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John Waldemar Filpus

A DISSERTATION

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ABSTRACT

THE ENERGETICS OF HYDROGEN ATOM RECOMBINATION

by John Waldemar Filpus

The dissociation-recombination cycle of hydrogen is likely to be important in the operation of a proposed microwave-plasma electrothermal rocket for deep-space propulsion and maneuvering. A series of preliminary experiments on a small-scale microwave-plasma electrothermal rocket system and two modelling studies, one involving vibrational and rotational molecular excitation and one on more macroscopic phenomena downstream from the plasma, are described.

Plasmas at pressures less than 100 Torr were studied in hydrogen, nitrogen, and argon, at flow rates up to 2 mg-mol per second, and incident microwave power between 300 and 600 W. Thrusts generated by the system were measured, by a vane-type thrust stand, and temperature profiles below the plasma were estimated, by a gas-dynamic technique, involving pressure ratios in flow through a nozzle. The measured thrusts were proportional to the square root of the gas-dynamic temperatures. The temperatures dropped rapidly from 1200 K in the plasma to 300 to 400 K just downstream, depending on the direction of flow of the coolant. Cooling of the plasma tube dominates the temperature profiles obtained. Directions for further improvement of the experimental arrangement are suggested, in the realm of improved matching of the input power and the capacity of the gas, moving the nozzle closer to the plasma, and increased plasma pressure.

The influence of vibrational and rotational energy of the recombined molecules on the rate of recombination and release of the energy of recombination is studied. The relaxation times for vibrational excitation are on the order of hundreds of times shorter than the residence time for the recombination reaction over a range of conditions that cover the range of practical designs. Molecular internal energy is found to be negligible for a practical electrothermal rocket system. The development of computer models of the recombination reaction zone, downstream of the plasma, is described, and the models are compared with the experimental results. The models confirm the suggested improvements for the experimental arrangement. The results indicate that a two-dimensional, axially-dispersed model, with a catalytic surface, is necessary to model all the characteristics of the experimental results. The axial dispersion model is evaluated by a search technique on the initial derivatives. Initial work provides qualitative confirmation, though quantitative agreement is lacking, and directions for improvement of the model are indicated, by combining the two-dimensional model and the dispersion model, and by fitting model parameters and initial conditions to the results.

To my Parents

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NOMENCLATURE

Α	Cross-sectional Area of Flow Reactor
A _o	Outer Surface Area of Cooling Jacket
A _s	Surface Area of Reactor per Length
A _t	Area of Nozzle Throat
c _P	Heat Capacity of Reacting Mixture
C _{Pc}	Molar Heat Capacity of Coolant
c _{PV}	Vibrational Heat Capacity
D _{H-H2}	Diffusion Constant, Atomic Hydrogen Through Molecular
	Hydrogen
DHR	Heat of Recombination
D _i	Internal Diameter of Reactor
dX/dz _R	Change in Dissociation From Reaction
dX _v /dz	Change in Dissociation From Volume Reaction
dX _w /dz	Change in Dissociation From Surface Reaction
e _v	Vibrational Energy Density
F	Molar Flow Rate of Hydrogen into Plasma
f	Fanning Friction Factor
Fc	Molar Flow Rate of Coolant
g	Standard Gravity
g _c	Gravitational Constant
G(r)	Local Mass Flux
h	Planck's Constant

xii

h _c	Heat-Transfer Coefficient from Surface to Coolant
h _i	Heat-Transfer Coefficient from Gas to Surface
h _m	Mass-Transfer Coefficient
I _{sp} (m)	Measured Specific Impulse
I _{sp} (th)	Theoretical Specific Impulse
К	Equilibrium Constant
k	Boltzmann's Constant
k _{VT}	Rate constant for Vibrational-Translational Collisional
	Relaxation
k _w	Surface Reaction Rate Constant
^k 1	Reaction Rate Constant, Hydrogen Atom as Third Body
k ₂	Reaction Rate Constant, Hydrogen Molecule as Third Body
M _w	Molecular Weight
^m O	Molecular Weight of Molecular Hydrogen
N _{Av}	Avogadro's Number
P	Pressure
P ₀	Stagnation Pressure
q	Heat Flux to Coolant
R	Gas Constant
r	Radius
r _{H2}	Volumetric Rate of Generation of Molecular Hydrogen by
	Recombination
Т	Temperature, Translational Temperature

T _c	Coolant Temperature
Т _е	Temperature Based on Total Relaxation of Vibrational
	Excitation
T _g (e)	Estimated Gas-Dynamic Temperature
Т _о	Temperature of Environment
т _v	Vibrational Temperature
T _{VO}	Initial Vibrational Temperature
T _w	Surface Temperature
т _о	Stagnation Temperature
u _b	Bulk Velocity of Flow
υ	Heat-Transfer Coefficient to Environment
U ₀	Overall Heat-Transfer Coefficient
x	Fraction of Hydrogen Dissociated
x _w	Dissociation at Surface
Y	Fraction of Recombination Energy Stored as Vibrational
	Excitation
z	Distance Below Plasma
Subscr	<u>ipts</u>
c	Coolant
v	Vibrational

w Surface Conditions

<u>Greek Letters</u>

γ	Specific	Heat	Ratio	

- λ Thermal Conductivity
- ν Fundamental Frequency of Vibration

<u>Others</u>

[] Concentration of Species

Chapter 1 - INTRODUCTION

Most currently used or envisioned concepts for systems for spacecraft propulsion and maneuvering rely on what may be called, in general, reaction propulsion systems. These consist of a means for accelerating a mass to some velocity relative to the spacecraft and releasing it. By Newton's Third Law, the spacecraft recoils, gaining momentum equal to that imparted to the released mass. If the released mass, also called reaction mass, is released in a continuous flow, or in frequent, short bursts, the spacecraft experiences a force, or thrust, equal to the product of the reaction mass flow rate and the relative velocity imparted to the reaction mass.

The reaction propulsion system most commonly used in space flight, to date, is, of course, the chemical rocket, which uses a stream of gas as the reaction mass, heated under pressure by chemical reactions within the gas, then accelerated by thermodynamic expansion through a nozzle. Alternatively, the reaction mass, sometimes called the working fluid, can be heated externally, for example, as in the NERVA nuclear rocket, by passage through a nuclear fission reactor. A totally different concept, under development to the point of prototype flight tests, ionizes the working fluid and uses electrostatic forces to accelerate the ions the ion engine. A third, under study, would use electromagnetic forces to accelerate solid bodies, then release them in rapid succession - the mass driver (O'Neill [1977]). These are only a few of the reaction propulsion systems that have received serious scientific and engineering study, while nearly every system that can perform the basic function has probably been considered. For example, a toy balloon, when blown up and

released uses the elastic forces of its rubber skin and the pressure of the air held inside to force the air out and the reaction causes the balloon to fly around. A similar technique is exemplified by the toy rockets that are filled with water, then pressurized by a hand air pump. When the rocket is released, the air forces the water out, and the rocket flies off. One particularly memorable science fiction novel (Anderson [1962]) describes the use of an aqueous solution of fermented malted barley, pressurized by dissolved carbon dioxide, and expanded through a nozzle to provide emergency spacecraft propulsion.

Much recent study has been directed at electric propulsion systems, ones in which the energy needed to accelerate the reaction mass is, at some point, in the form of electricity. These systems have certain advantages for certain applications. The performance of a chemical rocket is limited by the nature of the reactions involved, by the amount of energy available per unit mass of propellant and by the fact that the propellants have to include the products of the reaction. A nuclear thermal rocket, such as NERVA, has its own problems. An electrical propulsion system can be limited, in the amount of energy available per unit of reaction mass, only by the amount of energy and reaction mass flux available. In near-Earth orbits, the electricity could come from solar panels, making the potential energy store all but unlimited. For deep-space missions, nuclear reactors may be required to provide the electricity, but an electric propulsion system may be much more flexible than a nuclear thermal system, such as NERVA. Unlike the chemical rockets, non-chemical systems, such as NERVA and electric propulsion systems, can be somewhat less selective in their choice of working fluid. NERVA, for instance, was designed to use hydrogen as a propellant, for

its advantages in specific impulse (<u>vide infra</u>), to provide a large amount of thrust while using a small amount of propellant. No conventional chemical rocket can use hydrogen alone for reaction mass.

Electric propulsion systems that have been under study group themselves into three categories, depending on how the electrical energy is transferred to the working fluid. These groups are electrostatic systems, such as the ion engine, electromagnetic systems, such as the mass driver and rail gun, and electrothermal systems, in which the electricity is used to heat the working fluid and, as in a chemical rocket, thermodynamic expansion through a nozzle provides the thrust. An electrothermal propulsion system is, in fact, the first electric propulsion system to be used in practical application in space. This is the resistojet, in which the working fluid is heated by passing over and around a coil heated resistively, much as in an electric hair drier, before it flows out the nozzle. Certain of the latest series of INTELSAT communication satellites use augmented hydrazine thrusters for stationkeeping and attitude control. A standard hydrazine thruster uses the catalyzed decomposition of hydrazine to heat the decomposition products and force them through a nozzle to produce the thrust. The augmented thruster places a resistance heating coil before the nozzle, to further heat the working fluid electrically.

The resistojet has been studied for use with a wide range of propellants, besides the ammonia-nitrogen-hydrogen-hydrazine mixture used in the augmented hydrazine thruster. Early studies looked at using the waste products, water, carbon dioxide, ammonia, and methane, from a manned space station as propellants for the station-keeping and attitude control thrusters (Greco and Byke [1969], Halbach and Yoshida [1971]).

Deposition and other reactions between the working fluids and the surface materials led to the concept's abandonment. The resistojet has other technical problems, involving the transfer of heat from the resistance coil into the gas. Since the coil must be hotter than the working fluid, the materials selection problem is most critical, to provide the mechanical strength and electrical performance required at the temperatures called for. To allow the coil surface temperature to be as little above the fluid temperature as possible, the flow path is often tortuous, to provide as much contact area as possible. This aggravates the problem of deposition.

An alternative electrothermal propulsion concept, the microwaveplasma electrothermal rocket, is the subject of this work. In this system, shown schematically in Fig. 1, the electricity, from a solar panel, would power a microwave-frequency oscillator, and the microwaves generated would sustain a plasma in the working fluid, inside a resonant cavity, heating the working fluid, which would expand through a nozzle to produce thrust. This concept would have an important advantage over the resistojet, in that the working fluid would be heated from within, as in a chemical rocket, and the main unusual requirement for the plasma chamber wall is that it be transparent to microwaves. The heat and chemical resistance required are no different than for chemical rockets, and might be handled by techniques already standard for chemical rocket

An important mechanism by which energy might be coupled from the electromagnetic fields sustained by the microwaves to the working fluid is the dissociation-recombination cycle of a diatomic gas, such as hydrogen. In the plasma, a significant population of free atoms, Shaw



Figure 1. Schematic of Proposed Microwave-Plasma Electrothermal Propulsion System

[1959] reported 90% dissociation in a hydrogen plasma, might be maintained. On leaving the plasma, the atoms recombine, re-forming the molecules, and releasing the energy absorbed in their dissociating, and heating the gas still further. This mechanism could play such an important role that the system is sometimes referred to as the "free radical" [Hawkins and Nakanishi, 1981] or "atomic hydrogen" rocket. However, it should be clear that the system is, in its fundamental principles, electrothermal in nature.

A commonly-used figure of merit in evaluating and comparing the performance of reaction propulsion systems is the specific impulse, which has units of seconds. Experimentally, the specific impulse of a given experimental rocket is determined by measuring the thrust of the rocket in pounds (force), and dividing by the flow rate of propellant in pounds (mass) per second. In the SI system of units, the force in Newtons divided by the flow rate in kilograms per second must be divided by the standard acceleration of gravity, 9.8 m/s^2 , to give the correct units, and allow for the difference between the pound (force) and pound (mass) in the English system. An engine with a high specific impulse can produce a larger total impulse, or change in velocity, from a given amount of reaction mass than one with a lower specific impulse. Hence, all else being equal, as high a specific impulse as is consistent with other constraints is desirable in a spacecraft propulsion system, where total spacecraft mass is likely to be a critical constraint. The specific impulse can also be computed by dividing the exhaust velocity, in meters per second, by the standard acceleration of gravity. This permits estimation of the specific impulse for theoretical systems, by assuming that all the energy added to the propellant is converted to

linear kinetic energy, and computing the velocity from $E = \frac{1}{2} m v^2$. Table 1 lists the specific impulse for various common chemical rocket propellant mixtures, specifically those used in the first stage of the Saturn V and the Atlas boosters, the Titan and Ariane rockets, and the Centaur, Saturn V upper stages, and the Space Shuttle Main Engines, the design value for the NERVA nuclear rocket, and a range of values for various ion engine designs. Although the chemical rockets have lower specific impulse than the nuclear or ion engines, they will remain the propulsion system of choice for the foreseeable future, at least for surface to orbit operations. Neither the ion engine nor the NERVA nuclear rocket can generate enough thrust to lift themselves against Earth's gravity, though other nuclear rocket designs might get around the problems with NERVA, and be usable for direct launch (Kingsbury [1975]). Ion engines, and indirectly the NERVA atomic rocket design, are both limited in the amount of reaction mass flow they can handle for a given amount of system dry mass, thus limiting the total thrust they can generate. The NERVA design is limited by heat transfer from the reactor core to the working fluid/propellant.

Although the microwave-plasma electrothermal rocket is not purely a chemical rocket system, the importance of the dissociation-recombination cycle in the performance of the system, particularly when hydrogen is the working fluid, allows it to be treated as one, with the main reaction the recombination reaction of hydrogen:

$$H + H = H_2 (1)$$

The heat of reaction of this reaction is very high, 436 MJ/kg-mol of product at 298 K, and, combined with the low molecular weight of the

Table 1. Specific Impulse for Various Propellants.

Propellant	Specific Impulse (sec)	Reference
0 ₂ - Kerosene	300	Sutton [1976]
0 ₂ - H ₂	391	Sutton [1976]
N ₂ O ₄ - UDMH - Hydrazine	278	Sutton [1976]
Nuclear (NERVA)	825	Sutton [1976]
Ion	1500-8000	Sutton [1976]
Atomic Hydrogen		
H:H ₂ Ratio		
1:10	472	Palmer [1959]
1:5	660	Palmer [1959]
1:4	704	Stewart [1962]
1:1.6	1,046	Stewart [1962]
1:0.54	1,470	Stewart [1962]
1:0	2,103	Stewart [1962]

product, 2.016, if all the energy released in the reaction is transformed to the kinetic energy of the exhaust, this suggests that the exhaust velocity from a rocket fueled by atomic hydrogen alone would be as high as 21 km/s, with a corresponding specific impulse of 2100 s. By comparison, burning hydrogen with oxygen releases 242 MJ/kg-mol, producing an ultimate exhaust velocity of 3.7 km/s, due to water's molecular weight of 18, and specific impulse of 370 s. Table 1 also shows this sort of theoretical specific impulse for a rocket with a propellant of various proportions of molecular and atomic hydrogen, assuming total recombination of the free atoms. The table shows the promise of atomic hydrogen as a propellant: higher specific impulse than any commonly used chemical rocket, into the range of nuclear rockets and to match some ion engines. It seems likely that a rocket based on the recombination reaction of hydrogen can avoid the political and technical problems that killed NASA's NERVA nuclear rocket project. In addition, due to the different concepts behind the two systems, it seems likely that the microwave-plasma electrothermal rocket can generate higher total thrusts than an ion engine can, at similar system masses. The electrostatic heart of an ion engine is so limited as to how much reaction mass it can accelerate per unit area of the grids used that it becomes very expensive, in money and in engine mass, to scale the engine up to generate more than very low thrusts. These low thrust levels mean that all maneuvering must be leisurely, though the high specific impulse makes the ion engine ideal for long-duration, unmanned flights. NASA's proposed, though cancelled, probe to Comet Halley was intended to use an ion engine, for example. The microwave-plasma electrothermal rocket may be nearly so economical in reaction mass as as ion engine, with the added

benefit of easy scaling to thrust levels currently the regime of chemical rockets.

Atomic hydrogen, because of the large amount of energy released in its recombination reaction, and the high specific impulse potentially derivable from this energy, has long been desired as a rocket propellant (Stewart [1962]). However, the normal state of hydrogen, under reasonably accessible conditions, is as molecules, the equilibrium of the reaction in equation (1) is shifted far to the right. Hence, the free atoms must be generated from the molecular state. Atomic hydrogen is, hence, not truly a source of energy for propulsion, since the dissociation of the molecules consumes as much energy as the recombination would release. This isn't without precedent, since hydrogen itself is not found free in large quantities on Earth, so the hydrogen used in the liquid-hydrogen fueled rockets used today, such as the Space Shuttle Main Engines, must be liberated first from some hydrogen-containing compound. The most easily accessible source of hydrogen is, of course, the water of the oceans. The electrolytic dissociation of water to generate hydrogen is precisely the reverse of the combustion reaction of hydrogen with oxygen, used in the rockets.

Given that the hydrogen atoms must be generated before they can be used for propulsion or for other purposes, there are two obvious options as to how and where this can be done, in the case of a spacecraft with an atomic hydrogen-fueled engine. The atoms may be either generated on board, at need, from a supply of molecular hydrogen or generated at a base, either on-planet or in orbit, and stored on board until they were needed. Since most methods for generating atoms were both inefficient and heavy, early studies (<u>Ibid</u>., and references therein) concentrated on

the second option, of storing the free atoms. This proved difficult, as free hydrogen atoms are extremely reactive, under anything like normal conditions. A typical storage scheme involved freezing the atoms in a matrix of molecular hydrogen, at 20 K, at about one atom per ten molecules (Golden [1958]). A later storage method involves using magnetic fields to sort the spins of the elementary particles making up the atoms so that recombination is quantum-mechanically forbidden (Silvera and Walraven [1982]). This also involves very low temperatures, a major component of the system being super-fluid liquid helium, at less than 3 K. All storage methods have proven to be unwieldy and impractical for spaceflight, so the concept has been abandoned, and the concept of an atomic-hydrogen fueled rocket was neglected as impractical.

The concept has been revived, however, in the wake of the results of Shaw [1959], Mearns and Ekinci [1977], <u>inter alia</u>, showing that the microwave plasma could be an efficient source of free hydrogen atoms. In addition, recent advances in electronics and solar-cell technology, driven by the space program, have produced such a reduction in size and mass of such equipment and improvements in efficiency that a microwaveplasma electrothermal propulsion system, as described above, now appears feasible for interplanetary propulsion.

Although hydrogen's low molecular weight would produce the highest specific impulse, and hence might be preferred as a propellant, any diatomic gas could be used. It seems likely, from cosmochemical considerations, that oxygen might be the propellant of choice in the inner solar system. Although hydrogen is the most abundant element in the universe, as stars and giant planets like Jupiter are largely made of

hydrogen, and the ice moons of the giants are made largely of hydrogencontaining compounds, such as ammonia, methane, and water, the smaller, warmer, and hence rocky inner bodies of the solar system could not retain as much of the primordial hydrogen or hydrogenous compounds. Oxygen, the third most abundant element in the universe, after the inert helium, is the predominant element in the small, rocky bodies of the solar system, in its silicate, alumina, and other compounds. It would, no doubt, be a major by-product of any lunar or asteroidal mining and smelting operation. Hydrogen, on the other hand, is comparatively rare in the inner solar system, and would be far too valuable to throw away reaction mass, being mainly brought from Earth, or the ice moons of as Jupiter or Saturn, unless an asteroidal source of water is located. Research work has also been done using nitrogen (Asmussen, et al. [1984], Whitehair, et al. [1984]) and even helium (Whitehair, et al. [1986]) as working fluids in a microwave-plasma electrothermal rocket.

As part of a study of the microwave-plasma electrothermal propulsion system, and of other potential uses for microwave-frequency plasmas in propulsion, NASA-Lewis Research Center contracted with the plasma chemistry study group at Michigan State University to conduct experimental and theoretical studies of the microwave plasma (Grant # NSG-3299). This paper will describe three aspects of this joint study: First, a series of experiments, performed at NASA-Lewis Research Center, Cleveland, Ohio, to test the total concept and to measure the thrust that can be generated by a microwave-plasma electrothermal rocket, second, a theoretical examination of the last stage in the dissociation-recombination cycle, the energetics of hydrogen atom recombination, and last, a series of computer models of the recombination reaction to analyze and explain the experimental results.

Chapter 2 - TECHNICAL BACKGROUND

A number of technical, engineering, and scientific problems remain to be solved before the microwave-plasma electrothermal rocket takes any sort of role as a spacecraft propulsion option. The problems, in the order in which they're met along the energy pathway, include the efficiency of generating the microwaves, the transfer of the energy to the plasma, maintaining the plasma at operational flow rates and pressures, thermalizing the energy that may have been absorbed through non-thermal mechanisms, and controlling the heat of the exhausting working fluid. The first of these is a matter of electrical engineering, based on much prior work on microwave systems, and outside the scope of this work. The second may create interesting problems, for the plasma chamber required to pass a large flow rate of working fluid may be so much larger than our experimental systems that its primary resonant modes will be excited by radiation outside the microwave frequency band. How sensitive the plasma's behavior is to the frequency of the exciting radiation is a question for other work. It is clear that much of the detail design of the system is intimately related to the frequency that is used, and these considerations are also outside the scope of this work.

