

engineering significance. It is likely that any observable effect of an exothermal source on a turbulent gas flow will be found in measurements of bulk quantities because of the great difficulties in resolving precisely the three-dimensional spectrum from experimental information.

References

- ¹ Eschenroeder, A. Q., "Intensification of turbulence by chemical heat release," *Phys. Fluids* **7**, 1735-1743 (1964); also available as General Motors Defense Research Labs. TR 63-217D (August 1963).
- ² Mickelson, W. R. and Laurence, J. C., "Measurement and analysis of turbulent flow containing periodic flow fluctuations," NACA Research Memo. E53F19 (August 1953).
- ³ Scull, W. E. and Mickelson, W. R., "Flow and mixing processes in combustion chambers," *Basic Considerations in the Combustion of Hydrocarbon Fuels with Air*, NACA TR 1300, Chap. II (1957).
- ⁴ Hinze, J. O., *Turbulence. An Introduction to its Mechanism and Theory* (McGraw-Hill Publishing Co., Inc., New York, 1959), p. 193.
- ⁵ von Kármán, T., "Progress in the statistical theory of turbulence," *Proc. Natl. Acad. Sci. U.S.* **34**, 530-539 (1948).
- ⁶ Obukhoff, A. M., "On the distribution of energy in the spectrum of turbulent flow," *C. R. Acad. Sci. SSSR* **32**, 19-25 (1941).
- ⁷ Meksyn, D., "Differential integral equation for the spectrum of isotropic homogeneous turbulence," *Z. Physik* **174**, 301-313 (1963).
- ⁸ Batchelor, G. K., *The Theory of Homogeneous Turbulence* (Cambridge University Press, Cambridge, 1953), Chap. 5 and 6.
- ⁹ Eschenroeder, A. Q., "A solution for the inertial energy spectrum of isotropic turbulence," *Phys. Fluids* **8**, 598-602 (1965); also available as General Motors Defense Research Labs. TR64-02F (August 1964).
- ¹⁰ Lord Rayleigh, J.W.S., *Theory of Sound* (Macmillan and Co., Ltd., London, England, 1878; reprinted by Dover Publications, New York, 1945), articles 322f-322j.
- ¹¹ von Kármán, T. and Lin, C. C., "On the statistical theory of isotropic turbulence," *Advan. Appl. Mech.* **2**, 1-19 (1951).
- ¹² Kolmogoroff, A. N., "The local structure of turbulence in incompressible viscous fluid for very large Reynolds number," *C. R. Acad. Sci. SSSR* **30**, 301-314 (1941).
- ¹³ Heisenberg, W., "Zür statischen Theorie der Turbulenz," *Z. Physik* **124**, 628-657 (1943); also available in English transl. as NACA TM 1931 (1958).
- ¹⁴ Eschenroeder, A. Q., "The spectrum of turbulence in an exothermal gas flow," General Motors Defense Research Labs. TR63-217F (November 1963).
- ¹⁵ Bass, J., "Sur les bases mathématiques de la theorie de la turbulence d'Heisenberg," *C. R. Acad. Sci. Paris* **228**, 228-234 (1949).
- ¹⁶ Chandrasekhar, S., "On Heisenberg's elementary theory of turbulence," *Proc. Roy. Soc. (London)* **A200**, 20-33 (1950).
- ¹⁷ Proudman, I., "A comparison of Heisenberg's spectrum of turbulence with experiment," *Proc. Cambridge Phil. Soc.* **47**, 158-176 (1950).

OCTOBER 1965

AIAA JOURNAL

VOL. 3, NO. 10

Complex Kinetics in Adiabatic Flow: C—H—O (N) Systems

KENNETH A. WILDE*

Rohm and Haas Company, Huntsville, Ala.

