reaction (4a) seemed to occur at a faster rate than Eq. (3). Above 420°C the decomposition of the AP crystal became the dominant process.

In order to obtain some idea as to whether or not reaction Eq. (4a) might be exothermic, we considered the gas phase reaction,

$$3\ HClO_4\ (g) \rightarrow 2\ ClO_2 + HCl + \tfrac{7}{2}\ O_2 + H_2O \quad (4b)$$

The heats of formation of $HClO_4$ and ClO_2 were taken as 2 kcal/mole and 24.7 kcal/mole, respectively,[11] and the values of the other compounds were taken from standard thermodynamic tables. The calculated H° of the reaction (4b) is − 37 kcal/mole. This value plus the endothermicity of desorbing three moles of $HClO_4$ gives the overall H° of reaction (4a). Since $HClO_4$ is presumed to physically adsorb on the AP crystal surface[12] upon dissociation, the total energy necessary to desorb or evaporate three moles is probably less than 10 kcal. If disproportionation of $HClO_4$ is indeed occurring on the crystal surface, this calculation indicates that it is probably exothermic. These results support the arguments of Wenograd and Shinnar[4] cited earlier.

The results of the closed cell experiments provide some insight into the gaseous reactions that occur when the volatile products remain trapped. It appears that a complicated system of oxidation-reduction reactions is occurring. Both $HClO_4$ and ClO_2 serve as the major oxidizers, while NH_3 appears to be the major species which is oxidized. $HClO_4$ and ClO_2 appear to be reduced to Cl_2 and HCl, while NH_3 is oxidized to N_2, NO_2, and N_2O.

Conclusion

When AP is heated between 200° and 400°C, both decomposition and dissociative sublimation occur simultaneously on/in the crystal surface. An additional exothermic reaction occurring on the surface appears to be the disproportionation of adsorbed $HClO_4$ producing ClO_2 as a major product. The gaseous products of the various pyrolytic reactions are observed to undergo a complex series of oxidation-reduction reactions.

References

[1] Hall, A. R. and Pearson, G. S., "Ammonium Perchlorate: A Review of Its Role in Composite Propellant Combustion," R.P.E. TR 67/1, Jan. 1967, Ministry of Technology, London.

[2] Pellet, G. L. and Cofer, W. R. , "High Temperature Decomposition of Ammonium Perchlorate Using CO_2 Laser-Mass Spectrometry," AIAA Paper 69-143, New York, 1969.

[3] Acheson, R. J. and Jacobs, P. W. M., "The Thermal Decomposition of Ammonium Perchlorate Plus Magnesium Perchlorate Mixtures," AIAA 69-500, New York, 1969.

[4] Wenograd, J. and Shinnar, R., "Combustion of Ammonium Perchlorate—Some Negative Conclusions," *AIAA Journal*, Vol. 6, No. 5, May 1968, pp. 964–966.

[5] Hall, A. R. and Pearson, G. S., "Ammonium Perchlorate: A Review of Its Role in Composite Propellant Combustion," R.P.E. TR 67/1, Jan. 1967, Ministry of Technology, London.

[6] Verneker, V. R. P. and Maycock, J. N., "Mass-Spectrometric Study of the Thermal Decomposition of Ammonium Perchlorate," *Journal of Chemical Physics*, Vol. 47, No. 9, Nov. 1967, pp. 3618–3621.

[7] Manelis, G. B. and Rubstov, Y. I., "The Kinetics of the Thermal Decomposition of Ammonium Perchlorate," *Zhurnal Fizicheskoi Khimii*, Vol. 40, No. 4, April 1966, pp. 416–418.

[8] Guillory, W. A. and King, M. "The Thermal Decomposition of Methyl-Substituted Amine-Type Perchlorates," *Journal of Physical Chemistry*, Vol. 73, No. 12, Dec. 1969, pp. 4367–4369.

[9] Bircumshaw, L. L. and Newman, B. H., "The Thermal Decomposition of Ammonium Perchlorate, Part II," *Proceedings of the Royal Society of London, Series A*, Vol. 227, No. 1169, Jan. 1955, pp. 228–241.

