that proved disastrous to the control performance. Any compensation for this coupling effect requires information on the size of roll rate. It was decided that the best compensation for the deleterious effects would be the removal of the effect, e.g., a roll control channel. The roll control channel reduces roll rate to an acceptably low level (<2° sec).

With the decision to control roll rate in the vehicle, the analysis and understanding of planer on-off control systems can be applied to the problem.[1-3] With roll rate control, the vehicle spin rate is controlled to be within a threshold value, p, within a few seconds of system activation and the vehicle is brought under control or acquired for any arbitrary orientation. This overall stability did not exist in the system without roll control.

References

[1] Flugge-Lotz, I., *Discontinuous Automatic Control* (Princeton University Press, Princeton, N. J., 1953), Chapt. 2.

[2] Taylor, L. W. and Smith, J. W., "An analytic approach to the design of an automatic discontinuous control system," NASA TN-D-630 (1961).

[3] Pistiner, J., "On-off control system for attitude stabilization of a space vehicle," ARS J. **29**, 283–289 (1959).

Turbulence Effects in Chemical Reaction Kinetics Measurements

IRVIN GLASSMAN[*] AND IGOR J. EBERSTEIN[†]
Princeton University, Princeton, N. J.

I. Introduction

RECENT interest in the effect of turbulent flow on reaction kinetics has developed from consideration of such problems as recombination of atoms in hypersonic wakes,[1] efficient supersonic combustion,[2] etc. The authors' interest in the problem stems from their use of a flow reactor for the measurement of chemical reaction rates. This reactor is different from the classical flow reactor in that the gas flow is turbulent.[3] In the course of examining possible sources of errors that may arise in chemical kinetic measurements due to turbulent fluctuations, some simple phenomenological developments were evolved which could be of interest to other investigators. The developments are quite different from the detailed turbulent flow approaches of other investigators;[4, 5] however, they bring to light more clearly some of the important physical aspects of the problem.

II. Aspects of the Problem

Turbulence may affect the reaction rate in two ways. It may alter the fundamental chain mechanism either by selectively enhancing various elementary reactions of the chain or by altering the diffusion of free radicals. The second way, which is really a simplification of the first, is enhancement of the overall rate, the instantaneous value of which may be expressed in the form

$$\nu = dc/dt = -kc^n = -c^n B T^m e^{-E/RT} \qquad (1)$$

Thus the problem is first to ascertain whether or not the basic mechanism is affected by the turbulence. If this is not the case, and if steady-state kinetics do apply to the turbulent field, one must determine whether the rate at the means of the fluctuating quantities (T and c) differs significantly from the mean rate.

A third element of the problem is whether the turbulence enhances the eddy characteristics to a point where, for a one-dimensional system, longitudinal heat and mass transfers are such that they contribute to the temperature or concentration at a point and not just to the chemical reaction alone. This point is a simple extrapolation of the laminar flame propagation problem, where the temperature in the flame front is determined by the extent of the chemical reaction and by the amount of heat conducted back from the high temperature edge of the flame.[6] Only the laminar conductivity must be replaced by a turbulent eddy conductivity. If the effect of heat transfer is small, the adiabatic temperature profile may be related to the measured temperature profile by

$$\left(\frac{dT}{dx}\right)_{\text{ad}} = \left(\frac{dT}{dx}\right)_{\text{meas}} \left\{1 + \left[\frac{d^2T/dx^2}{(\dot{m}C_p/\epsilon A)(dT/dx)}\right]\right\} = \left(\frac{dT}{dx}\right)_{\text{meas}} (1 + \beta)$$

where β is the ratio of conductive to convective terms. For the adiabatic flow reactor mentioned previously, conditions are such that β is less than 1%, and conductivity effects may be neglected.[7]