Numerical studies of complex kinetics in adiabatic flow systems were extended to UDMH/ N_2H_4 — N_2O_4 and CH_2 — O_2 . The usual hydrodynamic equations for one-dimensional, adiabatic, frictionless, ideal-gas flow were solved along with general equations in matrix form for coupled chemical reaction kinetics starting with equilibrium at the nozzle entrance. The comparison of approximate and detailed kinetics indicated that simple pictures should give reasonable results for over-all performance parameters for most situations. However, the two levels of approximation usually require the same kinetic data, and the more comprehensive calculation is preferable. Comparison of calculated and experimental exhaust temperatures for CH_2 — O_2 (g) gave good agreement, whereas comparisons of vacuum specific impulse for CH_2 — O_2 (l) did not. The disagreement in the latter case was ascribed to the crudity of the combustion efficiency correction and/or expansion loss sources other than chemical kinetics.

NUMERICAL studies of H_2 — F_2 ¹ have been extended to UDMH/ N_2H_4 — N_2O_4 (N_2 assumed inert) and CH_2 — O_2 . The usual hydrodynamic equations for one-dimensional, adiabatic, frictionless, ideal-gas flow were solved along with general equations in matrix form for coupled chemical-reaction kinetics, starting with equilibrium at the nozzle entrance. The same model and general equations have been discussed by a number of authors,²⁻⁵ each with different techniques for numerical solution of the equations. The main purpose of the present work was to make a two-fold comparison of calculated performance for detailed kinetics with various approximate kinetic treatments and with experimental results, within the limitations of the preceding simple hydrodynamic model.

Received January 25, 1965; revision received April 9, 1965. This work was performed under U. S. Army Ordnance Contract No. DA-01-021 ORD-11878.

* Senior Research Chemist, Physical Chemistry Group, Redstone Arsenal Research Division.

Kinetic Scheme

The reactions used, along with the rate parameters, are shown in Table 1. The rate constant equation was of the form

$$k_l = B_l T^{v_l} e^{-E_l/RT} \quad (1)$$

for the forward rate of reaction l , with the reverse rate found from the equilibrium constant. The phrase "detailed kinetics" is, of course, a relative term, and, in general, the level of complexity chosen is one for which reasonable, consistent experimental data are available. It should be noted that only for reaction III was it necessary to estimate rate parameters. The experimental data cited may be accurate to a factor of 2 at best, but this is adequate for some purposes, and the situation is improving constantly. In many cases data from different workers and/or techniques are in agreement, within the accuracy just cited. Thus it does not seem necessary to attempt to derive simplified models or approximate treatments when such data are available. On the other

Table 1 C—H—O reactions and rate parameters

Reaction	B_i , cm ³ , moles, sec	v_i	E_i , kcal/mole	Source
I) $H + OH + M = H_2O + M$ A	3×10^{19}	-1	0	Refs. 4 and 9
B	1×10^{20}			Ref. 7
II) $2H + M = H_2 + M$ A	4×10^{18}	-1	0	Average from Refs. 8-12
B	1.4×10^{19}			Ref. 7
III) $O + H + M = OH + M$	4×10^{18}	-1	0	Assumed same as B_{IIA}
IV) $2O + M = O_2 + M$	2×10^{18}	-1	0	Refs. 4 and 12
V) $CO + OH = CO_2 + H$	1×10^{13}	0	10	Refs. 4, 13, and 14
VI) $H_2O + H = H_2 + OH$	3×10^{14}	0	21.1	Ref. 15
VII) $H + O_2 = OH + O$	4.2×10^{12}	0.5	15.9	Ref. 16
VIII) $O + H_2 = OH + H$	3.6×10^{11}	0.5	8.9	Ref. 17
IX) $O + H_2O = 2OH$	8.3×10^{13}	0	18.1	Ref. 15