The performance of the plasma under operational conditions will require investigation once those conditions are defined, though experiment and modeling, such as that reported in this work, will supply some preliminary guidelines. The physics and chemistry within the plasma are outside the scope of this work, though the experimental system used can contribute some data for these studies, and this modelling and experimental work, and extensions of them, can help define the direction in

which final design should lead. The final design of the thermalization section and nozzle of an operational microwave-plasma electrothermal rocket will be based on a detailed understanding of the processes at work in these sections, which will come through an interactive combination of experiment and numerical modelling. For example, full dissociation and complete recombination would heat the working fluid more than 15,000 kelvin. Just what temperatures would be attained and where, and how to handle them is a topic for a long design process, and this work is intended to provide a beginning for this process. This work will address some aspects of this phase of the overall problem, specifically, the energetics of the working fluid after it leaves the plasma to flow through the nozzle. This paper completes work published by Chapman, et [1982], Filpus and Hawley [1984], and Morin, et al. [1982]. This al. work first reports a series of experimental work, at the NASA-Lewis Research Center, Cleveland, Ohio, to investigate the performance of a small-scale model of a microwave-plasma electrothermal rocket, attempting to measure, or at least estimate, the temperature profile below the plasma and the thrust generated by the experimental system.

Next, I consider the question of thermalization of non-thermal, vibrational and rotational excitation, energy transfer in the plasma. In the dissociation-recombination cycle, it has been suggested (Villermaux [1964a,b]) that a large fraction of the recombination energy may be manifest as vibrational energy of the recombined molecules for long times. This work employs a computer model to estimate the amount and the relaxation time for such excitation under expected operational conditions. Last, this work describes an attempt to construct a numerical model of the recombination system, in an effort to predict the performance of proposed systems, and to verify the model by fitting its predictions to the experimental results.

Chapter 3 - EQUILIBRIUM CONSIDERATIONS

The recombination of free hydrogen atoms releases 436 MJ per kg-mol of molecular hydrogen produced. For this energy to be useful in a propulsion application, it must be turned to directed kinetic energy of flow of the gas. The object of this study is to determine the conditions under which the production of such kinetic energy, either directed, or random on the molecular level, which can become directed by thermodynamic effects in flow through a nozzle, can be maximized.

The first, and simplest, approximation is to assume that a stream of hydrogen gas is dissociated completely, then allowed to recombine fully, with all of the energy released in the recombination serving to heat the molecular gas, which is then allowed to expand through a nozzle. This produces the figures in Table 1, an exhaust velocity of 20.9 km/s, and a specific impulse of 2100 seconds, as described above. However, this is equivalent to a temperature rise of some 15,000 K, from the kinetic theory heat capacity for molecular hydrogen of 7/2 R, 29,100 J/kg-mol K. Besides the staggering, though not totally insurmountable problems involved in handling gases at such temperatures, about two and a half times the temperature of the surface of the sun, thermal dissociation will occur, at any reasonable temperature, limiting the extent of the recombination. At 1 atmosphere pressure, the equilibrium dissociation at 5000 K is over 90 per cent (Fig. 2, from Snellenberger [1980]), for instance.

The next step, then, is to consider the effects of chemical equilibrium on the extent of the recombination reaction. As a simplified model of the system, the inlet gas was assumed to be at 300 K, and




allowed to react adiabatically to equilibrium, then no further reaction occurred in the nozzle, frozen flow. Again, from the kinetic theory of gases, the heat capacity of atomic hydrogen was taken to be 5/2 R, or 20,800 J/kg-mol K. The equilibrium constant was computed from the exact heat capacities (see appendix C). Table 2 shows the equilibrium temperature, dissociation, and specific impulse produced by a fully dissociated hydrogen stream over a range of pressures. The specific impulses were computed based on the theoretical adiabatic expansion into a perfect vacuum, assuming no further reaction, or frozen flow (Equations 3a and 3b, p. 39). Tables 3 and 4 show the same values for a range of initial dissociations at pressures of 100 kPa, 1 atm, and 2500 kPa, 25 atm, respectively.

These tables show that thermal equilibrium does limit the performance of an atomic hydrogen rocket short of that which a simpler model would predict, particularly sharply at high atom concentrations and low pressures. However, these limits are still high enough, even at low pressures and relatively low concentrations at higher pressures, to generate performance, in terms of specific impulse, above that of chemical rockets and comparable to nuclear rockets. It should be clear from Table 1 that a specific impulse of 1000 seconds is a useful benchmark to shoot for, well above chemical rocket performance and comparable to nuclear rockets. A fully dissociated stream would produce this impulse at a recombination pressure of 10 kPa (1/10 atm), while at 100 kPa (1 atm), 30% dissociation suffices to generate the same level of specific impulse.

Table	2.	Calculated	Specific	Impulses	-	Pressure	Dependence.
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Adiabatic equilibrium recombination from fully dissociated 300 K Hydrogen stream.

Pressure	Equilibrium Temperature	Equilibrium Dissociation	Specific Impulse	
$(atm = 10^5 Pa)$	(K)		(sec)	
.1	3559	.706	1200	
.2	3707	.692	1223	
.5	3920	.673	1258	
1.0	4096	.658	1285	
2.0	4287	.641	1314	
5.0	4564	.616	1356	
10.	4794	.595	1389	
25.	5131	.565	1437	

Table 3.	Calculated Specific Impulses - Dissociation
	Dependence (Medium Pressure)

Adiabatic equilibrium recombination from 1 atm 300 K Hydrogen stream.

Initial Dissociation	Equilibrium Temperature (K)	Equilibrium Dissociation	Specific Impulse (sec)
.1	1707	7.5*10 ⁻⁵	731
.2	2656	.023	940
.3	3049	.086	1026
. 4	3282	.161	1080
.5	3424	.241	1122
.6	3598	.324	1158
.7	3726	.407	1191
. 8	3847	.491	1223
.9	3968	.575	1254
1.0	4096	.658	1285

Table 4	•	Calculated	Specific	Impu]	ses	-	Dissociation
		Dep	pendence	(High	Pres	ssu	ıre)

Adiabatic equilibrium recombination from 25 atm 300 K Hydrogen stream.

Initial Dissociation	Equilibrium Temperature (K)	Equilibrium Dissociation	Specific Impulse (sec)
.1	1708	1.5*10 ⁻⁵	731
.2	2830	.009	973
.3	3465	.051	1099
. 4	3850	.113	1176
.5	4133	.182	1233
.6	4365	.256	1281
.7	4570	.332	1324
.8	4760	.410	1363
.9	4944	.487	1400
1.0	5131	.565	1437

To improve further on this approximation, the finite reaction rate of the recombination must be considered. This is done by making a mathematical model of the reaction system, and solving the equations involved. A numerical solution, using a computer, is called for. Detailed description of such modelling is included in Chapter 6 of this paper, below.

Chapter 4 - EXPERIMENTS

As part of the NASA-supported study of the microwave-plasma "free radical" rocket concept, an experimental program was initiated at NASA-Lewis Research Center, Cleveland, Ohio. The portion of this program that pertains to this work had three primary goals. First, the measurement of thrust from an experimental model of a microwave-plasma rocket, and investigation of some of the parameters that might affect the thrust as measured. Increases in the measured thrust with the plasma over that meausred in cold flow, the magnitude of the increase and what parameters affected the increase were primary targets of the investigation. Second, determination of some of the conditions downstream of the plasma, for verification of numerical models. Specifically, temperature estimations via a gas-dynamic method were sought, especially if a profile of this temperature below the plasma could be established. Third, investigation of different configurations of the plasma tube, to decide which might overcome some of the limitations of the experimental arrangement, or would be better suited for practical applications.

<u>Apparatus</u>

The experimental apparatus consisted of two separate sections, the microwave-plasma generator, shown in schematic form in Figure 3, and the thrust stand, shown in schematic in Figure 6. In the microwave-plasma generation section, the gases used were commercial grade bottled gases, fed through micrometer variable leak control valves, with the flow rates





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measured by Hastings-Raydist flow meters, calibrated in air with conversion factors for other gases. The gases were fed to a flow manifold, where the gases were selected and mixed, and thence to the discharge tube. In transpiration flow experiments, the gas was fed to the jacket of the discharge tube, and flowed through the discharge tube walls into the discharge tube. Then, the gas flowed from the discharge tube through its nozzle into the tank of the vacuum facility. The thrust stand was located inside the vacuum tank, and the vane was positioned to intercept most of the discharge jet. The plasma pressure was assumed to be the pressure measured at the upstream end of the discharge tube by a Barocel capacitance manometer, connected to the discharge tube by a further eighteen inches of rubber hose. A Bourdon tube manometer served to measure the jacket pressure in transpiration flow experiments, and to measure the upstream pressure of the venturi meter used to measure the flow rate of the cooling air. A water manometer was used to measure the throat pressure drop of the venturi meter, and the standard equation, with a calibrated efficiency, was used to determine the flow rate. Copper-constantan thermocouples were used to measure the temperature of the cooling air and, on some occasions, the temperature at the upstream end of the discharge tube. The alumina tube used for transpiration flow experiments was opaque, so a glass window was installed in the upstream end of the discharge tube to permit visual monitoring of the plasma.

The microwave oscillator used had a frequency of 2.45 GHz, filtered to a narrow band, and the output power could be adjusted between 300 and 700 watts. The microwaves were passed through a water-cooled, ferrite core isolator, and a 40 dB directional coupler, where the power incident

on and reflected from the plasma cavity were measured, with thermistortype power meters. About one meter of flexible wave guide allowed for the adjustments required in tuning the cavity, and led from the directional coupler to the right-angle wave-guide-to-coaxial transition to the coaxial probe that led into the microwave resonant cavity. The cavity (Figure 4), of a Michigan State University-developed design described in Mertz, <u>et al</u>., [1974, 1976] and Mallavarpu, <u>et al</u>., [1978], was cylindrical, diameter 8 inches, with the discharge tube running coaxially through it. It was water cooled, though the water flow rate and temperature were not monitored. The length of the resonant section of the cavity and the depth to which the coaxial probe could be inserted into the cavity could be adjusted independently to tune the cavity to attain resonance, so the minimum amount of the microwaves incident on the cavity were reflected.

A number of different configurations of the plasma tube were used in this study. The first one used was called a venturi tube (Figure 5(a)). Constructed of quartz, the design included an plasma chamber of about 22 mm. inside diameter, then it necked down sharply, to a throat of some 3 mm. diameter, then the inner wall expanded as a straight cone over some 23 cm. in length back to about 22 mm. diameter. There was a second quartz tube coaxial with the main plasma tube, over the plasma chamber and nozzle, with an overall outside diameter of 34 mm. This outer jacket was ported so that air could be blown over the inner tube, to cool it, with the air inlet above the microwave cavity, and outlets on the end of the nozzle, so that the air and the plasma gas flowed cocurrently.



Figure 4. Schematic of Resonant Cavity



(a) Venturi Tube



(b) Straight Tube



(c) Quartz Nozzle Tube

Figure 5. Cross-Sections of Plasma Tubes

Surveying the literature (Kallis, et al. [1972]) suggested that the low, six-degree, divergence angle of the venturi tube's nozzle would be inadequate for proper expansion at the low flow rates under consideration. Also, the nozzle throat was too large to produce pressures in the plasma chamber in the range of interest, except under gas flow rates beyond the capacity of the vacuum system. Therefore, a nozzle was designed with a 1 mm. throat, between a 45° converging section and a 35° diverging section, both straight cones. Several nozzles of this design were machined into boron nitride plugs sized to fit into a 22 mm. i. d. tube. These plugs were on the order of an inch long. O-rings were used to seal the space between the tube and the nozzle plug. Some of the nozzle plugs were constructed with shoulders, so the plug would sit just inside the end of the plasma tube, held in place by tantalum strapping. One plug was constructed without these shoulders, to fit entirely within the tube and so, with a straight plasma tube, providing a range of distances between the plasma and the nozzle. Friction between the 0rings and the wall of the plasma tube held the nozzle plug in place. The straight plasma tubes (Figure 5(b)) were jacketed and ported so that cooling air could be flowed through them either with or against the flow of the plasma gas, or they could be sealed off and evacuated, to provide an insulating vacuum jacket around the plasma.

Similar high-divergence nozzles were fabricated into the ends of quartz plasma tubes (Figure 5(c)). However, the properties of the material limited the diameter of the throat to about 2 mm. These tubes were jacketed, but with only one port, so only vacuum jacketing could be used. In an attempt to reach very high plasma pressures, what were termed capillary tubes were fabricated. These were similar to the quartz nozzled tubes described above, except that the 22-mm. i. d. plasma chamber and the converging portion of the nozzle were replaced by a nominally 1 mm. i. d. quartz capillary tube, passing through the center of the 34 mm. o. d. vacuum jacket. Last, plasma tubes of porous alumina were fabricated, with boron nitride nozzle plugs, and a quartz jacket. These were used in transpiration flow experiments, where the plasma gas was fed to the jacket and then through the porous walls, to control the wall temperature by transpiration cooling.

The thrust stand used in the experimental series (Figure 6) consisted of an aluminum disc vane, or target, counterweighted to pivot on a vertical length of piano wire, whose lower end was fixed, and whose upper end could be twisted by a worm and pinion gear system. When a jet of gas impinged on the target, displacing it from its rest position, twisting the piano wire, as a torsion wire, would supply a force that, when this force balanced the force of the jet on the vane, would return the vane to its rest position. At relatively small amounts of torsion, the force so applied would be proportional to how far the wire was twisted. Thus, the amount of twist needed to return the target to its rest position was proportional to the force the jet imposed on it. The amount of twist of the wire was determined by the resistance of a potentiometer tied to the shaft of the worm gear that drove the pinion to which the wire was attached. The motion of the target was magnetically damped, and its position determined by measuring the light passing through a V-shaped slit in a vane counterbalancing the target, from a light source to a detector, both made by Opcon.

The thrust stand was calibrated directly, using 1.5 g. weights hung so their weight would exert force along the same axis as the impinging



Figure 6. Experimental Apparatus - Schematic - Thrust Stand

jet. All results are reported as measured, with no allowance made for inaccuracy from a number of likely sources. A certain amount of hysterisis was detected, in that the vane position for a given shaft position would vary depending on which way the vane had been moving. This was compensated for by always bringing the target to its rest position from the same direction, and over-shooting and returning if necessary.

Subtler effects were ignored. At sufficiently low pressures, when the mean free path of the molecules of the impinging jet would be comparable to the distance between the nozzle and the target, the jet may be in molecular flow, and the recoil from molecules rebounding from a target-type thrust stand may double the measured thrust over that which would be exerted by the jet upon its source, by Newton's third law. Lacking information about the interaction between the jet and the vane, and as relative thrust levels seemed sufficient for this preliminary study, the question of molecular flow was neglected.

A handful of other subtle effects were discovered in the course of the experimental work, and, in general, likewise neglected. The torsion wire was apparently not exactly centered in the pinion, inducing a slight lateral movement to the entire target and counter weight system when the pinion was rotated. Hence, the target was not in exactly the same position after the wire was twisted, even though the optical detector read the same value, in a thrust measurement. The amount of the movement was judged small enough to be negligible, and there was no way to easily account for it. There was a significant, though still inexplicable, pressure dependence on the performance of the optical system. With the vane held in position, so that the amount of light passing from the source to the detector was constant, the output from the detector

would change as the pressure in the vacuum tank changed. The details are given below. This could be neglected, because the pressure change in the tank during an experimental series would be small enough that the change in the Opcon output due to the pressure change would be much smaller than that involved in the thrust measurements. Since much of the work centered on comparing hot and cold flow measurements, at the same flow rate, and the vacuum system would maintain the same tank pressure at the same flow rate into the tank, the Opcon pressure effects would have no effect on the results. A hysterisis in this pressure effect with changing pressures was minimized by allowing enough time for the optical system to settle down before taking a reading when the tank pressure was changed. One other effect was a transient, in which the vane of the thrust stand would sometimes swing towards the jet when the plasma lit, and away when the plasma was turned off, before swinging to follow the increased or reduced thrust. This was diagnosed as an actual physical movement of the target vane, and not a transient in the position sensor, but has not been studied further. One hypothesis is that it was an electromagnetically induced coupling between the plasma and the aluminum vane, which could have affected the thrust measurements when the plasma was on. However, when the jet expanded freely into the vacuum tank, the thrust ratio between hot and cold flows, at the same flow rate, was usually very close to the ratio of the back pressure above the nozzle. This is as thermodynamic theory would indicate, suggesting that there was no great influence from any electromagnetic interaction between the plasma and the target.

Preliminary testing, using air jets, showed a significant pluming effect, particularly at low flow rates. The measured specific impulse dropped off with greater distance between the jet and the target. Since, for a simple tube jet, this occurred mainly beyond 15 cm. from the jet, it was judged that the measured specific impulse would be accurate for work with nozzles if they were kept within this 15 cm. of the target.

The thrust stand was installed inside one of the vacuum tanks at NASA-Lewis Research Center. The tank, 1.6 m. diameter by 6 m. long, was serviced by a roughing pump with a booster, which would hold the tank pressure, when sealed and no gas flow, to about 1 milliTorr, 0.1 Pa. Once it neared this pressure, any of four oil-diffusion pumps could be brought onto line. The work here would use two of these, and the no-flow pressure would reach 10^{-6} Torr, 10^{-4} Pa.

Procedure

To make an experimental series of runs, first, the vacuum tank's pumps were turned on, and the tank pressure brought to the desired range by the appropriate selection of pumps. The electronic equipment was turned on, and allowed to warm up, while the tank was pumping down. Once the pressure and the instruments had all stabilized, the thrust stand was zeroed by, first, raising a mechanical stop which marked the intended rest position of the target, and applying, through the torsion wire, a small amount of force (ca. 0.01 N) to hold the target against the stop. This was also the parked position of the target between experimental runs. Then, the output offset from the optical sensor was adjusted so that the output voltage read 0.00 (\pm 0.005) V. Then, the stop was lowered, freeing the target to swing, and the torsion wire

rotated until the target would settle down with the optical sensor output again reading $0.00 (\pm 0.01)$ V. The voltage drop across two legs of the potentiometer was noted, as the null thrust reading of the thrust stand. The pressure in the tank and in the plasma tube were noted, for later reference, as were the ambient temperature and the temperature of the cooling air.

Once the null values were recorded, the desired working fluid was selected and the flow manifold adjusted so that either the desired flow rate through the discharge tube or the intended cold flow pressure was established, without the microwave power fed to the cavity, to establish cold flow values. The flow rate, pressure in the discharge tube, and tank pressure, were recorded. Then, the target, swinging freely, was brought, by means of twisting the torsion wire, to settle at the point where the optical sensor output once again read $0.00 (\pm 0.01)$ V, a procedure called, for short, a thrust measurement. Due to a coincidence in the characteristics of the original elements of the thrust stand, one millipound (4.5 mN) of force on the vane was balanced by a twist represented as about one volt across the potentiometer. Later modifications for a greater range of measurable thrust changed this simple relationship.

This procedure was repeated at as many flow rates or cold pressures as were to be studied in the series of experiments at hand. Then, the microwave generator was turned on. By some combination of lowering the discharge tube pressure (via the gas flow rate), adjusting the cavity length and probe depth, and "tickling" the discharge tube with a Tesla coil, in some arrangements through a probe leading into the resonant cavity inside the discharge tube, the gas inside the discharge tube was

made to break down, establishing or "lighting" the plasma. The desired flow rate, one at which cold flow measurements had been made, was reestablished, with the cavity being re-adjusted, "tuned", so the plasma would not blow out as the pressure was raised. The desired microwave power level was established, with the cavity tuned to minimize the power reflected from the cavity, as a rule, in the desired resonant mode of the cavity. Each of the two cavity adjustments, the length of the resonant cavity and the depth of the coaxial probe, would be adjusted in turn, to reach a local minimum while the other was held constant, until neither reduced the reflected power. Once the plasma was stabilized, the pressure in the discharge tube was recorded, and the exact flow rate. A thrust measurement was taken, the cavity dimensions recorded, and the tank pressure noted. If the discharge tube was being air cooled, the outlet temperature of the air, and the inlet pressure and pressure drop to the throat of the venturi meter were recorded. This procedure was then repeated at all flow rates at which cold flow data had been taken, and plasmas could be maintained in the given cavity mode, or until the tube should fail.

Gas-Dynamic Temperature Theory

The temperature estimates made on the system were made using a reasonably non-invasive technique using the laws of gas dynamics, and hence are called gas-dynamic temperatures. From fluid-flow theory (Shapiro [1953]) in ideal and complete expansion through a nozzle, in choked flow, with velocity in the throat at Mach 1, the stagnation temperature and pressure, the mass flux at the throat, and the molecular

weight and heat capacity ratio of the gas are related by the following equation:

 $T_0 = \gamma P_0^2 g M_w / R / (F/A_t)^2 [2 / (\gamma + 1)]^{(\gamma+1)/(\gamma-1)}$ (2)

Hence, assuming constant thermodynamic nozzle efficiency, and constant gas properties, molecular weight and heat capacity ratio, the pressure required to force a given flow rate through a given nozzle is proportional to the square root of the temperature of the gas. In the experimental program, this was used to estimate the temperature downstream of the plasma by comparing the back pressure needed to force the desired flow through the nozzle into the vacuum tank at ambient temperature, and with the plasma lit. The ambient absolute temperature multiplied by the square of the ratio of the pressure with the plasma to that without is the gas-dynamic temperature.