III. Steady-State Considerations

In the description of turbulence given by Hinze,[8] flow in the smallest eddies is no longer turbulent but viscous, and molecular effects are dominant. Batchelor[9] states that the energy of turbulent motion dies away effectively to zero long before length scales comparable with the molecular mean free path are reached. It seems reasonable to assume from Refs. 8 and 9 that the only means by which the chemical kinetics within the smallest eddies of the turbulent field can be affected are turbulent pressure fluctuations in the fluid and molecular diffusion of species into or out of the tiny eddy. If the mean distance travelled by a tiny laminar pocket during its lifetime is sufficiently small so that it does not travel into regimes whose concentration and temperature are drastically different, then it will not encounter steep gradients, and the rate of change of conditions in the eddy due to diffusion effects will be slow.

For flow in a circular pipe, such an eddy, "lifepath" l is likely to be less than the pipe diameter D, and, for Reynolds numbers used in the flow reactor ($Re \sim 10{,}000$), l is approximately 0.2 D.[10] From these criteria, it is found that in the flow reactor an eddy encounters a 2% change in concentration and a 2°C difference in temperature. It seems safe to say that these gradients are sufficiently shallow so that diffusion will not cause any rapid fluctuations of temperature or concentration within an eddy. As regards pressure fluctuations and temperature fluctuations due to compressibility, Wight[11] has shown that small amplitude fluctuations do not affect significantly the chemical kinetics. From information given by Lewis and von Elbe[10] and Laurence,[12] a characteristic time of turbulent oscillation may be estimated. For conditions in the flow reactor, a characteristic turbulent time of 20 to 30 msec is obtained.

A mechanism for the thermal decomposition of hydrazine was proposed,[7] and the resulting set of differential equations was integrated numerically. The results that are presented in Fig. 1 show that the time necessary to reach a chemical steady state is generally less than 0.1 msec when the temperature is in the 1000°K range. Under these conditions, the chemical transient time is only 0.5% of the characteristic time of turbulent fluctuation just given. Actually, the time

---

Presented at the ARS 17th Annual Meeting, Los Angeles, Calif., November 13–18, 1962; revision received April 17, 1963. The work reported here was performed for the Air Force Office of Scientific Research under Grant No. AF 62-90.

[*] Associate Professor, Guggenheim Laboratories for the Aerospace Propulsion Sciences, Department of Aeronautical Engineering. Associate Fellow Member AIAA.

[†] Research Assistant, Guggenheim Laboratories for the Aerospace Propulsion Sciences, Department of Aeronautical Engineering. Student Member AIAA.

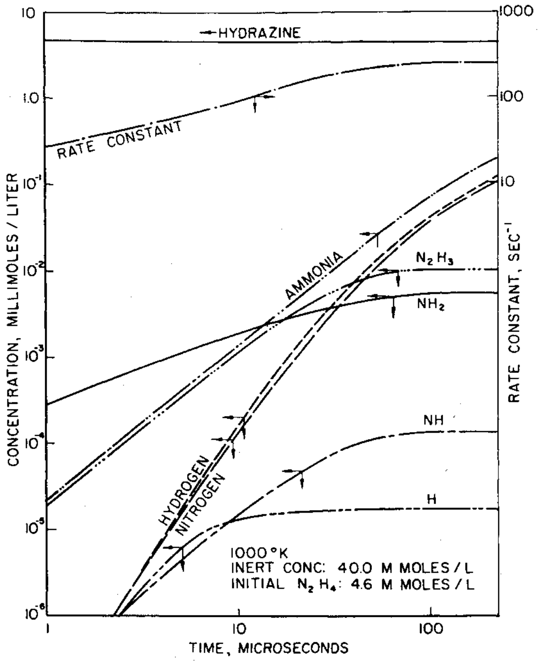

Fig. 1 Hydrazine decomposition at 1000°K showing buildup to steady-state concentration of radicals

required by the free radical system to adjust to a temperature change of a few degrees is likely to be less than the time required to reach steady state. Thus, it is safe to assume that steady-state kinetics do prevail in the flow reactor. But it is quite likely that, in flows containing steep gradients, high scales, and high intensities of turbulence, smaller characteristic times prevail, and a simple steady-state analysis of the kinetics is not permissible. Thus turbulent flames, some supersonic combustion schemes, and wakes in hypersonic reentry must be examined with great caution.

