Causes, Magnitude, and Effects of Temperature Fluctuations (Flickering) of Catalytic Wires and Gauzes

An experimental study has confirmed a theoretical prediction that, when an exothermic mass transfer limited chemical reaction occurs on a single catalytic wire for which the parameter a [Equation (11)] is large, temperature fluctuations (flickering) of large amplitude must be induced by concentration fluctuations. A simplified model is presented for predicting the magnitude of flickering in industrial convertors for which the parameter a is usually large. The model should be useful in estimating the influence of improved mixing of the reactants on the reduction in precious metal loss from the gauze.

W. M. EDWARDS
J. E. ZUNIGA-CHAVES
F. L. WORLEY, JR.
and DAN LUSS

Department of Chemical Engineering
University of Houston
Houston, Texas 77004

SCOPE

The industrial ammonia oxidation process utilizes a catalytic gauze consisting of 10 to 40 layers of platinum-rhodium wire screens. Observations of these gauzes reveal localized regions of high luminosity whose intensity fluctuates randomly with time, a phenomenon referred to as *flickering*. Nowak (1969) reported that the rate of precious metal loss in the ammonia oxidation process, which accounts for about 5% of the manufacturing costs, can be represented by an Arrhenius temperature dependence with an activation energy of about 40,000 cal/g mole. Due to this convex temperature dependence, temperature oscillations (flickering) increase the metal loss above the level corresponding to uniform temperature operation at the same average temperature. Thus, information about the magnitude and causes of flickering could lead to a design which reduces these precious metal losses.

Ervin and Luss (1972) used numerical simulation to show that large amplitude flickering can be induced by the fluctuations of the turbulent transport coefficients (caused by velocity fluctuations) if the parameter a, which is the ratio of the characteristic time for changes in wire diameter to the characteristic time for surface concentration changes, was of order unity or less. However, under the conditions prevailing in industrial convertors the parameter a is very large, and for this case numerical simulations indicate that the magnitude of flickering induced by velocity fluctuations is negligible. A model presented here shows that if the parameter a is large and the reactants are not completely mixed on a molecular level, concentration fluctuations can induce flickering of large amplitude. Edwards et al. (1973) measured large amplitude flickering during the catalytic oxidation of butane in air on single platinum wires for which a was rather large. The experiments demonstrated the existence of a correlation between flickering and the turbulence of the reacting gas but did not enable a determination of the specific cause for flickering.

The main objective of this work was to determine the primary cause of flickering of single catalytic wires for which the parameter a is much larger than unity. To this end a high resolution infrared detector was used to measure localized surface temperature fluctuations on single platinum wires during the catalytic oxidation of either hydrogen or ammonia in air. By changing the feed port location and method of injection various intensities of concentration fluctuations were obtained in the same turbulent flow field. The results of this study were used to develop a theoretical model for predicting the causes and magnitude of flickering under the conditions prevailing in industrial convertors.

CONCLUSIONS AND SIGNIFICANCE

A series of measurements of the root mean square temperature fluctuations in the same turbulent flow field and various levels of concentration fluctuations indicated that concentration fluctuations must be the primary cause for flickering of the magnitude observed in industrial convertors. The theoretical predictions of Equation (23) adequately described the relation between local flickering on a single wire and local concentration fluctuation intensity. A comparison of the probability density functions of the fluctuations about the mean of the wire's temperature with those of the concentration and velocity of the reacting gas further confirm the conclusion that flickering was induced by concentration and not velocity fluctuations. The spectral density functions of the temperature fluctuations do not enable a conclusive determination of the cause of flickering.

A simplified model was developed for estimating the magnitude of flickering in industrial gauze convertors [Equation (41)]. The model predicts that under the conditions prevailing in typical high pressure ammonia convertors imperfect mixing and concentration fluctuations are the main causes for flickering. Thus, equipment modifications which reduce the concentration fluctuations upstream of the gauze will decrease the magnitude of flickering. This in turn will reduce the precious metal loss and the deterioration rate of the catalytic gauze.

Correspondence concerning this paper should be addressed to D. Luss. W. M. Edwards is with the M. W. Kellogg Company, Houston, Texas.

Catalytic gauze convertors deteriorate with time due to precious metal losses (mainly in the form of volatile oxides). The precious metal loss varies from plant to plant and often has a significant impact on the economics of the process. For example, in the high pressure ammonia oxidation process, the metal losses may account for about 5% of the manufacturing costs (Newman and Hulbert, 1971; Gillespie and Kenson, 1971; Heywood, 1973) and, according to Nowak (1969), can be correlated by the empirical expression

$$-\frac{dM}{dt} = f(O_2)\exp(-E_m/RT) \tag{1}$$

where $E_m \simeq 40{,}000$ cal/g mole.

Large amplitude random temperature fluctuations (flickering) have been observed in commercial convertors. One of the main disadvantages of flickering is its deleterious influence on the rate of precious metal losses from catalytic gauzes. An instructive parameter for gauging the influence of flickering is the relative metal loss $r(T)$, defined as the ratio of the metal loss with flickering to that during uniform temperature operation with the same average temperature and average reactant concentration.

$$r(T) = \frac{\left\langle \frac{dM}{dt} \right\rangle}{\left(\frac{dM}{dt}\right)_{T=<T>}} = \frac{\left\langle \exp\left(-\frac{E_m}{RT}\right)\right\rangle}{\exp\left(-\frac{E_m}{R<T>}\right)} \tag{2}$$

where $<\ >$ denotes the time average of a stationary process. Since $\exp(-E/RT)$ is a convex function of the temperature $r(T) \geq 1$. When the probability density function (pdf) of the temperature fluctuations is known, (2) can be used to calculate the effect of flickering on the metal loss. Experiments carried out in this laboratory with single wires indicate that when no information is available about the pdf of the flickering a Gaussian distribution should be good approximation. Typical values of $r(T)$ are reported in Table 1 using this assumption and operating conditions similar to those existing in industrial ammonia oxidation convertors. It is noted that the relative metal loss increases rapidly with increasing root mean square temperature fluctuations.

The temperature and surface concentration of a single catalytic wire on which a single chemical reaction occurs can be described by the equations

$$\frac{d(AS)}{dt} = k_1(S)\,C - r \tag{3}$$

$$A\rho c_p \frac{\partial T}{\partial t} = k_w A \frac{\partial^2 T}{\partial s^2} + hP(T_g - T) + P(-\Delta H)r \tag{4}$$

$$(S) + (AS) = L \tag{5}$$

Edwards et al. (1973) have shown that when the reaction is mass transfer controlled the maximal temperature rise is given by

$$<\Delta T_{ad}> = <\Delta T_{ad}{}^{*}> + \frac{Ak_w}{P<h>}\frac{\partial^2 T}{\partial s^2} \tag{6}$$

where

$$<\Delta T_{ad}{}^{*}> = \frac{(-\Delta H)<C>}{\rho_f c_{p_f}}\left(\frac{N_{Pr}}{N_{Sc}}\right)^{2/3} = \frac{(-\Delta H)<x_g>}{c_{p_f} M_f} N_{Le}{}^{-2/3} \tag{7}$$

The second term on the right-hand side of (6), which accounts for the influence of thermal conduction, is negligible when compared with $<\Delta T_{ad}{}^{*}>$ for wires with length to diameter ratio greater than 200.

Table 1. Values of $r(T)$ as a Function of the Time Average Temperature and the Root Mean Square Temperature Fluctuations Assuming a Gaussian Temperature Oscillation pdf and E_m = 40,000 cal/g.mole

	$<T>$, °C			
T'_{rms}, °C	800	850	900	950
20	1.05	1.04	1.033	1.028
40	1.22	1.18	1.15	1.12
60	1.54	1.43	1.35	1.29

The turbulent mass transfer coefficient to a cylinder can be expressed as (Treybal, p. 59, 1968)

$$N_{Sh} = \frac{k_c\, d}{D_{AB}} = \alpha + \beta u^n \tag{8}$$

where α and β are two empirical constants. Local turbulent transport coefficients fluctuate with time and can be expressed as the sum of their stationary average and a fluctuating component, which is denoted by a prime. When the fluctuating velocity component u' is much smaller than the time averaged velocity $<u>$, the ratio between the instantaneous to the time averaged mass transfer coefficient may be approximated by

$$\frac{k_c}{<k_c>} = 1 + N\frac{u'}{<u>} \tag{9}$$

where

$$N = \frac{n\beta<u>^n}{<N_{Sh}>} = n\left(1 - \frac{\alpha}{<N_{Sh}>}\right) \tag{10}$$

and n is an empirical constant, which is about 0.5. Analogy between heat and mass transfer implies that when the Lewis number is close to unity the right-hand side of (9) describes also the ratio of $h/<h>$.

