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NON-EQUILIBRIUM EFFECTS IN HIGH
TEMPERATURE CHEMICAL REACTIONS

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ABSTRACT

Reaction rate data have been collected for chemical reactions occurring at high temperatures during reentry of space vehicles. Large differences in reaction rate data are reported by various authors in the literature.

The principle of detailed balancing is used in modeling kinetics of chemical reactions at high temperatures. Although this principle does not hold for certain transient or incubation times in the initial phase of the reaction, it does seem to be valid for the rates of internal energy transitions that occur within molecules and atoms. That is, for every rate of transition within the internal energy states of atoms or molecules, there is an inverse rate that is related through an equilibrium expression involving the energy difference of the transition.

Future goals include theoretical modeling to include internal energy transitions into overall rate expressions that can then be used to predict radiation heating effects for reentry vehicles under non-equilibrium conditions.

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INTRODUCTION

Data from Space Shuttle flights and experimental work indicate that non-equilibrium radiation due to chemical non-equilibrium in the shock layer of reentry vehicles may result in a significant added heat load.(1,2,3) For OTV and AOTV with higher reentry velocities, these non-equilibrium effects may be even more significant.(4)

This work is a continuation of work from last summer which will focus in on reaction rate data reported in the literature and also consider further the principle of detailed balancing as applied to transitions within the internal energy states of molecules.

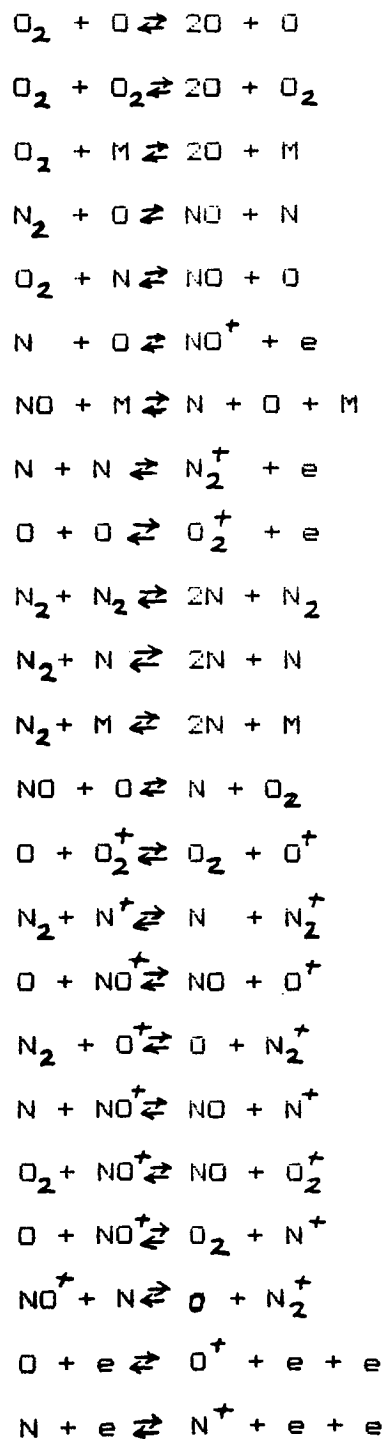
CHEMICAL REACTION RATES

At an altitude of 80-100 kilometers, the reactant substances in the atmosphere include N, O, N₂, O₂, NO, various positive ions and electrons. However, with these few reactants, a multitude of reactions with various interdependent relationships could possibly occur upon the initiation of a shock wave by a reentry vehicle. The low pressure at these altitudes and the high energy input due to the shock wave from Mach 20-35 results in a region of chemical non-equilibrium between the reentry vehicle's surface and the shock front. This chemical non-

equilibrium is not just due to the progress of reactions from reactants to products in the ordinary sense of chemical reactions. A more significant and complicating factor is that internal energies of atoms and molecules also take a finite time to change with the rapid input of energy. During this time of internal energy equilibration, the ordinary rate constant of a chemical reaction is not definable. This time of internal energy equilibration has been referred to in the literature as an incubation time or a pre-quasistationary time. (5,6,7)

The chemical reactions that could occur are many and some of the representative ones are given on the next page.

Carlson and Rieper (8) considered only the first twelve reactions given on the next page in their investigations on medium shock waves (5-7 km/sec). Their numerical predictions agreed with their experimental data on the electron temperature variation in these shock waves.



Chul Park(9,10) has used all of the above reactions in a computer program(NEQAIR) to calculate the extent of reactions and radiation in the non-equilibrium zone for a shock wave speed of 10km/sec. At this higher shock speed, calculated results did not fit the limited experimental data from shock tube experiments.