IV. Mean Rates

The variation of the rate with respect to temperature and concentration is found readily from Eq. (1). It follows that

$$\frac{d\nu}{\nu} = n\frac{dc}{c} + \left[m + \frac{E}{RT}\right]\frac{dT}{T} \tag{2}$$

Equation (2) permits one to estimate the relative importance of concentration and temperature in fluctuating fields, if, as a first approximation, one assumes that the same percentage fluctuation occurs in both. If $|n| \ll |m + (E/RT)|$ temperature effects predominate, and if the inequality is reversed, concentration effects predominate.

In complex combustion reactions, the overall order is somewhere about, but never greater than, 2, and the activation energy ranges from about 20 to 40 kcal/mole. A reasonable choice of m is $\frac{1}{2}$, and for temperatures of concern it thus reasonably may be assumed that the inequality $|n| \ll |m + (E/RT)|$ holds.‡

In the flow reactor mentioned earlier, where measurements were made on the decomposition of ethylene oxide[14] in the temperature range of 900° to 1200°K, the activation energy was found to be 45 kcal/mole and the overall order unity. Consequently,

$$|m + (E/RT)| = \tfrac{1}{2} + [45{,}000/(1.99)(1000)] \gg 1$$

For a flow scheme in which the recombination of atoms is the main chemical event, the importance of the concentration term immediately becomes evident. The activation energy of recombination reactions is about zero and the overall order 3. The temperature dependence through the T^m term can vary with the third body, but, for comparisons such as those being made here, m can be taken as $-\frac{1}{3}$.[15] It follows then that the inequality $|n| \gg |m + (E/RT)|$ holds.

The fluctuating temperature may be represented as follows:

$$T(t)/\langle T\rangle = 1 + a_n f(t) \tag{3}$$

where $-1 \leq f(t) \leq 1$, and

$$\langle T\rangle = \frac{1}{\tau}\int_0^\tau T(t)dt$$

By definition, the mean temperature $\langle T\rangle$ is a constant independent of time. If Eq. (3) is integrated over a time τ sufficiently long to give the mean temperature, the left-hand side of the equation becomes one. It follows that the integral of $f(t)$ over the time period τ must be zero.

Writing the overall rate in terms of an Arrhenius expression, the following equation is obtained:

$$\frac{k(T)}{k(\langle T\rangle)} = \exp\left[\frac{E}{R\langle T\rangle}\left(1 - \frac{\langle T\rangle}{T}\right)\right] \tag{4}$$

It follows from Eq. (3) that

$$1 - \frac{\langle T\rangle}{T} = \frac{a_n f(t)}{1 + a_n f(t)} \approx a_n f(t)$$

for small a_n. This expression may be substituted in Eq. (4). The quantity in brackets can be expanded in series and the result integrated to give a mean value of k. Note again that the integral of $f(t)$ is zero. The following result is obtained:

$$\delta = \frac{\langle k\rangle - k(\langle T\rangle)}{k(\langle T\rangle)} \leq e^b - (1 + b) \approx \frac{1}{2}b^2 \tag{5}$$

where $b = Ea_n/R\langle T\rangle$.

Assume the temperature fluctuation to be ±10% of the total temperature spread. This total spread is usually less than 100°K in the reactor. A typical operating temperature is 800°K, and a typical first-order rate constant is 100 sec^{-1}. A typical activation energy is 30 kcal/g-mole. Under these conditions $a_n = \frac{1}{80}$, and $b = 0.236$. It follows that $\delta \leq 2.8\%$. Although this value is hardly insignificant, it is certainly quite tolerable considering the deviations usually found in chemical kinetic measurements. However, it should be remarked that, under conditions of high turbulence, the difference between the mean rate and rate at the mean temperature may be significant.