Ervin and Luss (1972) used a numerical simulation to demonstrate that fluctuations of the transport coefficients may induce flickering on a wire. The magnitude of this induced temperature fluctuation was found to be strongly dependent on the parameter

$$a = \frac{A\rho\, c_p<k_c><C>}{LP<h>} = \frac{A\rho\, c_p<\Delta T_{ad}{}^{*}>}{LP(-\Delta H)} = \frac{A\rho\, c_p<x_g>N_{Le}{}^{-2/3}}{LP\, c_{p_f}<M_f>} \tag{11}$$

which is the ratio of the characteristic time for changes in wire temperature to the characteristic time for surface concentration changes. The numerical computations indicated that appreciable temperature oscillations were induced by fluctuating transport coefficients only when a was of order one or less.

Estimation of the parameter a requires information about the concentration of active surface sites per unit surface area L. The atomic radius of a platinum atom is 1.39A. Hence, $L \leq 2 \times 10^{-9}$ g atom/cm^2. A high temperature steady state can exist only if the reactant mole fraction exceeds the value corresponding to extinction x_e. Some estimates of a lower bound on the parameter a are reported in Table 2 for reactions on a 0.025-mm platinum wire, based on the assumptions of $L = 2 \times 10^{-9}$ and $<x> = x_e$. These estimates indicate that for all these cases a is at least of order 100. In the industrial ammonia oxidation process $<x_g> \simeq 0.11$ and $d_w = 0.075$ mm, yielding 9900 as the lower bound on a. A similar

Table 2. Estimation of a Lower Bound on the Parameter a From Experiments with a 0.025-mm Platinum Wire

Reactant	N_{Le}	$\Delta T^*_{ad}/g$ [K°]	T_g [°C]	x_e	Min (a)
Butane	2.30	47,500	145	0.0087	140
Hydrogen	0.27	19,600	24	0.010	710
Ammonia	0.895	8,000	24	0.040	1,240

magnitude is attained in the HCN process. The model of Ervin and Luss (1972) predicts that for these high values of a the amplitude of the flickering is negligibly small, and that fluctuations in the transport coefficients cannot induce the large amplitude flickering observed in industrial convertors.

In the following discussion, a model is described which explains flickering for systems having high values of the parameter a. The main assumption of the model is that for mass transfer controlling conditions and large values of a the surface concentration of the adsorbed reactant satisfies the pseudo steady state relation

$$r = k_1(S)C = k_cC \tag{12}$$

Substitution of (12) into (4) and neglecting the effect of axial conduction yields

$$\frac{A\rho\, c_p}{P}\frac{dT}{dt} = h(T_g - T) + k_cC(-\Delta H) \tag{13}$$

Equation (13) can be rewritten as

$$\frac{A\rho\, c_p}{P<h><T-T_g>}\frac{dT'}{dt} = -\left(1+\frac{h'}{<h>}\right)\left(1+\frac{T'}{<T-T_g>}-\frac{T_g'}{<T-T_g>}\right) + \left(1+\frac{k_c'}{<k_c>}\right)\left(1+\frac{C'}{<C>}\right) \tag{14}$$

where we have expressed the transport coefficients, the concentrations, and the temperature as a sum of a stationary average and a fluctuating component, and used the relations

$$\frac{d<T>}{dt} = 0 \tag{15}$$

$$\frac{(-\Delta H)<k_c><C>}{<h><T-T_g>} = 1 \tag{16}$$

Substitution of (9) into (14) and neglecting second-order terms yields

$$\frac{A\rho\, c_p}{P<h>}\frac{dT'}{dt} + T' = T_g' + \frac{<T-T_g>C'}{<C>} \tag{17}$$

Assuming that the gas temperature is uniform ($T_g' = 0$) Fourier transformation of (17) yields

$$G_{T'}(f) = \frac{<T-T_g>^2\, G_{C'}(f)}{<C>^2\,[1+(2\pi f\tau)^2]} \tag{18}$$

where

$$\tau = \frac{A\rho\, c_p}{P<h>} \tag{19}$$

and $G_{T'}(f)$ and $G_{C'}(f)$ are the power spectral density functions of the wire temperature fluctuations and of the feed concentration fluctuations, respectively.

The one-dimensional spectral density function of the velocity fluctuations in an isotropic turbulent flow field can be usually approximated very well for low frequencies by (Hinze, 1959)

$$\frac{G_{u'}(f)}{4<u'^2>\tau_E} = \frac{1}{1+(2\pi f\,\tau_E)^2} = \frac{1}{1+(f/f_{1/2})^2} \tag{20}$$

where τ_E is the Eulerian time scale and $f_{1/2}$ is the half power frequency. The power spectral density of concentration fluctuations in a turbulent field should be rather similar to that of velocity fluctuations and can be approximated by

$$\frac{G_{C'}(f)}{4<C'^2>\tau_C} = \frac{1}{1+(2\pi f\tau_C)^2} \tag{21}$$

where τ_C is the Eulerian concentration time scale. Experimental measurements of the spectral density function of scalar fluctuations in a turbulent flow field have been reported by Becker et al. (1966), Lee and Brodkey (1964), and Freymuth and Uberoi (1971). Substitution of (21) into (18), integration over all possible frequencies and application of the definition of power spectral density function

$$\int_0^\infty G_{T'}(f)\,df = <T'^2>, \tag{22}$$

yields

$$\frac{<T'^2>}{<T-T_g>^2} = \frac{\tau_C<C'^2>}{(\tau_C+\tau)<C>^2} \tag{23}$$

Substitution of (21) and (23) in (18) yields

$$\frac{G_{T'}(f)}{4<T'^2>} = \frac{(\tau_C+\tau)}{[1+(2\pi f\tau)^2]\,[1+(2\pi f\tau_C)^2]} \tag{24}$$

Edwards et al. (1973) have shown that if flickering is induced by fluctuations of the transport coefficients then the experimental data should satisfy the relation

$$\frac{G_{T'}(f)}{4<T'^2>} = \frac{(\tau_w+\tau_E)}{[1+(2\pi f\tau_E)^2]\,[1+(2\pi f\tau_w)^2]} \tag{25}$$

where τ_w is computed from

$$\tan^{-1}(2\pi f_{1/2}\,\tau_w) - \frac{\tau_E}{\tau_w}\tan^{-1}(2\pi f_{1/2}\,\tau_E) - \frac{\pi}{4}\left(1-\frac{\tau_E}{\tau_w}\right) = 0 \tag{26}$$

Hinze (1959, p. 231) has shown that for isotropic turbulent mixing the ratio τ_E/τ_C is equal to $\sqrt{N_{Sc}}$. For a mixture of a reactant in excess air N_{Sc} is close to unity so the values of τ_E and τ_C should be about the same. In addition, computations indicate that for our experimental conditions τ_w and τ are about equal. Hence, a comparison of (24) and (25) indicates that the temperature spectral density function cannot be used to determine whether flickering is induced by velocity fluctuations or by concentration fluctuations. However, measurements of the temperature fluctuations in the same flow field at various levels of concentration fluctuations can be used to test the validity of (23) and to determine the main cause of flickering. In the first part of this work we report an experimental study of temperature fluctuations on single catalytic wires. The results are then applied to predict the causes and magnitude of flickering in catalytic gauze convertors.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental data obtained to determine the cause of flickering include measurements of instantaneous values of

local surface temperature and reactant concentration. Instantaneous wire surface temperatures were measured with an infrared detector while concentration fluctuations were measured with an aspirating probe unit manufactured by Thermo Systems, Inc. The temperature measurements were made on single platinum wires placed normal to the flow direction of a turbulent reactant (either ammonia or hydrogen)-air mixture. The test assembly (Figure 1) which includes gas flow meters, mixing nozzles, flow channel, probe holder, and infrared detection unit is the same as that described by Edwards et al. (1973), but includes a redesigned flow channel, wire probe, and mixing devices.

