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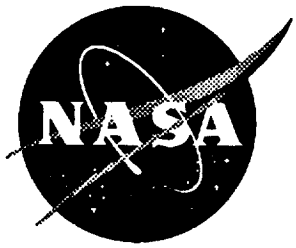

Implementation of a Vibrationally Linked Chemical Reaction Model for DSMC

A. B. Carlson
Langley Research Center, Hampton, Virginia

G. A. Bird
GAB Consulting Pty Ltd, Australia

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National Aeronautics and
Space Administration
Langley Research Center
Hampton, Virginia 23681-0001

IMPLEMENTATION OF A VIBRATIONALLY LINKED CHEMICAL REACTION MODEL FOR DSMC

Ann B. Carlson
Langley Research Center, Hampton, VA

and

G. A. Bird
GAB Consulting Pty Ltd, Australia

Abstract

A new procedure closely linking dissociation and exchange reactions in air to the vibrational levels of the diatomic molecules has been implemented in both one- and two-dimensional versions of DSMC programs. The previous modeling of chemical reactions with DSMC was based on the continuum reaction rates for the various possible reactions. The new method is more closely related to the actual physics of dissociation and is more appropriate to the particle nature of DSMC.

Two cases are presented; the relaxation to equilibrium of undissociated air initially at 10 000 K, and the axisymmetric calculation of shuttle forebody heating during reentry at 92.35 km and 7500 m/s. Although reaction rates are not used in determining the dissociations or exchange reactions, the new method produces rates which agree astonishingly well with the published rates derived from experiment. The results for gas properties and surface properties also agree quite well with the results produced by earlier DSMC models, equilibrium air calculations and experiment.

Introduction

A new model for chemical reactions in air with DSMC, closely linking reactions to vibrational states, is proposed by Bird in his new text.[1] The calculations employ the quantum model for vibration with the realistic anharmonic (or unequally spaced) levels. At each inelastic collision, the Larsen-Borgnakke redistribution of energy is employed, using the serial procedure in which each active internal mode interacts separately with the translational mode. This is modified for the consideration of dissociation in that the pre-collisional rotational as well as the vibrational and translational energy is distributed between the vibrational and translational modes. Dissociation occurs when the vibrational energy reaches or exceeds the value that corresponds to the dissociation energy. The general Larsen-Borgnakke redistribution of energy is also applied to forward exchange reactions, which occur when the vibrational energy exceeds the activation energy for the reaction. Reverse exchange reaction rates are based on equilibrium collision theory and are calculated using the partition functions and the forward rates produced by this theory. The probability of recombination for each collision of two atoms is also based on equilibrium collision theory. Details of the above theory are provided in Chapter's 5,6 and 11 of Bird's text.

The first test case uses the one-dimensional DSMC program to predict the relaxation to equilibrium of undissociated air initially at 10 000K. Both the reaction rate based chemistry and the new modeling technique were used to investigate the unsteady relaxation of the gas and the final equilibrium composition and temperature. The equilibrium composition obtained was compared to that given by the program AIRNEW[2] for a corresponding enthalpy and density.

The second test case involves the prediction of surface heating to the shuttle forebody during reentry at 92.35 km and 7500 m/s. The G2[3] program (with the reaction rate based chemistry) was used to predict the flowfield properties and surface heating. The code was then modified to incorporate the new chemistry technique and the calculation repeated to investigate any differences in the prediction. Both results are compared with corresponding shuttle flight data at this condition for a point on the forebody.

Uncertainties in the new model are discussed with some evaluation of their impact on the solution quality.

Symbols

A, B	constants
C_1, C_2	constants in the vibrational collision number equation
k_f	forward reaction rate coefficient
n	number density (m^3)
T	temperature (K)
x	linear distance parameter (m)
Z_v	vibrational collision number
σ_r	reaction cross-section
σ_T	total collision cross-section
ω	temperature exponent of the coefficient of viscosity

Modeling Details

While the general explanation of the new modeling technique can be found in Bird's textbook, a few of the details require some further explanation. There are also some parameters which are highly uncertain and which influence the results to varying degrees.