This use of the gas dynamic principle to estimate the gas temperature requires the assumption of constant molecular weight and heat-capacity ratio between the cold and hot runs. However, the microwave plasma is not only likely to generate a sizeable number of free atoms in a diatomic working fluid, the "free radical rocket" concept requires it to, changing the molecular weight and heat capacity of the gas. Since the experiments were intended to demonstrate this concept, some reconciliation between this and the contradictory assumptions implicit in the temperature measurement technique used is required.

The use of the gas-dynamic temperature measurements was justified on several grounds. First, at the plasma exit, using the venturi tube, gas-dynamic temperatures were determined that were consistent with spectroscopic measurements (Hawkins and Chapman [1982]), when only low dissociations were assumed (see also Morin, et al. [1982] Figure 11). Second, gas-dynamic temperature and specific impulse, from gas dynamic theory, vide infra (p. 54), should depend differently on molecular weight and heat capacity ratio, and this could be used, in theory, to estimate concentrations and corrected temperatures. The last lines in Table 5(b) (p. 59, below) show the estimated concentrations and corrected temperatures for a few of the experimental runs. In the other runs, the specific impulse, as measured, was too close to the same fraction of the theoretical specific impulse, based on the zerodissociation gas-dynamic temperature, with and without the plasma to make such an estimate, or the efficiency changed in the wrong direction, implying a negative dissociation. When such an estimate could be made, the concentrations were low, and the corrected temperatures, often, too low to be realistic, lower than the coolant temperature. Third, good information on the atom populations was lacking. This apparatus could not handle the titrant used in other free-atom measurement experiments (Chapman, et al. [1982]), nor was there room to install ESR (Bennett and Blackmore [1968]) or Lyman-Alpha Absorption equipment between the cavity and the vacuum tank. The apparatus used in the work reported by Chapman was not available to reproduce the work done here, and give estimates of the atom populations. Last, computer modeling of the system (vide infra, Chapter 6) tends to indicate that, under the conditions of the experiment, surface recombination should remove free atoms very quickly, particularly from atom concentrations sufficient to make a significant impact on the results.

Experimental Program

Once the thrust stand was installed and calibrated, and the gas flow and microwave cavity system installed, experimental work began with a venturi tube as the plasma tube, installed so that the throat of the nozzle was located at the edge of the cavity, on the side the gas exited on. The tank was pumped down using only the roughing and booster pumps. Five hundred to a thousand (indicated) sccm of hydrogen or helium flowing through the system did not raise the tank pressure to 10 mTorr. The microwave power was turned up to 600 W incident on the cavity, and the cavity tuned to minimize the reflected power. At the plasma pressures involved, less than 15 Torr, this meant a resonant cavity length on the order of 9 to 10 cm. The gas-dynamic temperatures were estimated to be up to 1800 K in hydrogen, and 1600 K in helium. The measured thrust was only negligibly higher with the plasma on than in cold flow, in either gas. Some 83% of the power absorbed by the cavity was taken off by the cooling air from a helium plasma, and some 75% when the plasma gas was hydrogen. The absence of a noticeable thrust increase despite the indicated temperature rise is probably due to the imperfect expansion through the low-divergence nozzle used, poorly designed for the low flow rates used (after Kallis, et al. [1972]), and, secondly, to cooling of the expanding gas by the air-cooled nozzle walls.

For safety reasons, nitrogen was used as the working fluid for an extensive series of studies in the same equipment. At a constant nitrogen flow of 1000 sccm (indicated) and constant incident microwave power of 600 W, the cooling air flow rate was varied between 2.0 and 3.7 g/s. As the air flow was decreased, its outlet temperature increased,

though the total heat load taken up by the air decreased. The thrust and gas-dynamic temperature both increased, very slightly, as the coolant flow decreased. However, these were not sufficient to account for the difference in the coolant heat loads, which still accounted for 60 to 70 per cent of the absorbed power.

Varying the nitrogen flow between 500 and 1500 sccm (indicated) with constant 600 W incident power and 3.6 g/s cooling air flow, produced gas-dynamic temperatures that ranged from 1700 to 3100 K, increasing with increased flow, and thrusts from 5 to 20 per cent above cold flow values. The cooling air heat load decreased slightly with the increasing flow, on the same order of magnitude as would be needed to account for the heating of the extra plasma gas flow. Due to plasma instabilities at lower power levels, one measurement was taken with 1700 sccm (indicated) nitrogen flow and 640 W incident microwave power. The cooling air heat load, though larger in net amount than the earlier, lower power runs, was a smaller fraction of the absorbed power.

Next, the gas flow was held constant at 1000 sccm (indicated) of nitrogen, the cooling air flow at 3.4 g/s, and the incident microwave power was varied from 300 to 670 W, with constant retuning to keep the reflected power minimized. As the incident power increased, the gasdynamic temperature also increased, from 1200 to 2500 K, the measured thrust increased, from 110 to 114 per cent of the cold flow value, and the cooling air heat load increased from 256 to 491 W, though the fraction of the absorbed power taken off in the cooling air dropped from 86 to 75 per cent. Adjusting the cooling air flow to keep its outlet temperature constant as the incident power varied kept the fraction of the absorbed power taken off by the cooling air very nearly constant.

An attempt was made, at constant incident power, 600 W, gas flow, 1000 sccm (indicated) nitrogen, and cooling air flow, 3.4 g/s, to locate a cavity tuning, a cavity length and probe depth, that might produce more thrust than the tuning for minimum reflected power. As the cavity was re-tuned, around the cavity length of 9.85 cm, and the reflected power rose as the resonance was lost, the gas-dynamic temperature dropped, as did the cooling air heat load, both reflecting the decrease in absorbed power. The measured thrust did not increase, having a rather broad peak before it fell off with the absorbed power, as the increasingly mis-tuned cavity could no longer sustain the plasma.

An attempt to light an argon plasma at about a 1000 sccm (indicated) flow rate generated a plasma that propagated through the nozzle. The plasma radiated microwaves, and was shut off quickly, for safety reasons. No with-plasma data were taken, and further work in argon was abandoned, for a time.

Then, the tube was replaced by a straight, quartz tube, with a boron-nitride nozzle plug in the end. The throat of the nozzle was some 35 cm. below the cavity, and the nozzle was close enough to the end of the tube for free expansion into the vacuum tank. The tube jacket was evacuated, to a jacket pressure of about 10^{-6} Torr. With 600 W incident microwave power, into nitrogen flows of 200 to 1000 sccm (indicated), it might take hours for the pressure and thrust to stabilize after the plasma was lit, or for the system to cool off again after the power was turned off. Gas-dynamic temperatures were eventually determined at 400 K, and thrusts of some 116 per cent of cold flow values.

In the same apparatus, well shielded to control stray microwave leakage, under 600 W incident power, plasmas in argon could be sustained to much higher pressures than could be seen in nitrogen. In addition, the gas-dynamic temperatures and thrust increases were much higher in argon than in nitrogen. The maximum came at 3600 sccm (indicated) of argon, which produced a plasma pressure of over 540 Torr, a gas-dynamic temperature of 675 K, and some 50% more thrust than in cold flow, which reached the limit of the thrust stand's capacity. Warm-up and cool-down transients could still be observed, but they were minor. At plasma pressures above about 100 Torr, argon plasmas would form into bundles of filaments, waving in the unsteady electromagnetic fields.

These high flow rates produced tank pressures of nearly 10 mTorr, as measured by ionization gauges. This was near the top of the range of such vacuum gauges, and the measurements were likely to be inaccurate. To see what effect the pressure in the tank might have, two of the oildiffusion pumps were turned on, and certain of the runs with argon plasmas were repeated. Then, the tank pressure stayed below 4 mTorr (indicated) again in the upper range of the ionization gauges. The gasdynamic temperatures and relative thrust increases, hot over cold, remained about the same as at higher tank pressures. However, both the cold and hot flow thrusts, as measured, increased about 25% over the measured values at higher tank pressure, though the ratio between the two remained constant. In addition, a large (amplitude on the order of 0.1 V), erratic, long-period (on the order of minutes) oscillation in the indicated position of the target was noted at tank pressures in the vicinity of 2 mTorr, which made certain thrust measurements difficult. To see the effects of an intermediate tank pressure range, some of the

argon plasma experiments were repeated with one oil-diffusion pump on. The results were intermediate between those with only the mechanical pumps and those with two ODP's, without any consistent pattern, however. At low argon flow rates, the tank pressure and results were close to those obtained with two ODP's, while at high flows, the system behaved almost as though there were no ODP's on. It seems likely that the single oil-diffusion pump could not stabilize the tank pressure against the higher argon flows. The oscillation near 2 mTorr tank pressure was observed again.

The plasma tube was to be replaced, so the pressure sensitivity of the thrust stand target position sensor was investigated in the meantime. With the vane held in one position, and all else held constant, as the tank pressure was raised above 1 mTorr by a controlled leak, the output voltage from the detector would drop. When the leak was closed, and the pressure allowed to drop again, the voltage would rise again, with a noticeable hysterisis. On pumping the tank down from atmospheric pressure, ca. 760 Torr, the voltage from the optical sensor would drop, at first, reaching a broad minimum around 60 Torr pressure at about 65 mV below the initial value. Then, slowly at first but with increasing speed, the voltage would rise again, crossing the initial value at about 3 Torr, until it levels off again below 1 mTorr, about 230 mV above the voltage at atmospheric pressure, and remains constant down to 10^{-6} Torr. The decrease from atmospheric pressure to 60 Torr might be explainable as reflecting the increased transmission through the rarefying atmosphere, since the system was wired so that a more negative potential reflected an increased intensity of light on the detector. However, the

behavior at lower pressures, when the intensity seemed to drop as the pressure did, does not fit this model. Consultation with the manufacturer provided no assistance, as they had not had such an effect reported before. Few of their other customers used their equipment in vacuum environments. For reasons given above, this pressure effect was neglected in further work.

The next plasma tube to be installed was another straight quartz 22-mm tube, with the floating boron-nitride nozzle plug. The plug was installed in the exit plane of the cavity, and the cooling air routed to flow counter-current to the plasma gas. With only the mechanical vacuum pumps turned on, attempts were made to run low-power plasmas in nitrogen, but the nozzle throat plugged up quickly. Clearing the nozzle and repeating the attempts produced the same results. Then the nozzle plug was moved downstream some 2.5 in (6.4 cm), and the throat remained clear. However, in nitrogen over a flow range of 10 to 700 sccm, no substantial increase in either thrust or gas-dynamic temperature was observed with the plasma turned on. The gas-dynamic temperature is plotted versus nitrogen flow rate in Figure 7. Similar results were obtained with hydrogen as the working fluid. The cooling air temperature reached 400 K, and the heat load was some 60 per cent of the absorbed microwave power.

Switching working fluids, to argon, again produced dramatically better results. Over a range of flow rates from 700 to 4000 sccm, corresponding to plasma pressures of 183 to 723 Torr, 600 Watts of absorbed microwave power, of which 360 to 400 Watts were taken off in the cooling air, produced gas-dynamic temperatures of 1100 to 1400 K, and thrusts of 103 to 121 per cent of the cold-flow values. As a rule, these values





varied directly with the flow rate, except for the heat load on the cooling air, which, as was expected, had the opposite trend. The gasdynamic temperature, though, bucked this general trend, with its highest value at the lowest flow rate, and a minimum with flow rate at about 2400 sccm, and increased above that. This was due to the effect of the plasma pressure on the size of the plasma. Below 1600 sccm, the filamentary high-pressure plasma reached to the nozzle, and a diffuse plasma appeared below the nozzle plug. Thus the low-flow gas-dynamic temperatures reflected conditions effectively within the plasma itself. There was also a large gap in the thrust increases between the low and high flow experiments, with the low flow increments being some three to seven per cent of the corresponding cold flow values, and the higher flows having increases of some 13 to 21 per cent of their corresponding cold flow thrusts.

The highest pressure, though, moved the nozzle plug against the friction between the O-ring and the wall, to about 8.5 in. (23 cm.) below the cavity. Repeating the experiments done earlier with the nozzle at the new position produced the same negative results with hydrogen and nitrogen as working fluids. After the cold flow measurements were taken in argon, the thrust stand was accidentally disabled, by inadvertantly overrunning the potentiometer used to detect the position of the torsion wire, thus dislodging the potentiometer and making it impossible to record the position accurately. This was not expected to be an important loss of data, since the thrust stand could be easily repaired, though it would require a major interruption in the program to open the vacuum tank to make the repairs, and the runs could be repeated later. In addition, the approximately 12 cm. of cooled 22 mm. quartz tube below

the nozzle would interfere with the free expansion of the gas and limit the accuracy of the thrust measurements. The hot flow experiments were done, without the thrust stand, and the plasma stayed above the nozzle, producing gas-dynamic temperatures of 360 to 570 K, increasing with increasing flow rate, and other results paralleled the earlier runs.

Then, the thrust stand was repaired, and the cooling air was repiped, so that it would flow co-current to the plasma gas. The experiments were repeated, to see what effect the coolant flow geometry might have. With hydrogen or nitrogen as the working fluid, the gas-dynamic temperature was a consistent 430 K, and the hot thrust 115 per cent of the cold thrust, regardless of flow rate. In argon, the gas-dynamic temperatures ranged from 480 to 720 K, with thrusts 123 to 130 per cent of the corresponding cold flow values, varying directly with the flow rate.

The nozzle plug was then moved to the end of the tube, some 14.5 in. (35 cm.) below the cavity, and, after the first cold-flow measurements, the thrust stand was again accidentally disabled. Pressing on, despite this, though with the free expansion into the tank the thrust measurements would be most accurate with the nozzle there, but they could be made again after the tank could be opened again, the experimental series was repeated with the cooling air flowing both co-current and counter-current to the plasma gas. In either hydrogen or nitrogen, the gas-dynamic temperature was 400 K with co-current air flow, regardless of gas flow rate, but barely above the ambient 300 K with counter-current air flow. In argon plasmas, the gas-dynamic temperature depended directly on the argon flow rate, ranging from 300 to 378 K in countercurrent flow and 460 to 630 K in co-current.

While the tank was opened to move the nozzle plug back to 2.5 in. (6.4 cm.) below the cavity, the thrust stand was repaired again. Then the experimental series was repeated, with co-current cooling air flow. Nitrogen and hydrogen continued to yield parallel results, recording gas-dynamic temperatures of 570 K, and thrusts of 120% of the cold flow values, again nearly independent of gas flow rate. The much higher pressures associated with the higher argon flows moved the nozzle plug again, to 8.5 in. (23 cm.) below the cavity, during the cold flow measurements. The nozzle was moved again to 5.5 in. (14 cm.) below the cavity, and the series of experiments was repeated with co-current air flow. In the diatomic gases, the thrust increased 15 to 20 per cent when the plasma was turned on, and the gas-dynamic temperature reached 450 K, with little flow rate dependence. In argon, the tendency of the nozzle plug to creep downstream under the pressure difference could be allowed for by alternating hot and cold runs at the same flow rate. The gasdynamic temperatures were quite erratic, around 660 K, and the thrust increased between 16 and 30 per cent over the cold-flow values.

The dependence of gas-dynamic temperature with distance below the cavity, shown in Figure 8 for hydrogen, with all flow rates shown and not differentiated, as there was little consistent correlation between flow rate and gas-dynamic temperature, as seen in Figure 9, save that the coolant flow geometry is distinguished by the different symbols, seemed most strongly determined by the heat transfer to the cooling air. If the air and either diatomic gas were flowing counter-currently, the relatively cool (300 K) inlet air would cool the plasma gas from the plasma temperatures nearly to its own temperature within 6 cm. The air temperature would be raised only very slightly by this, however, and the



Figure 8. Gas-Dynamic Temperature vs. Distance From Plasma In Hydrogen - All Flow Rates



Figure 9. Gas-Dynamic Temperature vs. Mass Flow Rate In Hydrogen - 6.4 cm Below Plasma

rest of the heating of the cooling air would take place from the plasma itself. When the fluids were in co-current flow, the gas-dynamic temperature profile would be roughly what would be expected in a co-current double pipe heat exchanger. In argon (Figure 10) the heat transfer downstream from the plasma was somewhat less efficient than in the diatomic gases. Still, most of the heat transfer would occur directly from the plasma. At most, 12% of the cooling air heat load could be accounted for by transfer from the plasma gas below the plasma.

A minor problem developed in co-current air flow. The downstream port on the straight, jacketed tubes (see Figure 5(b)) was, when the tubes were installed, inside the vacuum tank, and a short length of rubber hose was used to connect the port to a vent through the tank wall. During counter-current flow, this was the inlet for the cooling air, so cool air was fed through the hose. However, in co-current flow, this was the outlet for the cooling air, and the air could be so hot that the hose would fail. To prevent this, the air flow had to be kept high enough that the hose could handle the exit temperature of the air.

Next, a capillary flow tube was installed. No plasma was attained in this configuration. The gas in the central bore could not be made to break down, though the residual gas in the vacuum jacket sometimes would.

The 22-mm. i. d., quartz nozzle tube (Figure 5(c)) was the next configuration tried. The long period transients found in earlier vacuumjacketed tubes recurred. Despite the vacuum jacket, its outer wall was hot to the touch below the plasma cavity, and the inside of the resonant cavity was also hot, when the plasma was lit. A thermocouple stuck into



the cavity read over 200 F, 360 K, though the electromagnetic fields in the cavity may have distorted the readings.

An attempt was made to excite the TE_{012} mode of the cavity, that should concentrate the electric field strength near the axis of the cavity and of the coaxial plasma tube. Empty cavity studies predicted that the mode could be found in a cavity 6.8 cm. long, with a probe very near the wall. A resonance was found, at cavity lengths between 7 and 7.2 cm., depending on the plasma pressure, with the probe around 7 cm. from the cavity axis. At low pressures, the local minimum of reflected power found here was much higher than the minimum found at around 9.8 cm., which had been used so far. But, at higher pressures, the reflected power in the longer mode climbed, while that in the shorter mode dropped (see Figure 11). The new mode could sustain plasmas with around one per cent reflected power to as high pressures as were studied, to failure, melting through the inner tube, of the vacuum-jacketed tubes.

When this happened, at a plasma pressure of 60 Torr of hydrogen, the quartz nozzle tube was replaced with another of the straight tubes, with a boron-nitride nozzle end plug, putting the nozzle again about 35 cm. below the cavity. To inhibit surface recombination, this tube had been coated with Dri-film (R), however, no substantial difference in system performance was noted.

Specific Impulse - Measured and Theory

The measured specific impulse $(I_{sp}(m))$ reported here was determined, as described in the Introduction, by dividing the thrust measured


using the thrust stand, in Newtons, by the gas flow rate, in kilograms per second, and dividing again by the standard acceleration of gravity, 9.8 meters per second per second. Any gas at absolute temperature T_0 , when allowed to flow through a perfect nozzle into a perfect vacuum, will generate a thrust equivalent to that produced by converting the enthalpy needed to raise the gas from absolute zero to T_0 to linear kinetic energy of the gas (Shapiro [1953]). The theoretical specific impulse, I_{sp} (th), corresponding to this may be computed by the following equations, which assume constant heat capacities:

$$I_{sp}(th) = (2 C_p T_0 / M_w)^{1/2} / g (3a)$$

or

$$I_{sp}(th) = (2 \gamma R T_0 / (\gamma - 1) / M_w)^{1/2} / g (3b)$$

The efficiencies given in Table 5 were computed by dividing the measured specific impulse by the theoretical specific impulse given by equations (3), assuming the zero-dissociation gas-dynamic temperature, and zero dissociation in the stream. The corrected temperatures and estimated dissociations were calculated by assuming the nozzle efficiency remained constant from the cold to the hot flows, and solving equations (2) and (3), with the dependence of specific heat on composition, for the concentration and temperature that provided the measured back pressure and specific impulse ratio.