The rectangular cross section (25 × 152 mm) flow channel (Figure 2) was constructed from two (203 × 1650 mm.) 3.2-mm thick aluminum plates separated by 25-mm square aluminum bar stock. The channel was insulated with a 38-mm thick layer of fiberglass. The feed gas, air, or nitrogen, entered the flow channel through a 12.5-mm diameter opening into a short (127 mm long) diverging section. In order to break up the incoming jet and to provide a uniform velocity distribution, the gas was passed through two 30-mesh stainless steel screens (100 mm apart) followed by a section packed with 6.3 mm I.D. 102-mm long stainless steel tubes. The flow inside these tubes was laminar for the experimental conditions used.

The catalytic wire probe (Figure 3) was positioned 700 mm downstream from the exit of the stainless steel tubes (56 channel half heights). The probe opening (12.5 × 50 mm) in the bottom of the channel was sealed with a spring loaded fiber plate to prevent gas leakage.

A 25-mm. diameter sapphire window transmitting radiation in the 1-8μ range was installed in the top plate to permit direct viewing of the platinum wire with the infrared unit. This unit measured the instantaneous local wire surface temperature of a 0.04 mm. diameter spot. The root mean square noise level of the measured temperature fluctuations was 0.7°C. The gas temperature was measured with a mercury in glass thermometer inserted through a port in the side of the channel near the catalytic wire. Details of the method of measurement, calibration, recording, and data processing were described by Edwards et al. (1973) and Edwards (1973).

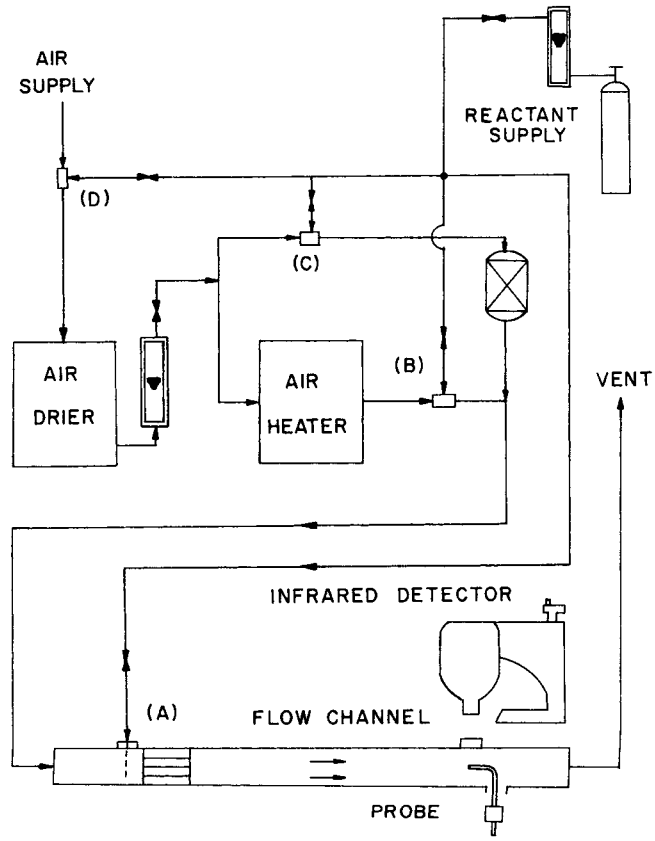

Fig. 1. Schematic of test assembly.

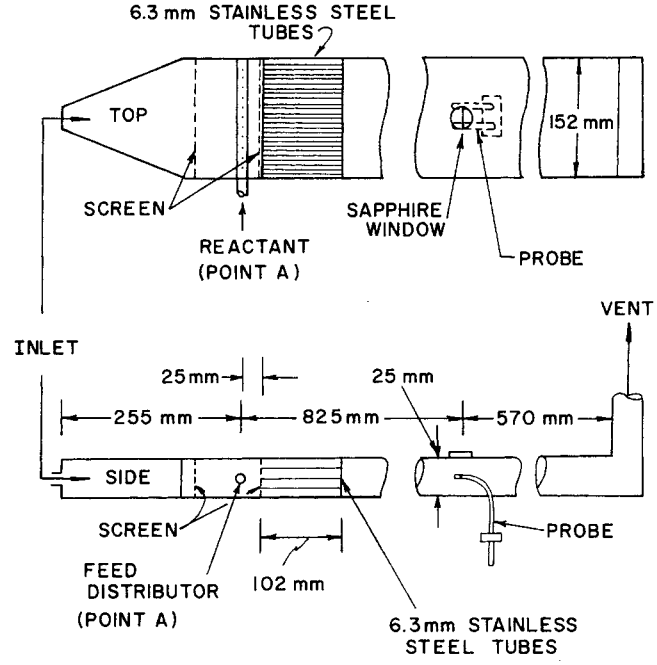

Fig. 2. Schematic of flow channel.

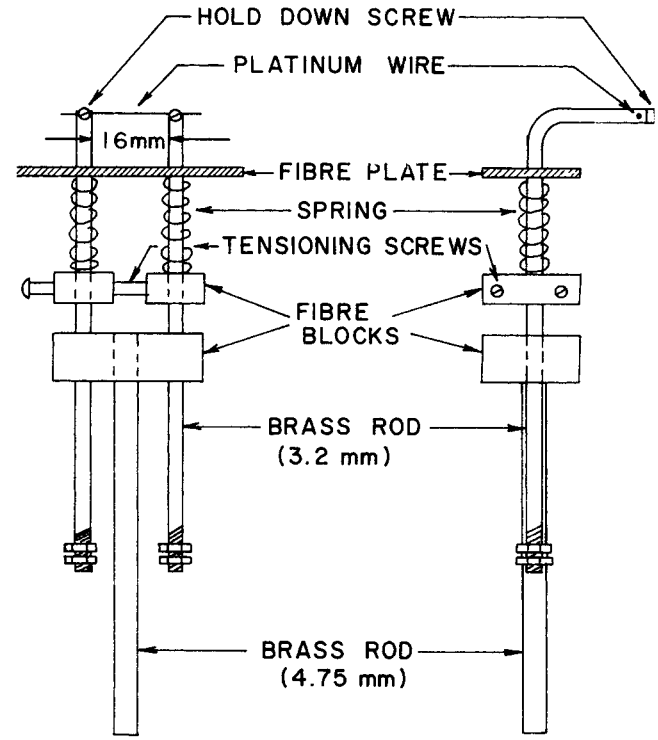

Fig. 3. Catalytic wire probe.

A wide range of reactant concentration fluctuations was obtained by varying the method of reactant injection and/or by changing the injection point (labeled A, B, C, and D in Figure 1). The reactant injector at point A consisted of a 6.3-mm stainless steel tube placed normal to the air flow in the channel between the two 30-mesh screens. The gas was injected through eleven 0.34-mm diameter holes spaced 12.5 mm apart. This distributor could be rotated so that the reactant could be injected at any prescribed angle relative to the bulk flow axis. Feed point B was a tee connection and the reactant was injected through nine 0.24-mm diameter holes in a steel plate. Feed point C was similar to B and contained nine 0.5-mm

diameter holes in a plastic plate. A 50-mm I.D. packed bed containing 100 cm³ of 0.065-mm diameter glass beads topped by 100 cm³ of 3-mm diameter glass beads was placed between points C and the channel inlet in order to improve the mixing and therefore reduce the magnitude of concentration fluctuations. Feed point D consisted of a tee connection ahead of the 1m. high packed bed air drier shown in Figure 1.

Instantaneous concentration fluctuations for nonreacting turbulent helium-air or hydrogen-nitrogen mixtures were measured with a Thermo Systems Model 1441A aspirating probe (Figure 4) in conjunction with a Thermo Systems Model 1010A constant temperature anemometer system. The design and principles of operation of this probe have been described by Blackshear and Fingerson (1962). Edwards (1973) discussed the conditions under which the measurements of the aspirating probe can be considered valid.

EXPERIMENTAL RESULTS AND DISCUSSION

Edwards et al. (1973) have shown that for butane oxidation the temperature fluctuations behave as a stationary process for times much longer than those required for a single experiment and that conduction due to end effects had a negligible influence on the time averaged temperature and root mean square temperature fluctuations at the center of wires of diameter 0.075 mm or less. In the experiments reported here, it has been assumed that the same is also true for either ammonia or hydrogen oxidation.