Most uncertain are the values of the constants in the equation for vibrational collision number (Bird's Equation 6.59).

$$Z_v = (C_1/T^{\omega}) \quad exp(C_2 T^{-1/2}) \tag{1}$$

The values used in this study are listed in Table I. They are based primarily on the data of Millikan and White[5], but there is very little in the data to justify any of the values except for the $N_2 - N_2$, $O_2 - O_2$ and $NO - NO$ cases. Fortunately, the vibrational excitation of the molecules in the calculation seems to be relatively insensitive to the choice of constants over a wide range of C_1 and C_2. However, in the calculation of forward exchange reactions, a value of Z_v based on the activation energy for the reaction is used. The rates of the forward exchange reactions do appear to be quite sensitive to the selection of these parameters. While the current values give reasonably good comparisons with the experimental reaction rates, better vibrational relaxation data, particularly at high temperatures, is needed to lend confidence to the calculations.

The possibility of dissociation is checked in the current programs every time a collision occurs between two atoms which have total collision energy exceeding the dissociation energy. It is theoretically appropriate to add a vibration relaxation number to the process, such that only some fraction of the collisions with sufficient energy are considered. However, a problem arises in calculating what this relaxation number should be. The effective temperature of such collisions is very high, 20 000 K or greater. Landau-Teller theory for vibrational relaxation predicts collision numbers on the order of unity for these temperatures. Equation 1, an experimental fit to data at much lower temperatures, gives values of approximately 20 for these collisions. Setting the collision number identically equal to 1 (checking for dissociation each time a sufficiently energetic collision occurs) gives dissociation rates much more in accordance with the experimental rates, and was the method employed in these calculations. If more relaxation rate data were available at high temperatures, it might be possible to formulate an equation Z_v which could be used over the entire temperature range.

In checking for possible dissociation, a redistribution of energy between the translational and vibrational modes is made. The selection of possible levels for the acceptance rejection scheme must extend beyond the dissociation energy. For this purpose, notional levels are assumed of even spacing equal to half that of the spacing between the two levels which span the dissociation energy. The polynomial used to generate the anharmonic levels up to the dissociation limit is the empirical Dunham series recommended by Herzberg.[4] The Dunham series covers all levels below dissociation, but cannot be used to generate levels much beyond dissociation because it soon begins to generate negative spacings. It would be more correct to fit the levels near and beyond the dissociation energy to some polynomial which would produce rapidly decreasing but still positive level spacings. However, the current choice is adequate for preliminary calculations and leads to realistic results.

Probabilities for recombination and reverse exchange reactions are determined from calculations of the partition functions and equilibrium collision theory. The values used in the current simulations are given in Tables II and III.

Relaxation of Air to Equilibrium

One-dimensional versions of DSMC codes were used to calculate the relaxation of a homogeneous gas from an initial temperature of 10 000 K to equilibrium. The density in the calculation was fixed at 0.01288 kg/m^3 and the enthaply was fixed by the initial temperature. The transient behavior of the gas was recorded to determine the chemical reaction rates and gas temperature histories. The two versions of chemical modeling produce very similar results. The equilibrium temperature differs by approximately 150 K and the new method takes somewhat longer to reach equilibrium. A comparison of the translational temperature history for the two calculations is provided in Fig. 1. While the compressed nature of the logarithmic time scale makes it appear that the new chemistry case may not have reached equilibrium, at least a hundred thousand iterations were performed with essentially unchanged results for both temperature and species densities.

The results are compared in Table IV with the AIRNEW prediction for equilibrium air at the same density and enthalpy. While both versions agree reasonably well, the new chemistry is in slightly better agreement with the AIRNEW species concentrations, while the previous model predicts an equilibrium temperature closer to the AIRNEW result.

The earlier method of calculating reactions with DSMC uses the reaction rate set of Gupta, et al.[6] While the new method does not use reaction rates to predict chemical reactions, it is interesting to compare the reaction rates produced with this published set. Figures 2-4 compare the actual rates produced by the simulation with the calculated rates based on Gupta's tabulation. The rates are calculated using the instantaneous temperature and densities in the flow. For dissociation, the fraction of collisions between each species and the third body efficiencies are also considered to obtain an overall rate. The agreement between the experimental rates and the rates produced by the DSMC program with the new chemistry is excellent.

