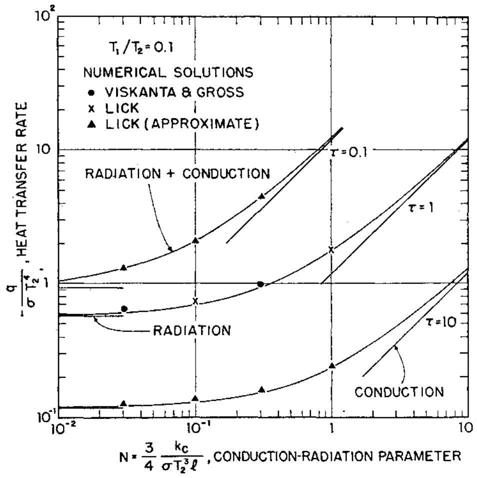

Fig. 2 Heat transfer rate for simultaneous radiation and conduction between two infinite isothermal parallel black plates containing a gray, constant conductivity gas in the gap between the plates

agreement with both the exact numerical calculations and the approximate calculations of Lick obtained using various asymptotic expansions.

In view of the success of the radiation slip argument, at least for the particular example considered, it would appear worth while to apply this concept to more complicated geometries, including problems where molecular conduction is present simultaneously, and to gas flows where radiant heat transfer is of importance (see, e.g., Goulard[11]). It also would appear that the exploitation of the simple mean free path arguments presented, by a more detailed photon transport theory, could assist materially in the difficult calculations of radiation transition regimes where the surfaces present and the radiating medium have more complicated properties than those considered.

References

[1] Goulard, R., "Similarity parameters in radiation gasdynamics," School of Aeronaut. and Eng. Sci., Purdue Univ., A & ES 62-8 (September 1962); also to appear in *Papers Presented in Honor of Modesto Panetti*, Politecnico di Torino (Accademia Nazionale dei Lincei, Rome, 1963).

[2] Rosseland, S., *Astrophysik auf Atom-Theoretischer Grundlage* (Springer-Verlag, Berlin, 1931), pp. 41–44.

[3] Fay, J. A., "Energy transfer in a dense plasma," Dept. Mech. Eng., Mass. Inst. Tech., Fluid Mech. Lab. Publ. 63-1 (January 1963); also to appear in *Proceedings of the 7th Lockheed Symposium on Magnetohydrodynamics* (Stanford University Press, Stanford, Calif., 1963).

[4] Usiskin, C. M. and Sparrow, E. M., "Thermal radiation between parallel plates separated by an absorbing-emitting nonisothermal gas," Intern. J. Heat Mass Transfer 1, 28–36 (1960).

[5] Kennard, E. H., *Kinetic Theory of Gases* (McGraw-Hill Book Co. Inc., New York, 1938), p. 315.

[6] Eddington, A. S., *Internal Constitution of Stars* (Cambridge University Press, Cambridge, 1926).

[7] Milne, E. A., "Thermodynamics of stars," *Handbuch der Astrophysik* (Springer-Verlag, Berlin, 1930), Vol. 3, Part 1, pp. 65–225.

[8] Sherman, F. S. and Talbot, L., "Experiment versus kinetic theory for rarefied gases," *Rarefied Gas Dynamics* (Pergamon Press, London, 1960), pp. 161–191.

[9] Sarofim, A. F., "Radiant heat transmission in enclosures," Sc. D. Thesis, Dept. Chem. Eng., Mass. Inst. Tech. (1962).

[10] Viskanta, R. and Grosh, R. J., "Heat transfer by simultaneous conduction and radiation," J. Heat Transfer **C84**, 63–72 (1962).

[11] Goulard, R., "The coupling of radiation and convection in detached shock layers," J. Quant. Spectr. Radiative Transfer 1, 249–257 (1961).

[12] Lick, W. J., private communication, Harvard Univ. (1963).

Reduction of Frozen Flow Losses by Nonequilibrium Heating

Michael Ming Chen*
Avco Research and Advanced Development Division,
Wilmington, Mass.