Preliminary experiments demonstrated that when the reactant was injected at either one of the feed points labeled as B, C and D in Figure 1, there existed no gradient in the time averaged concentration at the wire station. However, when either hydrogen or ammonia were injected at point A, gradients in the time averaged concentration existed at the wire station. Moreover, it was found that the concentration fluctuation intensity, the probability density function (pdf), and the spectral density function (sdf) were sensitive to the angular position of the distributor at point A. The intensity of the concentration fluctuations at the catalytic wire station depended on the feed port location and was in the following order A >> B > C > D.

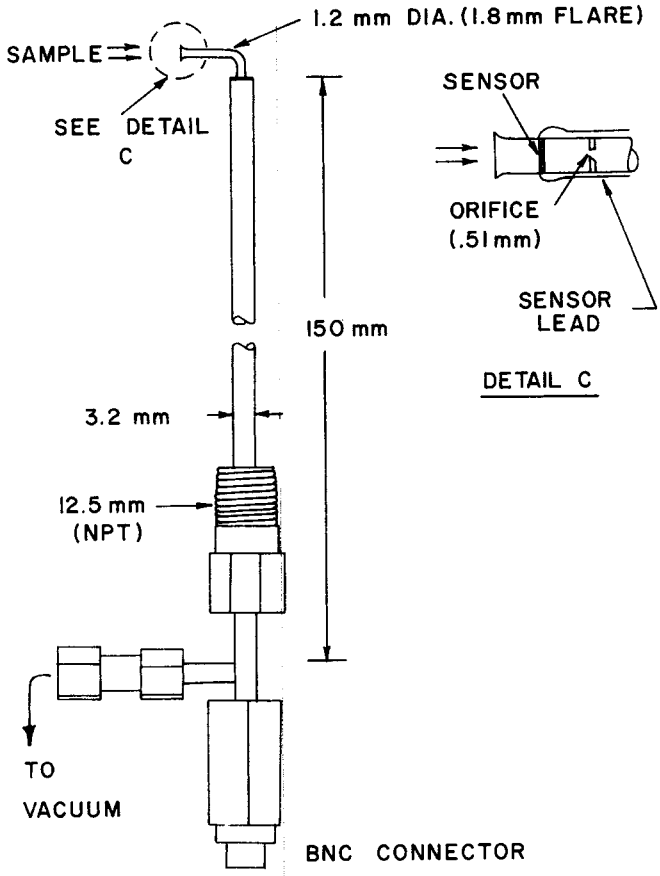

Fig. 4. Schematic of the aspirating probe.

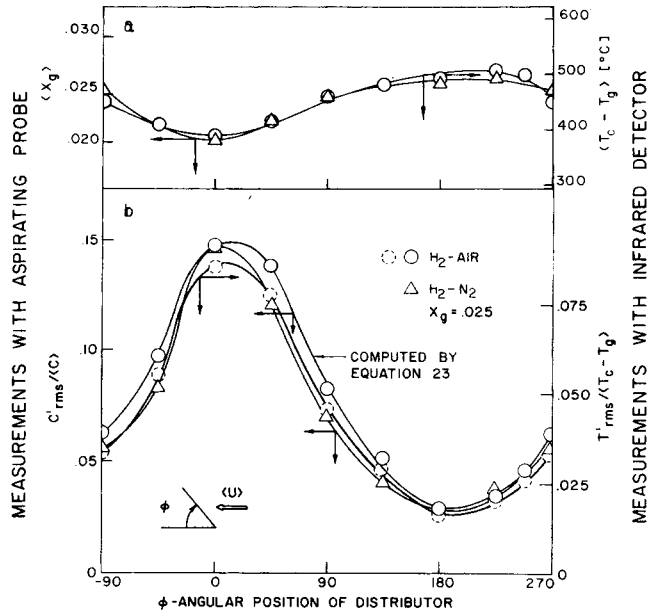

Fig. 5. The effect of the angular position of the feed distributor on: $\langle X_g \rangle$ and $C'_{rms}/\langle C \rangle$ as measured by the aspirating probe, on $\langle T_c - T_g \rangle$ and $T'_{rms}/\langle T_c - T_g \rangle$ for a 0.075-mm wire as measured by the infrared detector, and on $C'_{rms}/\langle C \rangle$ as computed from $T'_{rms}/\langle T_c - T_g \rangle$ by Equation (23).

A series of experiments were carried out to determine the relation between the concentration fluctuations (as measured by the aspirating probe for a hydrogen-nitrogen mixture) and the root mean square temperature fluctuations (as measured by the infrared detector) at the center of platinum wires during the oxidation of hydrogen in air. In all the experiments reported here, unless otherwise specified, the channel Reynolds number was 4000, the turbulent intensity ($u'_{rms}/\langle u \rangle$) was 0.11, T_g = 24°C, and d = 0.075 mm.

Experiments with a mixture of 3%v H_2 in air yielded values of T'_{rms} equal to 0.84, 1.10, and 2.7°C and $C'_{rms}/\langle C \rangle$ equal to 0.002, 0.004, and 0.006 when the hydrogen was injected from feed points D, C, and B, respectively. These results indicate a direct correlation between the concentration and temperature fluctuations and point out that in the absence of concentration fluctuations T'_{rms} will be very small (the noise level of the detector was 0.7°C). The above measured values of $C'_{rms}/\langle C \rangle$ are accurate to only one significant digit due to the poor signal to noise ratio. Thus, in order to obtain data suitable for a critical examination of the theoretical predictions it was necessary to use injection point A, which yields high values of concentration fluctuations at the wire station.

Experiments with the aspirating probe as well as chromatographic analysis of samples taken at various points across the channel revealed that gradients in the time averaged concentration existed next to the wire when injection point A was used to obtain a mixture of 2.5%v H_2 in air. Moreover, the time averaged concentration next to the wire depended on the angular position of the feed distributor. A comparison of $\langle x_g \rangle$ and $\langle T_c - T_g \rangle$ shown in Figure 5a indicates that the variations in the time averaged concentration next to the wire were responsible for

the variation of the time averaged temperature rise of the wire with ϕ and its deviation from 475°C. (If mixing of the reactants were such that no gradients in the time averaged concentration existed then for this mass transfer limited reaction $<T_c - T_g>$ would have been 475°C. The injection angle ϕ is defined as 0 for injection in the direction of air flow and positive when measured in the clockwise direction, for example, vertical upwards injection corresponds to 90°.)

Figure 5b describes the effect of the angular position of the feed distributor (point A) on the measured concentration and temperature fluctuations. The results indicate a close similarity between $C'_{rms}/<C>$ and $T'_{rms}/<T_c - T_g>$. Thus, while $C'_{rms}/<C>$ changes by a factor of about five as the distributor is rotated, the ratio of $(C'_{rms}/<C>)/(T'_{rms}/<T_c - T_g>)$ changes by no more than 8%. The values of T'_{rms} obtained in these experiments were quite large compared to the values obtained at points B, C, and D, and ranged from 8.6° to 33.4°C. Since peak to peak temperature fluctuations are about six times larger than T'_{rms}, the temperature fluctuations could be observed visually.

The assumption that flickering is induced by concentration fluctuations when $a >> 1$ led to the development of Equation (23) in the theoretical section. In order to test its validity it was used to compute $C'_{rms}/<C>$ from the measured values of $T'_{rms}/<T_c - T_g>$. To accomplish these computations, values of τ and τ_c must be known. The value of τ was determined from heat transfer experiments as 0.070 sec. Measurements with the aspirating probe showed that τ_c varied between 0.030 and 0.039 s depending on the injection angle. The computed values of $C'_{rms}/<C>$ shown in Figure 5b agree very well with the values measured by the aspirating probe, and support the validity of Equation (23).

Figure 6a describes the measured values of $T'_{rms}/<T_c - T_g>$ as a function of the wire diameter for a mixture of 2.5% vol. H_2 in air. The mixture was injected at point A using two different angular positions of the distributor. The temperature fluctuations in these cases almost doubled as the wire diameter was decreased from 0.125 to 0.025 mm. The magnitude of $<T_c - T_g>$ in these experiments was about 475°C, and the flickering was quite large in some cases.