Shuttle Forebody Heating at 92.35 km

Previous results for Space Shuttle forebody heating with DSMC have been published by Moss and Bird.[7] These calculations were performed at an altitude of 92.35 km and above. With advanced computers and codes, it should now be possible to extend the DSMC calculations into the lower altitude range. At the 92.35 km and lower altitudes, chemistry in the flow is significant and an accurate chemical model is essential. The G2 code, with the earlier chemical model, has been run for this case using the same equivalent axisymmetric body approximation as used by Moss and Bird. The case was then run using the new chemistry. Flowfield and surface property comparisons are made.

Stagnation streamline plots of the temperature and composition through the shock are shown in Figs. 5-7. Results for the two methods are similar, but significant differences in the vibrational temperature and the level of nitrogen dissociation are evident. The earlier model ignores the physical link between vibration and dissociation. Thus, the dissociation rates could be correct even if the vibrational excitation was too low. The surface heat transfer (Fig. 8) is about 10 percent higher with the new chemistry modeling. The experimental data point appears to agree more closely with the previous chemistry. However, as noted in the paper by Moss and Bird, assumptions about the surface properties of the shuttle forebody make a significant difference in the heat transfer prediction. The simulation assumes the surface is diffuse with full thermal accommodation. Preliminary calculations with a 20 percent specular surface indicate that the heating is reduced to a level where the method agrees with the experimental value while the previous method underpredicts the surface heating. Without more detailed knowledge of the surface properties, the best conclusion is that both methods produce a solution which is in reasonable agreement with the experimental result.

Conclusions

A new method for the calculation of chemistry in air with DSMC has been introduced and implemented in one- and two-dimensional versions of DSMC codes. Initial applications of the new method for two test cases are very encouraging. The new method offers a better physical basis for the computation of reactions in a particle simulation, closely linking dissociation with the vibrational levels of the diatomic molecules. Although much improvement seems possible in the definition of some of the physical input parameters, the results show startlingly good agreement with experimentally determined reaction rates. Application to a Space Shuttle reentry case gives flowfield and surface property results in general agreement with earlier predictions and measurement.

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Table I

Constants fo the evaluation of the vibrational collision number

Molecule 1	Molecule 2	C_1	C_2
N_2	N_2	9.1	220.
N_2	O_2	0.91	220.
N_2	N	1800.	73.5
N_2	O	1750.	73.5
N_2	NO	10.	203.
O_2	N_2	9.	203.
O_2	O_2	56.5	153.5
O_2	N	1813.	73.5
O_2	O	1780.	73.5
O_2	NO	125.	144.
NO	N_2	10.	203.
NO	O_2	125.	144
NO	N	131.	144.
NO	O	131.	144.
NO	NO	862.	52.3

Table II

Constants for recombination probability

$$\sigma_R/\sigma_T = AnT^B$$

Molecule	A	B
N_2	$1.\times10^{-26}$	-1.00
O_2	$9.\times10^{-27}$	-0.78
NO	$6.\times10^{-27}$	-0.90

Table III

Constants for reverse exchange reaction probability

$$\sigma_R/\sigma_T = AT^B$$

Reaction	A	B
$O_2 + N \rightarrow O + NO$	.5876	-.1345
$NO + N \rightarrow N_2 + O$	.6735	-.3394

Table IV

Species concentrations at equilibrium

Species	AIRNEW (T=5250 K)	Previous Chem (T=5260 K)	New Chem (T=5100 K)
N_2	1.94×10^{23}	1.98×10^{23}	1.98×10^{23}
O_2	1.04×10^{20}	2.70×10^{20}	0.86×10^{20}
N	3.00×10^{22}	1.96×10^{22}	2.35×10^{22}
O	1.13×10^{23}	1.12×10^{23}	1.15×10^{23}
NO	2.46×10^{21}	4.17×10^{21}	1.48×10^{21}