Introduction

The energy absorbed in the dissociation of a polyatomic propellant in nuclear or electrothermal rockets often represents a large portion of the total energy input. Current information on recombination rates appears to preclude any significant recombination of these dissociated particles in a nozzle of reasonable length. Thus the unreclaimed dissociation energy constitutes a serious loss mechanism. This energy loss, called the frozen flow loss, has been estimated for various propellants,[1] usually with the assumption that the propellant is dissociated to equilibrium compositions corresponding to the stagnation or throat enthalpies. This type of assumptions leads to the well-known conclusion that in order to reduce frozen flow losses one should operate at as high a pressure as practicable. Small improvements in frozen flow loss due to temperature nonuniformities and regenerative heating also have been investigated.[2–4]

All these studies have neglected the problem of dissociation kinetics. As will be indicated below, under certain circumstances, it is possible to heat the propellant to high enthalpies rapidly without significant dissociation. These preliminary calculations indicate that nonequilibrium heating is a promising means for reducing frozen flow losses of high specific impulse engines.

Discussion

The dissociation reaction rate is usually comparable to the recombination rate. Therefore the assumption of equilibrium dissociation but nonequilibrium recombination in rocket nozzle calculations is valid only for nozzles where the propellant is heated in low velocity or essentially stagnant conditions. If a nozzle is constructed in such a manner that the propellant is heated and simultaneously accelerated to high speeds, dissociation equilibrium may not be satisfied. At sufficiently high heating rates and acceleration rate, it is conceivable that the heated propellant may be accelerated before significant dissociation takes place.

In order to obtain an order of magnitude estimate of the feasibility of nonequilibrium heating, one may compare the time required for dissociation to the characteristic time of the nozzle flow as well as the characteristic times of the pertinent heating processes. The dissociation time constant is approximately

$$\tau_d \approx 1/\beta N_m = 1/\alpha K_N N_m \qquad (1)$$

where the relationship between the dissociation coefficient and recombination coefficient has been used. Based on Rink's summary of recent data[5] and Keck's theoretical temperature dependence,[6] α can be taken approximately as $8\,(10)^{-30}\,T^{-1}$ cc^2/molecule^2-sec. The result of the calculation is shown in Table 1 as a function of pressure.

The characteristic residence time of the propellant travelling at near sonic or higher velocities in a nozzle is related to the gas enthalpy and the nozzle length. Neglecting dissociation

---

Received March 18, 1963. The author wishes to express his gratitude to NASA, who supported his research, to H. Bethe, K. Burkhard, and C. Averitt for discussions and assistance, and to L. Shields for the numerical calculations.

* Senior Staff Scientist, Research Directorate.

energy, one has the approximate relationship

$$\tau_r \approx \frac{L}{(kT/m_m)^{1/2}} \tag{2}$$

where L should be taken as $D \cot\theta$ in case of very long nozzles. The results are shown in Table 1. Comparison of this with the dissociation time constant indicates that dissociation can be curbed if pL is small, as indicated in Table 2. It is seen that, for an arc-jet engine with $L = 0$ (1 cm) and propellant temperature near 7000°K or a nuclear rocket with $L = 0$ (10^2 cm) and propellant temperature near 3500°K, dissociation can be reduced if $p < 1$ atm.

It remains to be shown that it is physically possible to heat the propellant to such high temperatures within the short time allowed. Clearly, chemical heating is not capable of reaching such high heating rates, since it is limited by rate constants similar to those of dissociation. Other forms of heating, such as the volume heating due to electrical discharges in arc-jet engines and the surface heating due to thermal conduction from a hot wall in electrothermal rockets and some nuclear rocket configurations, are not limited by chemical reaction rates. The limiting heating rate for these processes will be examined below.