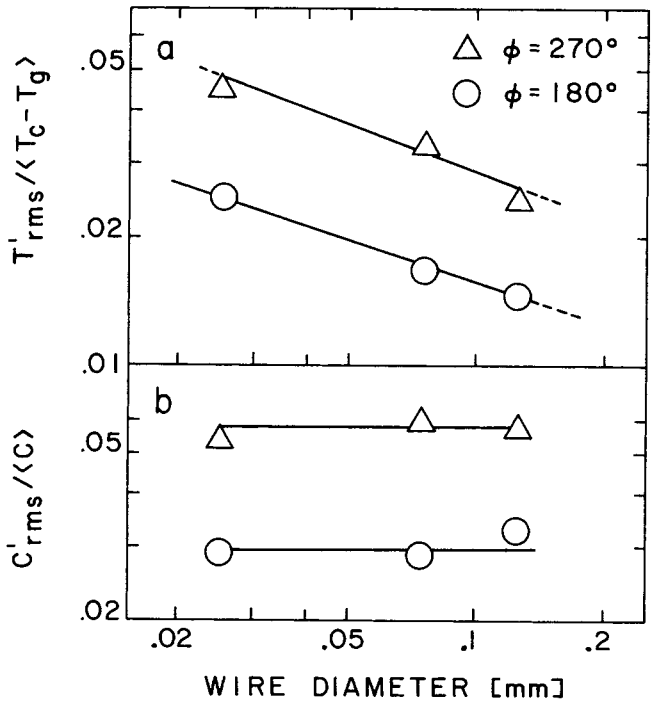

Fig. 6. (a) The effect of wire diameter and position of distributor on the temperature fluctuation for a mixture containing 2.5% H_2 in air; (b) Computed values of $C'_{rms}/<C>$ from $T'_{rms}/<T_c - T_g>$ using Equation (23).

The above measurements of T'_{rms} were used as a further test of the validity of Equation (23). The values of τ as measured by heat transfer experiments were 0.011, 0.070, and 0.141 s for wires of 0.025, 0.075, and 0.125 mm diameter, respectively. Measurements with the aspirating probe determined τ_c as 0.039 and 0.030 s for $\phi = 180°$ and 270°, respectively. Figure 6b presents the values of $C'_{rms}/<C>$ calculated by Equation (23) from the measured temperature fluctuations and the measured values of τ and τ_c. The computed concentration fluctuations are independent of the diameter of the wire used for measuring the temperature fluctuations and agree within 4% with values of $C'_{rms}/<C>$ measured directly by the aspirating probe. These results strongly support Equation (23) and the notion that when the parameter a is large compared to unity temperature fluctuations are induced mainly by concentration fluctuations in the reacting gas mixture.

It should be noted that Equation (23) was derived assuming that Equation (21) is an adequate representation of the concentration spectral density function (sdf). Fortunately, the constants appearing in (23) are rather insensitive to the exact form of the concentration sdf as is often the case with results based on integrals of assumed profiles. This insensitivity to the sdf enables application of (23) even when Equation (21) is no more a proper representation of the concentration sdf. On the other hand, the temperature fluctuation sdf is rather sensitive to the exact form of the concentration fluctuation sdf (especially when $\tau_c > \tau$) and Equation (24) cannot be expected to be valid when (21) is not. However, Equation (18) should be valid regardless of the form of the sdf of the concentration fluctuations, provided that the hypothesis about the cause of flickering is correct.

The sdf of the temperature fluctuations was measured for various reactions, wires, and operating conditions. Figure 7 describes the normalized sdf $G_{T'}(f)/G_{T'}(0)$ for a 0.075-mm wire using mixtures of either ammonia or hydrogen in air injected at point C. According to Equation (24) this normalized sdf should satisfy the relation

$$\frac{G_{T'}(f)}{G_{T'}(0)} = \frac{1}{[1 + (2\pi f\tau)^2]\,[1 + (2\pi f\tau_c)^2]} \qquad (27)$$

For the experiments shown in Figure 7, τ was determined to be 0.07 s, while τ_c was measured with the aspirating probe (H_2-N_2 mixture) and found to be 0.03 s. The experimental results agree well with the theoretical curve which uses the value of τ_c for the H_2-N_2 mixture. This agreement is not a critical test of the validity of (27) since $\tau > \tau_c$ and the theoretical curve is rather insensitive to τ_c in the range of frequencies for which the measurements were made. A critical test of the theory requires experiments with very thin wires for which $\tau < \tau_c$. Experiments with a 0.025-mm diameter wire ($\tau = 0.011$ s) have been inconclusive in this respect due to vibrations of the wire which introduced large errors in the measurements. Thus, the sdf of the temperature fluctuations, in contrast to the root mean square, was not useful in determining the major cause for flickering. Additional information concerning the sdf is presented by Zuniga (1974).

Instantaneous velocity measurements by a hot wire indicated that the pdf of the velocity fluctuations at the catalytic wire station was skewed with the mode smaller than the average. Changes of the angular position of the feed distributor did not affect the magnitude of the veloc-

ity fluctuations or the pdf. However, rotation of the distributor affected both the magnitude and the shape of the pdf of the temperature fluctuation on the wire. Figure 8 describes the temperature fluctuation pdf on a 0.075-mm wire during the oxidation of a mixture of 2.5% vol. hydrogen in air. The pdf's are skewed, and the position of the mode relative to the average depends on the angular position of the distributor. Measurements of the concentration fluctuation pdf of 2.5% vol. hydrogen in nitrogen showed that they were also skewed and very similar to those of the temperature fluctuation pdf. The similarity between the temperature and concentration fluctuation pdf's, and

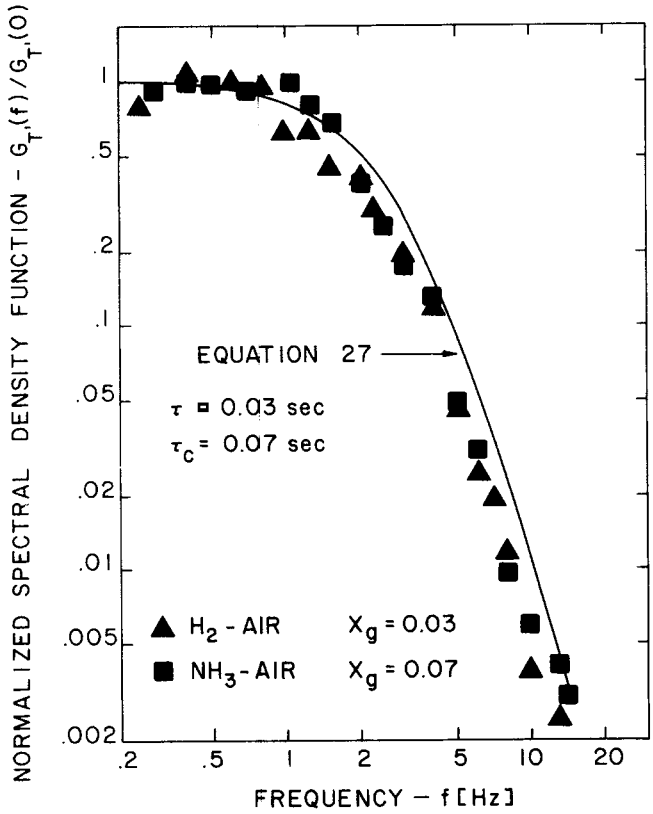

Fig. 7. The normalized spectral density function of temperature fluctuations at the center of a 0.075-mm diameter wire during the oxidation of either ammonia or hydrogen in air.

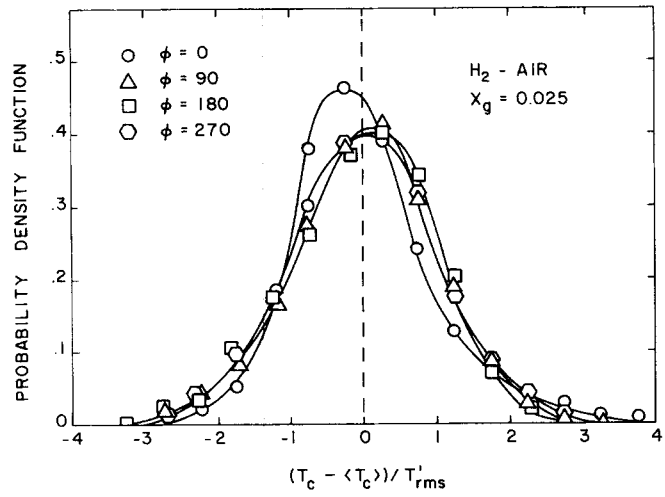

Fig. 8. The probability density function of temperature fluctuations on a 0.075-mm wire as a function of the angular position of the feed distributor.