hand, it also does not appear feasible to include more detailed kinetic features even though there are some data on refinements of the model of Table 1. For example, recombination rate constants are available with individual third bodies for some reactions, but only appropriate average values were used here. Minor species such as H_2O_2 , HO_2 , and O_3 were also neglected, even though some rate data are available for reactions involving them. When nitrogen was present, there was also some NO, but it was neglected since the quantity was small and not very important energetically at the oxidizer/fuel ratios of interest. Some rate data¹⁸ are available on the "catalysis" of H and OH recombination by NO through the intermediate HNO, but the effect would be small, and the added complications were considered to be unjustified. A number of other assumptions, with even less data available, are common in studies of this type, such as the use of forward and reverse rates related by conventional equilibrium constants, and fast vibrational and rotational relaxation times. Some recent work¹⁹ on vibrational relaxation in nozzles possibly indicates faster equilibrium than would be predicted from time constants measured by other techniques. Wray²⁰ has studied oxygen recombination directly in shocked ozone mixtures and found rates that compare favorably with those deduced from more conventional O_2 dissociation measurements in shock tubes. Most of the elementary reactions possible among the species considered are in Table 1. The possible reactions in such a system have been discussed by Westenberg and Fristrom¹³ in connection with premixed hydrocarbon-oxygen flames.

Approximate and Detailed Kinetics for UDMH/ N_2H_4 — N_2O_4 †

There have been many approximate treatments of kinetics in nozzles since the pioneering work of Altman and Penner,²² but the work of Bray^{23,24} has achieved widespread popularity and has perhaps the soundest basis. The close relationship between Bray's work and that of Penner has also been shown.²² It was observed in the numerical treatment of the expansion involving a single recombination reaction that the flow could often be described by a near-equilibrium portion, a short transition region, followed by chemically frozen flow. Bray suggested a sudden-freezing approximation, in which a point is chosen to divide the flow into equilibrium and frozen portions. The transition point was chosen where the net reaction rate equaled the dissociation rate. The rationale for this choice was that the net rate was small relative to either the recombination or dissociation rate in the near-equilibrium region, and large relative to the dissociation rate in the near-frozen region, since the dissociation reaction must have a large activation energy. Hence the dissociation rate should decrease rapidly along the expansion. Since equilibrium flow was assumed up to the freezing point, the

resulting equilibrium composition was used to determine the reaction rates for the freezing point. The extension of these ideas to multicomponent, coupled-reaction systems presents some difficulties, but has been done for a number of models.

One approach is to determine freezing points for the individual reactions. Besides the problem of what to do with a number of freezing points, these points cannot be determined unambiguously in many situations.⁴ Another approach, more empirical in spirit, is to assign freezing points to species rather than to reactions.²⁵ The equilibrium rate of change of a species is equated to the algebraic sum of the recombination reaction rates in which the species is involved, with the two-body "shuffling" reactions assumed to be rapid and always near equilibrium. A most important recombining species is then chosen for purposes of approximate analysis and/or correlation of experimental data. The most sophisticated extension^{26,27} of the Bray criterion involves the average molecular weight as the flow parameter that freezes. The molecular weight can be changed only by the recombination reactions (I-IV in Table 1), so that the freezing point can be defined where the equilibrium rate of change of the molecular weight becomes equal to the sum of the recombination rates. Approximate analytical solutions have also been developed^{28,29} for the case of a single recombination reaction. The exit radical concentration for these solutions is dependent mainly on the initial conditions and only weakly on the final conditions at the exit plane; this would be expected if the sudden-freezing picture holds.

A number of comparisons have been made between the results from the kinetics of Table 1 and various approximate treatments for the system UDMH/ N_2H_4 (50%)— N_2O_4 . The vacuum specific impulses calculated to compare with those of Simkin and Koppang are shown in Table 2.³⁰ These authors used an approximate scheme involving a freezing point for H atoms, based on the work of Kushida,²⁵ and an effective rate constant based on the data and analysis of Bahn and Harp.³¹

The extent of the preceding agreement should not be regarded as a measure of the success of the approximate kinetic model, but rather as a measure of the agreement of the original experimental data and the detailed kinetics. The column labeled set B is for the k_1 and k_2 values given recently by Sugden and Rosenfeld.⁸ All of the subsequent compari-

Table 2 Vacuum specific impulse^a (I_{vac} , sec) as a function of area ratio

Exit area ratio	Approximate ³⁰	Detailed kinetics		Equilibrium
		Set A	Set B	
20	318	319.7	321.7	327
40	329	330.3	334.0	339
60	334	336.2	340.1	345

^a $P_e = 100$ psia; oxidizer/fuel weight ratio, $O/F = 2$; nominal throat diameter = 14.74 cm.; and expansion half-angle = 13.75°.

