

obtain a straight line for the portion of the curve which ought to be in the logarithmic region and plays no role in the model used to compute turbulent flows. To obtain the skin-friction coefficient from the slope of the straight-line portion of the curve, it is customary to assume that the von Kármán constant retains its value for flows over smooth surfaces (see Ref. 2, p. 177). It is thus seen that the argument for parallel log-law portions for smooth and rough flows is an essential part of bringing the experimental data into tractable form. The shift  $\Delta y^+$  employed by Rotta is simply the difference between the smooth and rough log-law portions of the curves on semilog plot as  $u^+$  vs  $y^+$  (see Fig. 4.29 and 4.30 of Ref. 1) and bears no relationship to the shift of virtual origin  $\Delta z$ .

The virtual origin  $y = 0$  is a distance  $\Delta z$  below the crests of the roughness elements. The  $y$  in Eqs. (7) and (9) in Mills paper are indeed measured from the virtual origin. Thus the contradiction in the eddy-viscosity formulas and the wall boundary conditions "invented" by Mills does not exist. The appearance of  $\Delta y$  in Eq. (7) only affects the rate of approach to Eq. (9) when performing integration. However, this problem has been clearly overshadowed by the questions of where to start the solution and what the boundary conditions should be because the sublayer is reduced or nonexistent. It has been found by experience that the logarithmic boundary conditions, Eq. (9), are satisfactorily applied if  $y_0^+ \geq 50$  and  $u_0/u_e \geq 0.15$  are satisfied simultaneously.

Mills' objection 2 toward the end of his Comment simply states the obvious: Of course we are well aware that Eqs. (8) and (10) will have different forms for different roughness geometries (see Ref. 1, p. 129, Fig. 4.27). Unfortunately, so far only the sand-grain type roughness has been well researched and documented.

Before we conclude, we would like to offer a word of caution. If the agreement between "theory" and all the available experimental data on the subject is quite good (so good that it may be difficult to beat these predictions by other turbulence models), it is perhaps advisable to be cautious in light of this agreement before raising objections which do not bear up under the weight of the theoretical, computational or experimental evidence.

### References

- <sup>1</sup>Cebeci, T. and Smith, A.M.O., *Analysis of Turbulent Boundary Layers*, Academic Press, New York, 1974.
- <sup>2</sup>Cebeci, T. and Bradshaw, P., *Momentum Transfer in Boundary Layers*, McGraw-Hill/Hemisphere, Washington, D.C., 1977.

## Comment on "Pressure Dependence of Burning Rate of Composite Solid Propellants"

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### Nomenclature

- $C_i$  = arbitrary constants  
 $E$  = activation energy  
 $k_f$  = kinetic rate constant

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- $k_0, k_2$  = arbitrary constants  
 $P$  = pressure  
 $R$  = universal gas constant  
 $\dot{r}$  = regression rate  
 $T$  = temperature  
 $\Delta V^*$  = volume of activation  
 $T_f$  = flame temperature  
 $T_s$  = surface temperature

IN a recent contribution, Rastogi et al.<sup>1</sup> derived an expression for the pressure dependence of the regression rate of solid propellants by appealing to a model of the gas phase as a flow reactor. Because their reasoning is defective, the formula finally obtained is only an empirical correlation with no insights into mechanisms.

A pivotal and incorrect assumption in the derivation is their Eq. (8), which writes a rate constant

$$k_f = k_0 \exp(-P\Delta V^*/RT) \quad (1)$$

in which  $k_0$  is independent of pressure and temperature. For any gas phase oxidation of a fuel,  $k_0$  is certainly not temperature independent. A usual assumption is the Arrhenius form which converts Eq. (1) to

$$k_f = k_2 \exp[-(E/RT)(E + P\Delta V^*)] \quad (2)$$

To now make their mathematical simplification of linearizing the exponential with only a 5% error, a necessary condition is:  $(E + P\Delta V^*)/RT < 0.3$ .

