\partial T}{\partial n} = 0 \tag{8c}$$

Let $i = A$ in Eq. 2, multiply that equation by λ, multiply Eq. 3 by ρC_p and add the resulting equations to obtain, after using Eq. 4,

$$\left[\frac{D}{Dt} - \nabla \cdot D_t \nabla\right][\lambda C_A + \rho C_p T] = 0 \tag{9}$$

If there is no reaction, A and temperature behave as *tracers* which enter in the A stream and passively mix with the B stream. They satisfy:

$$\left[\frac{D}{Dt} - \nabla \cdot D_t \nabla\right] C_A^0 = \left[\frac{D}{Dt} - \nabla \cdot D_t \nabla\right] T^0 = 0 \tag{10}$$

Both the "enthalpy", $\lambda C_A + \rho C_p T$, and tracers, C_A^0 and T^0, satisfy the same equation (Eqs. 9 and 10). We make the boundary conditions the same with the following nondimensional quantities,

$$\frac{C_A^0 - 0}{C_{AO} - 0} = \frac{T^0 - T_B}{T_A - T_B} = f \tag{11}$$

$$\frac{(\lambda C_A + \rho C_p T) - (0 + \rho C_p T_B)}{(\lambda C_{AO} + \rho C_p T_A) - (0 + \rho C_p T_B)} = g \tag{12}$$

Then,

$$\left[\frac{D}{Dt} - \nabla \cdot D_t \nabla\right] g = \left[\frac{D}{Dt} - \nabla \cdot D_t \nabla\right] f = 0 \tag{13}$$

and

$$A \text{ inlet}, \quad g = f = 1 \tag{14a}$$

$$B \text{ inlet}, \quad g = f = 0 \tag{14b}$$

$$\text{tube walls}, \quad \frac{\partial g}{\partial n} = \frac{\partial f}{\partial n} = 0 \tag{14c}$$

so everywhere inside the reactor

$$g = f \tag{15}$$

or

$$\lambda C_A + \rho C_p (T - T_B) = [\lambda C_{Ao} + \rho C_p (T_A - T_B)] f \tag{16}$$

So the time-average temperatures and concentrations in turbulent reacting fluids are linearly related to the time-average tracer concentration. Equation 16 can be used in turbulent systems in which Eq. 4 is satisfied to obtain the local time average concentration C_A from measurement of time average temperature T, and time average tracer f. The need to measure f can be eliminated by raising the temperature of the B stream so that the inlet temperature difference is the adiabatic temperature rise for complete conversion of A, that is,

$$\lambda C_{AO} + \rho C_p (T_A - T_B) = 0 \tag{17}$$

Then Eq. 16 reduces to

$$\frac{C_A}{C_{AO}} = \frac{\rho C_p (T_B - T)}{\lambda C_{AO}} = \frac{T_B - T}{T_B - T_A} \tag{18}$$

Note that the "enthalpy," $\lambda C_A + \rho C_p T$, is now the same everywhere in the reactor.

The equations for B are obtained by making the A stream the warmer one,

$$\lambda C_{BO} + n \rho C_P (T_B - T_A) = 0 \tag{19}$$

so

$$\frac{C_B}{C_{BO}} = \frac{n \rho C_p (T_A - T)}{\lambda C_{BO}} = \frac{T_A - T}{T_A - T_B} \tag{20}$$

A somewhat different derivation of the above equations is given by Singh (1973). Although Singh used Eqs. 17 and 18 and Eqs. 19 and 20 in two separate measurements, only one is needed if f is known since, subtracting Eq. 2 for A from the same equation for B and then nondimensionalizing as before, leads to

$$\frac{nC_A - C_B + C_{BO}}{nC_{AO} + C_{BO}} = f \tag{21}$$

where f is the nondimensional tracer profile given by Eq. 11. [Equation 21 also holds instantaneously when the molecular diffusivities of A and B are equal and in that form is the starting point for the "conserved scalar" method of treating nonpre-