First consider electric heating. In order to heat a diatomic gas to stagnation temperature T, the necessary energy per particle is $\frac{7}{2}kT$. This energy must come from the acceleration of electrons in the electric field, amounting to about $\frac{1}{2}(e^2E^2/m_e)\tau$ per collision. The problem of how to provide a small number of electrons without dissociation will not be discussed in detail here because of space limitations. It suffices to mention that seeding and nonequilibrium ionization are both promising schemes. Assuming the electron mole fraction to be X_e, the time required to heat the neutrals to T_0 is then

$$\tau_e \approx \frac{\frac{7}{2}kT_0}{(X_e/2)(e^2E^2/m_e)\tau} \approx 7\left(\frac{\pi k T_0}{8m_e}\right)^{1/2} \frac{p}{X_e}\frac{Q_{em}}{e^2E^2} \tag{3}$$

It is seen that the heating time can be reduced by increasing the degree of ionization or the electric field. Since ionization also may introduce frozen flow problems, one probably would wish to limit X_e to the vicinity of 1%. On the other hand, electric field also cannot be increased indefinitely. Because of the large disparity between the electronic and molecular masses, their collisions are inefficient energy exchange processes. Thus too high an electric field, or too high a heating rate, may not result in the proper thermalization of the energy input. The time required for electron-neutral energy exchange is[7]

Table 1 Characteristic times for various physical processes in a rocket nozzle[a]

Process	At 3500°K	5000°K	7000°K
Dissociation	$2\,(10)^{-4}\,\frac{1}{p}$	$(10)^{-5}\,\frac{1}{p}$	$\frac{1}{2}\,(10)^{-6}\,\frac{1}{p}$
Joule heating	$5\,(10)^{-4}\,\frac{p}{E^2X_e}$	$4\,(10)^{-5}\,\frac{p}{E^2X_e}$	$3\,(10)^{-5}\,\frac{p}{E^2X_e}$
Electron-neutral energy transfer	$20\,(10)^{-8}\,\frac{1}{p}$	$2\,(10)^{-8}\,\frac{1}{p}$	$3\,(10)^{-8}\frac{1}{p}$
Heat conduction from hot surface	$\frac{1}{2}\,(10)^{-2}\,r^2p$	$2\,(10)^{-3}\,r^2p$	$(10)^{-3}\,r^2p$
Approx. residence time in nozzle	$2\,(10)^{-6}\,L$	$2\,(10)^{-6}\,L$	$1.5\,(10)^{-6}\,L$

[a] Units of time are in seconds, p in atmospheres, E in volts/cm, L and r in cm; X_e denotes electron mole fraction. Calculations are based on an assumed electron-neutral cross section of $(10)^{-15}$ cm², recombination coefficient of $8(10)^{-30}\,T^{-1}\,cc^2$/molecule²-sec, with hydrogen as propellant.

Table 2 Conditions for nondissociating flow in a rocket nozzle[a]

	3500°K	5000°K	7000°K
Approx. conditions for the gas not to dissociate in a rocket nozzle of length L	$pL \ll 100$	$pL \ll 5$	$pL \ll 0.3$
Nondissociative joule heating	$\frac{E}{p} > \frac{0.5}{(X_e)^{1/2}}$	$\frac{E}{p} > \frac{2}{(X_e)^{1/2}}$	$\frac{E}{p} > \frac{8}{(X_e)^{1/2}}$
Thermalization of joule heating	$\frac{E}{p} < \frac{150}{(X_e)^{1/2}}$	$\frac{E}{p} < \frac{40}{(X_e)^{1/2}}$	$\frac{E}{p} < \frac{30}{(X_e)^{1/2}}$
Nondissociative surface heating	$pr < 0.2$	$pr < 0.07$	$pr > 0.02$

[a] Units of time are in seconds, p in atmospheres, E in volts/cm, L and r in cm; X_e denotes electron mole fraction. Calculations are based on an assumed electron-neutral cross section of $(10)^{-15}$ cm², recombination coefficient of $8(10)^{-30}\,T^{-1}\,cc^2$/molecule²-sec, with hydrogen as propellant.

$$\tau_{en} = \frac{1}{2}\frac{m_m}{m_e}\frac{1}{M_m v_e Q_{em}} \tag{4}$$

Assuming that the electron-neutral collision cross sections[7] are of the order of 10^{-15} cm², the calculated time constants are shown in Table 1.