† Comparison of approximate and detailed calculations for this system have also been made very recently by Sarli et al.²¹

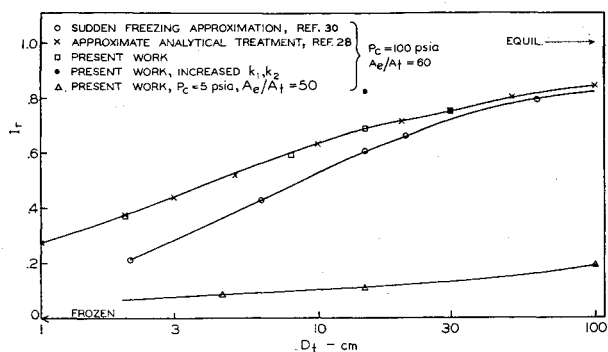


Fig. 1 Comparison of performance predicted by several approximate treatments.

sons in this section were made with set A. The data for k_1 in Ref. 8 are higher by a factor of 3 than Sugden's previous work,⁷ which was apparently based on an inadequate interpretation of the data.⁸ However, a recent value for k_1 reported by Schott and Bird⁹ is comparable to the set A value. The data for k_2 , set B, are also higher by a factor of 3 than the highest of the previous data for H_2 as a third body.¹⁰

A more meaningful test of the approximate treatments would be a comparison of their prediction of performance variation with experimental parameters of interest such as nozzle size, i.e., throat diameter D_t ; chamber pressure P_c ; and expansion ratio A_e/A_t . Such a comparison is shown in Fig. 1 for variation of throat diameter and chamber pressure. The ordinate I_r is the reduced specific impulse ($I_{\text{kinetic}} - I_{\text{frozen}} / I_{\text{equil}} - I_{\text{frozen}}$). The approximate analytical solution of Ref. 28 was presented as curves of I_r vs D_t for various rate constants for a general recombination reaction. An effective k of $3 \times 10^{15} \text{ cm}^6 \text{ moles}^{-2} \text{ sec}^{-1}$ was chosen to fit the detailed kinetic result at $D_t = 10 \text{ cm}$, resulting in a good representation of the throat diameter variation. The sudden freezing approximation would be only slightly poorer, with a point fitted. The lowest line on Fig. 1 is the detailed kinetic result for a lower chamber pressure, 5 psia. Here the predictions of the approximate theories were poorer. The approximate analytical approach gave $I_r \sim 0.005$ at $D_t = 10$, whereas the sudden freezing criterion indicated frozen flow by two orders of magnitude. That is, the "required" net equilibrium reaction rate was at least that much less than the available rate everywhere in the expansion.

Comparison of Calculated and Experimental Parameters for $\text{CH}_2\text{-O}_2$

A detailed kinetic calculation deals with only one of several sources of experimental variance of equilibrium parameters,

so that comparisons must be made with caution and some reservation. Since the nozzle expansion process is of primary concern, it is a requirement of any experimental data that near-equilibrium conditions prevail at the beginning of the expansion, i.e., that there be a high c^* efficiency. Olson,³² in a general comparison of experimental, frozen, and equilibrium specific impulse, has divided the experimental impulse by the c^* efficiency to obtain a rough measure of experimental expansion losses, if the c^* efficiency is greater than about 90%. In a survey of the available data, two studies appeared as likely candidates for comparison, one³³ on RP1-O_2 (g) and one³⁴ for RP1-O_2 (l).

The reaction scheme of Table 1 with set A rate constants was used to compare the experimental exhaust temperatures T_e of Ref. 33 for the following conditions: $P_c = 500 \text{ psia}$, $O/F = 2.6\text{-}6$, expansion half-angle = 15° , $A_e/A_t = 5.23$, and throat diameter $D_t = 1.35 \text{ cm}$. The results obtained are shown in Fig. 2. The kinetic calculations are given for two exit plane conditions, exhaust pressure $P_e = 1 \text{ atm}$ (open circles), and area ratio $(A_e/A_t) = 5.23$ (closed circles), since the experimental data were given for these nominal values as an exit condition. The experimental temperatures were estimated in Ref. 33 to be $100\text{-}150^\circ\text{K}$ low because of heat losses. Consideration of this correction would give good agreement between calculated and experimental values in the range of O/F ratios of $2.5\text{-}3.5$, but would give higher experimental results for $O/F > 4$. The differences are not great (up to 100°K), and little significance can be attached to them in view of the ranges of the calculated and experimental values and the assumptions involved.