Thrust Measurement Study

An extensive study was done, at 600 W incident microwave power. using the 7-cm cavity mode, with hydrogen as working fluid over the range of flow rates 220 to 1400 μ mol/s and corresponding plasma pressures of 12 to 57 Torr, with 4.7 g/s cooling air flow, the nozzle at the end of the tube, some 36 cm below the cavity, and into both ranges of tank pressure. The results are shown in Table 5, and the specific impulse is plotted vs. flow rate in Figure 12. The theoretical specific impulses are computed based on a non-dissociated hydrogen flow at room temperature, about 300 K, for the cold flow cases and at the gas-dynamic temperature for hot flow. There was some increase in measured specific impulse with flow rate, both with and without plasma, at high tank pressures. At low tank pressures, the measured specific impulse declined very slightly with flow rate. There was a slight kink, in that the very lowest flow rate showed a higher specific impulse than did the next higher ones. The measured specific impulse at low tank pressures was from two to five times as high as that the corresponding flow rates produced at the high tank pressures, when there was no such dependence expected. This was all independent of whether there was a plasma or not, and the ratio between the hot and cold flow values remained roughly constant, and comparable to the pressure ratios, consistent with using the gas-dynamic temperature as the gas temperature. At the low tank pressures, as can be seen in Figure 12, the cold flow specific impulse was measured to be higher than that predicted by an ideal, adiabatic, expansion into a perfect vacuum (as after Shapiro [1953]). Similarly, so was the hot flow value, if one assumed zero dissociation and used the

[a] High Back Pressure						
Gas Flow Rate (10 mol/s)	220	360	500	600	1100	14 00
Cold Flow:						
Thrust (mN)	.30	.52	.72	1.02	2.41	3.58
Pressure (Torr)	10.0	15.0	20.0	25.0	40.0	50.0
I _{sp} [m](s)	72	75	74	81	113	132
I_{sp} [Th] (s)	290	290	290	290	290	29 0
Efficiency	.25	.26	.26	.28	.39	.46
Tank Pressure (mflorr)	1.9	2.8	3.2	3.6	4.4	5.2
Hot Flow:						
Absorbed Power (W)	539	600	599	600	596	597
Cooling Air:						
Flow (g/s)	4.7	4.6	4.6	4.7	4.7	4.7
Outlet Temp. (K)	375	385	383	382	376	374
Heat Load (W)	392	423	414	407	392	384
Pressure (Torr)	11.7	17.6	23.2	28.9	46.24	57.5
Gas Dynamic Temperature (K)	405	405	405	395	394	391
Thrust (mN)	.46	.62	.91	1.17	2.77	4.07
I _{sp} [m](s)	107	89	93	94	130	1 50
I _{sp} [Th] (s)	340	340	340	336	336	334
Efficiency	.31	.26	.27	.28	.39	.46

.

Table 5. Experimental Results.

Table 5 (cont'd.)

[b] Low Back Pressure						
Gas_Flow Rate (10° mol/s)	220	350	500	640	1100	1400
Cold Flow:						
Thrust (mN)	1.44	3.29	3.21	4.14	6.85	8.63
Pressure (Torr)	9.8	15.0	20.0	25.0	40.0	50.0
I_{sp} [m] (s)	337	333	331	333	324	318
I_{sp} [Th] (s)	290	290	290	290	290	290
Efficiency 1	1.16	1.15	1.14	1.15	1.12	1.10
Tank Pressure (mTorr)	.048	.074	.14	.16	.24	.3
Hot Flow:						
Absorbed Power (W)	532	548	556	566	558	553
Cooling Air:						
Flow (g/s)	4.7	4.7	4.7	4.7	4.7	4.7
Outlet Temp. (K)	376	377	378	378	374	373
Heat Load (W)	392	397	400	400	384	376
Pressure (Torr)	11.6	17.3	23.1	28.8	46.0	57.2
Gas Dynamic Temperature (K)	413	408	404	407	398	393
Thrust (mN)	1.61	2.64	3.67	4.66	7.78	9.74
I_{sp} [m] (s)	381	385	378	374	367	359
I_{sp} [Th] (s)	344	342	340	341	337	335
Efficiency	1.11	1.13	1.11	1.10	1.09	1.07
Dissociation	.183	.064	.092	.175	.095	.082
Corrected	349	384	370	346	364	363

Gas Dynamic Temperature (K)



Figure 12. Specific Impulse vs. Mass Flow Rate In Hydrogen Effect of Plasma and Tank Pressure

zero-dissociation gas-dynamic temperature to compute the specific impulse. So, for that matter, was the hot flow value higher than that computed by assuming a constant nozzle efficiency to estimate the atom concentration and a corrected temperature, the last two lines in Table 5, since the cold-flow efficiency was over 100 per cent.

The increased specific impulse, at constant gas-dynamic temperature, at the higher flow rates and tank pressures, is most likely due to pluming effects, with higher flow rates producing narrower jets of gas. In addition, at low flow rates and high tank pressures, the flow through the nozzle can separate from the nozzle walls, and the environmental gas flows into and increases the boundary layer, thus decreasing the nozzle's efficiency of expansion. A third effect may occur when the pressure is low enough that free molecular flow occurs, and the recoil from the molecules bouncing off the target may as much as double the thrust measured with a target-type thrust stand above that measured by a stand that measures the thrust imparted to the engine itself. Even these tests have been reported to show some dependence of the measured specific impulse on the background pressure. Since no effort was made to hold the tank pressure constant, the vacuum system maintained different tank pressures at different flow rates. This might explain the observed flow rate dependence at low tank pressures and at the lowest flow rates at high tank pressures, as a small fraction of the difference between the two tank pressure ranges.

Attempts to operate a transpiration flow tube proved unsuccessful. Thermal shock would crack the porous ceramic (alumina) tubes, changing the uniformity of the porosity. Breakdown in the inlet jacket also proved problematic. Last, and most important, the plasma had a tendency

to migrate into the dead area of the tube above the transpiration flow region, so much of the gas would end up by-passing the plasma entirely.

Discussion

To gain some idea of the performance of a practical microwave plasma electrothermal rocket, based on the experimental results, it is useful to construct a theoretical engine concept whose performance may be extrapolated from the performance of the experimental system. For this theoretical performance, all of the energy that was lost to the cooling air, in the experimental system, is assumed to be confined to the working fluid, and heating it further, with all other energy losses assumed to be constant. Table 6 compares this theoretical thrust with the thrust measured in the experiment for a selected number of runs from those included in Table 5. For each case, the measured thrust and cooling air heat load are listed, with the measured specific impulse. Then, a computed specific impulse and thrust, with the ratio between the measured thrust and that computed, an efficiency, for three conceptual, idealized, models of the engine. First, for ideal nozzle flow, assuming the zero-dissociation gas-dynamic temperature and zero dissociation in the working fluid. This efficiency is called the nozzle efficiency, though it obviously includes the characteristics of the thrust stand. Then. the ideal nozzle performance of the theoretical system, in which all the heat taken off by the cooling air is retained within the working fluid. Last, the performance that might be measured if the nozzle efficiency, the ratio of the the measured performance to the ideal, was the

		Experimen	ntal Result	S
Mass	Tank Pressure Regime	Thrust	Specific	Cooling Air Heat Load
(mg/s)		(mN)	(s)	(W)
.436	High	.46	107	392
.433	Low	1.6	381	392
2.17	High	2.8	130	392
2.16	Low	7.8	367	384
4.28	High	7.5	178	394
4.28	Low	14.7	350	376

Table 6. Theoretical Thrust Efficiencies

Ideal Nozzle Flow

Mass Flow (mg/s)	Tank Pressure Regime	Gas-Dynamic Temperature (K)	Predicted Thrust (mN)	Specific Impulse (s)	Nozzle Efficiency (%)
.436	High	410	1.5	350	31
.433	Low	420	1.5	355	107
2.17	High	400	7.4	347	37
2.16	Low	405	7.4	349	105
4.28	High	395	14.5	346	51
4.28	Low	395	14.5	346	101

Table 6 (cont'd.)

.433

2.17

2.16

4.28

4.28

LOW

High

Low

High

LOW

Mass Flow (mg/s)	Tank Pressure Regime	Predicted Thrust (mN)	Specific Impulse (s)	Efficiency
(()		(0)
.436	High	18.7	4338	2.5
.433	Low	18.7	4354	8.8
2.17	High	42.7	1999	6.5
2.16	Low	41.4	1954	19.8
4.28	High	60.1	1426	12.5
4.28	Low	58.7	1395	25.
	Theoreti	cal - Real M	<u>lozzle</u>	
Mass	Tank Pressure	Predicted	Specific	Efficiency
(mg/s)		(mN)	(S)	(%)
.436	High	5.6	1326	8.1

20.0

15.9

43.6

30.8

59.1

4672

749

2055

734

1441

8.2

17.

18.

24.

25.

Theoretical - Ideal Nozzle

same in the theoretical system as in the real one. Since these efficiencies are the ratios of the thrusts, and the energy involved is proportional to the square of the thrust, squaring the given efficiencies will give the efficiencies in energy terms.

Estimating temperatures from these theoretical performances, by solving Equation 3a for T_0 , gave values ranging from 6500 K at the highest flow to 63,000 K at the lowest, with no dissociation. Under the conditions of the experiment (Table 5), adiabatic thermal dissociation would bring the atom-molecule mixture to equilibrium at about 30 per cent dissociated and 3100 K at the highest flow rate/pressure, and full dissociation, 100 per cent atoms, at 34,000 K at the lowest flow and pressure. This would reduce the ideal nozzle specific impulse, to 1070 seconds in the first case and to 3800 seconds in the second. These extreme predicted temperatures, particularly at low flow rates, demonstrate the "overkill" inherent in the experimental arrangement. The microwave flux incident on the cavity is so high that, especially at low flow rates, there is no practical mechanism by which the working fluid can absorb more than a small fraction of the incident microwave energy.

This may explain, to some degree, the need for cooling the plasma cavity, by showing how much of the microwave power absorbed by the cavity cannot be taken off by the working fluid without drastic effects. However, it seems more complicated than that, since plasmas have been maintained for long periods at low flow rates, and incident power levels similar to those used in the experiments described above, without any cooling of the plasma chamber. On the contrary, the cooling air jacket can be sealed off and evacuated, in an attempt to insulate the plasma

chamber and the recombination zone from their surroundings. Even so, with that path by which energy might leave the plasma cut off, and all the energy absorbed by the plasma supposedly remaining in the working fluid, the performance never approached the theoretical levels predicted above. There was, at best, a negligible improvement in the performance over that in cooled plasma tubes. How the energy is lost from the plasma gas remains unexplained. The observed heating of the outer wall of the vacuum jacket and inside the resonant cavity suggests that the vacuum jacket is not the insulator it was expected to be. Perhaps there were radiative losses, though in what wavelength is unknown. There was not enough visible light given off by the plasma to account for more than a small fraction of the lost energy. Another consideration comes from the manner in which plasma tubes fail while holding plasmas. At low flow rates and pressures, even vacuum-jacketed tubes can hold a plasma for long periods, with no maximum time yet found, under some conditions. However, at high flow rates and pressures, the tube fails quickly. The power that must be absorbed by the walls is (very slightly) higher at low flows than at high, for the same absorbed power. Hence, it might be expected that the tube walls might fail at least as fast in low flows as in high. The greater stress due to the greater pressure at high flows may lead to faster failures at high flow rates, however. Air-cooled tubes have also failed, though, at very high plasma pressures and flow rates, though the pressure was still very much lower than the over atmospheric pressure in the cooling air jacket. Since the differential pressure across the wall of the tube is actually less at higher plasma pressure, when the jacket is open to the atmosphere, the stress on the wall in a cooled tube is less, hence it should not fail so fast. What

appears to happen is that the plasma shrinks at higher pressures, and the energy transfer to the wall must pass through a smaller area. The quartz of the tube walls cannot conduct the heat away fast enough, without heating up at the contact point, and the smaller the area the hotter it gets, and, eventually, it melts.

There are a number of ways to improve the experimental design to avoid the problem of overcooling the gas. The microwave power level must be better matched to the capacity of the gas. The cavity resonant mode and the gas flow pattern can be selected to reduce the danger to the tube walls. One potential method, transpiration flow, was tried and could not be made to work. The distance between the plasma and the nozzle can be reduced to reduce the downstream cooling, it is to be hoped, without reducing the accuracy of the thrust measurements. A possible alternative design, for both experiment and applications, is regenerative cooling, where the feed to the plasma is ducted past the nozzle to cool the nozzle and pre-heat the feed. This is a common design in more conventional chemical rocketry. Another possible experimental arrangement, under discussion when this work was being done, would be to mount the entire cavity, plasma tube, and nozzle in a vacuum tank, on a thrust stand. This would help diagnose the origin of the back-pressure dependence, by determining whether the effect is due to the interaction between the impinging jet and the vane. It would also help reduce the effect of cooling by reducing the distance that would be required between the plasma and the nozzle.

Chapter 5 - VIBRATIONAL ENERGY MODELING

An important consideration in evaluating the practical utility of the microwave-plasma electrothermal propulsion system is the rate of energy release in the recombination reaction. A side factor in this consideration is the form which the energy, when released, should take. On the microscopic scale, this energy can take the form of translational kinetic energy, vibrational energy, or rotational energy. The latter two are also called internal energy of the molecules. This internal energy is not to be confused with the thermodynamic internal energy of the gas, which includes the translational energy on the molecular level. The first is most useful, as what is usually called heat is the randomly directed kinetic energy of the molecules of a substance, and thermodynamic effects transform this random motion into directed motion in a nozzle, to produce thrust.

The conventional assumption in chemical reaction engineering is to assume that the energy is immediately manifested as heat, and that the internal energy of the molecules is either negligible, or reaches equilibrium, thermalizes, quickly. However, the exact pathway of the transformation of energy from chemical potential energy through internal energy to translational energy greatly influences the rate of the reaction, as well as the rate at which the reaction generates useful energy. Theoretical models (Whitlock, <u>et al</u>., [1974]) of the hydrogen recombination reaction propose that highly vibrationally-rotationally excited states may serve as transition states, and experimental reaction rate determinations (Trainor, <u>et al</u>., [1973]) provide some support to the models. Simulations of the recombination reaction (Levitskii and Polak,

[1973]) suggest that, at very high temperatures, over 80 per cent of the recombination energy may be manifested as internal energy of the recombined molecules. In addition, experimental results (Villermaux, [1964a,b]) have been interpreted as showing a "high" degree of vibrational excitation, and "slow" relaxation to translational energy, in the recombined molecules. However, the extent of the excitation and the rate of relaxation were not clearly quantified.

This could be significant, because, if the recombined molecules still possess a significant fraction of the energy of recombination as internal energy when they reach the nozzle exit, the performance of the rocket could be seriously degraded from that predicted based on the normal assumption of total thermalization of internal energy. A study was therefore done to examine the effects of vibrational excitation on the performance of a hydrogen-propellant, microwave-plasma, electrothermal propulsion system. Rotational energy, since the levels are so much more closely spaced than the vibrational levels, was assumed to thermalize much more quickly than the vibrational energy, hence vibrational relaxation would provide an upper bound for the total relaxation of internal energy.

One of the models of the recombination section, below the plasma, was modified to account for above-equilibrium vibrational excitation of the recombined atoms, and for collisional relaxation of this excitation. To model the vibrational excitation, the hydrogen molecular gas was modelled using two temperatures: the translational temperature T, which describes the distribution of translational kinetic energy; and the

vibrational temperature T_V , which describes the distribution of vibrational energy, as described by a simple one-dimensional oscillator model. The vibrational energy E_V is given as a function of T by the following equation (Herzberg [1950]):

$$E_{V}(T) = N_{Av} h \nu / (e^{h \nu} / k T - 1)$$
 (4)

where N_{AV} is Avogadro's number, h is Planck's constant, ν is the groundstate frequency of the oscillator, and k is Boltzmann's constant. Differentiating this with respect to T gives a vibrational heat capacity C_{PV} :

$$C_{PV}(T) - (E_V(T) / T)^2 e^{h \nu / k T} / R (5)$$

where R is the gas constant.

The energy of recombination was computed based on both T and $\rm T_V$ by:

$$DH_R(T,T_V) = DH_R(0.,0.) + 3/2 R T - E_V(T_V)$$
 (6)

with $DH_R(0.,0.)$ computed so that $DH_R(298,298)$ agrees with the literature values for the standard heat of dissociation for hydrogen. If it is assumed that the energy of recombination is distributed between translational and vibrational energy so that Y $DH_R(T,T_V)$ goes into vibrational energy, and (1 - Y) $DH_R(T,T_V)$ goes into translational energy, where Y is a parameter between 0 and 1, the mass, translational energy, and vibrational energy balance equations in an adiabatic, gas-phase, plugflow reactor can be written as follows:

$$F dX/dz + r_{H_2} A = 0 (7)$$

$$-F [(1 - X) C_{PH_2} + 2 X C_{PH}] dT/dz + ((1 - Y)(-r_{H_2})[-DH_R(T,T_V)] + k_{VT} [E_V(T_V) - E_V(T)]) A = 0 (8)$$

$$-F (1 - X) C_{PV} dT_V/dz + (Y (-r_{H_2}) [-DH_R(T,T_V)] - k_{VT} [E_V(T_V) - E_V(T)]) A = 0 (9)$$

where F is the molar flow rate based on undissociated hydrogen, X is half the flow rate of hydrogen atoms divided by F (the fraction dissociated), A is the cross-sectional area of the reactor, z is the distance along the reactor, r_{H_2} is the rate of production of molecular hydrogen per unit volume by recombination, and k_{VT} is the rate of collisional vibrational-translational relaxation, per unit volume.

The adiabatic inviscid-flow reactor model (Eqns. (13), (15), and (16), p.83, below), with Equation (9), properly transformed, added and Equation (15) modified to:

$$\frac{\{m_0 \ u_b^2 \ / \ g_c \ [1 \ / \ (1 \ + \ X) \ dX/dz \ - \ dA/dz \ / \ A] \ +}{(1 \ - \ Y) \ DH_R \ dX/dz \ + \ k_{VT} \ A \ [E_V(T_V) \ - \ E_V(T)] \ / \ F\}}$$
(8a)
$$(m_0 \ u_b^2 \ / \ g_c \ T \ + \ C_P)$$

was solved using Computer Program 1 in Appendix B, via a Runge-Kutta-4 method, as described in Appendix A. The parameter Y was treated as a constant, user adjustable parameter, over each run of the computer program.

Figure 13 shows the output from a number of simulations using this model, using the parameters of the modelled run (Table 8, p. 85), with initial temperature 300 K and values of Y of 0., 10^{-5} , and 10^{-3} . The Figure shows the translational temperature profile for all three cases (solid curve), indistinguishable at the scale of the Figure, and the vibrational temperature profiles for the three values of Y and corresponding initial values for vibrational temperature of 300, 400, and 600 K (shortest, medium, and longest dashed curves, respectively). The initial values of the vibrational temperatures were selected to minimize the steepness of the initial portions of the curves, since any value selected would very quickly reach the same profile, as seen in Figure 14. It is also expected that, with finite values of the Y parameter, there would be some population of excited molecules leaving the plasma. The dissociation within the plasma would be accompanied by recombination, the plasma conditions merely throwing the equilibrium towards the atoms side of the reaction. Thus, at finite values of Y, there would be some vibrational excitation generated within the plasma. The shortest dashed curve is seen to drop below the solid curve, and so do both other dashed curves, where they meet, though the scale of the Figure is too large to show this. This is due to the fact that the heat of recombination includes some vibrational energy when assuming equilibrium thermalization, hence there is an equilibrium value of the parameter Y, and if the value of Y input to the program is less than this equilibrium value, the vibrational temperature will lag behind the translational temperature.







Figure 14. Modelled Translational and Vibrational Temperature Profiles - XO = 0.99 - Y = 1. (Low Pressure)

Experimentation with the program, at very short reactor lengths, showed that T_{ij} very quickly, on the order of microseconds in residence time and microns of reactor length, reaches values close to the curves shown if the assumed initial value is varied. This is shown in Figure 14, where the two curves, (b) and (c), vary only in their initial value for T_{y} . To save computational time, T_{y0} should be selected so that dT_{y} /dz is zero at the start of the reactor, which is an option in the program, selected by feeding an initial value of T_{y} less than 0. Figure 14 shows the output for the modelled run (Table 8, p. 78), with initial dissociation 0.99 and parameter Y = 1.0, showing the translational temperature profile (solid curve), and vibrational temperature profiles for initial vibrational temperatures of 1200 K (longer dashed curve) and 3000 K (short dashed curve). The small increase in the translational temperature reflects the small degree of recombination that takes place in the very low residence time of the simulated length of reactor. The vibrational temperature has, very quickly, reached a very nearly constant value, about 40 K above the translational temperature. Figure 15 shows the translational (solid curve) and vibrational (dashed curve) temperature profiles for the same parameters as in Figure 14, with initial vibrational temperature of 3000 K and at a pressure a hundred times higher, some 3.5 atm. Within the 1.5 nanometers of reactor length plotted in the Figure, the vibrational temperature drops to about 70 K above the translational temperature, and slowly continues to drop.