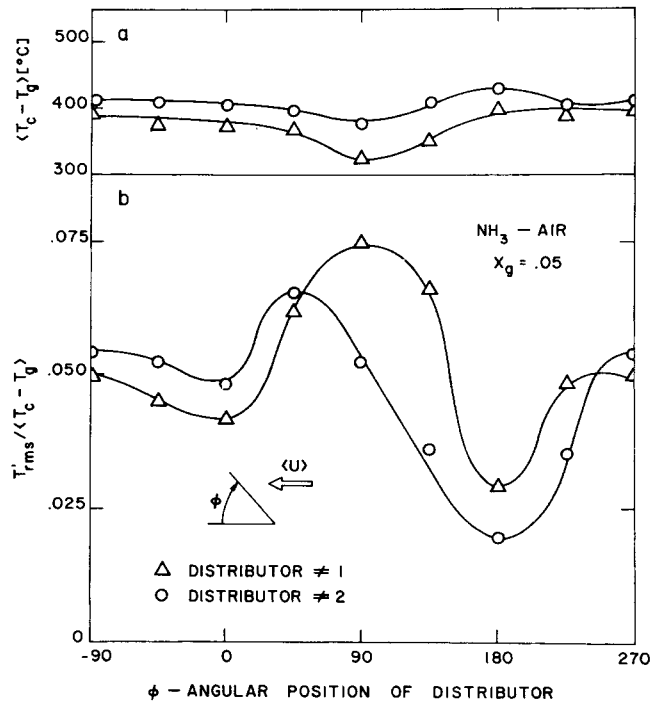

Fig. 9. The influence of the angular position of the distributor and the size of the holes in the distributor on the magnitude of: (a) $\langle T_c - T_g \rangle$ and (b) $T'_{rms}/\langle T_c - T_g \rangle$ during the oxidation of ammonia on a 0.075-mm wire.

the lack of any correlation between the velocity and temperature fluctuations further supports the argument that temperature fluctuations are induced mainly by the concentration fluctuations and not by velocity fluctuations.

Temperature fluctuations were measured during the oxidation of ammonia in air on a 0.075-mm diameter wire using two geometrically similar distributors, one of which (#2) had 0.51-mm diameter injection holes as compared with the 0.34-mm diameter holes for the standard distributor. The results (Figure 9) indicate that both T'_{rms} and $\langle T_c - T_g \rangle$ depend on the size of the holes as well as on the angular position of the distributor. This result is of course similar to that obtained with hydrogen. A comparison of Figures 9 and 5 indicates that the maxima in T'_{rms} were attained at different angular positions of the standard distributor during the oxidation of either hydrogen or ammonia. This must be due to the difference in the effect of ϕ on the magnitude of the concentration fluctuations for different reactants. Unfortunately, $C'_{rms}/\langle C \rangle$ for ammonia cannot be measured using the aspirating probe due to the small difference in the thermal conductivities of air and ammonia. When the distributor at point A was used to obtain the 2.5% vol. mixture of H_2 the injection velocity of the jets was 1.39×10^4 cm/s. However, when a 5% vol. mixture of NH_3 was prepared the injection velocities were 2.84×10^4 and 1.29×10^4 cm/s for feed distributors 1 and 2, respectively. This difference in the injection velocities and the density of H_2 and NH_3 is responsible for the variation in the effect of ϕ on $C'_{rms}/\langle C \rangle$.

There is no question, however, that concentration fluctuations are the main factor affecting the magnitude of temperature fluctuations in both the hydrogen and ammonia oxidation reactions. This conclusion was further confirmed by passing a premixed mixture (5.0% vol.) of ammonia in air over the catalytic wire at $N_{Re} = 3200$ and $T_g = 24$°C. The measured T'_{rms}(0.76°C) was very close

to the root mean square noise level of the detector (0.70°C). Thus, we conclude from our experiments that large temperature fluctuations are caused mainly by concentration fluctuations of the reactants when the parameter a is large.

CAUSES AND MAGNITUDE OF FLICKERING IN GAUZE CONVERTORS

A theoretical model of gauze convertors will be used here to predict the main causes of flickering and to estimate its magnitude. The model assumes that: (1) the reaction rate is limited by mass transfer; (2) the parameter a is large; (3) plug flow of the gas through each gauze; (4) the length of the effective flow path through a single gauze is l and the surface area of a single gauze is $a_v l$ per unit cross section of the reactor; (5) the local temperature of each gauze layer is uniform in the flow direction and the rate of heat transfer by conduction and radiation between successive gauze layers is negligible; and (6) the effect of axial concentration dispersion can be ignored.

The concentration of the gaseous reactant flowing through gauze i is described by the equation

$$u_i \frac{dC}{dz} = -k_{C,i}\, a_v C \tag{28}$$

Defining C_i as the concentration of the gas stream leaving gauze i we obtain from (28)

$$\frac{C_i}{C_{i-1}} = \exp\left(-\frac{k_{C,i}\, a_v l}{u_i}\right) = \exp(-N_{St,i}\, a_v l) = \xi_i \tag{29}$$

The mass transfer coefficient for a long cylinder can be described by the correlation (Treybal, 1968)

$$N_{Sh} = 0.43 + 0.53\, N_{Sc}^{0.31}\, N_{Re,w}^{0.5} \tag{30}$$

For a typical high pressure ammonia oxidation convertor the gauze wire Reynolds number is about 35 and the Stanton number is essentially a constant changing by less than 15% as the gas average film temperature increases from 500° to 900°C. Thus, it will be assumed that ξ_i is the same for all the gauze layers, yielding

$$\frac{C_i}{C_o} = \xi^i \tag{31}$$

At steady state the heat loss from any gauze is equal to the heat generated by the reaction. Hence, the temperature of each gauze satisfies

$$T_i - T_{gi,lm} = \frac{(-\Delta H) k_c\, C_{i,lm}}{h} = \frac{(-\Delta H) C_o}{\rho_f c_{pf}} \frac{C_{i,lm}}{C_o} N_{Le}^{-2/3} \tag{32}$$

where we have used the heat and mass transfer analogy

$$\frac{k_c\, \rho_f c_{pf}}{h} = N_{Le}^{-2/3} \tag{33}$$

and the subscript i, lm denotes the logarithmic average across gauze i. An enthalpy balance yields

$$T_{gi,lm} - T_{go} = \frac{(-\Delta H)(C_o - C_{i,lm})}{\rho_f C_{pf}} = \frac{(-\Delta H) C_o}{\rho_f c_{pf}} \left(1 - \frac{C_{i,lm}}{C_o}\right) \tag{34}$$

Addition of (34) and (32) yields

$$T_i - T_{go} = \frac{(-\Delta H) C_o}{\rho_f c_{pf}} \left[1 + (1 - N_{Le}^{-2/3}) \frac{(1-\xi)\xi^{i-1}}{\ln \xi}\right] \tag{35}$$

If $\tau << \tau_c$ and τ_E this relation can be used to predict the temperature fluctuation T_i'. Substitution of

$$C_o = \langle C_o \rangle + C' \tag{36}$$

$$\xi = \langle \xi \rangle + \xi' \tag{37}$$

into (35) yields after discarding second-order terms

$$\frac{T_i'}{\langle T_i \rangle - T_{go}} = \frac{C_o'}{\langle C_o \rangle} + K_i \frac{\xi'}{\langle \xi \rangle} \tag{38}$$

where

$$K_i = \frac{(-\Delta H)\langle C_o \rangle (1 - N_{Le}^{-2/3})}{\rho_f c_{pf} (\langle T_i \rangle - T_{go})} \left[\left(\frac{(i-1)\langle \xi \rangle^{i-1} - i\langle \xi \rangle^i}{\ln \langle \xi \rangle}\right) - \frac{\langle \xi \rangle^{i-1} - \langle \xi \rangle^i}{(\ln \langle \xi \rangle)^2}\right] \tag{39}$$