Commonly assumed values of  $E/RT$  range indefinitely upward from about 2. Indeed a whole field of combustion analysis rests on an assumption of asymptotically large activation energy.<sup>2</sup> Without the linearization, the form of the resulting integration would be more complicated:

$$\dot{r}^2 = C_1 P [e^{-bQ} + C_2 + C_3 Q + C_4 Q^2 + C_5 Q^3 + \dots] \quad (3)$$

where  $Q = E + P\Delta V^*$ .

The text reference<sup>3</sup> cited by the authors does not apply to the present problem because 1) it defines

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^*}{RT}$$

which applies only to isothermal pressure changes; 2) it is presented only in the context of liquid solutions; and 3) it notes that at higher pressures  $\Delta V^*$  depends on pressure. There is little known about  $\Delta V^*$  for gases.

Another error was made in obtaining their Eq. (6) by assuming no change in specific volume of the process, since in propellant combustion the volume of products exceeds the volume of reactants. That fact must be accounted for by making the missing molecular weight in Eq. (6) dependent on  $C_f$  through whatever stoichiometry is assumed.

As it stands, the expression for burning rate Eq. (13) cannot be correct because it also requires that the variable  $L$  be both the reactor length and the divisor in the gas side surface temperature gradient in Eq. (1), such that

$$\frac{\partial T}{\partial x} = \frac{T_f - T_s}{L}$$

The thus assumed linear temperature profile across the gas phase cannot be universally, if ever, true. What few temperature measurements have been made by various investigators<sup>4</sup> impeach the linear assumption. The expression  $[(T_f - T_s)/L]$  estimates the gradient in the center of the zone, not at the regressing surface.

All of these objections taken together should spell a rejection of the rationale for this correlation of burning rate with pressure.

## References

- <sup>1</sup>Rastogi, R. P., Singh, H. J., Dupak, D., and Srivastava, A. K., "Pressure Dependence of Burning Rate of Composite Solid Propellants," *AIAA Journal*, Vol. 16, May 1978, pp. 534-536.
- <sup>2</sup>Williams, F. A., "Theory of Combustion in Laminar Flows," *Annual Review of Fluid Mechanics*, Vol. 3, 1971, pp. 171-188.
- <sup>3</sup>Moelwyn-Hughes, E. A., *Chemical Statics and Kinetics of Solutions*, Academic Press, London, 1971, p. 410.
- <sup>4</sup>Kubota, N., Ohlemiller, T. J., Caveny, L. H., and Summerfield, M., "Site and Mode of Action of Platonizers in Double Base Propellants," *AIAA Journal*, Vol. 12, Dec. 1974, pp. 1709-1714.

## Reply by Authors to Nelson, Adams, and Ward

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IN a recent Note<sup>1</sup> we tried to emphasize that pressure dependence of burning rate of composite solid propellants may depend on chemical factors and, accordingly, we postulated a reactor model. Recently, Nelson et al. questioned the validity of that model. They questioned the basic relation [Eq. (8)] of that Note,

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\left(\frac{\Delta V^*}{RT}\right) \quad (1)$$

which predicts that rate constant  $k$  would increase with pressure  $P$  when the volume of activation  $\Delta V^*$  is negative. The relation is obtained from transition state theory<sup>2</sup> and would be valid for gaseous as well as condensed phase reactions. Wherever a tightly activated complex is formed, there is a likelihood that  $\Delta V^*$  will be negative. It is true that not many gas reactions have been studied, but it is also true that the pressure effect would be significant. However, we agree with Nelson et al. that in our Eq. (8)  $k_0$  would depend on temperature, so that

$$k_1 = k_2 \exp[-(1/RT)(E + P\Delta V^*)] \quad (2)$$

where  $k_2$  is another constant and  $E$  is the energy of activation. Equation (2) can be substituted in Eqs. (10) and (11) of our Note and a solution can be obtained for some cases,<sup>3</sup> including the case when  $(E/RT)$  is greater than 15, which would certainly be the case in combustion reactions.<sup>4</sup>