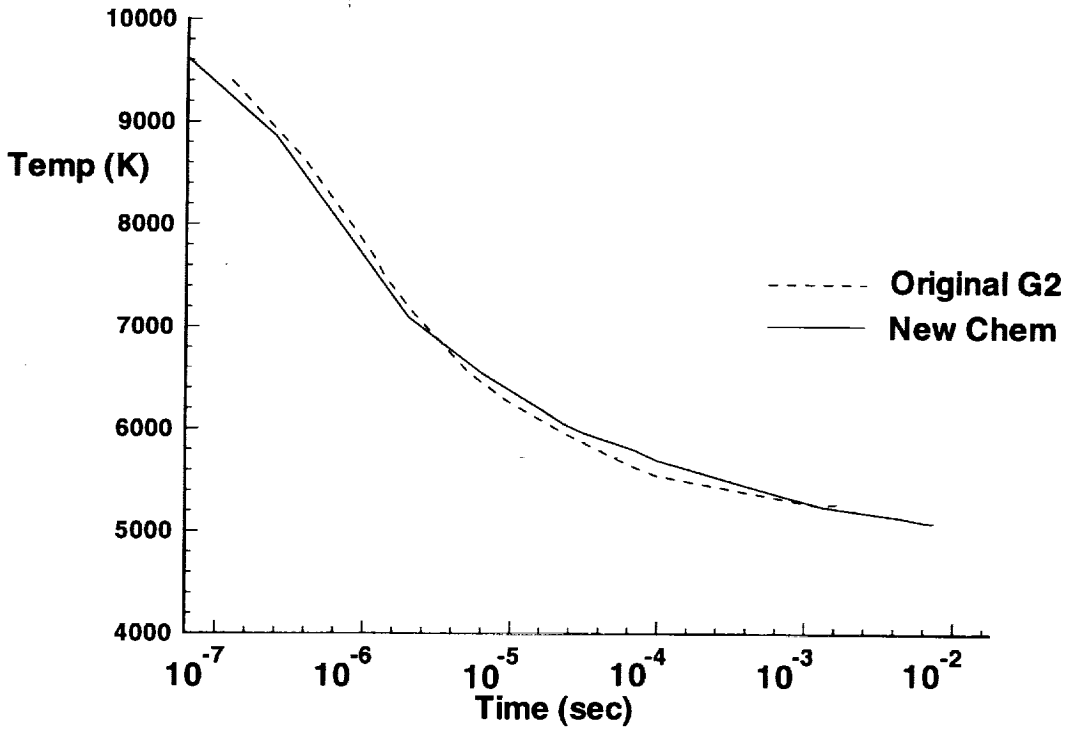

Fig. 1 Relaxation of air from 10 000 K to equilibrium

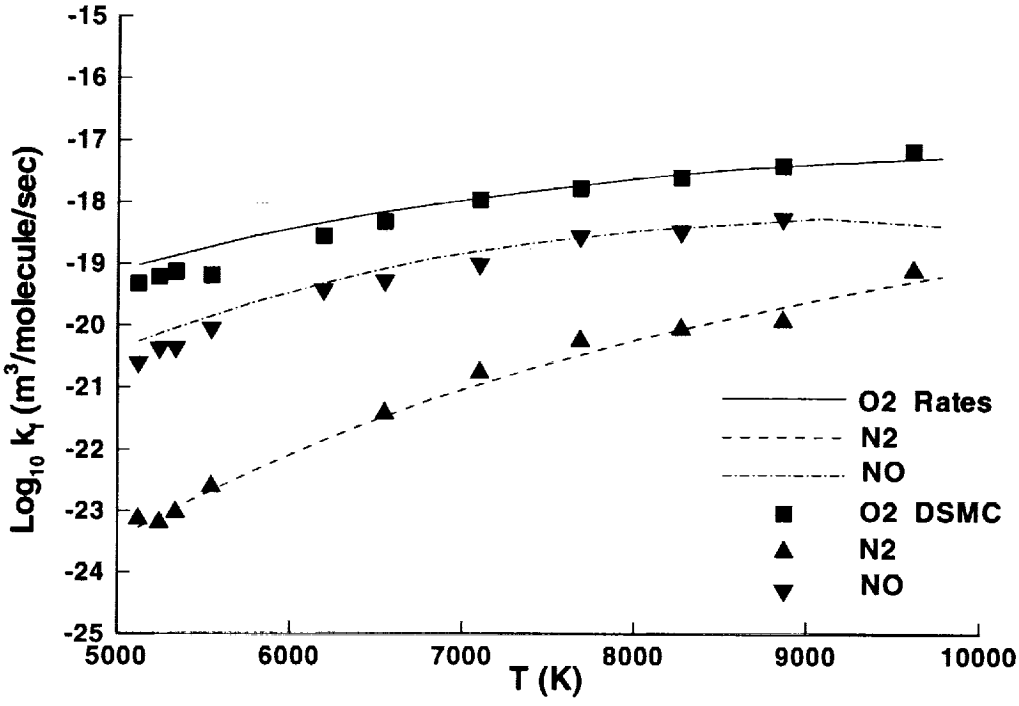

Fig. 2 Dissociaion rate coefficients