[10] Bircumshaw, L. L. and Newman, B. H., "The Thermal Decomposition of Ammonium Perchlorate, Part I," *Proceedings of the Royal Society of London, Series A*, Vol. 227, No. 1168, Dec. 1954, pp. 115–132.

[11] Heath, G. A. and Majer, J. R., "Mass Spectrometric Study of the Thermal Decomposition of Ammonium Perchlorate," *Transactions of the Faraday Society*, Vol. 60, Pt. 2, 1964, pp. 1783–1791.

[12] Schultz, R. D. and Dekker, A. O. "Absolute Thermal Decomposition Rates of Solids, Part II," *Journal of Chemical Physics*, Vol. 23, No. 11, Nov. 1955, pp. 2133–2138.

New Outer Boundary Conditions for the Similar Boundary-Layer Equations

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In the numerical integration of the similar boundary-layer equations, the outer boundary conditions, which should be applied at infinity, are necessarily applied at some reasonable finite distance with a resulting loss of accuracy. (In some methods of solution, this also leads to loss of uniqueness of the solution e.g., see Ref. 1.) This inaccuracy can, in principle, be reduced to any desired degree by applying the outer boundary conditions at a sufficiently large distance from the surface. However, an attractive alternative was introduced by Libby and Chen[2] that consists of matching a numerical inner solution to an asymptotic series for the outer solution. This procedure was applied by Libby in Refs. 2 and 3 to the quasilinearization method of integrating the similar boundary-layer equations with unit Prandtl number. In this paper, we treat the outer boundary conditions in a more general manner, not tied to any particular numerical method of solution. We show the derivation of outer boundary conditions from the asymptotic form of the similar boundary-layer equations with unit Prandtl number, and also note results for the incompressible case with arbitrary Prandtl number.

The laminar similar boundary-layer equations for steady two-dimensional ideal gas flows with unit Prandtl number and constant wall temperature are[4]

$$f''' + ff'' + \beta(1 + S - f'^2) = 0 \quad (1)$$

$$S'' + fS' = 0 \quad (2)$$

subject to the inner and outer boundary conditions

$$f(0) = f'(0) = 0,\ S(0) = S_w \qquad f'(\infty) = 1,\ S'(\infty) = 0 \quad (3)$$

where f and β are defined as usual, primes denote differentiation with respect to η, and S is defined in terms of the stagnation enthalpy $S = (h_s/h_{se}) - 1$.

To find an outer solution we first introduce a new variable $\phi = 1 - f'$ in terms of which

$$f = \eta - \int_0^\eta \phi d\eta = \eta - \eta_0 + \int_\eta^\infty \phi d\eta$$

where we have defined

$$\eta_0 = \int_0^\infty \phi d\eta$$

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With this Eqs. (1) and (2) are then rewritten

$$\phi'' + (\eta - \eta_0)\phi' - \beta(2\phi + S) = -\beta\phi^2 - \phi' \int_\eta^\infty \phi d\eta$$

$$S'' + (\eta - \eta_0)S' = -S' \int_\eta^\infty \phi d\eta$$

If we now assume η sufficiently large that $|\phi| \ll 1$, the right-hand sides of the preceding two equations are negligibly small and may be dropped, giving the following outer equations:

$$\begin{aligned} \phi'' + (\eta - \eta_0)\phi' - 2\beta\phi &= \beta S \\ S'' + (\eta - \eta_0)S' &= 0 \end{aligned} \tag{4}$$