The fears of Nelson et al. that induction of Eq. (2) would make the subsequent development of the theory of pressure dependence based on our model difficult are not genuine. Since we are primarily interested in getting an expression for pressure dependence of burning rate, considerable simplifications can be achieved. Rewriting our Eq. (9) with the help of Eq. (2) we get

$$-k_2 \exp\left[\frac{-E}{RT}\right] \exp\left[\frac{-P\Delta V^*}{RT}\right] dVdT - \frac{\dot{m}TR}{P} \frac{dC_f}{C_f} dT = 0 \quad (3)$$

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Since the magnitude of  $P\Delta V^*/RT$  under the chamber conditions would be approximately of the order of  $10^{-2}$ , the second exponential of the first factor of Eq. (3) can be linearized and the subsequent integration under the proper limit would yield:

$$\int_0^V \int_{T_s}^{T_f} k_2 \exp\left[\frac{-E}{RT}\right] \frac{1 - P\Delta V^*}{RT} dVdT = - \int_{C_{fs}}^{C_{fe}} \int_{T_s}^{T_f} \frac{\dot{m}TR}{P} \frac{dC_f}{C_f} dT \quad (4)$$

or

$$\begin{aligned} k_2 V \left[ \left\{ T_f \exp\left[\frac{-E}{RT_f}\right] - T_s \exp\left[\frac{-E}{RT_s}\right] \right\} \right. \\ \left. - \frac{P\Delta V^*}{R} \left( \ln T_f \exp\left[\frac{-E}{RT_f}\right] - \ln T_s \exp\left[\frac{-E}{RT_s}\right] \right) \right] \\ - \int_{T_s}^{T_f} \exp\left[\frac{-E}{RT}\right] \frac{E}{RT} \left( 1 - \frac{P\Delta V^*}{RT} \ln T \right) dT \\ = \frac{\dot{m}R}{2P} (T_f^2 - T_s^2) \ln \frac{C_{fs}}{C_{fe}} \end{aligned} \quad (5)$$

A further simplification can be achieved by considering that  $(P\Delta V^*/RT) \ln T \ll 1$ , Eq. (5) can be rewritten as

$$k_2 V \left[ f_1(T) - \frac{P\Delta V^*}{R} f_2(T) \right] = \frac{\dot{m}R}{2P} (T_f^2 - T_s^2) \ln \frac{C_{fs}}{C_{fe}} \quad (6)$$

where

$$\begin{aligned} f_1(T) &= T_f \exp[-E/RT_f] - T_s \exp[-E/RT_s] \\ &- \int_{T_s}^{T_f} \exp[-E/RT] (E/RT) dT \end{aligned}$$

and

$$f_2(T) = \ln T_f \exp[-E/RT_f] - \ln T_s \exp[-E/RT_s]$$

Approximate methods can be applied to estimate  $f_1(T)$ . However, for the present purpose, it is not necessary to know them explicitly since we are concerned with pressure-dependent quantities only. Thus a modified form of our Eq. (12) would be

$$L = \frac{R\dot{m}(T_f^2 - T_s^2) \ln(C_{fs}/C_{fe})}{2k_2 P [f_1(T) - (P\Delta V^*/R)f_2(T)]} \quad (7)$$

Incorporating Eq. (7) into heat balance equation of Ref. 1 leads to identical results

$$(\dot{r}/P)^2 = (a/P) - b \quad (8)$$

with

$$a = \frac{2\lambda_{gs}(T_f - T_s)k_2 f_1(T)}{\rho_p^2 R [C_s(T_s - T_0) - Q_h](T_f^2 - T_s^2) \ln(C_{fs}/C_{fe})}$$

$$b = \frac{2\lambda_{gs}(T_f - T_s)k_2 \Delta V^* f_2(T)}{\rho_p^2 R^2 [C_s(T_s - T_0) - Q_h](T_f^2 - T_s^2) \ln(C_{fs}/C_{fe})}$$

The objection of Nelson et al. to Eq. (6) of Ref. 1 is not sound since  $1/\rho_g$  represents the specific volume of reactants only. Similarly, in view of the fact that not many