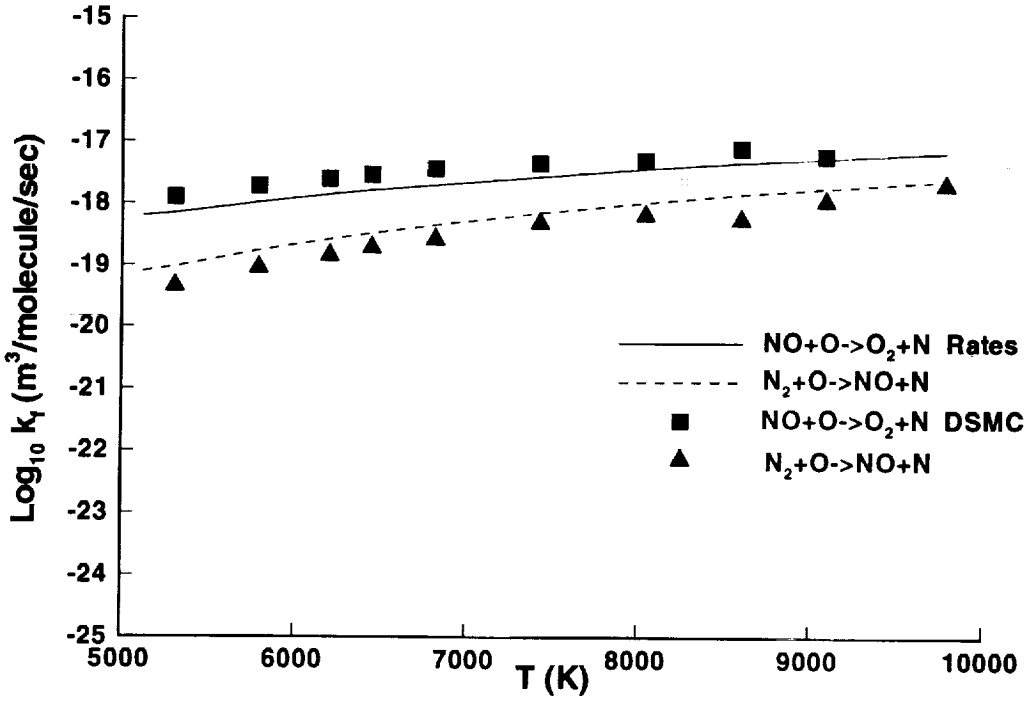

Fig. 3 Forward exchange reaction rate coefficients

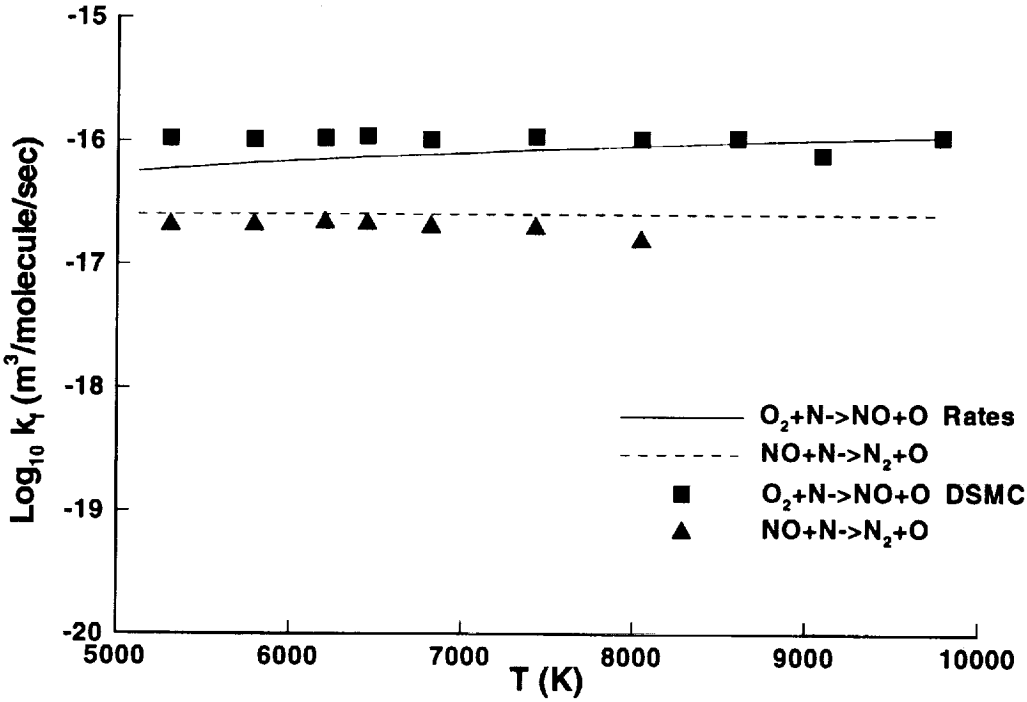