References

[1] Vaglio-Laurin, R., Bloom, M., and Byrne, R., "Aerophysical aspects of slender body theory," ARS Preprint 2674-62 (November 1962).

[2] Libby, P. A., "Theoretical analysis of turbulent mixing of reactive gases with application to supersonic combustion of hydrogen," ARS J. **32**, 388–396 (1962).

[3] Crocco, L., Glassman, I., and Smith, I. E., "A new flow reactor for high temperature reaction kinetics," Jet Propulsion **27**, 1266–1267 (1957).

[4] Corrsin, S., "The reactant concentration spectrum in turbulent mixing with a first-order reaction," J. Fluid Mech. **11**, 407–416 (1961).

[5] Predvoditelev, A. S., "The rates of chemical reactions in turbulent streams," Inzh. Fiz. Zh. **11**, 3–10 (1960).

[6] Frank-Kamenetski, D. A., *Diffusion and Heat Exchange in Chemical Kinetics* (Princeton University Press, Princeton, N. J., 1955), Chap. VIII.

[7] Glassman, I. and Eberstein, I. J., "Reaction kinetics in turbulent flow," ARS Preprint 2672-62 (November 1962).

---

‡ m at times has been given values ranging from 0 to +1 in order better to correlate experimental data.[13] For combustion systems, m contains the temperature dependency of the collision frequency and other pre-exponential factors.

[8] Hinze, J. O., *Turbulence, An Introduction to Its Mechanism and Theory* (McGraw-Hill Book Co., Inc., New York, 1959), pp. 3–7.

[9] Batchelor, G. K., *The Theory of Homogeneous Turbulence* (Cambridge University Press, Cambridge, England, 1953).

[10] Lewis, B. and von Elbe, G., *Combustion, Flames and Explosions of Gases* (Academic Press Inc., New York, 1951), p. 488.

[11] Wight, H. M., "Study of the influence of sound waves on chemical reaction rates," Aeronutronic Div., Ford Motor Co., TR U-858 (1960).

[12] Laurence, J. C., "Intensity, scale, and spectra of turbulence in mixing region of free subsonic jet," NACA Rept. 1292 (1956).

[13] Penner, S., *Chemistry Problems in Jet Propulsion* (Pergamon Press, New York, 1957), p. 217.

[14] Crocco, L., Glassman, I., and Smith, I. E., "Kinetics and mechanism of ethylene oxide decomposition at high temperatures," J. Chem. Phys. **31**, 506 (1959).

[15] Zinman, W. C., "Recent advances in chemical kinetics of homogeneous reactions in dissociated air," ARS J. **30**, 233–250 (1960).

Plane Jet in a Moving Medium

A. Pozzi* and B. Sabatini†
University of Naples, Naples, Italy

It is well known that major difficulties in the viscous theory of jets occur from the impossibility of obtaining similar solutions when conditions are different from those of Schlichting.[2]

The purpose of this paper is to show how it is possible to obtain "nearly similar" solutions and to give a solution of the linearized equation.

Basic Equations and "Nearly Similar" Solutions

The equations governing the motion of an incompressible plane jet in a moving medium in the boundary-layer approximation are‡

$$u_x + v_y = 0 \tag{1}$$

$$uu_x + vu_y = \nu u_{yy} \tag{2}$$

Related boundary conditions are

$$\begin{aligned} u(0, y) &= u_i \quad \text{for} \quad y < h \\ u(0, y) &= u_e \quad \text{for} \quad y > h \end{aligned} \tag{3}$$

$$\begin{aligned} v(x,0) &= 0 \qquad u_y(x,0) = 0 \\ u(x, \infty) &= u_e \end{aligned} \tag{4}$$

where $2h$ is the height of the jet at $x = 0$, u_i its velocity, and u_e the external (constant) velocity.