Lastly, the characteristic time constant for surface heating, such as the heating of a gas stream flowing in a hot tube, will be examined. In this instance only the gas particles in the vicinity of the solid surface is heated directly. The remaining body of gas must be heated by gaseous thermal conduction. The time required for conduction to overcome the thermal inertial effects of heat capacity can be estimated by using the macroscopic concept of "heat diffusivity" $K/\rho c_p$, or it can be estimated from the equivalent microscopic consideration of the random walk. Since the energy transferred per collision is of the order of mean thermal energy, the time required to heat a cylindrical body of gas with radius r is just the time required for a particle to travel the distance r by random walk:

$$\tau_c = \frac{r^2 N_m Q_{mm}}{v_m} = r^2 N_m Q_{mm}\left(\frac{\pi m_m}{8kT}\right)^{1/2} \tag{5}$$

Assuming $Q_{mm} \approx 10^{-15}$, numerical results of this also are shown in Table 1.

By comparing the time constants shown in Table 1, approximate criteria for nondissociative rocket nozzle design can be obtained. These are shown in Table 2. It is seen that there are wide design margins within which net dissociation can be reduced effectively by nonequilibrium heating.

Illustrative Example

In the foregoing approximate calculations, nozzle geometry was not considered specifically. As an example, a numerical calculation of a one-dimensional nonequilibrium flow has been made for a simple nozzle, consisting of a constant area subsonic section and a diverging supersonic section. Heating is assumed to take place in the subsonic section at such a rate that

$$T_0/T_0^* = x/L \tag{6}$$

Using the same rate constants as before, the results of the calculation are shown in Fig. 1. It is seen that the results are

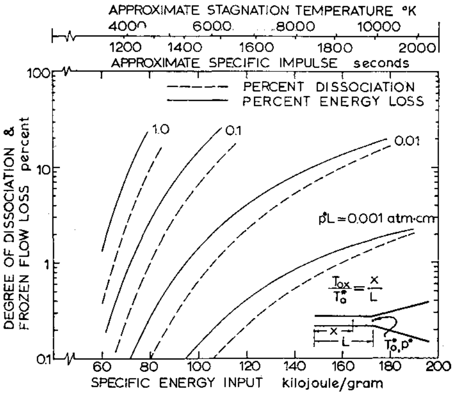

Fig. 1 Estimated dissociation and frozen flow loss for a nozzle with constant area heat addition

not substantially different from the conclusions in Table 2.

The nozzle and heat input distribution used in this calculation are not substantially different from some actual nozzles in current use. Indeed, nonequilibrium heating actually may be taking place in some arc-jet engine nozzles, which usually operate with pL of the order of unity.[4]

Concluding Remarks

Although the preliminary calculations presented in the foregoing indicate that nonequilibrium heating is feasible, more detailed investigations of the kinetics and aerodynamics are necessary to evaluate quantitatively its effectiveness in reducing frozen flow loss. In particular, the influence of electron impact dissociation[7] at high electron concentrations and temperatures should be investigated. It is hoped that this note will stimulate interest among propulsion engineers in these endeavors.

References

[1] Page, R. J., "Current status and prospects of electrothermal propulsion," ARS Preprint 2649-62 (November 1962).

[2] Noeske, H. O. and Kasner, R. R., "Analytical investigations of a bipropellant arc jet," ARS J. **32,** 1701–1708 (1962).

[3] Mironer, A. and Macomber, H., "Spatial non-uniformity effects in electrothermal propulsion," ARS J. **32,** 1412–1413 (1962).

[4] Chen, M. M., "Effect of non-equilibrium flow in thermal arc jet engines," Summary Report to NASA Lewis Research Center, Contract NAS-8-1607, Avco Corp., Research and Advanced Development Div. RAD-TR-62-25 (September 1962).

[5] Rink, J. P., "Shock tube determination of dissociation rates of hydrogen," J. Chem. Phys. **36,** 262–265 (1962).

[6] Keck, J. C., "Statistical theory of chemical reactions," J. Chem. Phys. **29,** 410–415 (1958); also "Variational theory of chemical reaction rates applied to three-body recombination," Avco Everett Rept. 66 (September 1959).

[7] Massey, H. S. W. and Burhop, E. H. S., *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), pp. 1–16, 189–281.

On Two Alternative Motivations of Reference-State Expressions for Turbulent Flows with Mass Transfers

Eldon L. Knuth*
University of California, Los Angeles, Calif.