Fig. 4 Reverse exchange reaction coefficients

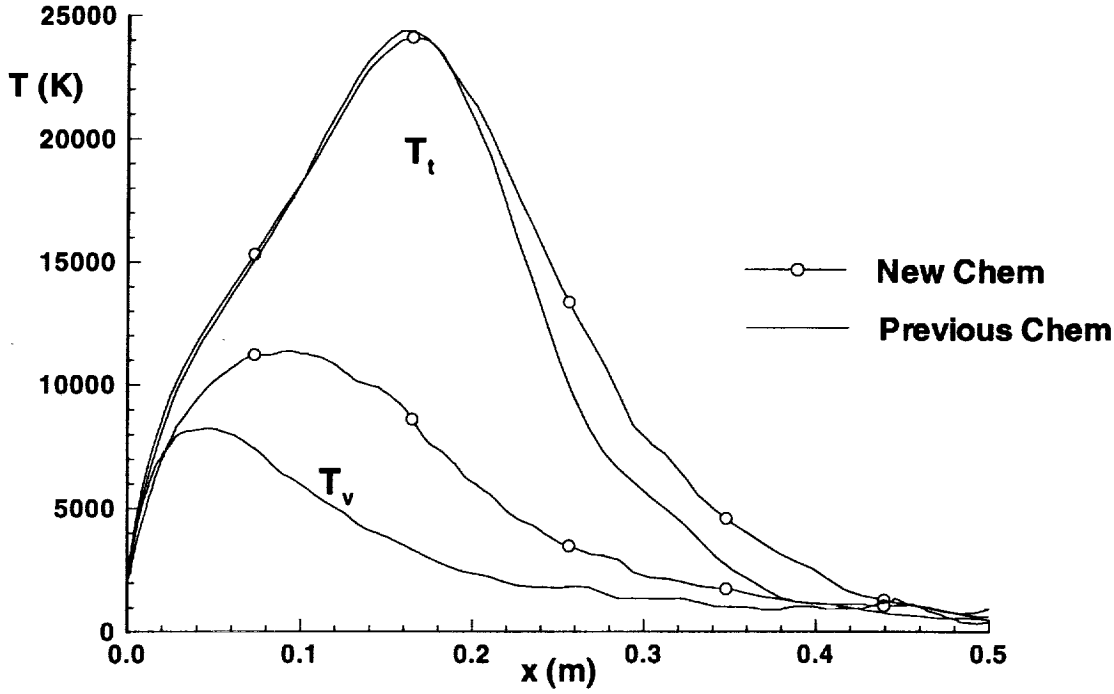

Fig. 5 Stagnation line temperatures - 93 km Shuttle forebody

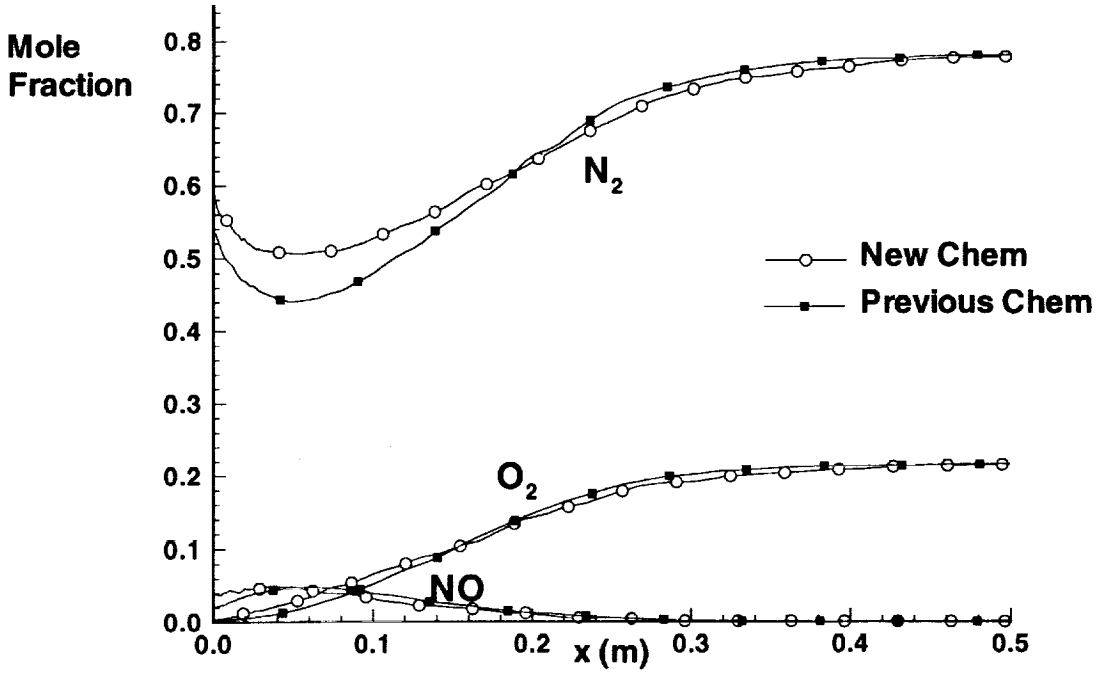