There are still discrepancies in the literature for reaction rate data as reported by various authors. Some of these are given in Table 1 below.

Some of these differences in reaction rate data are small in magnitude and would not affect the results of computations drastically. However, many of the reactions have orders of magnitude differences in the rate constants and also differences in the temperature dependency of the reactions. These include the nitrogen, oxygen and nitric oxide dissociations as well as the impact ionization reactions.

Further work on the effect of varying the rate constants upon the output of computer programs would seem to be a worthwhile effort. Better agreement with experimental data may be obtained by adjusting rate parameters within the computer program itself.

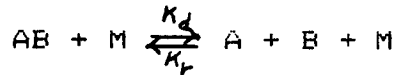
Table 1. Reaction Rate Data

Rate Constant, $k = AT^{-s} e^{-B/T}$ (cc/mole-sec)

Reaction	A	s	B	Ref.
$N_2 + N_2 \rightleftharpoons N + N + N_2$	3.7(21)	1.6	113,200	10
	4.7(17)	0.5	113,200	11
	2.3(29)	3.5	113,200	12
$N_2 + N \rightleftharpoons N + N + N$	1.1(22)	1.6	113,200	10
	4.1(22)	1.5	113,200	11
	8.5(25)	2.5	113,200	12
$O_2 + O_2 \rightleftharpoons O + O + O_2$	2.8(19)	1.0	59,500	10
	3.2(19)	1.0	59,500	11
	6.2(24)	2.5	59,500	13
$O_2 + O \rightleftharpoons O + O + O$	8.3(19)	1.0	59,500	10
	2.0(19)	1.0	59,500	11
	4.0(18)	1.0	59,500	13
$N_2 + O \rightleftharpoons NO + N$	3.2(13)	0.1	37,700	10
	7.3(13)	0.0	38,000	11
	1.8(14)	0.0	38,300	13
$NO + M \rightleftharpoons N + O + M$ (M = O or N)	2.3(17)	0.5	75,500	10
	3.9(20)	1.5	75,500	11
	1.4(14)	0.0	74,600	14
	5.2(15)	0.0	75,800	15
$NO + M \rightleftharpoons N + O + M$ (M = O, N or NO)	4.6(17)	0.5	75,500	10
	7.8(20)	1.5	75,500	11
	3.0(14)	0.0	76,400	14
	5.2(15)	0.0	75,800	15
$N + O \rightleftharpoons NO^+ + e$	1.5(10)	-0.37	32,000	10
	1.4(6)	-1.5	31,900	11
	3.0(13)	0.5	32,500	16
$N + N \rightleftharpoons N_2^+ + e$	1.8(10)	-0.77	67,500	10
	1.4(13)	0.0	67,800	11
	$5.4 \times 10^{13} T^{-\frac{1}{2}} (1 + 1.3 \times 10^{-4} T + 3.3 \times 10^{-8} T^2 - 10^{-12} T^3) e^{-\frac{67300}{T}}$			
$O + O \rightleftharpoons O_2^+ + e$	3.9(10)	-0.49	80,600	10
	1.6(17)	0.96	80,800	11
	$1.9 \times 10^{13} T^{-\frac{1}{2}} (1 + 7.5 \times 10^{-5} T + 2.2 \times 10^{-8} T^2) e^{-\frac{80100}{T}}$			

DETAILED BALANCING PRINCIPLE

For ordinary, one-step chemical reactions, the principle of detailed balancing can be shown to follow from equilibrium relationships. Consider the reaction



at equilibrium, $k_d (AB) (M) = k_r (A) (B) (M)$

and therefore $k_d / k_r = (A) (B) / (AB) = K$, the equilibrium constant.