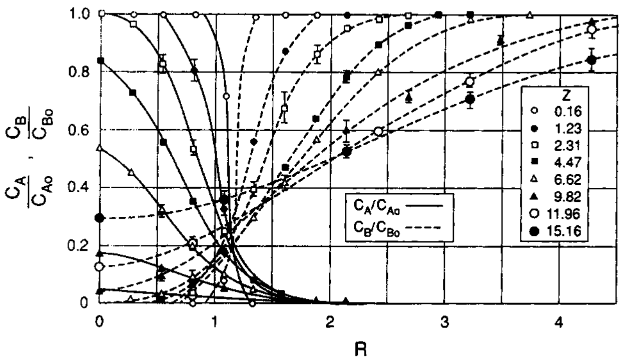

Figure 1. Profiles of C_A/C_{AO} and C_B/C_{BO} from Eqs. 18 and 20.

Instantaneous reaction, HCl + NaOH; $\beta = 1$; 0.00476 m diameter jet in a 0.0762 diameter tube; jet Reynolds number of 9,400; volumetric flow rate ratio of outer to inner tube of 5.

mixed turbulent reactions (Toor, 1962; Lin and O'Brien, 1974; Li and Toor, 1986; Bilger et al., 1991).]

Equations 11, 18, 20 and 21 allow three independent experiments which can be used to test the proposed method. The nondimensional temperature profile f can be measured in the absence of reaction with hot and cold water using Eq. 11. This result depends upon the total thermal diffusivity. Then two independent thermal experiments, one using Eqs. 17 and 18 and one, Eqs. 19 and 20, give C_A and C_B which depend upon both total mass and total thermal diffusivity. If all the total diffusivities are equal, then the combination of C_A and C_B given by Eq. 21 should give the same value of f as obtained in the nonreacting experiment.

Experiments of this type were carried out in a confined jet apparatus (0.00476-m-dia. jet centered in a 0.0762-m-dia. tube) with a jet Reynolds number of 9,400 and a volumetric flow rate ratio of outer to inner liquid of 5.

In the purely thermal measurement of f the inlet water temperature difference was 0.4°C. The resulting time-average temperature profiles were measured with a traversing thermocouple made from 36 gauge chromel-constantan wire which had a glass coated 0.78 mm diameter beaded tip. The resulting profiles are shown in Figures 2 through 5 where they are labeled hot-cold water.

Reaction experiments followed using the instantaneous HCl-NaOH reaction as well as the slower but still rapid reaction between dissolved CO_2 and NaOH. The reaction experiments were in the same apparatus with the same flow rates as the nonreacting experiment. Reactant inlet concentrations varied from 0.012 to 0.81 kmol/m^3 while inlet temperature differences varied from 0.27 to 0.99°C in order to satisfy Eqs. 17 or 19. The resulting values of C_A and C_B, obtained from Eqs. 18 and 20, are shown in Figure 1 for the instantaneous reaction when the feed concentration ratio was stoichiometric. Data at other feed ratios are in Singh (1973) as are individual reactant concentrations for the CO_2-NaOH system which are not shown here.

All the measured values of C_A and C_B, including those not shown here, were then used to compute f at each position and in Figures 2 through 5 these are compared with each other and with the f measured without reaction. Because the reaction contributions are strong functions of position, the data are shown over a wide range of axial and radial position.

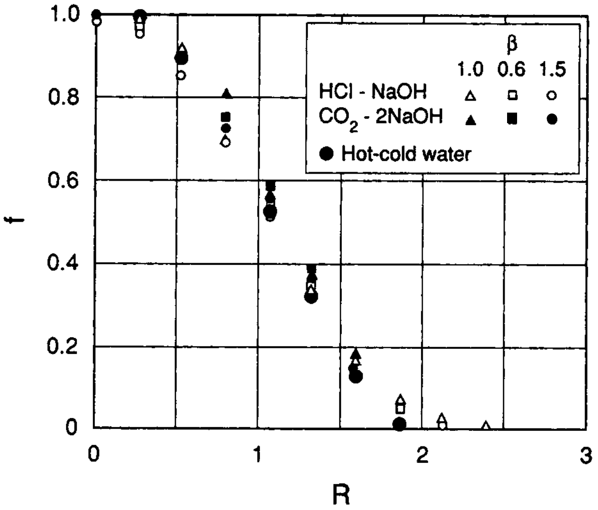

Figure 2. f from Eq. 11 using hot and cold water and f from Eq. 21 with C_A and C_B from Eqs. 18 and 20.