These equations are linear and can be integrated to give

$$\begin{aligned} \phi &= A \exp[-\tfrac{1}{2}(\eta - \eta_0)^2]\Psi(\beta + \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}[\eta - \eta_0]^2) - \tfrac{1}{2}S \\ S &= B \exp[-\tfrac{1}{2}(\eta - \eta_0)^2]\Psi(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}[\eta - \eta_0]^2) \end{aligned} \tag{5}$$

where Ψ is the confluent hypergeometric function of the second kind.[5] [The second solution of Eq. (4) has algebraic, rather than exponential, decay as $\eta \to \infty$, and is therefore eliminated.] The constants A and B may be determined by matching with the inner solutions. However, instead of doing this we may use these outer solutions to obtain a new outer boundary condition. This is done by differentiating ϕ and S, and using these derivatives to eliminate A and B. As can be seen, the forms of the resulting equations are

$$(\phi + \tfrac{1}{2}S)'/(\phi + \tfrac{1}{2}S) = \text{function of } (\eta - \eta_0) \text{ and } \beta$$

$$S'/S = \text{function of } (\eta - \eta_0)$$

Actually, doing this with Eqs. (5) would be rather complicated and not particularly convenient to use. Fortunately, these solutions are more accurate than need be, since we have assumed $\eta \gg 1$, so an asymptotic approximation for ϕ may be used. One may be generated as follows.

Considering only Eq. (4), we introduce the new variables

$$\theta = (\phi + \tfrac{1}{2}S)'/(\phi + \tfrac{1}{2}S),\ z = \eta - \eta_0$$

which, substituted in Eq. (4), give

$$z^{-2}\theta_z + (\theta/z + 1)\theta/z - 2\beta/z^2 = 0$$

The leading terms of the asymptotic expansion for Ψ,

$$\Psi(a, b;\ x) = x^{-a}[1 - a(a - b + 1)/x + \ldots]$$

for $x \gg 1$, suggest a series expansion for θ of the form

$$\theta = -z[a + b/z^2 + c/z^4 + \ldots]$$

where $a, b, c, \ldots$ are $O(1)$ but may be functions of β/z^2, since we wish our results to also be applicable to cases in which β/z^2 may be $O(1)$. Substitution of the series in the differential equation and separation of terms of different orders in z yield the set of equations

$$a(1 - a) + 2\beta/z^2 = 0$$

$$a + za_z + (1 - 2a)b = 0$$

$$b - zb_z + b^2 - (1 - 2a)c = 0$$

etc., which may be solved to give $a = \frac{1}{2}(1 + \sigma)$ and

$$\theta = -\tfrac{1}{2}z(1 + \sigma)\{1 + 1/\sigma^2z^2 - [(5 - \sigma)/2\sigma^5]/z^4 + \ldots\} \tag{6}$$

where we have introduced $\sigma = (1 + 8\beta/z^2)^{1/2}$. [There is also a second solution in which $a = \frac{1}{2}(1 - \sigma)$; this solution corresponds to the algebraic decay case that was eliminated.] The equivalent expression for S'/S is found by setting $\sigma = 1$.

To the order of approximation being entertained we may replace z by f, so that the outer boundary conditions are, returning to our original variables,

$$\begin{aligned} &S' + fS(1 + 1/f^2 - 2/f^4) = 0 \\ &(f' - \tfrac{1}{2}S)' - \tfrac{1}{2}f(1 - f' + \tfrac{1}{2}S)(1 + \sigma)\{1 + 1/\sigma^2f^2 - [(5 - \sigma)/2\sigma^5]/f^4\} = 0 \end{aligned} \tag{7}$$

where, now, $\sigma = (1 + 8\beta/f^2)^{1/2}$. These two differential boundary conditions may be applied in place of Eqs. (3) at any suitable outer boundary η where S and $1 - f'$ are not too large. The error in S and $1 - f'$ generated by the use of Eqs. (7) is of order

$$(|S| + |1 - f'|)(f^{-1} + |S| + |1 - f'|)$$

evaluated at the outer boundary η, while the error arising from the application of the infinity boundary conditions (3) at η is of order $|S| + |1 - f'|$.