Figures 14 and 15 show that, at high temperatures, the vibrational temperature very quickly reaches a value somewhat above the translational temperature, even with the assumption of Y = 1.0, and thereafter



Figure 15. Modelled Translational and Vibrational Temperature Profiles - XO = 0.99 - Y = 1. (High Pressure)

the difference between the two temperatures decreases very slowly. This relaxation takes place on a time scale on the order of $.1 \mu$ sec, compared to the msec time for the reaction and residence time in a recombination reactor. It appears that the vibrational temperature has reached a quasi-steady-state value, at which the rate of excitation from recombination is almost exactly balanced by an equal rate of collisional relaxation. At very much lower temperatures, the initial difference is much larger, as at small Y it is very noticeable, and the difference drops much more slowly to the steady-state value, on a msec time scale. This suggests that an important value is this steady-state value, or offset, that difference between the vibrational and translational temperatures at which collisional relaxation transfers energy out of the vibrational mode as fast as the recombination reaction adds energy to the vibrational mode. This is determined by setting dT_v/dz in equation (9), above, to 0, and solving the following equation for $T_{\rm V}$ at a given T, X, P, and Y:

$$\{Y (-r_{H_2})[-DH_R(T,T_V)] - k_{VT} [E_V(T_V) - E_V(T)]\} A = 0$$
 (10)

which is transformed to:

$$(Y - r_{H_2})[-DH_R(T,0)] + k_{VT} E_V(T) \} / (Y (-r_{H_2}) + k_{VT}) - E_V(T_V)$$
 (11)

Table 7 gives the results of solving this equation, based on certain assumptions. The offsets T_V -T as given in the table are linearized, assuming that:

$$E_{V}(T_{V}) - E_{V}(T) - C_{PV}(T) (T_{V}-T)$$
 (12)

x	T(K) 300	0	5	500	700		100	0
	<u>⊥</u>	<u>T</u> e <u>−</u> T	<u>Ty-T</u>	<u>Te-T</u>	<u> </u>	<u>e</u> T	<u>⊤v-</u> ⊤	I <u>I</u>
	YP	YP	YP	YP	YP	YP	YР	YP
	(K/Pa)	(K/Pa)	(K/Pa)	(K/Pa)	(K/Pa) (K	(/Pa) ((K/Pa) (K/Pa)
.01	7400.	1.8e-3	.020	5.1 0- 6	8.4 e- 5 3	.3 e- 7	1.4 e- 6	3.6e-8
.15	1.7 e+ 5	.033	.63	1.3 e- 4	2.7e-3 8	.7 e- 6	4.6 e- 5	9 .5e-7
.30	3.5 e+ 5	.052	2.1	3.4 e- 4	9.0e-3 2	.3e-5	1.6e-4	2 .5e- 6
.50	4.8 e+ 5	.048	6.2	6.6 e- 4	.027 4	.5e- 5	4.7e-4	5.0 e- 6
.70	5.6e+5	.031	17.	9.8 c- 4	.074 6	.8e-5	1.3e-3	7.6e-6
.90	6 .2e+ 5	.011	65.	1.2e-3	.31 9	.1e-5	5 .5e- 3	1.0e-5
1.00*	6.2e+10	0.	5.9e+7	0.	3.8e+6 0).	5 .9e +5	0.

Table 7. Temperature Offsets for Collisional Relaxation -Recombinational Excitation Vibrational Steady State

* As X goes to 1.0, total dissociation, offsets become independent of pressure. Table gives offsets computed near X = 1.0 at P = 100,000 Pa. T_V goes to infinity at finite $T_e - T$.

Notes: aen = a x 10ⁿ . Offsets linearized, assuming constant C_{PV} at value at T. True T_V values lower than table predicts. For example, at P = 100,000 Pa, T = 300 K, X = .01, Y = 1.0, table predicts T_V -T = 7.4 x 10⁸ K. Exact T_V value 2550 K. Most important at low temperatures.

This is valid here only if k_{VT} is much greater than Y (- r_{H_2}). Under this assumption, these offsets are directly proportional to [Y $(-r_{H_2})$] / k_{VT} , hence the table gives values of (T_V-T) / Y P. This linearization, particularly at low temperatures and high values of Y, greatly overestimates the vibrational temperature at steady state. Also, since $k_{\rm VT}$ is proportional to the molecular hydrogen density and to the total gas density, whereas the recombination reaction is three-body, at low atom concentrations and far from chemical equilibrium, the offsets are directly proportional to the pressure. Hence, the table gives values of (T_V-T) / Y P. At total dissociation, though, k_{VT} goes to 0, and the offsets become independent of pressure and of Y. The table gives linearized offsets $(T_{V}-T)$ computed for values of X close to 1.0 at 100,000 Pa, approximately 1 atmosphere pressure. Particularly at lower temperatures, the linearization with pressure may not exactly hold at lower dissociations, as well, and the numbers in the table were computed for a pressure of 100,000 Pa. The second column under each temperature in the table gives an estimate, similarly linearized, as to the total energy tied up in vibrational excitation at the steady-state, in terms of a temperature T_o, which is the temperature the gas would have if all the excess vibrational energy were turned to translational energy.

Since the offsets in Table 7 are given divided by Y, they can be interpreted as the offsets for Y = 1.0, and thus give the upper bounds for the offsets in any real case. The table shows that the offsets go up with fraction dissociated, as the recombination rate increases. However, the T_{p} -T offset peaks, and drops to 0. at full dissociation. This comes from the reduction of the population of hydrogen molecules as dissociation nears completion, and the vibrational temperature must be infinite for there to be a non-zero excitation energy with no molecules present. The offsets drop sharply with temperature, due largely to the increase in the rate of exchange relaxation, the dominant mechanism for collisional relaxation when there are atoms present. In exchange relaxation, a free atom strikes a vibrating molecule, and knocks one of the atoms in the molecule free, forming a less excited molecule with the remaining atom. Additional reduction with temperature comes from the reduction of the recombination rate, in both the rate constants and the concentrations of the atoms and of the third bodies.

In conclusion, the conditions necessary to reduce the influence of the internal energy of the recombined molecules on the macroscopic energetics of recombination are near-equilibrium dissociation, high temperatures, and low pressures. Under these conditions, any excess vibrational energy will relax down to thermal equilibrium, or as near as the recombination excitation will allow, very quickly, and the steadystate value will be close to true thermal equilibrium. In a practical microwave-plasma electrothermal rocket, however, high operating pressures are likely to be the rule, to force the recombination reaction towards completion, and generate high temperatures. However, the pressure dependence is much less than the temperature dependence. Under conditions that are somewhat conservative, for these considerations, for a practical electrothermal propulsion system, 3000 K temperature, and 20 atmospheres pressure, the T_a -T offset will be less than 0.3 K and the

relaxation to this value is likely to be on the order of microseconds, a negligible concern in the design of the system. The assumption of immediate thermalization will be sufficiently valid for accurate design.

Villermaux's experiments [1964a,b], which reported high vibrational excitation and slow relaxation, were performed at very much the other end of this regime. The temperatures were low, around 300 K, and the pressures were relatively high, 30 to 300 Torr. Under these conditions, very sensitive instruments may detect the temperature offsets of the magnitude calculated here.

Chapter 6 - COMPUTER MODELLING

In order to help design further experiments, and potentially to predict the performance of practical microwave-plasma electrothermal rocket systems, development of a numerical model of the recombination section, downstream of the plasma, of such a system was initiated. The recombination section is modelled as a gas-phase chemical reactor, with the reactants being a mixture of atomic and molecular hydrogen, and the main reaction being the reversible recombination of atomic hydrogen. The reaction rate constants and other physical constants used and their sources are described in Appendix C. The model has gone through a long and somewhat evolutionary process of testing and relaxation of assumptions, in attempting to fit the results computed from the model to the experimental data, to ascertain what factors need to be considered in the model, to verify the model's applicability, and to justify confidence in the model's predictions for further work. The reactor described by the model was an adiabatic, gas-phase, one-dimensional, plug-flow model at first. To make the model more realistic, and to correct the discrepancies found between the model and the experimental results, cooling, surface reaction, radial diffusion, making the model twodimensional, and last, axial dispersion were added in turn. The equations were solved, at first, as an initial value problem by a specially-written version of a fourth-order Runge-Kutta technique (see Appendix A), then, as difficulties with the dispersion model turned up, other implicit techniques were tried, culminating with the IMSL DGEAR subroutine.

Adiabatic, Gas-Phase, Plug Flow Model

As described in Chapman, <u>et al</u>. (1982), at that point the model was of a one-dimensional, adiabatic, gas-phase, inviscid flow, constant pressure reactor. The equations for the model were as follows:

$$dX/dz = A (k_1 [H] + k_2 [H_2]) ([H_2] - K [H]^2) / F (13)$$

 $dT/dz = - DH_R dX/dz / C_P (14)$

Inviscid flow pressure effects were added, after Shapiro [1953], for some inconclusive investigation of nozzle flow. This changed equation (14), above, and added another equation, as follows:

$$dT/dz = \frac{\left(\frac{m_0 u_b^2}{g_c} / g_c \left[1 / (1 + X) dX/dz - dA/dz / A\right] + DH_R dX/dz\right)}{(m_0 u_b^2 / g_c T + C_P)}$$

$$dP/dz = -m_0 u_b^2 / g_c \left[dT/dz / T + dX/dz / (1 + X) - dA/dz / A\right] \times P / [R T (1 + X)] (16)$$
Here we are the eigenberities in the flow equations at capic values.

However, the singularities in the flow equations at sonic velocity proved intractable, so the investigation was abandoned. Viscous losses were added to a model for a cooled reactor, changing the energy and mechanical energy balance equations to:

$$(m_{0} u_{b}^{2} / g_{c} [dX/dz / (1 + X) - dA/dz / A] + DH_{R} dX/dz - dT/dz = \frac{u_{b}^{4} f / [D_{i} R T (1 + X)] + U_{0} A_{s} (T_{c} - T) / F}{(m_{0} u_{b}^{2} / g_{c} T + C_{p})}$$

$$dP/dz = \{-m_{0} u_{b}^{2} / g_{c} [dT/dz / T + dX/dz / (1 + X) - dA/dz / A] - f u_{b}^{2} / g_{c} D_{i}\} P / [R T (1 + X)] (18)$$

The model considering viscous losses predicted, in the straight-tube geometry of the experimental apparatus, pressure drops much less than one percent of the total system pressure over the length of the reactor, so the viscous loss terms were neglected in further investigation.

This model, equations (13), (15), and (16), with parameters given in Table 8, yields the temperature profile shown in Figure 16. This modelled profile is so incompatible with the experimental profile shown in Figure 11 that is is obvious that the assumptions used in developing the model need to be reevaluated.

Table	8.	Parameters	for	Modelled	Run	
Tante	0.	Falametels	TOL	MODELLED	Kull	

Modelled Gas	Hydrogen
Initial Conditions	
Fraction Dissociated	0.10
Gas Temperature (K)	1200.
Gas Pressure (Torr)	26.5
Coolant Temperature (K)	400.
System Parameters	
Gas Flow Rate (mg/s)	0.77
Tube Internal Diameter (cm)	2.2
Coolant (Air) Flow Rate (g/s)	5.0
Coolant Flow Direction	co-current
Adiabatic Equilibrium Conditions	
Fraction Dissociated	0.02
Temperature (K)	2300.



Cooled Model

The change in the experimental profile with the change in coolant flow geometry argues for the inclusion of cooling of the modelled reactor, changing the energy balance equation to:

$$dT/dz = \{m_0 u_b^2 / g_c [dX/dz / (1 + X) - dA/dz / A] + DH_R dX/dz + U_0 A_c (T_2 - T) / F\} / (m_0 u_b^2 / g_c T + C_P) (19)$$

Simulations, by trial and error, assuming zero dissociation, constant coolant temperature and constant overall heat-transfer coefficient, produced some fairly good fits to the experimental results. In Figure 17, the solid curve, which corresponds to an initial gas temperature of 700 K, coolant temperature of 370 K, and overall heat-transfer coefficient of 1 W/m^2 K, is seen to fit the data from 6 cm out fairly well. However, the initial temperature is much lower than that measured at the exit of the cavity. The dashed curve in Figure 17 assumes a more realistic gas temperature of 1200 K, and requires a heat-transfer coefficient of 3.7 W/m^2 K to bring the temperature down to match the experimental 600 K at 6 cm, and a coolant temperature of 400 K to keep the temperature at 36 cm comparable to the experimental values. However, in between 6 and 36 cm, the model predicts a lower temperature than the experiment recorded, and the 400 K coolant temperature is somewhat higher than that used in the experiments.

To see whether these heat-transfer coefficients are indeed reasonable, the fluid-flow regime must be determined. Assuming the viscosity of the plasma is roughly that of normal, equilibrium-dissociated



hydrogen, reasonable at low dissociations, as the viscosity of atomic hydrogen is 0.7 times that of molecular hydrogen (Browning and Fox (1964)), close enough to 1.0 for these purposes, at the highest flow rate used in the experiments, 0.77 mg/s, that used in the sample run, the Reynolds number is about 5 at 300 K, and about 12 at 1200 K. This put the flow clearly in the laminar regime. The question of entrance effects must be considered, as the flow profiles in and exiting the plasma are unknown. Entrance effects in heat transfer are correlated by the Graetz number, the product of the Reynolds number, the Prandtl number, and the ratio of the diameter to the length of the tube. Theoretical analyses indicate that the Nusselt number reaches a limiting value of 3.66, in the case with constant wall temperature, for Graetz numbers less than 4.0 (Perry and Chilton, [1973], pp. 10-12,10-13). Since the Prandtl number for simple gases is about 0.7, at 1200 K, entrance effects are smoothed out after about 2 tube diameters, 4 cm in the experimental system, so the flow may be assumed to be fully developed laminar flow, with this constant Nusselt number, with reasonable accuracy.

The Graetz number dependence is such that the Nusselt number, and hence the heat-transfer coefficient, is infinity at the entrance to the tube, and decreases with tube length. This may suffice to produce the shift in heat-transfer coefficient predicted by the fitting of the model to the data. However, the entrance zone is very short, and the flow through the plasma is probably laminar already, hence, this effect is probably minor. At a constant Nusselt number and tube diameter, the heat-transfer coefficient is directly proportional to the thermal conductivity. Literature values for the thermal conductivity of hydrogen (<u>Ibid.</u>, p. 3-215) show a marked increase as the temperature goes up, by about a factor of 2.5 over the range from 400 to 1200 K. However, after correcting for an apparent error in the table in Perry and Chilton ([1973], p. 3-215) (see Appendix C), the internal heat-transfer coefficient, in the experimental system, for a Nusselt number of 3.66 should range from 37 W/m^2K at 400 K to 88 W/m^2K at 1200 K. From annulus flow correlations (<u>Ibid.</u>, p. 10-15) and the flow rate and properties of the air used as coolant, the heat-transfer coefficient in the cooling jacket is calculated to be around 75 W/m^2K . Thus, the overall heat-transfer coefficient should range from about 25 W/m^2K at a gas temperature of 400 K to about 40 W/m^2K at a gas temperature of 1200 K, well above the values that produced an apparently good fit. The temperature profile for the modelled run at zero dissociation and with a constant Nusselt number of 3.66 and assuming normal hydrogen thermal conductivity is shown in Figure 18.

Although assuming normal hydrogen thermal conductivity is only completely appropriate when zero or equilibrium dissociation is also assumed, for this work the assumption of a constant thermal conductivity with dissociation was made. First, it was made to simplify the computation, however, it can be readily justified on other grounds (see Appendix C).

Relaxing the initial assumption, of constant coolant temperature, by including the energy balance equation for the coolant in the model:

 $dT_c/dz = [-U_0 A_s (T_c - T) + U_o A_o (T_o - T_c)] / F_c C_{Pc}$ (20)


showed that the original assumption was largely justifiable. At the flow rates used in the experiments, the total heat content of the gas would not raise the coolant temperature more than around 5 kelvin. The second term in equation (20), above, allows for natural convective and radiative losses to the environment, with coefficients from Perry and Chilton [1973], p. 10-11. Inclusion of these effects has a larger effect on the coolant temperature than does the heat transfer from the gas, cooling the coolant by some 10 kelvin over the length of the reactor. The environment of the experimental system was fairly complex, and there was a fan blowing air across the outside of the cooling jacket between the cavity and the vacuum tank. The presence of this forced convective cooling was found to make a difference of about 5 kelvin in the outlet temperature of the cooling air. However, this additional cooling could not be modeled, but a 10 kelvin temperature drop for the coolant is probably conservative. All in all, although the measured coolant temperatures did not reach 400 K, assuming the coolant temperature to be a constant at this value is probably not an unreasonable simplification of the model. Even better is that used in the sample runs for co-current flow situations, with this temperature being the initial, cavity exit, temperature for the coolant. The maximum coolant temperature possible in the experiments was 420 K, which assumes that all the 600 W of microwave power absorbed by the cavity in a typical experiment was taken off by the coolant flow normally used.

As Figures 17 and 18 show, the good fit values for heat-transfer coefficients are much less than those calculated based on the properties of the gas. Thus, the simple, no reaction, heat exchanger model for the experimental system is inadequate, and reaction must be considered. Assuming a ten per cent initial dissociation, and gas-phase reaction only, in a cooled reactor, as per the modelled run, the model produced the temperature profile of Figure 19. The agreement with experiment is still poor, though improving, and trial and error on the initial conditions ought to produce even better fits. Before this was done, though, further testing of the assumptions in the model was done, to judge whether the further trial and error would be meaningful.

Surface Reaction

The next assumption to be checked was that of a gas-phase reaction only. The model was modified to include a second-order, reversible, surface recombination reaction, with rate constants after Wood and Wise [1962] (see Appendix C). The mass balance equation was modified to include surface recombination as follows:

$$dX_{v} / dz = A (k_{1} [H] + k_{2} [H_{2}]) ([H_{2}] - K [H]^{2}) / F (21)$$
$$dX_{w} / dz = A_{s} k_{w} ([H_{2}]_{w} - K_{w} [H]_{w}^{2}) / F (22)$$
$$dX / dz = dX_{v} / dz + dX_{w} / dz (23)$$

At first, it was assumed that the energy released in surface recombina-



tion would remain in the surface, and be taken up by the coolant, making the energy balance equations:

$$dT/dz = \{m_0 u_b^2 / g_c [dX/xz / (1 + X) - dA/dz / A] + DH_R dX_v/dz + U_0 A_s (T_c - T) / F\} / (m_0 u_b^2 / g_c T + C_p) (24)$$
$$dT_c/dz = \frac{[-U_0 A_s (T_c - T) + U_0 A_o (T_o - T_c) - F DH_{Rw} dX_w/dz]}{[-U_0 A_s (T_c - T) + U_0 A_o (T_o - T_c) - F DH_{Rw} dX_w/dz]} (25)$$

F_c C_{Pc}

Figure 20 shows the temperature profile for the sample run, under these assumptions, integrating equations (16), (21), (22), (23), (24), and (25), and it is virtually identical to that in Figure 18, which assumes no dissociation. The lower curve in Figure 21 shows, to a greatly enlarged axial scale, the simulated extent of dissociation under the assumptions of Figure 20. The upper curve in Figure 21 shows the same profile without surface recombination, replacing equations (21), (22), (23), and (24) with (13) and (20). Under the assumptions used here, the model predicts that surface recombination should consume nearly all the free atoms in the first tenth of a millimeter of the reactor. Under the assumption of total transfer of surface recombination energy to the coolant, little recombination energy remains to heat the gas.

The lowest curve in Figure 22 is the initial section of the temperature profile from Figure 20, expanded to the same axial scale as Figure 21. The top curve in Figure 22 is the temperature profile for a similar run, under the assumption that the surface recombination energy is taken up by the gas, then lost to the coolant by convection -integrating equations (16), (19), (20), (21), (22), and (23). The middle curve is an intermediate case, in which the surface recombination energy





Fraction Dissociated



is transferred to both the gas and the coolant by convection. This was done by estimating a wall temperature T_w such that:

$$F DH_{Rw} dX_w/dz = \{h_i (T_w - T) + h_c (T_w - T_c)\} A_s$$
 (26)

and rewriting the energy balance equations as follows:

$$dT/dz = \{m_0 u_b^2 / g_c [dX/dz / (1 + X) - dA/dz / A] + DH_R dX_v/dz + h_i A_s (T_v - T) / F\} / (m_0 u_b^2 / g_c T + C_p) (27)$$
$$dT_c/dz = [-h_c A_s (T_c - T_v) + U_o A_o (T_o - T_c)] / F_c C_{Pc} (28)$$

The middle curve in Figure 22 is, therefore, the result of integrating equations (16), (21), (22), (23), (27), and (28), such that equation (26) is satisfied. Although both the top and the middle curves in the Figure show a sharp peak in gas temperature, to above 2000 K, after the peak, the gas still cools far more quickly than the experiments reported.

So far, the surface reaction rate constants had been computed based on the bulk temperature of the gas. However, they should properly be computed based on the temperature of the surface. Since the wall temperature computed to satisfy equation (26) was usually much higher than the bulk temperature, when there was surface reaction, there should be a significant difference, by reducing the surface, and hence the total, recombination rate. A trial and error approach (see Appendix A) was implemented to solve equation (26) for the surface temperature at which the rate of energy generation balanced the rate of energy removal. Figure 23 shows the temperature profile under this "hot wall" assumption, for the gas, lower curve, and the wall, upper curve, to the scale of Figure 22. Figure 24 shows the gas temperature profile from the same





run to the scale of Figure 20. The peak in the gas temperature is moved downstream, but not sufficiently far to keep the gas from being cooled very quickly to the coolant temperature.

A further, similar consideration, is whether the surface reaction is diffusion controlled, under the experimental conditions. That is, it was to be considered whether the rate of recombination at the surface might be limited by the rate of transport of atoms to the surface. This was checked by calculating the value for the concentration of atoms at the wall such that the rate of convective mass transport of atoms to the wall would equal the rate of consumption of atoms in surface recombination, again, by trial and error (see Appendix A). The equation that had to be satisfied was as follows:

$$h_{m} A_{e} ([H] - [H]_{w}) / [1 + X_{w}/(1 + X_{w})] = F dX_{w}/dz$$
 (29)

The convective mass transfer coefficient was computed using a Sherwood number, analogous to the Nusselt number in heat transfer, and so, by a conventional analogy between heat, mass, and momentum transport (Bird, <u>et al</u>. [1960], p. 645) also assumed constant at 3.66. The diffusion coefficient and density needed for the Sherwood number computation were computed under bulk conditions. The gas temperature profile derived from integrating equations (16), (21), (22), (23), (27), and (28), such that equations (26) and (29) are satisfied, for the modelled run is shown, to the scale of Figure 21, in Figure 25, and, with the wall and coolant temperature profiles, to the scale of Figure 20, in Figure 26. The peak is shifted yet further downstream, very slightly, as the surface concentration, corresponding to 0.8 per cent dissociation against the bulk 10 per cent, is lowered enough to have an impact, however slight, on the





surface reaction rate. The surface reaction consumes the free atoms very quickly, even so, as shown by Figure 27, which compares the profiles of dissociated fraction for volume recombination only (upper curve) and for volume with surface recombination (lower curve), over the first 7 cm of the recombination zone.

