References

[1]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.

[2]Williams, F. A., "Theory of Combustion in Laminar Flows," *Annual Review of Fluid Mechanics*,, Vol. 3, 1971, pp. 171-188.

[3]Moelwyn-Hughes, E. A., *Chemical Statics and Kinetics of Solutions*, Academic Press, London, 1971, p. 410.

[4]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

R. P. Rastogi,* H. J. Singh,†
and A. K. Srivastava‡
University of Gorakhpur, Gorakhpur, India

In a recent Note[1] 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,

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

which predicts that rate constant k would increase with pressure P when the volume of activation ΔV^* is negative. The relation is obtained from transition state theory[2] and would be valid for gaseous as well as condensed phase reactions. Wherever a tightly activated complex is formed, there is a likelihood that ΔV^* 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

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

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,[3] including the case when (E/RT) is greater than 15, which would certainly be the case in combustion reactions.[4]

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

$$-k_2 \exp\left[\frac{-E}{RT}\right] \exp\left[\frac{-P\Delta V^*}{RT}\right] \mathrm{d}V \mathrm{d}T - \frac{\dot{m}TR}{P}\frac{\mathrm{d}C_f}{C_f}\mathrm{d}T = 0 \tag{3}$$

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:

$$\int_0^V \int_{T_s}^{T_f} k_2 \exp\left[\frac{-E}{RT}\right] \frac{1 - P\Delta V^*}{RT} \mathrm{d}V \mathrm{d}T = -\int_{C_{fs}}^{C_{fe}} \int_{T_s}^{T_f} \frac{\dot{m}TR}{P} \frac{\mathrm{d}C_f}{C_f} \mathrm{d}T \tag{4}$$

or

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

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

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

where

$$f_1(T) = T_f \exp[-E/RT_f] - T_s \exp[-E/RT_s) - \int_{T_s}^{T_f} \exp[-E/RT](E/RT)\mathrm{d}T$$

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

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

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

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

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

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*Professor of Chemistry. Associate Fellow AIAA.

†Lecturer in Chemistry.

‡Research Fellow.

measurements of temperature profile in the gas phase are available, the assumption of linear temperature gradient across the reaction zone is the only way out.

The model which we proposed in Ref. 1 breaks new ground, although it has to be subjected to further modification. There have been reports that the decomposition temperature of ammonium perchlorate[5] is reduced by increase of pressure, indicating thereby that the kinetics of oxidizer decomposition is pressure dependent. Further heat of gasification would also be pressure dependent,[6] since enthalpy for real gases can be pressure dependent.[7] There is a need for further investigation of the model and the underlying pressure-dependent processes so that a clearer picture may emerge.

References

[1] Rastogi, R. P., Singh, H. J., Deepak, D., and Srivastava, A. K., "Pressure Dependence of Burning Rate of Composite Solid Propellants," *AIAA Journal*, Vol. 16, May 1978, pp. 534-536.

[2] Hamann, S. D., *Physico-Chemical Effects of Pressure*, Butterworths Scientific Publications, London, 1957, p. 162.

[3] Yang, R. T. and Steinberg, M., "Reaction Kinetics and Differential Thermal Analysis," *Journal of Physical Chemistry*, Vol. 80, No. 9, 1976, p. 966.

[4] Ozawa, T., "Kinetic Analysis of Derivatives Curves in Thermal Analysis," *Journal of Thermal Analysis*, Vol. 2, 1970, pp. 301-304.

[5] Waesche, R. H. W. and Wenogard, J., "Effect of Pressure on the Kinetics of Decomposition of Ammonium Perchlorate," United Aircraft Research Laboratory, Conn., Tech. Rept., April 1967.

[6] Girdhar, H. L. and Arora, A. J., "Effect of Pressure on Heat of Explosion," *Combustion and Flame*, Vol. 28, 1977, pp. 291-293.

[7] Rastogi, R. P. and Mishra, R. R., *An Introduction to Chemical Thermodynamics*, Vikas Publishing House, Pvt. Ltd., New Delhi, India, 1978, p. 95.

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EXPERIMENTAL DIAGNOSTICS
IN COMBUSTION OF SOLIDS—v. 63

Edited by Thomas L. Boggs, Naval Weapons Center, and Ben T. Zinn, Georgia Institute of Technology

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As remarked in the 1977 volume, the particular diagnostic methods selected for presentation were largely undeveloped a decade ago. However, these more powerful methods now make possible a deeper and much more detailed understanding of the complex processes in combustion than we had thought feasible at that time.

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