Two different reactions with three different stoichiometric feed ratios; 2.31 jet diameters downstream from jet mouth. Same apparatus and flow rates as in Figure 1.

The data in Figures 2 through 5 (like similar data in Singh) show no consistent difference among the values of f found in the seven sets of experiments. Since these cover nonreacting as well as different kinds of reacting systems, with different feed concentration ratios, traversing a wide range of concentration and temperature profiles, they appear to validate the thermal method. Nevertheless, the relatively unknown effect of reaction on diffusivities suggests some caution in generalizing to other systems.

One-Dimensional Reactor in Eq. 1

We bulk weighted averages in the usual manner, so that they are appropriate for use in energy and material balances,

$$\bar{X}=\frac{1}{\bar{V}A_T}\int_{A_t} X\underline{V}\cdot\underline{n}dA, \quad X=T,C_A,C_B. \tag{22}$$

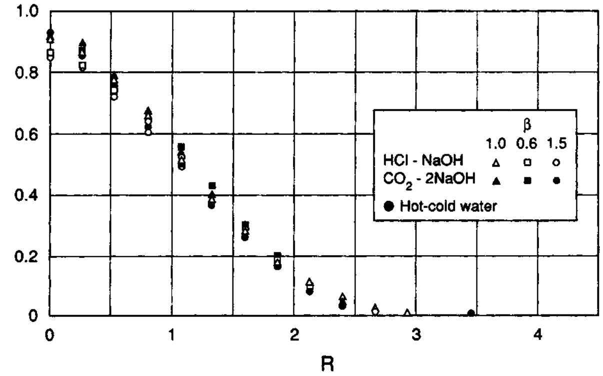

Figure 3. Same as Figure 2; however, 4.47 jet diameters downstream.

Two different reactions with three different stoichiometric feed ratios.

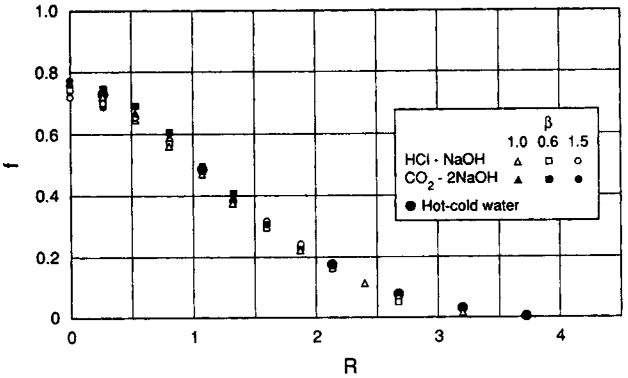

Figure 4. Same as Figure 2; however, 6.62 jet diameters downstream.

Two different reactions with three different stoichiometric feed ratios.

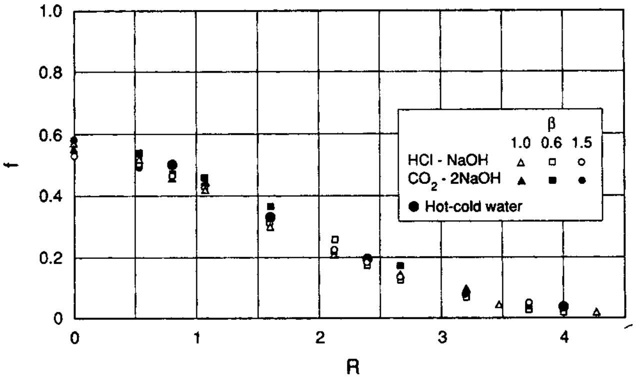

Figure 5. Same as Figure 2; however, 9.82 jet diameters downstream.