Figure 28 shows the gas and coolant temperature profiles for the modelled run, but with counter-current flow geometry. This was simulated by making the coolant flow rate negative when it was input to the program. The initial coolant temperature was assumed to be 305 K, to allow for the expected heat load and the roughly 300 K inlet air temperature, at the far end of the recombination zone. The profile is nearly identical to that of Figure 26, the main difference arising from the different coolant, and hence ultimate, temperatures. The simulation agrees fairly well with the experiment, in this case, predicting that the gas temperature should reach equilibrium with the coolant very quickly.

The effect of the mass flow rate through the system is shown in Figure 29, which shows gas temperature profiles for runs at the lowest hydrogen flow rate, and the corresponding plasma pressure, used in the axial dependence studies, .055 mg/s and 4.26 Torr (short dashed curve), and at twice the modelled run's flow rate and pressure, 1.54 mg/s and 52 Torr (long dashed curve), alongside the modelled run (solid curve). The Figure shows that the temperature profile becomes independent of the mass flow rate, beyond 5 cm below the plasma, over the range of flows studied in the experiments, which agrees with the experimental results. However, the model predicts that this is due to the gas temperature







coming into equilibrium with the coolant, and approaching the coolant temperature. Since the coolant, even if it absorbed all the incident microwave energy, could not exceed 420 K, the model does not explain the 600 K reported gas-dynamic temperature.

Figure 30 shows the simulated gas temperature profiles assuming initial dissociations of 0., .1, .2, and .3, with other parameters as in the modelled run. The higher the initial dissociation, the higher and, very slightly, the broader the initial peak in the temperature profile. The peak still disappears by 5 cm, however. A higher initial dissociation is probably not realistic, and would not, probably, improve matters enough. Figure 31 shows the effect of raising the initial temperature to 1500 and to 1800 K, from the modelled run's 1200 K, holding all other parameters as in the modelled run. As with increasing the initial dissociation, the increased initial temperature raises the peak and broadens it slightly. The net initial rise actually decreases with increasing temperature, however, and the peak disappears within 4 cm of reactor length, anyway.

Figure 32 shows the gas temperature profiles for a non-dissociated and 0.1-dissociation run, with the heat-transfer coefficients multiplied by 0.1 from the literature values, and all other parameters as in the modelled run. Comparing these curves with the two lowest curves in Figure 30 shows a dramatic difference. The cooling is much slower, the peak temperature is higher, and the peak is broader. It seems to suggest that the correlations used to estimate the heat-transfer coefficients have given values that are too high, compared to the real values, since these profiles are well above the experimental profiles, and adjusting the initial conditions and the heat-transfer coefficients may serve to



T0 = 1800 K---T0 = 1500 K___ T0 = 1200 KTemperature (K) ż Ó i Reactor Length (cm)



Ż



Figure 32. Modelled Temperature Profiles - Conductivity 0.1 Hydrogen Initial Dissociation Effect

bring the simulation into line with the experimental results. Yet, the adjustment on the heat-transfer coefficients is not reasonable. Engineering correlations, as were used in the simulations, tend to be conservative. In heat transfer work, conservative values for heat-transfer coefficients tend to be underestimates, to ensure the heat-transfer apparatus will continue to perform its designed task, even if it is somewhat fouled.

Another use of this adjustment is to investigate, to a first approximation, the behavior of other gases. If the product of the flow rate and the heat capacity of the second gas is the same as the product of the input flow rate to the simulation and the heat capacity of hydrogen, and the heat-transfer coefficients multiplied by the ratio of the thermal conductivity of the second gas to that of hydrogen, the output of the model will approximate the performance of the second gas. This assumes that the same constant Nusselt number applies, making the internal heat-transfer coefficient solely dependent on thermal conductivity. This also involves neglecting the reaction, or requiring zero dissociation, and neglecting the differing dynamics and thermodynamics of compressible fluid flow for the different gases. In argon, the thermal conductivity is about one-tenth that of hydrogen (Perry and Chilton [1973], p. 3-215). The argon flow rate used in the experiments whose results are plotted in Figure 13 corresponds to the hydrogen flow of the modelled run, when corrected for the differing heat capacities. Since argon is a monatomic gas, the zero-dissociation curve in Figure 32 compares rather well with Figure 13.

The thermal conductivity of nitrogen is about 0.15 that of hydrogen (<u>Ibid</u>.) over the range 300 to 1200 K. Simulating the experimental runs

in nitrogen by the modelled run at zero dissociation and with the heattransfer coefficients reduced by this factor produced the gas temperature profile shown by the upper curve in Figure 33. Also shown on the Figure are the experimental gas-dynamic temperatures determined in nitrogen flows, with co-current coolant flow. The agreement between the computed profile and the measured one is remarkable. However, this was done for a flow rate corresponding to the highest nitrogen flow used in the experiments. Reduce the flow rate by a factor of five, to match the lowest experimental flow, and the model produces the temperature profile shown by the lower curve in the Figure. Since the experimental temperatures were very close together over the whole range of flow rates, as shown by the cluster of experimental points, the model obviously does not accurately reproduce this lack of dependence on flow rate. The counter-current coolant flow experiments, as shown in Figure 10, show a much larger dependence on flow rate, much more as a simple heat-exchanger model, such as this model at zero dissociation, would predict. Only the point at 6.4 cm below the cavity showed any residual heating in counter-current flow.

Two-Dimensional Model

Since this modelling has shown that consideration of surface recombination necessitates sharp radial gradients in temperature and concentration, under the conditions of the experimental system, a twodimensional model was developed to further investigate the system and, it was hoped, to model the results better. The Peclet numbers, relating the bulk flows of mass and energy to the diffusion and conduction,



respectively, are 0.88 and 1.2, also respectively, using the transport properties as calculated at 1200 K and the tube diameter as the defining dimension. This further suggests that radial diffusion and conduction should be important. The energy and material balances for a twodimensional model are as follows:

First, defining

$$dX/dz_{R} = (k_{1} [H] + k_{2} [H_{2}]) ([H_{2}] - K [H]^{2}) / G(r) (30)$$
$$dX/dz = dX/dz_{R} + D_{H-H_{2}} d(r d[H]/dr)/dr / G(r) (31)$$
$$dT/dz = [DH_{R} dX/dz_{R} + \lambda d(r dT/dr)/dr / G(r)] / C_{P} (32)$$

with boundary conditions in the radial direction:

from symmetry:

$$dX/dr|_{r=0} = 0$$
 (33)
 $dT/dr|_{r=0} = 0$ (34)

from mass and energy conservation in wall recombination:

$$d[H]/dr_{w} = k_{w} ([H_{2}]_{w} - K_{w} [H]^{2}) [1 + X_{w}/(1 + X_{w})] / D_{H-H_{2}} (35)$$

$$\lambda dT/dr_{w} = DH_{R} k_{w} ([H_{2}]_{w} - K_{w} [H]^{2}) / A_{s} - q (36)$$

where

$$q = -h_c (T_c - T_w) (37)$$

Additional terms, as in equation (15), were included in the energy balance equation (32) to account somewhat for inviscid flow effects. These inviscid flow terms were based on the bulk velocity, computed from the mass-average temperature and composition. Similarly, equation (16) was used to give the pressure dependence, assumed constant across the reactor, based likewise on the mass-average state. That is, the bulk temperature was computed assuming the heat capacity per unit mass was independent of the variation of composition or temperature across the tube. The mass flux down the tube was assumed constant with length, and parabolic in cross-section, that of an isothermal laminar flow. The radial diffusion term was modified to ensure this, transforming equation (31) to:

$$dX/dz = dX/dz_R + D_{H-H_2} d(r d[H]/dr)/dr / G(r) / [1 - X/(1 + X)] (38)$$

This provides for the equal-mass counterflow, also apparent in equation (36), the surface boundary condition providing for conservation of mass in the surface reaction.

These equations were solved by the method of lines, that is, each of the transverse derivatives was written in its finite-difference form, rendering the axial derivative at each station across the tube as a function of the conditions at the stations on either side, as well as those at the station itself. To help ensure the conservation laws were followed, the transport properties used in the transverse derivatives were computed at the arithmetic average of the temperatures of the two stations involved. In the finite-difference form used, the mass flux through each radial segment was taken to be the average value based on the parabolic profile, and the conditions were assumed to be uniformly that of the station within each segment, centered except for the outermost one, which was taken to be at the wall. The wall boundary conditions, equations (35) through (37), were not explicitly invoked in solving the equations. Instead, the outermost section was assumed to be at the wall conditions, and that section's material and energy balances included the wall recombination reaction and losses through the wall, along with flow through that section. The first station was located on the center line of the reactor.

Experimentation with the number of stations used showed that there little difference in the radial profiles when five or nine stations was were specified, under the standard set of parameters. Hence, for computational economy, five stations were used in the model computations. This model produced results much like the earlier ones (Figure 34). Though the bulk, or mass-average, temperature profile is a little closer to the experiment, the improvement is not significant. This figure also shows a temperature profile that makes allowance for the assumptions involved in the gas-dynamic temperature measurement (dotted curve) by allowing, to a first approximation, for the change in molecular weight and heat capacity due to dissociation. This curve shows roughly the gasdynamic temperature profile that would be estimated under the assumptions made in the experimental program if the model accurately reflected the experimental system. This predicted gas-dynamic temperature $T_g(e)$ is computed from the bulk temperature T by

 $T_{g}(e) = T (7 + 3 X) (1 + X) / (5 + X) / 1.4 (39)$

The closeness of the predicted gas-dynamic temperature curve to the bulk temperature partially validates using the experimental gas-dynamic temperatures as a reasonable estimate for the gas temperature, ignoring the inaccuracy implicit in the assumptions used in computing the experimental values. Figure 35 shows the bulk temperature profile at the lowest flow from the experimental series, and the model continues to



Figure 34. Modelled Temperature Profiles for Modelled Run Two-Dimensional Model - Five Stations





predict a much higher dependence on flow rate than the experiment showed.

Axial Dispersion Model

The next modification to the model that was considered was the inclusion of axial dispersion. Since the first data point in the experimental system was located about three tube diameters downstream from the plasma, the Peclet numbers using this distance as the dimension were about 3. This supports the idea that axial dispersion should be considered, as diffusional transport is thus a significant fraction of the bulk flow. Adding axial thermal conduction (through the gas) to the two-dimensional model changes the energy balance equation (32) to:

 $C_p dT/dz - \lambda d^2T/dz^2 / G(r) - [DH_R dX/dz_R + \lambda d(r dT/dr)/dr / G(r)] (40)$ and adds an additional boundary condition:

$$dT/dz|_{z=\infty} = 0$$
 (41)

Analogous modification to the material balance equation (21) allows consideration of axial diffusion, as well. Solution of these equations by reducing the second-order differential equations to first-order equations by using the first axial derivatives as dependent variables and using a Runge-Kutta marching technique (see Appendix A) to solve the coupled system proved to yield unstable solutions (See also Coste <u>et al</u>. [1961]). Coste's solution technique was adopted to find stable solutions. The non-dispersion equations were solved, first, by using an implicit cell model, which, as Coste shows, is roughly equivalent to a dispersion model if the cell length is chosen appropriately, based on

the relative magnitude of velocity and dispersion coefficient. The cell length used was computed based on the thermal conductivity at bulk (mass-average) temperature and bulk flow velocity, computed at (mass-) average temperature and concentration. Once the end of the reactor was reached, the reduced, first-order, dispersion equations were integrated backwards, using the Runge-Kutta techniques on an arc-length method to reduce the problems from stiff equations. In addition, the program was modified to explicitly solve the boundary conditions at the walls (Equations (23)-(25)), by the trial and error method described in Appendix A, in hopes of reducing the instabilities further. This changed the distribution of stations within the reactor, so that the first station was effectively half a cell-width off the center line of the reactor, and the last station an equal distance from the wall. The two-dimensional model, in this version, could be used to fairly mimic the most highly developed one-dimensional model by using one radial station. In effect, this use would be equivalent to a one-dimensional, axial-dispersion model with surface reaction and heat and mass transfer to the walls using constant Nusselt and Sherwood numbers of 4.0. This is not out of line with actual Nusselt and Sherwood number values for well-developed laminar flow (Perry and Chilton, [1973], pp. 10-12,10-13). Comparing Figures 34 and 35 with Figures 26 and 29, respecively, shows that the two-dimensional model actually made little difference in the profile in the plug-flow case, as well. Runs with one station were therefore used to test-run the model and conserve computation time.

On the forward, implicit, cell-model integration, this technique generated temperature profiles little different from the non-dispersed model. The temperature was somewhat higher around 5 cm. downstream, though not significantly, and the initial peak had been passed at the first cell. However, this technique, on the backwards integration, still produced instability, of the sort reported by Coste, <u>et al</u>. [1961]. Coste's method probably only allows for stable integration of equations within a certain range of parameters, such as the relations among flow rate, dispersion coefficient, and reaction rate. It seems likely that the system considered here does not fit in this range, and so cannot be integrated stably either backwards or forwards. Therefore, a new integration technique was adopted, an implicit version of the Runge-Kutta method, as described by Cash [1975] (see Appendix A). This technique proved to consume excessive amounts of computer time, as developed from scratch, so an implicit-method integrator routine from the IMSL library, their routine DGEAR, was selected and the program rewritten to access the integrator.

At first, the initial derivatives of temperature and concentration were assumed to be those computed without consideration of axial dispersion. This resulted in instabilities, including instances of predicted negative concentrations of hydrogen atoms, and temperatures oscillating up and down along the tube. Assuming zero initial derivatives produced better results, though with its own inconsistencies. The program has never modeled more than the first five mm of the reactor under these assumptions, due to some uncorrectable difficulty in solving the surface equations. Beyond a certain point, perhaps in a certain range of nearsurface conditions, possibly high dissociations at low temperatures, the solution techniques seem to fail to find a solution for the boundary conditions, and the program runs indefinitely. It is unclear what the conditions that cause this are, since it seems that the program had

little problem solving the equations under very similar conditions. Various techniques for solving the equations describing the boundary conditions have been attempted, with various degrees of success but no breaking through to model the full length of the reactor.

Even these short runs, though, produce some results that might be significant in considering the value of the models. In the pseudo-onedimensional case, using a single station, the bulk dissociation rises briefly, then drops off slowly, much more slowly than in the non-disperse model. The bulk temperature drops off as sharply as in a nondisperse case, reaching 400 to 500 K in the first few mm below the atom source. However, the surface temperature and dissociation both rise sharply, to around 3000 K and over 0.5 dissociation. The surface concentration, however, still remains lower than the bulk, permitting mass transfer to the wall, despite the higher degree of dissociation, due to the increase in surface temperature. It is rather startling that the bulk gas temperature in the model drops as the surface temperature rises. Apparently the axial dispersion of energy is computed to be so much greater than the radial dispersion that radial conduction effects haven't shown up as far as the model has been able to go. Using multiple radial stations has produced much the same results, and, in addition, has predicted that radial gradients seem to persist and even intensify down the pipe. Differences between two stations seem to increase with distance, though radial transfer should damp out such differences. Besides the added computer time to compute the additional stations, the problem of the surface equations locking up seems to arise even faster when using a number of radial stations, so this is based on even shorter reactor sections than the quasi-one-dimensional results are.

One possible source for these results, counter-intuitive to the point of being non-physical, is the model itself, and its technique for handling the second-order equations. To solve a second-order differential equation, such as (40) above, the model rearranges the equation to the form of:

$$\lambda d(dT/dz)dz / G(r) - C_p dT/dz - [DH_R dX/dz_R + \lambda d(r dT/dr)/dr / G(r)]$$
(42)

Then, the coupled system of equations, with dT/dz as a separate dependent variable, is solved by using first-order methods. If it is assumed that the last two terms on the right side of equation (42) can be neglected, it reduces to

$$\lambda d(dT/dz)dz / G(r) = C_p dT/dz$$
 (43)

which can be integrated analytically to

$$dT/dz = dT/dz|_{z=0} \exp(G(r) C_p z / \lambda) (44)$$

 $T = T|_{z=0} + dT/dz|_{z=0} \lambda / G(r) / C_p [exp(G(r) C_p z / \lambda) - 1] (45)$

Equations (44) and (45) tend to blow up with increasing z, tending to infinity, either positive or negative depending on the initial derivative. Hence, it is to be hoped that the terms in equation (42) that were neglected should not be. Analysis assuming that those terms are constant only adds a linear term to the final equation for T, which will be swamped by the exponential term, given sufficient distance down the reactor. In addition, the terms enter the equation in a manner that seems contrary to physical expectation. It seems unreasonable that the generation term, the second term on the right side, should have a negative influence on the second derivative, and through it, on the first. Likewise, the radial conduction term has an influence opposite to that it would have in the non-disperse case. In the program, the subroutine that computes the dispersion terms does so by calling the subroutine used to compute the first derivatives for a non-disperse model, and subtracting the outputs from the subroutine from the dependent variables that are used as the first derivatives, and applying the appropriate multipliers, of flow rate, capacity, and dispersion constant. Perhaps this subtraction should be reversed, so that the system won't blow up, and will yield more physically reasonable results, yet repeated analysis of the system yields the model as given. It is unclear what the answer to this problem is. This might be one reason that Coste, <u>et al</u>., [1961] said that forward marching methods are unusable for this sort of secondorder differential equation problems.

The problems with the implementation of the Coste method program were eventually traced to incorrect initial conditions on the reverse integration. A more generalized program, using an arbitrary step size and a search method to find the downstream conditions to initiate the reverse integration, was developed, and it proved to yield results comparable to the Gear method. However, the reverse integration method required much more computer time, so the Gear method integrator was selected for further work.

It was eventually realized that randomly selected initial conditions would not necessarily yield results that would converge on the infinity boundary conditions (Equation 41). Indeed, a marching integration on the second-order equation (42) will produce, for example, values of temperature that will be driven away from the neighboring temperatures, downward if the temperature is less than the neighbors, upward if greater. Therefore it seemed reasonable and experimentation verified
that properly selected initial values for the derivatives may generate results that are realistic and reasonable. Since the IMSL DGEAR integrator proved as effective and efficient as any, it was selected and a search algorithm designed to find the appropriate initial derivatives (see Appendix A).

However, the search technique failed to find a set of initial derivatives, for the standard model, that would allow the integration to proceed beyond a short reactor length without yielding results that were assumed to be incompatible with the boundary conditions at infinity. Inconsistent results, to the point of having two runs with the same set of initial derivatives invoking contradictory indicators, and a relatively strong dependence of the point towards which the search would converge on the value of the integration and surface boundary conditions convergence parameter indicated a possible numerical instability in the integration. A possible way around this would be to search for initial conditions that would allow integration to some preset length, back up to some point where the variation in the search is expected to be small, and search for the derivatives at that point that would permit integration to proceed further. This might cause a slight discontinuity in the derivatives at the transition points, however. Investigation of this technique is left for future work.

Before the instabilities appeared, though, the simulation reached a point at which most of the changes within the modelled reactor seemed to have completed, and the search had reached the point where this regime had been fairly well established, with differences from one run to the next being smaller than the precision of the output. The movement of the search convergence point with the convergence parameter was within this range. The temperature profile from the longest run, standard conditions, quasi-one-dimensional, using the diffusion coefficient and conductivity for the values of the mass and thermal dispersion coefficients respectively, is shown in Figure 36 (solid curve), along with the same profile from the plug-flow model (dashes). Comparing the curves shows that the temperature peak when dispersion is considered is much lower than that in the plug-flow situation, and the peak is much broader. The profile of fraction dissociated is shown in Figure 37, again paired with the plug-flow profile, and the decay of the free atoms is much slower.

However, the temperature peak is largely dissipated at 5 cm. below the reactor. The model is approaching the results of the experiment, but has not yet reached them. A fully two-dimensional dispersion model might provide results more in agreement with experiment, and the program developed in this work could be used provided sufficient computation time is available. The search for the quasi-one-dimensional case involved large amounts, on the order of hours, of computer time, and a n-station case requires a 2n-dimensional search. Or else, the initial conditions might be adjusted to fit the experiment better.

Figure 38 shows the temperature profiles calculated at the low flow rate and pressure (solid line), and at the standard flow rate (long dashes), from the dispersion model, and the low flow rate from the plugflow model (short dashes). Inclusion of dispersion has a much greater effect at the lower flow rate than at the higher, in broadening the peak, and the dependence on flow rate is much lower in the dispersed than in the plug-flow. Thus, the lack of flow-rate dependence seen in the experiments is seen as an indication that axial dispersion needs to be considered. The modelled results do not yet match the experiment in









every detail, but further adjustment of initial conditions and the dispersion coefficients may provide much better fits.