Comparison calculations were also made for the experimental thrust measurements of Ref. 34 for various O/F ratios and a high area ratio 48.39 (Fig. 3) and a low area ratio 5.49 (Fig. 4). The points labeled "corrected experimental" were derived from the average of the given data band by dividing by the observed c^* efficiency and the flow divergence correction for a 15° half-angle nozzle, $0.983 [1/2(1 + \cos 15^\circ)]$. The kinetic runs were much higher than the experimental results for both area ratios. It does not appear likely that the calculated results of Figs. 3 and 4 could be brought down to the corrected experimental points with reasonable values of the rate constants, since values near the lower limits of the most important rate constants k_I and k_{II} were used. The major part of the difference between the calculated and experimental curves must be ascribed to the crudity of the combustion efficiency correction and/or expansion loss sources other than chemical kinetics.

Discussion

The comparisons of approximate and detailed kinetic treatments indicate that simple pictures should give reason-

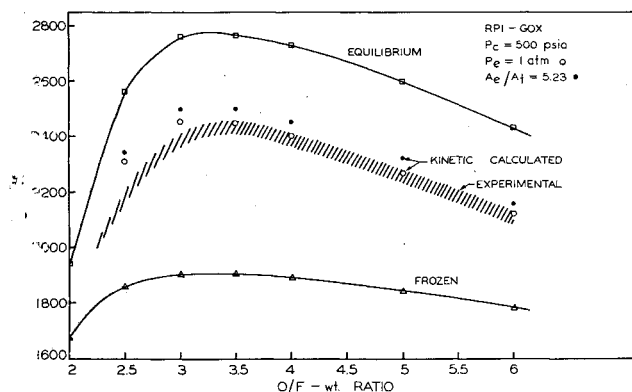


Fig. 2 Comparison of calculated and experimental exhaust temperatures as a function of O/F ratio.

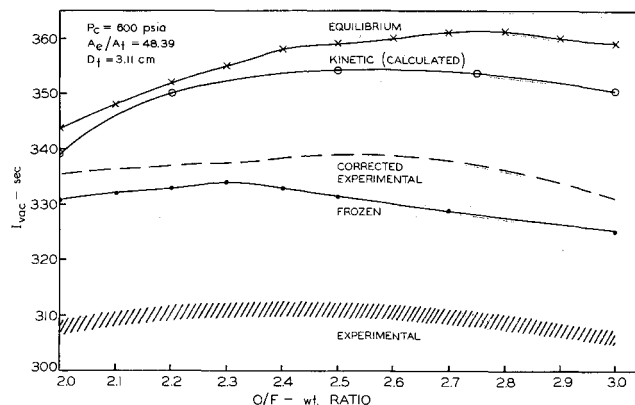


Fig. 3 Comparison calculations for experimental thrust measurements from Ref. 34 and a high area ratio.

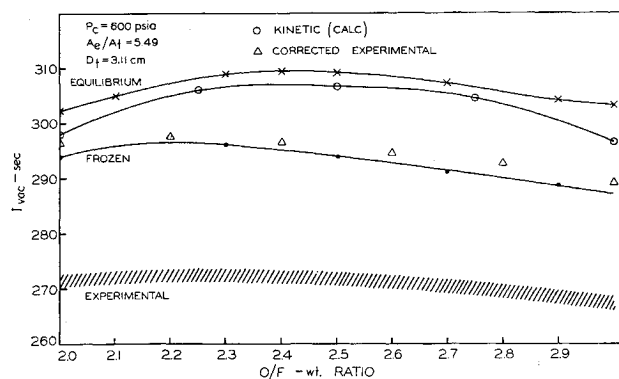


Fig. 4 Comparison calculations for experimental thrust measurements from Ref. 34 and a low area ratio.