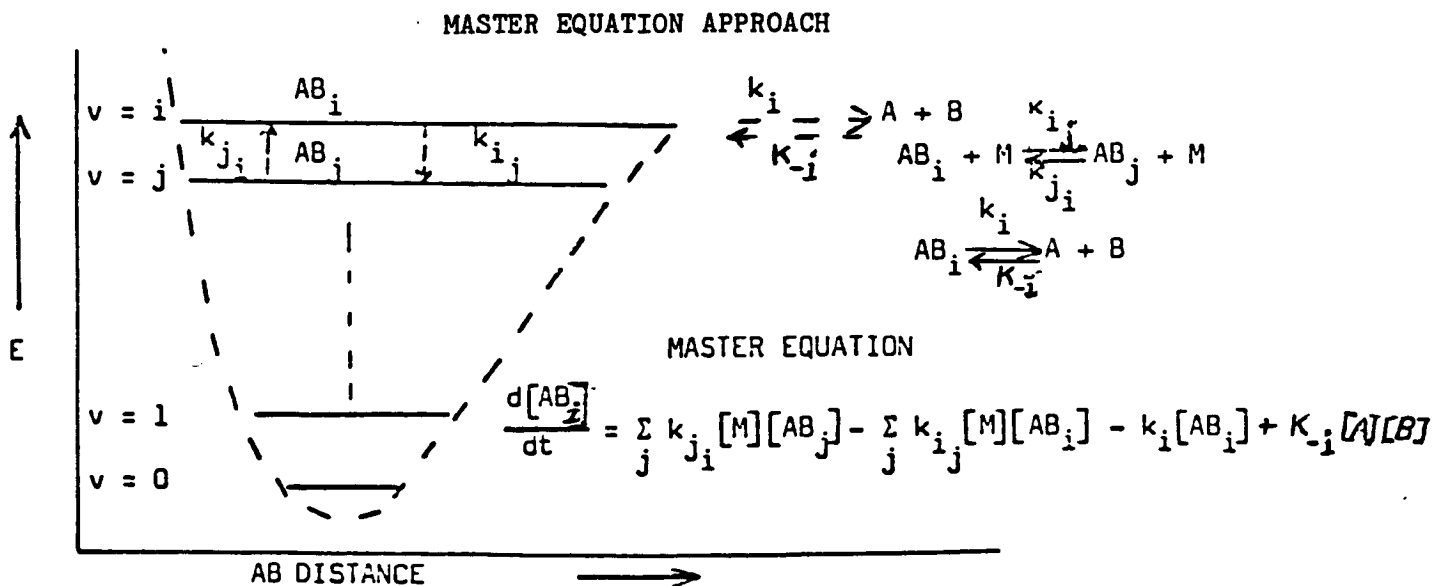
Even away from equilibrium, $k_d / k_r = K$ because the k 's do not depend upon concentrations.

Usually k_d and k_r are not both available from experimental data. Especially at high temperatures, k_r is expressed as k_d / K in computer programs and calculations involving these rates of reactions.

Work last summer led to the conclusion that this relationship, $k_d / k_r = K$, also called the principle of detailed balancing, does not hold under certain conditions. If a large, sudden change in temperature occurs in a system, such as that generated by a high energy shock wave, then the equilibration of energy into the internal states will take a finite time and this time may become comparable to the reaction time of the system. When this occurs, the ordinary chemical rate constant is not well defined since

it usually represents an average rate of reaction over many individual rates from internal energy states. There is then an incubation time before the reaction rate reaches a steady-state or defined value. During this incubation time, the principle of detailed balancing does not hold for overall chemical reaction rates. (7)

During the incubation time, internal energy transitions become important and the approach to considering all of these transitions is summarized in the "Master Equation Approach" which is shown diagrammatically below.



This equation could be solved if all k_{ij} , k_{ji} , k_i and k_j are known. Approximations to this equation have been tried using detailed balancing for the internal energy transitions (k_{ij} and k_{ji}), and also assuming a harmonic oscillator. This development is shown in several references such as "Introduction to Physical Gas Dynamics" by Vincenti and Kruger. (18) This particular development is for vibration levels only and is briefly summarized below.

$$k_{ji} [AB_j] = k_{ij} [AB_i]$$

$$\frac{k_{ji}}{k_{ij}} = \frac{[AB_i]}{[AB_j]} = K = e^{-\frac{(E_i - E_j)}{KT}} = e^{-\frac{h\nu}{KT}}$$

$$\therefore \frac{k_{ji}}{k_{ij}} = e^{-\frac{h\nu}{KT}}$$

$$k_{ij} = i k_{i,0}, \quad i-j=1$$

$$k_{i,0} = \frac{1 - e^{-h\nu/KT}}{\tau}$$

$\tau = \text{RELAXATION TIME}$

$$\frac{d[AB_i]}{dt} = k_{i,0} [-i[AB_i] + (i+1)[AB_{i+1}] + e^{-\frac{h\nu}{KT}} (-i+1)[AB_i] + i[AB_{i-1}]]$$