For turbulent flows without mass transfers, reference-temperature (or reference-enthalpy) expressions obtained using two alternative motivations are found to be equivalent to good approximation. For example, Eckert,[1] guided apparently by the expression evolved empirically for laminar flows, finds that

$$T^* = 0.50\,T_w + 0.50\,T_\infty + 0.22\,r_0{}^*u_\infty{}^2/2c_p{}^* \qquad (1)$$

correlates satisfactorily data for turbulent flows over flat plates; Burggraf,[2] equating the reference enthalpy and the enthalpy at the outer edge of the laminar sublayer, obtains an expression that may be written (for constant specific heat)

$$T^* = \left(1 - \frac{Pr^*}{s_{h0}{}^*}\frac{u_{s0}}{u_\infty}\right)T_w + \frac{Pr^*}{s_{h0}{}^*}\frac{u_{s0}}{u_\infty}T_\infty + \frac{Pr^*}{s_{h0}{}^*}\frac{u_{s0}}{u_\infty}\left(1 - \frac{s_{h0}{}^*}{r_0{}^*}\frac{u_{s0}}{u_\infty}\right)\frac{r_0{}^*u_\infty{}^2}{2c_p{}^*} \qquad (2)$$

where T is temperature, u velocity parallel to surface, c_p constant-pressure specific heat, Pr Prandtl number, r recovery factor, s_h Reynolds-analogy factor for heat transfer, subscripts w, s, ∞, and 0 refer, respectively, to wall, outer edge of laminar sublayer, outer edge of boundary layer, and zero-blowing conditions, and the asterisk indicates that the property is to be evaluated at the reference state. For

$$\frac{Pr^*}{s_{h0}{}^*}\frac{u_{s0}}{u_\infty} = \frac{s_{h0}{}^*}{r_0{}^*}\frac{u_{s0}}{u_\infty} = \frac{1}{2}$$

(a typical value), Eqs. (1) and (2) are equivalent to good approximation. The purpose of the present note is to compare extensions of Eqs. (1) and (2) to the case of turbulent flows with mass transfers.

Expressions for the reference state (reference temperature and reference composition) for laminar boundary layer flow with mass transfer have been developed by Knuth.[3] The development of the reference-temperature expression was guided by an analysis of Couette flow in which the variation of the specific heat with composition was taken into account. The purposes of the present note are satisfied, however, if one uses the simplified expression obtained by applying the methods of Ref. 3 to a model in which the specific heat is constant with a value fixed by the reference state. One obtains

$$T^* = 0.50\,T_w + 0.50\,T_\infty + 0.17\,r_0{}^*u_\infty{}^2/2c_p{}^* + 0.08(c_p{}^c/c_p{}^*)\,Pr^*B_f{}^*(T_w - T_\infty) \qquad (3)$$

where

$$B_f{}^* \equiv [(\rho v)_w/\rho^*u_\infty](2/C_{f0}{}^*)$$

and where ρ is density, v is velocity normal to surface, C_f is friction coefficient, and superscript c refers to coolant. The expression for reference composition involves, in general, logarithmic terms; the linearized expression

$$c^{c*} = 0.50\,c_w{}^c + 0.50\,c_\infty{}^c \qquad (4)$$

may be used, however, for low blowing rates or small molecular-weight differences. In a study of the limited available data, it was concluded[4] that, for Mach numbers up to 3 and for injection of nitrogen into air, Eq. (3) correlates satisfactorily the data for turbulent boundary layer flows with mass transfers.

In the alternative motivation of reference-state expressions for turbulent flows with mass additions, one would equate the reference temperature and composition to the temperature and composition at the outer edge of the laminar sublayer. For a model in which the specific heat is constant with value fixed by the reference state, an expression for the temperature at the outer edge of the laminar sublayer is given by Eq. (15) of Ref. 4. Solving for T_s,

$$T_s = T_w - \frac{r_s{}^*u_s{}^2}{2c_p{}^*} + \frac{k^*(dT/dy)_w}{(\rho v)_w c_p{}^c}\left[\left(\frac{\tau_s}{\tau_w}\right)^{(c_p{}^c/c_p{}^*)Pr^*} - 1\right]$$

Received January 14, 1963.

* Associate Professor and Head of Molecular-Beam Laboratory. Associate Fellow Member AIAA.