able results for over-all performance for most situations involving chemical kinetic lag. However, as has been pointed out,⁴ the approximate and detailed treatments require the same kinetic data and the results of an equilibrium performance program, so that it would seem preferable to make the more complete consideration, particularly if exit compositions and temperatures are of interest. If one has experimental data from which to deduce empirical effective rate constants with an approximate method, then the results of such a correlation are not needed in any case. Extrapolation of such effective rate parameters to markedly different conditions should be made with great caution.

The significance of comparisons of calculated and experimental flow parameters is limited by present accuracy of high-temperature kinetic parameters (\sim factor of 3) and by flow complications such as nonequilibrium initial compositions, heat losses, boundary-layer effects, etc. Within these limitations, however, it is often possible to draw interesting qualitative and semi-quantitative conclusions from such comparisons.

References

- Wilde, K. A., "Numerical study of hydrogen-fluorine kinetics in nozzles," *AIAA J.* **2**, 374-376 (1964).
- Eschenroeder, A. Q., Boyer, D. W., and Hall, J. G., "Nonequilibrium expansions of air with coupled chemical reactions," *Phys. Fluids* **5**, 615-624 (1962).
- Emanuel, G. and Vincenti, W. G., "Method for calculation of the one-dimensional nonequilibrium flow of a general gas mixture through a hypersonic nozzle," Arnold Engineering Development Center, AEDC-TDR-62-131 (June 1962).
- Westenberg, A. A. and Favin, S., "Complex chemical kinetics in supersonic nozzle flow," *Ninth Symposium (International) on Combustion* (Academic Press, New York, 1963), pp. 785-798.
- Sarli, V. J., Blackman, A. W., and Buswell, R. F., "Kinetics of hydrogen-air flow systems. II. Calculations of nozzle flows for ramjets," *Ninth Symposium (International) on Combustion* (Academic Press, New York, 1963), pp. 231-240.
- Bulewicz, E. M. and Sugden, T. M., "The recombination of hydrogen atoms and hydroxyl radicals in hydrogen flame gases," *Trans. Faraday Soc.* **54**, 1855-1860 (1958).
- Rosenfeld, J. L. and Sugden, T. M., "Burning velocity and free radical recombination rates in low temperature hydrogen flames. II. Rate constants for recombination reactions," *Combustion Flame* **8**, 44-50 (1964).
- Patch, R. W., "Shock-tube measurement of dissociation rates of hydrogen," *J. Chem. Phys.* **36**, 262-265 (1962).
- Schott, G. L. and Bird, P. F., "Kinetic studies of hydroxyl radicals in shock waves. IV. Recombination rates in rich hydrogen-oxygen mixtures," *J. Chem. Phys.* **41**, 2869-2876 (1964).
- Rink, J. P., "Shock tube determination of dissociation rates of hydrogen," *J. Chem. Phys.* **36**, 262-265 (1962).
- Sutton, E. A., "Measurement of the dissociation rates of hydrogen and deuterium," *J. Chem. Phys.* **36**, 2923-2931 (1962).
- Rink, J. P., Knight, H. T., and Duff, R. E., "Shock tube determination dissociation rates of oxygen," *J. Chem. Phys.* **34**, 1942-1947 (1961).
- Westenberg, A. A. and Fristrom, R. M., "Methane-oxygen flame structure. IV. Chemical kinetic considerations," *J. Phys. Chem.* **65**, 560-591 (1961).
- Fenimore, C. P. and Jones, G. W., "The reaction of hydrogen atoms with carbon dioxide at 1200-1350°K," *J. Phys. Chem.* **62**, 1578-1581 (1958).
- Kaufman, F. and Del Greco, F. P., "Fast reactions of OH radicals," *Ninth Symposium (International) on Combustion* (Academic Press, New York, 1963), pp. 659-666.