Fig. 6 Stagnation line molecular distribution - Shuttle forebody 93 km

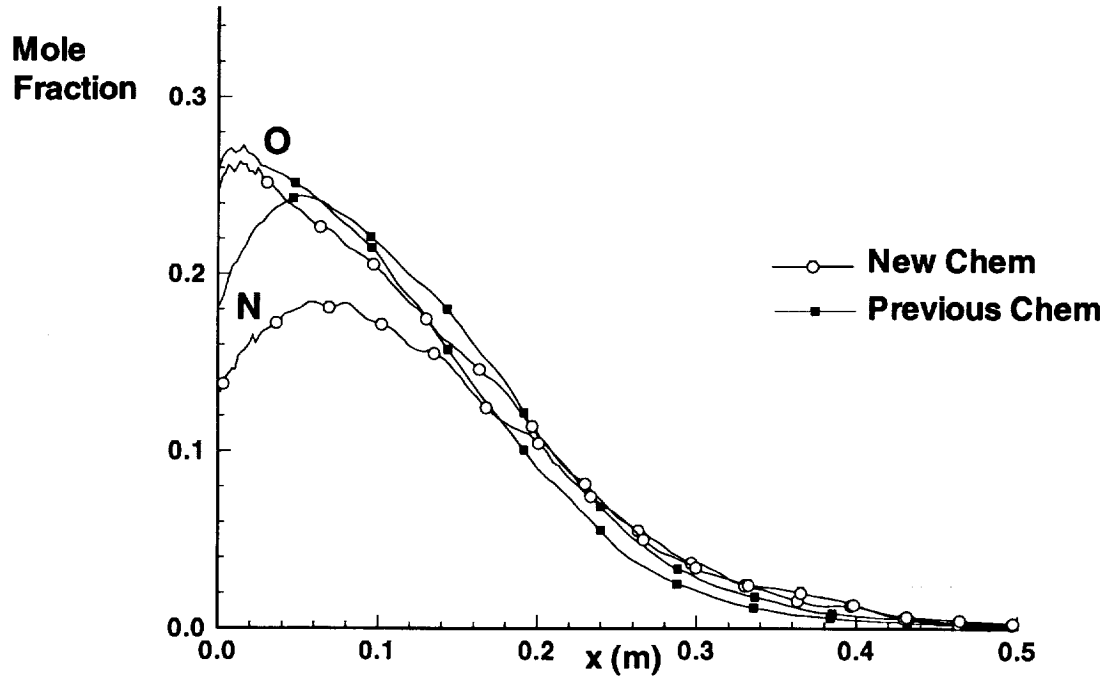

Fig. 7 Stagnation line atomic distribution - Shuttle forebody 93 km