The aforementioned results can be extended to incompressible flow with arbitrary Prandtl number with relatively little effort. In this case Eq. (2) becomes $S'' + PrfS' = 0$. The principal difficulty lies in the fact that $\phi = -\frac{1}{2}S$ is no longer a particular solution of Eq. (4). However, an asymptotic approximation to a particular solution can be shown to be

$$\phi_p = -\tfrac{1}{2}S[1 + (1 - Pr)(S'/S)az^{-1} \times (1 + b/z^2 + c/z^4 + \ldots)]$$

where

$$\begin{aligned} a &= [Pr(1 - Pr) + 2(\beta + 1)/z^2]^{-1} \\ b &= (2 - Pr)a - (2Pr - 1)z^2(a/z)_z \\ c &= (2 - Pr)ab - (2Pr - 1)z^4(ab/z^3)_z - z^3(a/z)_{zz} \end{aligned}$$

etc. Then, redefining $\theta = (\phi - \phi_p)'/(\phi - \phi_p)$, Eq. (6) gives the outer boundary condition on f'. For S we have

$$S' + PrfS[1 + (1/Prf^2) - (2/Pr^2f^4)] = 0$$

The numerical solutions of the differential Eqs. (1) and (2) using our outer boundary conditions (7) may be accomplished by a variety of methods, such as those used by Libby and by Nachtsheim and Swigert.[4] The use of iterative implicit methods also leads to relatively straightforward solutions (see, e.g., Christian, Hankey and Petty[6]); however, considerable computer memory capacity generally is required.

To test the accuracy of solutions obtained using Eqs. (7), a numerical experiment was performed in which an "exact" solution (computed with an accuracy of 10^{-10} in f' and S) was compared with approximate solutions using Eqs. (3) and (7) applied at three values of η_B. The exact solution was found† by using an explicit numerical integration technique similar to that used by Nachtsheim and the approximate solutions were found by using an iterative implicit technique. Details of both numerical techniques may be found in Ref. 6. Care was taken that the expected numerical errors were in all cases much smaller than the expected analytic errors. We chose $\beta = 0.1$, $S_w = -0.8$ as being representative values. The maximum errors are shown in Table 1.

Table 1 Comparison of errors arising from application of the outer boundary conditions at finite distances

	Maximum error		
		Eqs. (7)	
η_B	Eqs. (3)	Actual	Estimated
3.0	2.4×10^{-2}	1.4×10^{-3}	3.3×10^{-3}
4.0	1.6×10^{-3}	1.4×10^{-5}	1.5×10^{-5}
5.0	4.2×10^{-5}	7.8×10^{-8}	3.2×10^{-8}

† The author wishes to acknowledge his gratitude to J. W. Christian for supplying this exact solution.

As can be seen, the improvement arising from the use of the nonasymptotic boundary conditions (7) is significant and the actual and estimated errors are in reasonable agreement. The procedure we have used in this Note may be applied to a variety of boundary-value problems with asymptotic boundary conditions, the principal requirements being that some foreknowledge of the asymptotic behavior of the solutions is needed and that the outer differential equations can be reduced to homogeneous form.

References

[1] Nachtsheim, P. R. and Swigert, P., "Satisfaction of Asymptotic Boundary Conditions in Numerical Solution of Systems of Nonlinear Equations of Boundary-Layer Type," TN D-3004, 1965, NASA.

[2] Libby, P. A. and Chen, K. K., "Remarks on Quasilinearization Applied in Boundary-Layer Calculations," *AIAA Journal*, Vol. 4, No. 5, May 1966, pp. 937–939.

[3] Libby, P. A. and Liu, T. M., "Some Similar Laminar Flows Obtained by Quasilinearization," *AIAA Journal*, Vol. 6, No. 8, August 1968, pp. 1541–1548.

[4] Cohen, C. B. and Reshotko, E., "Similar Solutions for the Compressible Laminar Boundary Layer with Heat Transfer and Pressure Gradient," Rept. 1293, 1956, NACA.

[5] Slater, L. J., *Confluent Hypergeometric Functions*, Cambridge University Press, London, 1960.

[6] Christian, J. W., Hankey, W. L., and Petty, J. S., "Similar Solutions of the Attached and Separated Compressible Laminar Boundary Layer with Heat Transfer and Pressure Gradient," ARL Rept. 70-0023, Feb. 1970, Aerospace Research Lab., Wright-Patterson Air Force Base, Ohio.