- Baldwin, R. R., "Discussion on paper of Kaufman and Del Greco," *Ninth Symposium (International) on Combustion* (Academic Press, New York, 1963), p. 667.
- Clyne, M. A. A. and Thrush, B. A., "Rates of elementary processes in the chain reaction between hydrogen and oxygen. I. Reactions of oxygen atoms," *Proc. Roy. Soc. (London)* **A275**, 554-558 (1963).
- Bulewicz, E. M. and Sugden, T. M., "Flame photometric studies of reactions induced by nitric oxide in hydrogen-oxygen-nitrogen flames. I. The catalyzed recombination of atomic hydrogen and hydroxyl radicals," *Proc. Roy. Soc. (London)* **A277**, 143-154 (1964).
- Hurle, I. R., Russo, A. L., and Hall, J. G., "Spectroscopic studies of vibrational nonequilibrium in supersonic nozzle flows," *J. Chem. Phys.* **40**, 2076-1089 (1964).
- Wray, K. L., "Shock-tube study of the recombination of O atoms by Ar catalysts at high temperatures," *J. Chem. Phys.* **38**, 1518-1524 (1963).
- Sarli, V. J., Burniell, W. G., and Zupnik, T. F., "Investigation of nonequilibrium flow effects in high expansion ratio nozzles," NASA Contract Rept. CR-54221, United Aircraft Contract Research Labs. Rept. C-910096-13, UARL (December 3, 1964).
- Penner, S. S., Porter, J., and Kushida, R., "Rate and radiative transfer processes during flow in DeLaval nozzles," *Ninth Symposium (International) on Combustion* (Academic Press, New York, 1963), pp. 748-758.
- Bray, K. N. C., "Atomic recombination in a hypersonic wind tunnel nozzle," *J. Fluid Mech.* **6**, 1-32 (1959).
- Bray, K. N. C., "Chemical reactions in supersonic nozzle flows," *Ninth Symposium (International) on Combustion* (Academic Press, New York, 1963), pp. 770-782.
- Kushida, R., "Nonequilibrium chemical recombination effects in exhaust nozzle flow: An approximate method," *AIAA Progress in Astronautics and Rocketry: Liquid Rockets and Propellants* (Academic Press, New York, 1960), Vol. 2, pp. 385-409.
- Baier, R. W., Byron, S. R., and Armour, W. H., "Application of the Bray criterion for predicting atomic recombination effects in propulsion systems," *Proceedings 2nd Conference on Kinetics, Equilibria, and Performance of High-Temperature Systems* (Gordon and Breach, New York, 1963), pp. 321-336.
- Franciscus, L. C. and Lezberg, E. A., "Effects of exhaust nozzle recombination on hypersonic ramjet performance: II. Analytical investigation," *AIAA J.* **1**, 2077-2083 (1963).
- Wilde, K. A., "Effect of radical recombination kinetics on specific impulse of high temperature systems," *Jet Propulsion* **28**, 119-120 (1958).
- Smith, F. T., "On the analysis of recombination reactions in an expanding gas stream," *Seventh Symposium (International) on Combustion* (Butterworths Scientific Publications, London, 1959), pp. 93-97.
- Simkin, D. J. and Koppang, R. R., "Recombination losses in rocket nozzles with storable propellants," *AIAA J.* **1**, 2150-2152 (1963).
- Bahn, G. S. and Harp, J. L., Jr., "Experimental determination of effective reassociation rate constants for performance analysis of jet propulsion exhaust nozzles," *Proceedings 2nd Conference on Kinetics, Equilibria and Performance of High Temperature Systems* (Gordon and Breach, New York, 1963), pp. 337-348.
- Olson, W. T., "Recombination and condensation processes in high area ratio nozzles," *ARS J.* **32**, 672-680 (1962).
- Boynton, F. P., "Chemical kinetic analysis of rocket exhaust temperature measurements," *AIAA J.* **2**, 577-578 (1964).
- Fortini, A., Hendrix, C. D., and Huff, V. N., "Experimental altitude performance of JP-4 fuel and liquid-oxygen rocket engine with an area ratio of 48," NASA Memo 5-14-59E (May 1959).