Two different reactions with three different stoichiometric feed ratios.

Then integrating Eq. 16

$$\lambda\overline{C}_A+\rho C_p(\overline{T}-T_B)=[\lambda C_{AO}+\rho C_p(T_A-T_B)]\bar{f} \qquad (23)$$

Since $\bar{f}$ is constant, subtracting Eq. 23 from itself at the inlet gives Eq. 1, but now without the restriction of negligible downstream axial dispersion. Except for a symmetrical kind of feed device, axial dispersion at the inlet apparently would invalidate Eq. 1. (Vassilatos and Toor, 1965, incorrectly imply otherwise.) Of course, under ordinary circumstances axial dispersion can be neglected at both ends of the reactor.

The multidimensional thermal method, like the unidirectional version, is limited to single step reactions, but in both cases with such reactions has the convenient characteristic of being independent of the chemical species involved.

Notation

A = area
C = time-average concentration
C_p = heat capacity
D_i = molecular diffusivity
D_t = total diffusivity, Eq. 4
f = time-average nondimensional tracer concentration
F = fractional conversion
g = time-average nondimensional enthalpy
n = stoichiometric constant or distance normal to wall
$\underline{n}$ = outward normal
$\bar{r}$ = reaction rate
R = number of jet radii from centerline of jet
t = time
T = time-average temperature
$\underline{V}$ = velocity
$\bar{X}$ = T or C_i
Z = number of jet diameters downstream

Greek letters

α = molecular diffusivity of heat
β = C_{BO}/nC_{AO}
ϵ_h = eddy diffusivity of heat
ϵ_{mA} = eddy diffusivity of reactant A
ϵ_{mB} = eddy diffusivity of reactant B
λ = negative enthalpy change on reaction
ρ = density

Subscripts

A, B = reactants A and B or temperature of inlet streams A and B
i = A or B
O = inlet
t = total

Superscripts

— = bulk average
o = absence of reaction

Literature Cited

Bilger, R. W., L. R. Saetran and L. W. Krishnamoorthy, "Reaction in a Scalar Mixing Layer," *J. Fluid Mech.*, **23**, 211 (1991).

Hinze, J. O., *Turbulence*, McGraw-Hill, New York (1959).

Kerstein, A. R., and R. W. Dibble, "Measurement and Computation of Differential Diffusion in a Turbulent Jet," *Symp. on Turbulent Shear Flows*, Stanford University (1989).

Launder, B. E., "Heat and Mass Transport," *Topics in Applied Physics*, **12**, P. Bradshaw, ed., 2nd ed., Springer-Verlag, Berlin (1978).

Li, K. T., and H. L. Toor, "Chemical Indicators as Mixing Probes: A Possible Way to Measure Micromixing Simply," *I&EC Fund.*, **25**, 719 (1986).

Lin, C. H., and E. E. O'Brien, "Turbulent Shear Flow Mixing and Rapid Chemical Reactions: An Analogy," *J. Fluid Mech.*, **54**, 195 (1974).

Reynolds, A. J., "The Prediction of Turbulent Prandtl and Schmidt Numbers," *Int. J. Heat Mass Transf.*, **18**, 1055 (1975).

Roughton, F. J. W., and Britton Chance, *Technique of Organic Chemistry*, S. L. Friess, E. S. Lewis, and A. Weissberger, eds., Vol. VII, Pt. II, Interscience, New York, p. 703 (1963).

Singh, M., "Chemical Reactions in One and Two Dimensional Turbulent Flow Systems," PhD Thesis, Carnegie Mellon University, Pittsburgh (1973).

Toor, H. L., "Mass Transfer in Dilute Turbulent and Non-Turbulent Systems with Rapid Irreversible Reactions and Equal Diffusivities," *AIChE J.*, **8**, 70 (1962).

Vassilatos, G., and H. L. Toor, "Second-Order Chemical Reactions in a Nonhomogeneous Turbulent Fluid," *AIChE J.*, **11**, 666 (1965).

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