The fluctuations in ξ are induced by the turbulent velocity fluctuations and thus cause fluctuations in the mass transfer coefficient. Substitution of (9) into (29) yields

$$\frac{\xi'}{\langle \xi \rangle} = 1 - \langle \xi \rangle^{(1-N)u'/\langle u \rangle} \tag{40}$$

Substitution of (40) into (38), squaring, and time averaging yields

$$\frac{\langle T_i'^2 \rangle}{(\langle T_i \rangle - T_{go})^2} = \frac{\langle C_o'^2 \rangle}{\langle C_o \rangle^2} + 2K_i \frac{\langle C_o' \rangle (1 - \langle \xi \rangle^{(1-N)u'/\langle u \rangle})}{\langle C_o \rangle} + K_i^2 \langle (1 - \langle \xi \rangle^{(1-N)u'/\langle u \rangle})^2 \rangle \tag{41}$$

Computation of K_i for typical industrial conditions indicate that its value is usually much smaller than unity. This indicates that the main cause of flickering in industrial gauzes is the concentration fluctuations and not the turbulent velocity fluctuations. Numerical computations of the amplitude of temperature fluctuations caused either by velocity fluctuations or concentration fluctuations for a typical ammonia oxidation convertor for which $x_o = 0.11$, $N_{Le} = 0.895$, $\langle \xi \rangle = 0.5$, $T_{go} = 25°$, and $N = 0.45$ presented in Table 3 demonstrate this point.

When the time constant of a single wire is about equal to or larger than τ_C or τ_E the amplitude of the flickering will be attenuated and (41) will overestimate $\langle T_i'^2 \rangle$. In this case a numerical simulation of the transient behavior of the various gauze layers is required for predicting T_i'. Comparison of (23) and (41) indicates that T'_{rms} will be attenuated by a factor of $1/\sqrt{1 + \tau/\tau_c}$. For a typical high pressure ammonia convertor $d_w = 0.075$ mm and the wire Reynolds number is 35, yielding $\tau = 0.03$ s. The reactor diameter is about 1 m and the average gas velocity 2 m/s. Since $\Lambda_f \approx D/3$ then $\tau_E = \Lambda_f \langle u \rangle \approx \tau_c$ is approximately 0.166 s and $\tau/\tau_c = 0.18$. Thus, the attenuation of T'_{rms} due to the heat capacity of the wire should be very small in industrial convertors and (41) should yield a good prediction of T'_{rms}. It should be noted that in some of our single wire experiments $\tau > \tau_c$ and the attenuation was not negligible.

The above model predicts that flickering is a localized phenomenon induced mainly by concentration fluctuations.

TABLE 3. COMPUTATIONS OF K_i AND T'_{rms} FOR AN AMMONIA CONVERTER FOR WHICH $\langle x_0 \rangle = 0.11$, $N_{Le} = 0.895$, $\langle \xi \rangle = 0.5$, $T_{go} = 25°$, and $N = 0.45$

Layer number i	$\langle T_{gi} \rangle$ [C°]	$\langle T_i \rangle$ [C°]	$10^2 K_i$	T'_{rms} $u'_{rms} = 0.1 \langle u \rangle$ $C'_{rms} = 0$	T'_{rms} $u'_{rms} = 0$ $C'_{rms} = 0.05 \langle C \rangle$
1	253	887	2.3	0.7	43.1
2	547	865	3.9	1.2	42.0
3	695	853	3.3	1.0	41.4
4	768	848	2.4	0.7	41.2
5	805	845	1.5	0.5	41.0
10	841	842	0.1	0.03	40.9

We will now examine briefly the influence of conduction on flickering. The characteristic time for conduction along a single wire is

$$\tau_k = \rho c_p s^2/k \tag{42}$$

while that for heat losses by forced convection from a wire is

$$\tau_k = \frac{\rho c_p d}{4h} = \frac{\rho c_p d^2}{4 N_{Nu} k_f} \tag{43}$$

These two time scales are equal when

$$\frac{s}{d} = \left[\frac{k_w}{4 k_f N_{Nu}} \right]^{0.5} \tag{44}$$

Equation (44) predicts that under typical operating conditions the two time scales are equal when the wire length is about ten diameters. Hence, the influence of conduction is rather localized and is not expected to attenuate to a large extent local temperature fluctuations induced by instantaneous concentration fluctuations.

The above results indicate that flickering is induced primarily by concentration fluctuations. Hence, it is important to estimate the magnitude of concentration fluctuations in industrial convertors. The only theoretical correlations developed so far are restricted to a homogeneous isotropic turbulent flow field. Corrsin (1957) suggested that for an idealized mixer

$$\frac{\langle C'^2(t) \rangle}{\langle C'^2(0) \rangle} = \exp\left(-\frac{6\nu t}{\lambda^2} \right) \tag{45}$$

According to Hinze (1958, p. 186)

$$\frac{L_e}{\lambda} = \frac{4}{3} \frac{\Lambda_f}{\lambda} = \frac{\gamma}{15} \frac{u'_{rms} \lambda}{\nu} \tag{46}$$

where γ is a constant of about one. Substitution of $t = X/\langle u \rangle$ and (43) into (44) yields

$$\frac{\langle C'^2(t) \rangle}{\langle C'^2(0) \rangle} = \exp(-0.4\gamma m) \tag{47}$$

where

$$m = \frac{3}{4} \frac{X}{\Lambda_f} \frac{u'_{rms}}{\langle u \rangle} \tag{48}$$

Beek and Miller (1959) carried out a numerical computation of the spectral transfer of concentration fluctuations in the wave number space. Their graphical results indicate that after a short distance downstream from the mixer the concentration fluctuations decay exponentially as a function of m. Their design charts show a significant improvement in mixing when the number of inlet nozzles is increased. However, this result should be applied with care since it is based on the yet experimentally unproven conjecture that the size of the concentration eddies in the inlet is inversely proportional to the square root of the number of injection nozzles. Moreover, the calculations are restricted to the special cases in which the injection velocity is equal to final mixed stream velocity.

In a typical ammonia convertor the distance between the mixer and the gauze $X \simeq 20D$, $u'_{rms}/\langle u \rangle = 0.03$, and $\Lambda_f \simeq 0.4D$ so that $m \simeq 1.13$. For this case (47) predicts that $\langle C'^2(t) \rangle / \langle C'^2(0) \rangle = 0.64$, while the graphs of Beek and Miller predict 0.57 and 0.014 for the cases of one and 64 injection nozzles, respectively. Although the above predictions are a rough approximation, they indicate that under commercial conditions the distance between the mixer and the gauze is not sufficient to eliminate concentration fluctuations.

One of the main difficulties in estimating $C'_{rms}(t)$ is the lack of a reliable estimation technique for $C'_{rms}(0)$ in industrial mixers. Keeler et al. (1965) suggested for an ideal one-dimensional system the approximation

$$\frac{C'_{rms}(0)}{\langle C(0) \rangle} \simeq \sqrt{\frac{G}{I}} \tag{49}$$

where G and I are the main stream and tracer volumetric flow rates, respectively. Toor (1969) obtained the same result for an idealized mixer in pipe flow. This prediction is at best a crude estimate for an industrial gas mixer for which gradients in the time averaged concentrations usually exist next to the injection nozzles. For these mixers, the initial root mean square concentration has to be determined experimentally. Fortunately, in most practical cases the time averaged concentration gradients decay faster than the concentration fluctuations, and the graphs of Beek and Miller (1959) should be a good approximation for the decay of $\langle C'^2(t) \rangle$ at the center of the pipe at points where no gradients in the time averaged concentration exist. The decay rate next to the wall is expected to exceed that predicted by their graphs.

The prediction that C'_{rms} decays exponentially as a function of m is most useful for scale-up purposes and for equipment modifications. Thus, measurements of C'_{rms} at several points downstream from the mixer should enable one to predict the effect of changing the length of the inlet pipe on C'_{rms} at the gauze. This should enable design or modification of equipment to reduce concentration fluctuations and the accompanying flickering.

CONCLUDING REMARKS

The present study was concerned with the causes and magnitude of flickering of single wires and gauze convertors on which a single catalytic reaction occurs. Flickering has a deleterious influence on gauze convertors since it increases the precious metal loss. Dorawla and Douglas (1971) have shown that in complex reaction networks the yield of a desired intermediate can be increased by oscillatory operation. Wandrey and Renken (1973) have recently shown that periodic variation of the concentration of the feed to a gauze converter (frequency 0.5-2 per min.) has a significant influence on the selectivity (CO/

CO_2 ratio) during the oxidation of cyclohexane on a catalytic gauze. Therefore, it is most likely that concentration fluctuations which induce flickering affect the yield in industrial gauze convertors used for the production of HCN.