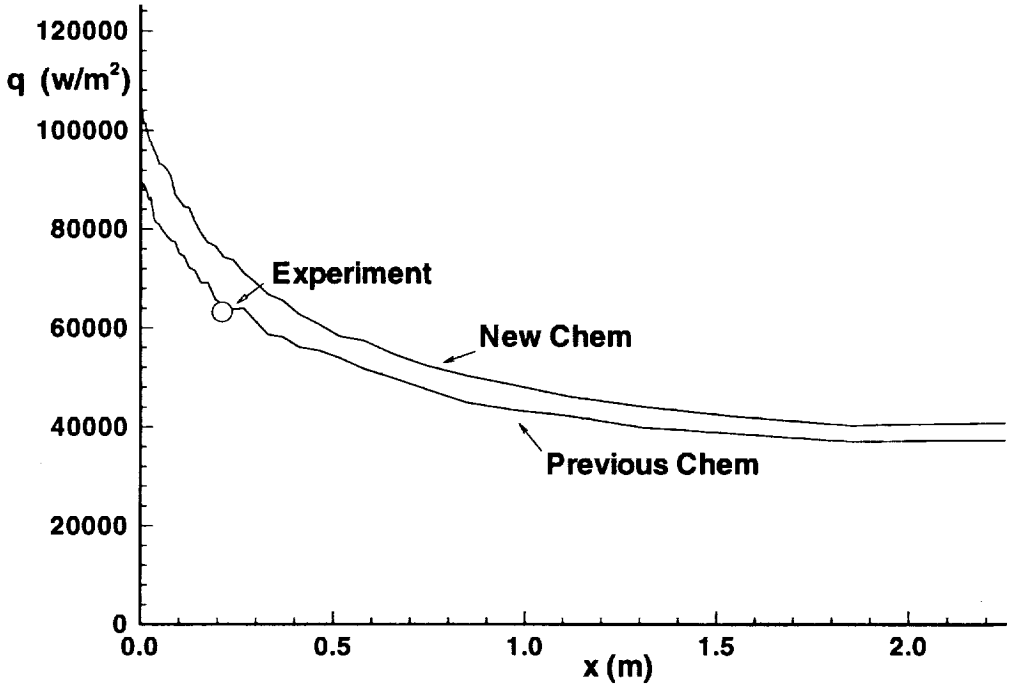

Fig. 8 Surface heat transfer - Shuttle forebody 93 km

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