Chapter 7 - CONCLUSIONS

A spacecraft propulsion and maneuvering system has been proposed that would use electrical energy, from a solar cell or other source, to heat the working fluid, or propellant, through a microwave-frequency plasma. The heated gas would then flow through a nozzle to generate thrust, much as in a conventional rocket. The main difference is that a chemical rocket heats the propellant with energy liberated by chemical reactions within it, whereas this system heats the propellant with energy obtained from outside it. A number of engineering problems remain to be solved before this microwave-plasma electrothermal rocket becomes practical. Among these problems is the basic one of how efficiently the energy is transferred, or coupled from the microwave-frequency electromagnetic fields to the gas. More specifically, it is desired to generate translational kinetic energy of the molecules of the propellant. This motion, random at first, can be turned to directed flow and thrust by a nozzle. One potential mechanism for this coupling is the dissociationrecombination cycle of a diatomic gas in the working fluid. In the plasma, the diatomic gas would dissociate, to recombine and release the energy absorbed in the dissociation downstream of the plasma. Hydrogen has a number of advantages as a propellant, particularly if this cycle is important, and this work examines several aspects of the use of hydrogen in this proposed system.

The work reported here is divided into three distinct sections. First, the paper describes a program of preliminary experimental work, intended to demonstrate the capability of the microwave-plasma to couple energy to the gas from the electromagnetic fields, to measure the thrust

and temperature profiles generated in the gas flowing through a microwave-plasma, and to test various experimental designs for their efficiency in coupling energy to the plasma. A modelling study was undertaken to evaluate the importance of vibrational and rotational excitation on the hydrogen recombination reaction and energy transfer in the reaction, and its effects on a practical microwave-plasma electrothermal rocket. A series of computer models have been developed to explain the experimental results and to provide a basis for the design of future experiments and practical microwave-plasma electrothermal propulsion systems. The three sections of this research each lead to their own independent conclusions, though there are also certain common conclusions from comparison of the results from different phases of the work.

The experimental work mainly involved relatively low-pressure, up to 100 Torr, plasmas in hydrogen, with flows to 2 mg-mol/s, and incident microwave powers between 300 and 600 W. Work was also done, for comparison and safety considerations, in nitrogen and argon, under similar conditions. The experiments showed that the microwave-plasma system can pump energy into the flowing gas. Thrusts were measured directly, using a vane-type thrust stand, and temperature profiles obtained, through a gas-dynamic technique, that were in rough proportion. That is to say, the thrusts obtained, at the same flow rate, were approximately proportional to the square root of the estimated temperature, in configurations of the apparatus in which the thrust measurements were most reliable. With the plasma, when the gas-dynamic temperature estimate was 400 K, the thrust was approximately 17 per cent higher than the thrust measured by flowing the same rate of cold, room temperature, roughly

300 K, gas through the apparatus. A predicted mode, TE₀₁₂, of the microwave resonant cavity was verified, for use at higher plasma pressures.

However, the experimental arrangement pumped the absorbed microwave energy out of the gas again as fast. The experiments' poor design forced this loss of most (60 to 80 per cent, and more) of the incident microwave energy to the coolant, as the gas could not carry off the "overkill" of microwave energy by any available mechanism. In addition, the cooling needed to protect the plasma chamber walls also cooled the region below the plasma, so the gas retained but a small fraction of the energy fed into it in the plasma at any distance downstream. If the temperature was estimated far enough downstream, though still within the apparatus, the gas and the coolant were at the same temperature. With the air coolant and the plasma gas flowing counter-currently, in hydrogen, the gas-dynamic temperatures were 300 K as close as 6 cm below the plasma. With the coolant flow reversed, that temperature had dropped to 600 K, from 1200 and more at the plasma exit, at 6 cm and had cooled to match the coolant, 400 K, by the end of the plasma tube, 36 cm below the plasma. Accurate thrust measurements required that the nozzle be at the end of the plasma tube, for free expansion into the vacuum tank housing the thrust stand, and some 36 cm from the plasma. This was so far downstream from the plasma that the gas and the coolant were nearly equilibrated. Though the values of the measured thrust were not in agreement with theoretical values, as computed from gas-dynamic theory, the measured values being from 25 to 110 per cent of the ideal, depending largely on the pressure around the thrust stand, their relative values

were in rough accord with the temperature estimations, as described above. The temperature profile, in hydrogen, especially, was very nearly independent of the flow rate.

The experiments demonstrated that the cavity resonant mode was a controlling factor on the plasma behavior, that different modes could sustain a plasma in different pressure regimes. Attempts to cool the wall by transpiration cooling proved unsuccessful, due to failure of the porous wall and migration of the plasma out of the transpiration region. An attempt to create high-pressure plasmas by a capillary tube design also was unsuccessful.

The experimental work was basically preliminary, but yielded a number of curious and potentially significant results for further experimentation. For example, there was an as yet unexplained extreme background pressure dependence of the measured thrusts, that had also been reported elsewhere, though not, I believe, to the degree reported here.

There are a number of ways to improve the experimental design to avoid the problem of overcooling the gas. The microwave power level must be better matched to the capacity of the gas. The cavity resonant mode and the gas flow pattern can be selected to reduce the danger to the tube walls. One potential method, transpiration flow, was tried and could not be made to work, due to failure of the porous wall and migration of the plasma out of the transpiration region. The distance between the plasma and the nozzle can be reduced to reduce the downstream cooling, it is to be hoped, without reducing the accuracy of the thrust measurements. A possible alternative design, for both experiment and applications, is regenerative cooling, where the feed to the plasma is ducted past the nozzle to cool the nozzle and pre-heat the feed. This is a common design in more conventional chemical rocketry. Another possible experimental arrangement, under discussion when this work was being done, would be to mount the entire cavity, plasma tube, and nozzle in a vacuum tank, on a thrust stand. This would help diagnose the origin of the back-pressure dependence, as well as reducing the distance for cooling between the plasma and the nozzle.

A potential sink for the recombination energy was thought to be the internal, vibrational and rotational energy of the recombined molecules. If the recombined molecules retained a significant fraction of the energy of recombination in these modes for a significant length of time before the energy would be transferred to translational kinetic energy, the performance of a rocket that relies on the dissociation-recombination cycle to transfer energy to the working fluid might be seriously degraded. A computer modelling study, based on a two-temperature model of vibrational excitation, was done to estimate how important this internal energy of the molecules would be in a practical system. This study showed that it is most likely that molecular internal energy considerations will not be important in practical electrothermal rocket design. At temperatures and pressures likely to be used in such designs, any internal energy excess will largely thermalize very quickly, within microseconds, compared to the millisecond time scale of the recombination reaction. The energy that would be stored in excess vibrational excitation is likely to be but a small fraction of the total energy released in the recombination reaction. Under practical conditions, this loss of energy would reduce the temperature of the recombined gas on the order of a few kelvin compared to the 3000 K operating temperature.

However, low temperature, high pressure work with atomic hydrogen may require consideration of internal energy.

Attempts to correlate the experimental results with the macroscopic computer models have verified that wall cooling must be considered in any model of the experimental arrangement as used, as the profound influence of the cooling geometry on the experimental temperature profile shows. In addition, the models show that the surface reaction is important, under the experimental conditions. This reaction creates conditions at the surface that imply large thermal and concentration gradients across the tube, hence two-dimensional models are required. Though many of the qualitative characteristics of the experimental results have been reproduced, quantitative agreement remains elusive. The absence of dependence on flow rate has been seen, but only as a result of total equilibration with the coolant. The reaction is all but complete and the temperature equilibrated by the time the model reaches the first experimental data point. However, the experiments show no flow rate dependence at a temperature too high to be explained by equilibration at that first point. In addition, some experimental results in nitrogen parallel those in hydrogen almost exactly, while the models suggest that, at some of the experimental flow rates in nitrogen, equilibration should not have occurred at that first point.

Further improvement and complication of the model are required, and one including axial dispersion has been developed to investigate the matter further. A solution technique involving a search for the initial derivatives is developed. Preliminary results indicate that dispersion may play a role in the performance of the experimental arrangement,

though instabilities limit the utility of the model. The work has indicated the directions further development should take, coupling the twodimensional and dispersion models together, and trial and error or theoretical studies to determine better values for the initial conditions and the dispersion coefficients.

The experiments have shown that the microwave-plasma electrothermal rocket may be feasible, various diagnostic techniques have been demonstrated, and some of the constraints on an experimental arrangement have been identified. The vibrational-energy modelling study has shown that one possible constraint on the performance of a microwave-plasma electrothermal rocket is unlikely to be an important factor in practical design of the system. The further modelling has shown that cooling, surface reaction, and axial mixing must be considered under the conditions of the experiment to adequately model the experiment. It has also indicated that these factors are likely to be important in other configurations. Flow rates and pressures must be much higher than those in the experiment before axial mixing and surface reaction can be neglected. Though much work remains before the microwave-plasma electrothermal rocket takes flight, this work, at least, has demonstrated its scientific feasibility. The major problem to be solved is the question of surface reaction, and keeping the energy in the gas.

APPENDICES

APPENDIX A

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Appendix A - COMPUTER PROGRAM DESCRIPTIONS

All inputs, outputs in Systeme Internationale units. If z input less than 0., ends computer run. Inputs echoed. Inputs free format.

Changes From Cyber to Vax

The computer work was begun on the MSU Computer Laboratory Control Data 6500 computer, and some work was done using a NASA-Lewis IBM 360. The 6500 was replaced with a Control Data Cyber 750-175, and then, for reasons of computer access, the programs were transferred to a MSU College of Engineering Digital Equipment VAX 11/750. This produced a few changes in the code, some mandated by the new computer, others facilitated by the VAX/VMS operating system.

Mandatory Changes:

1. To maintain consistency with the Cyber 64-bit word, double precison (Real*8) was required on the 32-bit VAX.

2. Code structures of the form A-B-C, permitted on the Cyber, are non-standard, and forbidden on the VAX.

3. Certain statement function structures would not work, and those statement functions had to be transformed into Function Subprograms.

Other Changes:

1. The program was redesigned to save sufficient data to permit a limited interrupt-restart capability.

2. The code was modularized, permitting more efficient debugging and modification.

3. A prompt for the initial inputs was added. The Cyber had a prompt utility that the IBM and VAX lack.

In Appendix B:

Program 1: Vibrational Energy Model. One-Dimensional, Plug Flow, Adiabatic, Gas-Phase Reactions.

Inputs: Initial values for z, X, T, P, and T_V , Hydrogen flow rate to plasma, Y, convergence value, area of reactor cross-section, nozzle throat area, position of end of reactor, printing interval. If input T_V less than 0, uses steady-state value as initial value.

Outputs: At initial z and print intervals, prints z, X, T, P, T_V , reactor flow area, bulk velocity, local sonic velocity, and Mach number.

Program 2: One-Dimensional Model. One-Dimensional, Plug Flow, Cooled, Reactive Surface.

Inputs: Initial values for z, X, T, P, and T_c . Mass flow rate in kg-mols molecular hydrogen fed to plasma per second, convergence control

parameter, the two area parameters, constant and throat areas, final reactor length, print interval, cooling air flow rate in kg-mols per second, a real-valued heat transfer-coefficient control parameter, UO, two integer-value mode control parameters, MODE and M2, and a realvalued viscous-flow control parameter, FR.

Control Parameters:

U0: If U0 greater than 0, internal heat transfer coefficient computed from conductivity and Nusselt number, then multiplied by U0, external coefficient is constant 47.06 \star U0 W/m² K.

If U0 equal to 0, internal heat transfer coefficient computed as though U0 - 1.0, external coefficient 0. Adiabatic with reacting walls.

If UO less than 0, then the absolute value of UO in W/m^2 K is used for both internal and external heat transfer coefficients.

MODE:

Value Result

<-0 Wall Temperature based on convective heat transfer alone, with surface recombination energy transferred to cooling air.

1 Non-reactive walls

- 2 Wall Temperature based on convective heat transfer alone, with surface recombination energy transferred to gas.
- 3, >4 Wall Temperature based on energy balance between convection to gas and to coolant, and surface recombination rate.
- 4 As MODE = 3, but wall reaction rates computed from bulk temperature, rather than wall temperature.

M2: If M2 = 0, Dissociation at surface assumed bulk value. Otherwise, computed based on mass balance at surface, with convective mass transfer balancing surface reaction.

FR: If FR = 0, inviscid flow. Otherwise, Fanning friction factor, from standard correlations, multiplied by FR to compute viscous losses.

Outputs: At initial z and at print intervals thereafter, prints z, X, T, P, T_c, Bulk Velocity, Flow area, Sonic Velocity, Estimated Corrected Gas Dynamic Temperature, and the Wall Temperature (at downstream print stations only).

Program 3: Two-Dimensional Model. Two-Dimensional, Plug Flow, Cooled, Reactive Surface.

Inputs: Initial Values for z, $\langle X \rangle$, $\langle T \rangle$, P, T_c, Mass flow rate, convergence limit, area parameters, reactor length, print interval, cooling air flow, real valued heat transfer control parameter UO, integer valued, 1 to 4, initial profile parameter INPRO, and the number of radial stations, at least 2, but not more than 10, with arrays dimensioned as given.

Control Parameters:

UO: As in One-dimensional model, but controls only external heat transfer coefficient. (Note: due to error in initial evaluation of

jacket heat transfer coefficient, UO should be 1.6 for most realistic simulation. Not a strong influence on results.)

INPRO:

Value Initial profile used

- 1 Uniform to wall at $\langle X \rangle_0$, $\langle T \rangle_0$
- 2 Center station at $\langle X \rangle_0$, $\langle T \rangle_0$, others at X = 0., T = T_{c0}.

3 Arbitrary Profile: Prompts for dissociation profile, from center to wall, then Temperature profile. Recomputes averages.

4 Cool sheath profile. As 1, but at wall station,
$$X = 0., T = T_{c0}$$
. Averages recomputed.

Other Error, run aborts.

Outputs: At initial axial position and at print intervals thereafter, prints z, $\langle X \rangle$, $\langle T \rangle$, P, T_c, Bulk Velocity, Flow area, Sonic Velocity, and Estimated Corrected Gas Dynamic Temperature, the last four based on the average composition and temperature, then the radial profile of dissociated fraction, from the center out to the wall, then the radial temperature profile in the same order. The local state variables should stack one above the other.

Program 4: Dispersion Model. (Gear method, search for initial derivatives, on VAX) Two-Dimensional, Dispersion, Cooled, Reactive Surface.

Inputs and Control Parameters: In file startg.dat: as Two-Dimensional Model, (one station valid) plus, IMSL DGEAR routine control parameters METH and MITER (see IMSL documentation), real-valued mass and energy dispersion control parameters, and a real-valued debugging print control parameter. If dispersion control parameters positive, dispersion coefficient is diffusion coefficient or thermal conductivity time control parameter; zero, plug flow in mass or energy; negative, dispersion coefficient is constant at absolute value in SI units. Debugging print will not print if parameter set to 0.

In file search.dat: From central to outer, for dissociation at all stations then for temperature -- a low value, a high value, and the current value of a search parameter, and two integer valued search control parameters. Last, on a separate line, a print control parameter.

The first search control parameter controls whether the search will be bounded if the associated variable is the next to invoke one of the runaway conditions. The second, if 1, will make the search bounded regardless of the history, and, if 0, the search will run freely. The first is set to the value of the second if the corresponding condition is not the first to reach runaway and to 1 if it is. The second search control value should be set to 1 only if you are sure, from watching the behavior of the search, that any invocation of the runaway conditions associated with that variable will set an absolute, global minimum or maximum of that parameter. In the sample case, quasi-one-dimensional, calling for a two-dimensional search, it was noticed that, as the search narrowed, the temperature runaway would only show up along a very narrow, diagonal region, between regions where the dissociation runaway dominated. To keep the search from looping, the temperature search was strictly bounded. In addition, it proved faster to search more or less parallel to that diagonal, rather than strictly orthogonally. Hence, the transformed search coordinate matrix was devised (vide infra). If either

the high or low value of the search parameter is equal to the current value, the search will step the difference between the high and low if the the runaway indicates that the search should continue in the direction corresponding to whichever is equal to the current value, regardless of the value of the search control variables. If the first search control value is 0, the search steps to the other value, if the control value is 1, it steps to half-way between, if the direction of the search is the other direction.

If the print control parameter is not 0, the program will print to the screen or to the *.log file after every print step. If it is 1, the program will stop once it reaches the target reactor length.

In file saves.dat: If defaulted, at least 4n+9 commas, will begin from startg.dat starting point. Else will start at last print position from last run.

In file hmat.dat: Matrix for linear transformation of search parameters to initial derivatives. Default, $4n^2$ commas, is identity matrix.

Output: Before each attempt and restart, prints initial derivatives. When print control parameter non-zero, as Program 5, with surface conditions on all print intervals, and beneath each local condition, first and second derivatives.

Program 5: Subroutine RK4: Final form of fourth-order Runge-Kutta integration subroutine. Additional features: generalized through use of parameter to specify function to be integrated, cascading return capability, integration to dependent variable value.

Area Function

Program models as 0.025 m straight, circular tube, with flow area AK, first area input parameter, followed by a straight-cone converging section 0.025 m long to a throat with area A2, second area input parameter, and another straight-cone diverging section 0.25 m long, back to flow area AK, and a straight tube with flow area AK thereafter.

Solution Methods

Differential Equations

For Programs 1-3, the systems of coupled differential equations were solved using a standard fourth-order Runge-Kutta method. Program 5 is the latest version of the integrator. With bold face representing vector notation, for a series of coupled differential equations:

$$dy(x)/dx = f(y,x)$$
 (A1)

with initial conditions:

$$y(x_0) - y_0$$
 (A2)

 $y(x_0 + h)$ may be estimated by:

$$k_{1} = f(y_{0}, x_{0}) \quad (A3)$$

$$k_{2} = f(y_{0} + k_{1} / 2, x_{0} + h/2) \quad (A4)$$

$$k_{3} = f(y_{0} + k_{2} / 2, x_{0} + h/2) \quad (A5)$$

$$k_{4} = f(y_{0} + k_{3}, x_{0} + h) \quad (A6)$$

$$y(x_{0} + h) = y_{0} + (k_{1} + 2 k_{2} + 2 k_{3} + k_{4}) h / 6 \quad (A7)$$

This approximation is improved by taking smaller values of h for the integration interval. In these programs, the integration is done over the print interval, then the step size is halved, and the integration repeated. If the sum of the squares of the ratio of the difference between the values of each dependent variable after the two integrations to the change of the value over the final integration, summed over the dependent variables, is larger than the input convergence value, the integration interval is halved, and the integration is repeated until convergence. The stiffness of the equations is controlled by having the integrator check to see if the change of any of the temperatures over the integration interval will be greater than one-tenth of the value of the temperature. If it is, then the integration interval is halved until it is not, and the final value of the interval is used over the rest of the print interval. There is a floor, so that if the integration interval becomes less than one-millionth of the print interval, the computer prints out "INTEGRATION DIVERGED" and the integrator subroutine returns to the main program, with the final value of the overall integration interval made negative. The program may then prompt for new input (Program 1), or reduce the interval fed to the integrator, and repeat until

that becomes too small, at which time it will prompt for new input (Programs 2 and 3).

Program 5 includes two new features that earlier versions of did not include. Instead of using the final length as the error flag, it calls for another integer input variable as an error flag, initially 0, returning it set to 1 if the integration diverged. The print statement was also removed. If that variable, through a common block, is set nonzero by the subroutine called to compute the derivatives, the integrator will return at once to the calling routine, with the error flag still set. Second, the subroutine requires input of an integer variable, zero or the index for one of the elements in the Y array and a target value for that element. If that variable is non-zero, the integration will run until the final value of the independent variable or until the designated element passes the target value, whichever occurs first. If the index is 0, integration is strictly controlled by the independent vari-This was implemented because the backwards integrations, using an able. arc-length method, would sometimes overshoot z=0. The variable selected should be monotonic over the integration range, of course, though the integrator can handle either increasing or decreasing target variables.

It was thought at first that an extension of the Runge-Kutta method, with dT/dz being used as a new dependent variable, might be applicable to solve the dispersion equations. However, this method provided unstable solutions, and a survey of the literature (Coste, <u>et</u> <u>al</u>. [1961]) showed that that was to be expected from forward-marching methods for solving the dispersion equations. Hence, Coste's method for solving such equations has been adopted. The non-dispersed equations are

solved first via a cell model, an implicit method, which, for appropriately chosen cell lengths, depending on the relationship between the dispersion coefficient and flow rate, approximates a dispersed flow reactor. Then, once the end of the reactor is reached, the values at the end of the reactor are used as input, and the exact equations integrated backwards along the reactor to give the exact profiles.

To solve the cell model (Program 4), which entails the solution of a large number of non-linear equations, first, the cell length was chosen to fit Coste's parameter based on the bulk or average conditions at the input to the reactor. Then, the conditions at the end of the cell were computed based on the axial derivatives of the conditions computed using the initial conditions. Certain limits were applied, temperatures and dissociations were kept positive, for instance, to maintain realism, and the cell length and conditions at the end of the cell recalculated. Then, for each dependent variable, the difference between the guessed value and the recalculated value was computed for both cases, and, if the difference was too large, a new value of the dependent variable was extrapolated or interpolated, as appropriate, linearly. Then, the limits were applied, and the process repeated until the sum of squares converged.