Turbulent Boundary-Layer Thicknesses on Yawed Cones

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Nomenclature

b = blowing parameter = $[(\rho v)_w/(\rho u)_e]2/C_{f_0}$
C_f = skin friction coefficient
L = model length
M = Mach number
MW = molecular weight
Re = Reynolds number based on model length
T = temperature
T^* = reference temperature
u = velocity parallel to model wall
v = velocity normal to model wall
α = angle of attack
δ = boundary-layer thickness
$\bar{\delta}$ = $[\delta(\alpha)/\delta(0)]/[\delta_c(\alpha)/\delta_c(0)]$
θ = momentum thickness
θ_c = cone half angle
ρ = density

Subscripts

∞ = freestream conditions
c = critical or calculated
e = boundary-layer edge conditions
0 = without mass addition
r = recovery conditions
w = wall conditions

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Introduction

INFORMATION on the growth and thickness of boundary layers is required in order to estimate viscous interaction effects, plasma attenuation, and wake characteristics. For unyawed cones, Ref. 1 is widely used for making engineering calculations of turbulent boundary layer properties both with and without mass addition (blowing). In the present Note data are presented which indicate the effect of α on δ along the windward and leeward rays of a yawed cone. Test conditions include M_∞'s ranging from 1.8 to 10.2, cases with and without heat transfer and with and without blowing. It is shown that the effect of crossflow on δ for all of these data can be satisfactorily represented by a single curve.

Experimental Data

Test conditions for the experimental data considered are summarized in Table 1. The new data without blowing reported herein were obtained in Tunnels *B* and *C* of the Arnold Engineering Development Center. Nominal reservoir conditions were 220 psia and 850°R at M_∞ = 6.05 and 1725 psia and 1900°R at M_∞ = 10.2. The test model was a 36-in. long, 9° half-angle cone equipped with a boundary-layer trip having a roughness height of 0.080 in. located near its nose. In one series of experiments the nose was sharp and wall temperature was near adiabatic, whereas in another series of experiments the nose radius was 0.15 in. and there was heat transfer to the wall.

The blowing data were taken on a 10-in. long, 9° half-angle cone equipped with a porous skin through which air could be ejected. The model had a nose radius of 0.053 in. and was tested without a boundary layer trip. A M_∞ = 8 airstream was generated by 1000 psia and 1340°R reservoir conditions. Without blowing the model boundary-layer was laminar; however, for the blowing tests the boundary layer became turbulent near the nose. Additional details on the experimental setup are presented in Ref. 2.

The δ's reported herein were measured at the model base. For the AEDC test the δ's represent averages of measurements taken from shadowgraph or color schlieren photographs from several runs. These results are summarized in Table 2. The δ's from the Ref. 2 test were determined from shadowgraph pictures whereas the δ's reported in Ref. 3 were determined from pitot pressure surveys. All of the δ's obtained from the blowing test are included in Table 3.

Results and Discussion

The windward data from Tables 2 and 3 and Ref. 3 are plotted in Fig. 1. The change in δ with α exhibited in Fig. 1 can be separated into two effects, 1) changes in δ caused by changes in local flow conditions as the cone is yawed, and 2) thinning of the boundary layer due to crossflow. In order to isolate these effects, changes in δ caused by changes in local conditions were calculated. The method of Ref. 1 was used with the following modifications which were obtained from

Table 1 Summary of test conditions

Symbol	Source	M_∞	T_w/T_r	θ_c (deg)	L (in.)	Re_∞ (10^6)	$\frac{(\rho v)_w}{(\rho u)_\infty}$
◇	Present Data	6.05	1	9	36	11.8	0
⊙		10.2	1	9	36	6.3	0
●		10.2	0.37 to 0.52	9	36	6.3	0
⊡	Ref. 2	8.0	0.69	9	10	4.0	0.013
■		8.0	0.55	9	10	4.0	0.017
△	Ref. 3	1.8	1	12.5	41.6	25	0
▽		4.25	1	12.5	41.6	51	0