IN TERMS OF ENERGY

$$\frac{dE_v}{dt} = k_{i,0} (1 - e^{-\frac{h\nu}{KT}}) \left[\frac{[AB] h\nu}{e^{-\frac{h\nu}{KT}} - 1} - E_v \right] = \frac{E_v^* - E_v}{\tau}$$

$$[AB] = \sum [AB_i] \quad E_v^* = \text{EQUILIBRIUM ENERGY}$$

Probably the best assumption in this development is the principle of detailed balancing for the internal energy states. At the molecular level, where elementary collisions cause internal energy transitions, the exchange from translational to vibrational energy or vice-versa in a collisional process should be reversible in time by energy conservation principles. Thus there is no reason to suspect the failing of the principle of detailed balancing at this elementary level unless some other energy equilibration procedure is occurring that is not known. Rotational energies are lower than vibrational energies, but those transitions are assumed to occur very quickly even at low pressures so that rotational energies and translational energies are very quickly equilibrated. The effect of anharmonicity of the vibrational mode within the molecule is an effect that should be considered. This effect becomes more pronounced at higher energies and it is these higher energies that are important for dissociation.

Thus the development of the Master Equation using detailed balancing and harmonic oscillator assumptions is a valid first approximation to calculation of rates of reaction in high energy shock waves. However, other approaches are also presently being worked on and these are summarized below.

OTHER APPROACHES TO NON-EQUILIBRIUM REACTION RATES

Dove, et al have calculated the effects of coupling for the internal modes upon the relaxation of internal energies for hydrogen.(19) They concluded that at high rotational energies ($J = 10$), coupling between translational, vibrational and rotational becomes almost as significant as translational-rotational coupling and is greater than translational-vibrational coupling. Thus at high rotational energies, equilibration in the internal energies occurs through combined rotational-vibrational energy level changes.

Koshi has calculated the effect of vibrational-dissociation and dissociation-vibrational coupling (CVDV effect) and compared it with experimental data on NO dissociation.(15) His agreement is very good and indicates that as the translational temperature increases, the vibrational temperature lags behind and seems to approach a limit in the range of 5000K even though the translational temperature is above 7500K. The CVDV effect is due to the reduction of the dissociation rate due to the lack of vibrational equilibration within the molecule and also the coupled effect of a slower vibrational equilibration time due to dissociation removing energy from the upper vibrational levels and thus depleting them too rapidly.

This could result in a "bottle-neck" effect. That is, with a very rapid and high energy input, such as that from a high energy shock wave, the dissociation rate is limited by internal energy transitions within vibrational levels and not by the dissociation of the molecule from highly excited vibrational energies into two atoms.

Carlson compared experimental results with calculations on nitrogen in moderate shock waves studies and included the CVDV effect as well as electronic-vibrational coupling. His calculated electronic temperature and the measured values agreed well within experimental error for this series of experiments. (8)

Finally, Chul Park has worked extensively on this problem and has written a computer program for predicting the non-equilibrium radiation in a shock front using available rate data. (9,10) His approach utilizes a two or three temperature model assuming different temperatures for different internal modes of energy and also a translational temperature. For some reactions, he uses the translational temperature, for some, the vibrational temperature and for others, the electronic temperature. Although this is an interesting approach, the calculated distances in the shock wave for peak and equilibrium temperatures, do not agree with experimental data.

SUMMARY

The most significant finding this summer was that there are large differences in important reaction rates as reported in the literature by various authors. These large differences could have significant effects on any computer programs or calculations of chemically reacting systems utilized in shock wave heat load predictions. It would be worthwhile to try some of these other rates in present computer programs and check the results with known data.

The principle of detailed balancing is used widely in calculations of reaction rates. It is not valid during short incubation times in high energy shock waves in terms of the overall dissociation or recombination rate expressions. It does appear to be valid at the micro energy level concerning transitions within molecules. These transitions occur when translational energy is exchanged for vibrational energy in a collision for example. However, another significant find this summer is that in collisional processes, multi-jump transitions in vibrational levels can and do occur. This does not violate the law of detailed balancing, but makes it more complicated to take this into account.

Further refinements in calculation on these high energy reactions would benefit from the use of coupling effects

such as some of those mentioned in this paper. These include translation-vibration-rotational coupling, electronic-vibrational coupling and vibration-dissociation, dissociation-vibration coupling.

Future investigations should include models with limiting expressions such as the vibrational temperature reaching a limit and thus simplify the overall rate expressions. This may or may not occur within a time period that is insignificant in high energy shock waves. Approaches utilizing partition functions and activated complex theory also should be investigated. One final approach for future work would include the information theory approach by such authors as Levine to predict products of chemical reactions on the basis of excess entropy. (20)

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I would also like to thank NASA and ASEE for these summer program opportunities for faculty such as myself to enrich our teaching and allow us to carry back some of this enthusiasm to our students who will become the engineers and scientists of tomorrow.

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