If it is assumed[3] that the slit is infinitesimal, initial conditions [Eq. (3)] are replaced by

$$\frac{d}{dx}\int_{-\infty}^{\infty}(u^2 - uu_e)dy = 0 \tag{5}$$

(This equation was obtained by integrating Eq. (2) between $-\infty$ and $+\infty$, taking into account the continuity equation).

Put in Eqs. (1) and (2)

$$\bar{u} = u - u_e \qquad \bar{v} = v \tag{6}$$

The continuity equation does not change, whereas the momentum equation becomes

$$\bar{u}\bar{u}_x + \bar{v}\bar{u}_y + u_e\bar{u}_x = \nu\bar{u}_{yy} \tag{7}$$

Now one assumes the stream function ψ to be a "nearly similar" function; i.e., one writes

$$\psi(x, y) = F(x) \sum_{i=0}^{\infty} f_i(\eta)m^i(x) \tag{8}$$

with

$$\eta = y/h(x) \tag{9}$$

Equations and boundary conditions make it possible to find the unknown functions $h(x)$, $m(x)$, and $F(x)$ to obtain

$$h = 3\nu^{1/2}x; \qquad m = 3u_e x^{1/3}; \qquad F(x) = \nu^{1/3}x^{1/3} \tag{10}$$

Note that the $f_0(\eta)$ in Eq. (10) is that of Schlichting's solution[3] for a jet in a medium at rest.

To obtain the velocity functions $f_i(\eta)$ of the expansion scheme (8), this expression is substituted in Eq. (7) and the $m^i(x)$ coefficients equated to zero.

Solutions of the Linearized Equation

As long as m is sufficiently small (i.e., $m^2 \ll m$), only the first term in the series expansion of Eq. (8) may be considered. The equation that determines the velocity function $f_1'(\eta)$ in Eq. (9) is then

$$f_1''' = -f_0'f_1' - 2f_0''f_1 - f_1''f_0 - \eta f_0'' - f_0' \tag{11}$$

subject to the boundary conditions

$$f_1(0) = 0 \qquad f_1''(0) = 0 \qquad f_1'(\infty) = 0 \tag{11$'$}$$

Moreover, to satisfy Eq. (5) up to terms of order m, it must be verified that

$$f_0(\infty) + 2\int_0^\infty f_0'f_1'\,d\eta = 0 \tag{11$''$}$$

Since it seems very difficult to solve Eq. (11) exactly, the following approximation is proposed:

Integrate Eq. (11) once:

$$f_1'' = -f_0'f_1' + 2f_0'\eta + f_0 - 2\int_0^\eta f_1f_0''\,d\eta \tag{12}$$

Now, as previously stated, condition (5) requires that

$$G(\eta) = f_0(\eta) - 2\int_0^\eta f_1f_0''\,d\eta \tag{13}$$

is zero when $\eta \rightarrow \infty$. Moreover, at $\eta = 0$ both function f_0 and $\int_0^\eta f_1f_0''\,d\eta$ are zero.

So, following an interative method, one assumes in Eq. (12), as first-approximation value of (13), $G(\eta) = 0$.

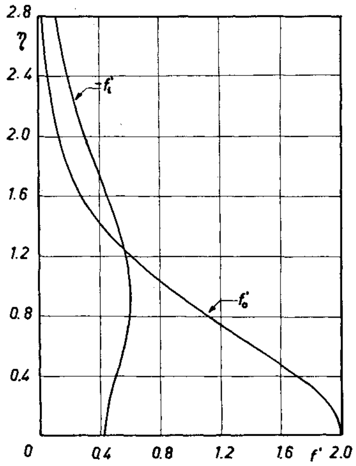

Fig. 1 Velocity functions

Received February 11, 1963. This work was sponsored by Consiglio Naxionale delli Ricerche.

* Associate Professor of Aerodynamics.

† Research Assistant of Aerodynamics.

‡ These equations also hold good for compressible fluids as long as $\mu\rho$ can be assumed constant.