Our analysis indicates that the parameter a is usually large in industrial reactors and that flickering of the magnitude observed in industrial ammonia convertors must be caused by imperfect mixing of the reactants. It is desirable to minimize the amplitude of the flickering in order to reduce the precious metal loss, and our analysis indicates that this can be accomplished by improving the mixing of the reactants. This prediction merits a test under commercial conditions and is supported by the observation of Heywood (1973) that when a catchment gauze was placed below the platinum gauze there was evidence for improved gas mixing and a reduction in the rate of deterioration of the gauze.

At the present time, mixing theory is restricted to certain idealized flow fields and mixing devices and is not suitable for predicting the performance of various industrial mixing devices. This study points out the need of improving our knowledge and understanding of mixing under industrial conditions. One of the difficulties in investigating mixing is that most probes for concentration fluctuations can be operated only with a very limited number of substances which are not normally encountered in industrial reactors. The fact that flickering of a single wire is directly related to the concentration fluctuations has led to the development of a new probe which can measure the intensity of concentration fluctuations of a number of gaseous mixtures of practical interest. This probe should be useful in many applications and will be described elsewhere.

ACKNOWLEDGMENT

The financial support of the NSF through grant GK 18226 is gratefully acknowledged.

NOTATION

a = capacity term defined by Equation (11)
a_v = gauze surface area per unit volume, cm^{-1}
A = wire cross-sectional area, cm^2
AS = occupied catalyst sites, g mole cm^{-2}
C = reactant concentration in fluid, g mole cm^{-3}
c_p = wire heat capacity, cal g^{-1} $°K^{-1}$
c_{pf} = fluid heat capacity, cal g^{-1} $°K^{-1}$
d = wire diameter, cm
D = diameter, cm
D_{AB} = binary diffusion coefficient, cm^2 s^{-1}
E_m = metal loss activation energy, cal g $mole^{-1}$
f = frequency, Hz
$f_{1/2}$ = half-power frequency, Hz
G = main stream volumetric flow rate, cm^3 s^{-1}
$G_y(f)$ = one-sided power spectral density of random process y
h = heat transfer coefficient, cal s^{-1} cm^{-2} $°K^{-1}$
ΔH = heat of reaction, cal g $mole^{-1}$
i = catalytic gauze layer number, integer
I = tracer injection volumetric flow rate, cm^3 s^{-1}
k_1 = mass transfer and adsorption rate constant, cm^3 g $mole^{-1}$ s^{-1}
k_c = mass transfer coefficient, cm s^{-1}
k = thermal conductivity, cal s^{-1} cm^{-1} $°K^{-1}$
K_i = constant defined by Equation (39)
l = flow path length through a single gauze layer, cm
L = total catalytic sites, g mole cm^{-2}
L_e = characteristic scale of turbulence, cm
M = weight of precious metal gauze, g
m = parameter defined by Equation (48)
M_f = molecular weight of fluid, g g $mole^{-1}$
n = empirical velocity exponent in Equation (10)
N = constant defined by Equation (10)
N_{Le} = Lewis number, $k_f/\rho_f D_{AB} c_{pf}$
N_{Nu} = Nusselt number, hD/k_f
N_{Pr} = Prandtl number, $c_{pf} \mu_f/k_f$
N_{Re} = Reynolds number, $D u/\nu_f$
N_{Sc} = Schmidt number, ν_f/D_{AB}
N_{Sh} = Sherwood number, $k_c D/D_{AB}$
N_{St} = Stanton number, k_c/u
P = wire perimeter, cm
r = surface reaction rate, g mole cm^{-2} s^{-1}
$r(T)$ = relative metal loss, Equation (1)
R = gas constant, cal g $mole^{-1}$ $°K^{-1}$
S = unoccupied catalytic sites, g mole cm^{-2}
s = distance along wire axis, cm
t = time, s
T = temperature, °K
u = fluid velocity, cm s^{-1}
X = distance from mixer, cm
x_g = mole fraction reactant in fluid
z = axial distance in catalytic gauze, cm

Greek Letters

α = constant in Equation (8)
β = constant in Equation (8)
γ = constant used in Equation (47)
λ = concentration microscale, cm
Λ_c = concentration macroscale, cm
Λ_f = velocity longitudinal macroscale, cm
μ = viscosity, g cm^{-1} s^{-1}
ν = kinematic viscosity, μ/ρ, cm^2 s^{-1}
ξ = defined by Equation (29)
ρ = wire density, g cm^{-3}
ρ_f = fluid density, g cm^{-3}
τ = wire time constant, Equation (19), s
τ_c = Eulerian time scale of concentration fluctuation, s
τ_E = Eulerian time scale of velocity fluctuations, s
τ_k = characteristic time for conduction along wire axis, s
τ_w = wire time constant defined by Equation (26)

Subscripts

ad = adiabatic
f = fluid
g = gas
o = inlet condition
w = wire

Superscripts

$'$ = fluctuating component

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Manuscript received December 20, 1973; revision received January 29 and accepted January 30, 1974.

Growth Rate of an Ice Crystal in Flowing Water and Salt Solutions

JOHN G. VLAHAKIS and ALLEN J. BARDUHN

Department of Chemical Engineering and Materials Science, Syracuse University Syracuse, New York 13210

The growth rate of an ice crystal in the basal plane has been measured in subcooled water flowing at velocities of 0.04 to 1 cm/s to test a theory of Fernandez and Barduhn (1967). The theory fits the data in pure water at all velocities and subcoolings studied here and at velocities up to 46 cm/s studied previously. The interfacial tension between ice and water calculated from these data is 33 ± 6 ergs/cm², a value in good agreement with those determined by others.

Measured growth rates of ice from solution do not follow the theory and in fact are as much as 150% higher in 0.5 to 1% NaCl solution than in pure water. High subcoolings and low flow velocities accentuate this anomaly.

SCOPE

To test further a theory of unconfined crystal growth of Fernandez and Barduhn (1967), the growth rate of ice crystals in the basal plane (*a*-axis direction) has been measured in flowing subcooled water, aqueous NaCl, and glucose solutions over a wide range of subcoolings, flow velocities, and solute concentrations. The theory presumes that transfer of the latent heat of crystallization, by convection to the flowing stream, controls the ice growth rate and yields an expression with no empirical constants which is

$$v = \left(\frac{a}{1+b}\right) V^{1/2}\,\Delta T^{3/2}$$

where a is a function of the known properties of pure water and ice and b of the solution. The equation predicts zero ice growth rate (v) in quiescent water ($V = 0$) which is known to be untrue, and an attempt is made to discover the lowest flow velocity for which the theory holds. Previous work showed the relation to hold well at flow velocities up to 46 cm/s, and kinetic contributions to ice growth have been shown to be negligible even at this high flow rate.

The term b in the equation is nearly proportional to the solute concentration and it is thus predicted that ice growth rates decrease regularly as the solute concentration is increased. Previous work shows this to be untrue, and a thorough experimental investigation of this is made.

CONCLUSIONS AND SIGNIFICANCE

The measurements of ice growth rates in pure water now include flow velocities as low as 0.042 cm/s, and the equation of Fernandez and Barduhn holds well here. Previous work included, it has now been shown that the theory holds over a range of flow velocities covering three orders of magnitude. A lower limit to its applicability has not yet been detected although such a limit must exist. Limitations of the apparatus did not permit use of lower flow rates.

The equation resulting from the theory has been verified experimentally for growth in pure water over a velocity range of 1100 to 1, a subcooling range of 40 to 1, and a growth rate range of 180 to 1. The theory, along with the experimental data, yield 33 ± 6 ergs/cm² for the interfacial tension between water and ice, a value in good agreement with that determined by others using entirely different means. The theory predicts the radius of curvature of the ice crystal tip to be inversely proportional to the subcooling, and this has been verified by photographic methods but the proportionality constant agrees poorly

Correspondence concerning this paper should be addressed to A. J. Barduhn. J. G. Vlahakis is with Sanitary Science Division, U.S. Army MERDC, Fort Belvoir, Virginia 22060.