Arc-Length Method

For the reverse integration and for the later Gear model integration, an arc-length method (after Bhatia and Hlavacec [1983]) was implemented to avoid stiffness problems. This method involves a new independent variable s and redefines the equations as follows:

$$dz/ds = 1 / (1 + |df/dz|^2)^{1/2}$$
 (A8)
 $df/ds = df/dz / (1 + |df/dz|^2)^{1/2}$ (A9)

where $|df/dz|^2$ is the sum of the squares of the elements of df/dz. This system of equations is integrated with respect to s, assuming as integrating intervals over s the print interval, and printing after the value of z has passed the print interval, regardless of whether the print interval has been hit exactly. Since dz/ds is always less than 1, it will print at least once in each print interval. To help limit the running time, the step size in s is adjusted after each call to the integrator to be the remaining length to the next print point divided by 16 dz/ds, as computed by finite difference over the last integration, or the print step, whichever is larger. This may negate the advantages of the arc-length method, and the adjustment, originally the full length divided by dz/ds, had to be reduced by a factor of 16 to avoid stepping too far past zero in some reverse integration cases.

Implicit Runge-Kutta Method

When the dispersion model equations could not be integrated stably on Coste's backwards integration, using the standard, explicit Runge-Kutta integrator described above, an implicit Runge-Kutta method, as described by Cash [1975] was implemented. This method would change the equations (A3)-(A7) above to:

$$k_{1} = f(y_{0}, x_{0}) \quad (A10)$$

$$k_{2} = f(y(x_{0} + h) - k_{4} / 2, x_{0} + h/2) \quad (A11)$$

$$k_{3} = f(y(x_{0} + h) - k_{2} / 2, x_{0} + h/2) \quad (A12)$$

$$k_{4} = f(y(x_{0} + h), x_{0} + h) \quad (A13)$$

$$y(x_{0} + h) - y_{0} = (k_{1} + 2 k_{2} + 2 k_{3} + k_{4}) h / 6 \quad (A14)$$

These equations were solved by assuming that, as an initial guess, $y(x_0 + h) - y_0 + h k_1$, and using equations (All)-(Al3) to compute the other k vectors, then substituting them into (Al4) to obtain a new guess, and repeating until the new guess was close enough to the last one.

When the integrators specially developed for this modeling proved intractably impractical, due to excessive computation time for appropriate reactor lengths, an appropriate "canned" integrator was sought. The subroutine DGEAR from the IMSL library was selected. This subroutine uses, at operator option, either implicit Adams methods or Gear's stiff, backward differentiation methods, with a variety of user-selectable corrector iteration methods to solve the system of algebraic equations generated.

Algebraic Equations

The surface conditions were estimated by solving the appropriate material and energy balances for the surface by a trial and error method. The first guess was that the surface conditions were those of the bulk gas or of the station closest to the wall, in a two-dimensional model. Then, the surface temperature needed to satisfy the energy balance, with generation at these conditions, was estimated, and the equilibrium conversion at this temperature was calculated, for the next guess. The signed error of closure in the material and energy balance equations was computed for each case, and the next guess taken from a bounded linear inter- or extrapolation, as appropriate, with bounds selected to maintain realistic values and to avoid runaway.

Initial Conditions (Dispersion Model)

After each print length integration is completed, the results are checked to see if each station's conditions, temperature and concentration, were likely to be compatible with the infinity boundary condition. The following conditions were originally considered to be incompatible with the boundary conditions, suggesting the condition would run away, eventually going to plus or minus infinity: 1) The variable, if the first derivative did not change, would become negative in the next print length. 2) The first and second derivatives of the variable were both positive. 3) The first, second, and third derivative were of the same sign. The third derivatives were calculated by a finite-difference

method. 4) The square of the first derivative, divided by the product of the value and the second derivative, was positive and less than unity.

The first and third, if the derivatives were negative, were assumed to mean a negative runaway, so that the initial guess of the derivative involved had to be increased. The others, and the third with positive derivatives, were taken to indicate positive runaway, requiring a lower initial guess. Initial derivative values were assumed, and the equations integrated until one of the runaway conditions turned up for one of the values. Then the initial value of the derivative of that value was adjusted appropriately, and the integration repeated, until the integration went the full length of the modelled reactor. The initial values were stepped along until both positive and negative runaway were indicated, then the point half-way between was selected. The variables would reach runaway in turns, though not strictly alternating, and they were clearly linked, so that finding a better value for one would shift the best value for another. This produced long running times, since the search is literally looking for an infinite integration length, even for pseudo-one-dimensional, one station case, and the program was redesigned to allow for interruption and restarting.

Inclusion of the last listed runaway condition produced dramatic changes in the performance of the search algorithm from that seen without that condition. That condition would occur much earlier than the others, and therefore a shorter integration would be needed to determine which section of the search area a point was in. The boundaries of the sections would change, as that condition might be satisfied earlier than one of the other conditions, and define a point as belonging in a different section than the other condition would. However, that condition

produced false positive responses in certain regions. Inclusion of that condition would send the search one way when a longer integration would send the search in exactly the opposite direction. In a preliminary, one-dimensional, two-variable modeling, part of one section disappeared entirely, since the runaway conditions on one variable would never be satisfied before one or the other of the runaway conditions on the other The transition from one runaway to the other occurred at a finite were. reactor length. This forced the search technique to a halt, with a false convergence on the transition from positive to negative runaway. Hence, condition 4 was dropped from further searching, except as a means to establish lower bounds. Likewise, on experimentation with a two-dimensional model, condition 2 and the negative runaway from condition 3 were seen to create false results, so they were also dropped. This left only condition 1, with the coolant temperature as the floor for the temperatures, and zero, or the wall dissociation, if the dissociation in question was higher than that at the wall, for the dissociation values, to mark negative runaway and the positive side of condition 3 to mark positive runaway.

Interruption and Restart Capability

Due to long normal running times, plus a number of bugs in the program that caused or required the program to stop, the program was equipped with a limited interrupt and restart capability. At each print point, the reactor state array was written into a special file called saves.dat. Each time the search algorithm was implemented, the values required for the algorithm were likewise written onto their own file, search.dat. Each of these files was rewound before the new information was written. On starting the program anew, these files were read, and, if saves.dat was not defaulted, the integration resumed at the last print point before the previous run was halted. Search.dat had to be initialized with the intended start point and step sizes, and saves.dat could be set to default to begin the integration from z=0.0.

Two problems with the program remain unresolved, though the program has been modified to recover from them. First, the search for the solution to the surface boundary conditions may not converge. Second, the computer would report an "undefined exponentiation" error, and halt. It was discovered that a simple halt and restart, as described above, could usually integrate right over the problem. I presume that the DGEAR algorithm chooses the points at which it calls the differential equation computation subroutines in such a way that which specific points are evaluated changes with where the DGEAR initiation takes place. The program was restructured so that if the surface conditions search did not converge or the exponentiation probably responsible would be undefined the program would perform the equivalent of a restart from the last print location.

Transformed Search Coordinates

The program calls a file hmat.dat, and reads off it a 2n by 2n matrix called HMAT, which holds the matrix for transforming the vector of search parameters, by matrix multiplication, to the initial derivatives used in the calculation. If the file is defaulted, with nothing but $4n^2$ commas, HMAT is assumed to be the identity matrix.

VARIABLE DICTIONARY

- A (AVG) Dimensionless Outer Radius of Cell
- A(3,3) (DELTA, TVSS) Array Containing Constants for Rate Constant Calculation
- A1 (AVG, DELTA2) Real Constant for Fewer Mode Problems
- A2 Throat area for Area Function. (DELTA2) Real Value of Loop Counter For Fewer Mode Problems.
- AK Constant Area for Area Function
- ALFA Common Block Name
- AMO Molecular Weight of undissociated gas
- AQ (Prog. 4, DELTA) Parameter For Quadratic Fit In Temperature Search
- AR(Z) Area Computation Function Subroutine
- AS Surface Area In Square Meters Per Meter Length (Perimeter) Assumes Circular Cross Section
- AVG Function Subroutine to Compute Mass-Averages
- B (AVG) Dimensionless Inner Radius of Cell
- BQ (Prog. 4, DELTA) Parameter for Quadratic Fit During Temperature Search
- BRAVO Common Block Name
- C(3,3) Array Containing Constants for Heat Capacity Calculations
- CHARLIE Common Block Name
- CP(I,T) Heat Capacity at Constant Pressure calculated as quadratic function of temperature T (I=: 1, Molecular Hydrogen; 2, Atomic Hydrogen; 3, ΔC_p of reaction) Constants in Array C
- CPM(X,T) Heat Capacity of Hydrogen Mixture with Dissociation X at Temperature T
- CPV (Prog. 1) Vibrational Heat Capacity of Molecular Hydrogen
- D2Y(47) (Prog. 4) Array of derivatives from a DELTA2 call

- D3Y(47) (Prog. 4) Array of finite-difference computed second and third derivatives.
- DAR(Z) Function Subroutine for finite-difference computation of derivative of area with respect to Z. Step size 1 μ m.
- DELTA Subroutine that Computes Local Derivatives Based on First-Order Conservation Equations
- DELTA2 Subroutine to Compute Derivatives Including Second Derivatives using Arc-Length Method
- DGO Standard Free Energy of Reaction at 298.15 K
- DGEAR (Prog 4) ISML Gear Method Integration Subroutine
- DH(T) Heat of Reaction Calculated From ΔC_p and DHO For Temperature T
- DHO Heat of Reaction Calculated at O K
- DH2HP(T) Diffusion Coefficient between Molecular and Atomic Hydrogen as Function of Temperature T
- DHH2P Mass Dispersion Coefficient
- DHS Energy Released By Surface Recombination
- DHT (Prog. 1, TVSS) Heat of Reaction Considering Vibrational Excitation
- DHV (Prog. 1, DELTA) Heat of Reaction Considering Vibrational Excitation
- DISP(2) (Prog. 4, ROCKET) Two element array containing Mass and Energy Dispersion Control Variables.
- DISPM (Prog. 4, DELTA2) Mass Dispersion Coefficient Control Variable
- DR Radial Spacing Between Stations, Dimensionless
- DS Value of Coefficient for Conversion From Direct to Arc-Length Method
- DTS Difference Between Actual Surface Temperature and That Needed to Balance Heat Flux
- DTS2 Storage Variable for Surface Temperature Difference During Search
- DTSO Storage Variable for Surface Temperature Difference During Search

- DUMMY (Prog. 4) Subroutine required for DGEAR integration (see IMSL documentation)
- DX (Prog. 1, TVSS) Variable used to Compute Reaction Rate
- DX0 (RK4) Initial Overall Step Size
- DXL (RK4) Dimensionless Step Size
- DXN(2) (Prog. 4) Array for Projection phase of Solution of Wall Boundary Conditions
- DX0 (RK4) Initial Interval for Control of Stiffness
- DXR (DELTA) Change in Dissociation Based on Reaction and Axial Flow Alone
- DXS Temporary Value, and Difference Between Real Surface Dissociation and That Necessary to Maintain Flux To Surface
- DXSO Storage Variable for DXS During Search
- DXW Change in Dissociation From Surface Reaction
- DY (DAR) Step-size for finite-difference derivative calculation
- DY(N) Array of Derivatives, parallel local Y(N) array
- DY4 (Prog. 1) Temporary Variable in computation of Vibrational Temperature Change
- DZ (ROCKET) Interval over which Integration Occurs.
- ECHO Common Block Name
- EDISP (Prog. 4, DELTA2) Energy Dispersion Coefficient Control Variable
- EGRESS (Prog. 4) Entry point for error recovery restart
- EK(Y,Z) Function Subroutine Computes Kinetic Energy of Flow at length Z and Conditions described by vector Y. Y(1)=X, Y(2)=T, Y(3)=P, assumes uniform
- ERR (ROCKET, DELTA) Relative Error Tolerance. (RK4) Relative Difference Between Successive Integrations.
- ERRX (Prog. 4, DELTA) Error Tolerance on XS search
- EV(T) (Prog. 1, DELTA, TVSS) Vibrational energy as function of Temperature T
- EVTV (Prog. 1, TVSS) Temporary Variable in computation
| FO | Molar Flow Rate of Gas into Plasma |
|----------|---|
| FCN | (Prog. 5) Dummy variable name for function to be integrated |
| FD | $(Prog. 2) - FFF / D_i$ |
| FFF(Y,Z) | (Prog. 2) Fanning Friction Factor Function Subroutine |
| FI | (Prog. 2, FFF) Temporary Variable |
| FOXTROT | (Prog. 2) Common Block Name |
| FR | (Prog. 2) Viscous Flow control variable |
| FXT(4) | Array for Values in Simplex Method Search |
| G2 | Debugging Print Control Variable |
| GAMMA | (Prog. 1) Fraction of Recombination Energy in Vibrational
Excitation.
(Prog. 4) Debugging Print Control Variable. |
| GOLF | (Prog. 1, TVSS) Temporary Variable in Computation
(Prog. 4) Common Block Name |
| Н | (Prog. 4) DGEAR Control Step Size (see IMSL documentation) |
| HI | Heat Transfer Coefficient From Outermost Station To Wall |
| HMAT | (Prog. 4, ROCKET) Matrix for Transformation of Search
Parameters |
| но | Coolant Heat Transfer Coefficient |
| HOTEL | Common Block Name |
| I | Loop Counter, Used Repeatedly |
| 11 | Loop Counter. (DELTA2) Locates Dissociation |
| 12 | Loop Counter. (DELTA2) Locates Temperature |
| 13 | (DELTA2) Locates Temperature Derivative |
| 14 | (DELTA2) Locates Dissociation Derivative |
| IB | (Prog. 4, ROCKET) Array of Second Search Control Parameters |
| ICON | (Prog. 4) Print, stop control variable |
| ID | (Prog. 4) Flag for Dispersion check in search Algorithm |

IER	(Prog. 4) DGEAR Error Flag Variable (see IMSL documentation)						
IF1	(Prog. 4) Flag Variable Used to Check for Non-Realistic Results						
IF2	(Prog. 4) Flag to tell whether to cascade return or call entry EGRESS on error result. (Prog. 5) Error Flag in Runge-Kutta integrator.						
IJ	Loop Counter						
IMAX	Marker For Maximum Value During Simplex Search						
IMIN	Marker For Minimum Value During Simplex Search						
INDEX	(Prog. 4) DGEAR Control Parameter (see IMSL documentation)						
INDIA	(Prog. 4) Common Block Name						
INPR	(Prog. 4) Default value for INPRO - 3						
INPRO	Initial Profile Control Variable (1-5)						
IS	(Prog. 4) Array of First Search Control Parameters						
ISN	(Prog. 4) Temporary Variable in Search Algorithm						
IT	(Prog. 5) Dummy Parameter for index of dependent variable that controls length of integration (- 0 for none)						
IWK	(Prog. 4) Array for DGEAR integration controls (see IMSL documentation)						
J	Loop Counter						
J1	Index For Dissociation Value						
J2	Index For Temperature Value						
J5	Loop Control Variable in Wall Boundary Condition Computation						
J6	Loop Control Variable in Wall Boundary Condition Computation						
к	(RK4) Loop Counter						
K(I,T)	Reaction Rate Constants as Function of Temperature T. I= 1) Hydrogen Molecules as Third Body, 2) Hydrogen Atoms as Third Body, 3) Surface Reaction. Constants in Array A. Form $k(T) =$						
	$a T^{b} e^{C/T}$						
KEQ(T)	Equilibrium Constant at Temperature T						
KOUNT	(RK4) Loop Counter						

KTH(T)	Thermal Conductivity of Hydrogen as Function of Temperature T					
KTHY	Heat Dispersion Coefficient					
KVT(Y)	(Prog. 1) Vibrational-Translational Relaxation Rate Constant					
KW	Mass Transfer Coefficient From Gas To Wall					
L	Loop Counter, Used Repeatedly					
Ll	Loop Counter					
L2	Loop Counter					
L3	Loop Counter					
L5	Loop Control Variable in Wall Boundary Condition Computation					
L7	Loop Control Variable in Wall Boundary Condition Computation					
L8	Loop Control Variable in Wall Boundary Condition Computation					
LAST	Marker For Last Point Changed in Simplex Method Search					
LCOUNT	(Prog. 4, DELTA) Loop counter					
LT	Loop Control Variable in Wall Boundary Condition Computation					
LX	Loop Control Variable in Wall Boundary Condition Computation					
M2	(Prog. 2) Control Variable					
METH	(Prog. 4) DGEAR Control Variable (see IMSL documentation)					
MIKE	(Prog. 2) Common Block Name					
MITER	(Prog. 4) DGEAR Control Variable (see IMSL documentation)					
MODE	(Prog. 2) Control Variable					
MODEL	(Prog. 4) Main Program Name					
N	(DELTA, DELTA2, RK4, AVG, DUMMY) Length of Y Array Submitted					
Nl	(ROCKET, RK4) Number of Radial Stations					
N2	(Prog. 4, ROCKET) - N1*2+5, Location of Last Non-Derivative Element in Y Array. (DELTA, DELTA2) Number of Radial Stations. (RK4) Location of First Temperature Value					

N3	(Prog. 4, ROCKET) = 4*N1+7, Total Number of Elements in Y Array. (DELTA) Location of First Temperature Value.
	(RK4) Location of Last Temperature Value.
N4	<pre>(Prog, 4, ROCKET) = N2+1, Number of First Derivative Element (<dx dz="">) in Y Array. (DELTA) = Number of Radial Stations Minus One, for Loop Counter that Computes all but Outermost Station</dx></pre>
N5	(Prog. 4, ROCKET) - N4+1, Location of First dX/dZ Element in Y Array
N6	(Prog. 4, ROCKET) - N3-1, Location of Last dT/dZ Element in Y Array
N7	(Prog. 4, ROCKET) - N1*2, For Search Counters
NCOUNT	Loop Control Variable for Debugging Printing
NF	(Prog. 4, DELTA2) Length of Y Array Submitted to Subroutine Delta From Delta2
PD	(Prog. 4, DUMMY) Array required for DGEAR integration (see IMSL documentation)
PI	Mathematical constant, $\pi = 3.14159$
POPPA	Common Block Name
QI	Heat Flux From Gas To Wall
QO	Heat Flux From Wall Into Coolant
R	Universal Gas Constant
R1	Dimensionless Inner Radius of Radial Cell
R2	Dimensionless Outer Radius of Radial Cell
RE	(Prog. 2, FFF) Reynolds Number
RK4	Runge-Kutta-4 integration subroutine
RNH1	Radial Diffusion Mass Flux Into Cell From Next Inner Cell
RNH2	Radial Diffusion Mass Flux Outward From Cell
ROCKET	(Prog. 1-3) Main Program Name (Prog. 4) Main Driver Subroutine Name
RQ1	Radial Thermal Flux by Conduction Into Cell From Next Inner Cell

- RQ2 Radial Thermal Flux by Conduction Outward From Cell
- SRC (Prog. 4) Array of search parameters
- SUM(2) (Prog. 4, DELTA) Array Used For Computation of New Point in Simplex Method Search
- TO Standard Temperature for Thermodynamic Data, 298.15 K
- TAIR Molar Flow Rate of Cooling Air
- TANGO (Prog. 1) Common Block Name
- TB Average Temperature Between Radial Stations, Used to Compute Fluxes and Transport Properties
- TG Estimate of Gas-Dynamic Temperature based on Mass-Average conditions
- THETA (Prog. 1) Fundamental Vibrational Frequency of Hydrogen Molecule Expressed as a Temperature
- T00 Far Upstream Temperature for Calculation of Danckwerts Boundary Conditions
- TOL (RK4) Error Tolerance
- TS Surface Temperature
- TS1 Non-Reaction Surface Temperature Based on Flux Balances
- TS2 Storage Variable for Surface Temperature During Search
- TSA (Prog. 4, DELTA) Surface Temperature From Flux Balances and Reaction at TS
- TSI Storage Variable for Surface Temperature During Search
- TSMIN Minimum Surface Temperature Value, Arbitrarily One-Tenth of Coolant Temperature
- TSN(2) Array for Projection phase of Solution of Wall Boundary Conditions
- TSO Storage Variable for Surface Temperature During Search
- TSX(2) Array for Projection phase of Solution of Wall Boundary Conditions
- TVSS (Prog. 1) Function Subroutine to estimate initial value of T_V based on $dT_v/dz = 0$. at z = 0.

- TW (Prog. 2) Temperature From Which Wall Reactions Were Computed
- U0 Coolant Heat-Transfer Coefficient Control Variable
- UB(Y,Z) Function Subroutine Computes Bulk Velocity at length Z and Conditions described by vector Y. Y(1)=X, Y(2)=T, Y(3)=P, assumes uniform, Ideal Gas Law.
- UI Coolant Heat-Transfer Coefficient Control Variable
- VB Bulk Velocity (Used when use of UB seemed precluded)
- VIS (Prog. 2, FFF) Viscosity of Reacting Mixture, computed from Prandtl number relations
- VMACH(Y,Z) Mach Number at length Z and conditions described by vector Y. Y(1)-X, Y(2)-T, Y(3)-P, assumes uniform, Ideal gas
- VS(Y) Function Subroutine (or statement function) Computes Velocity of Sound at Conditions described by vector Y. Y(1)=X, Y(2)=T, assumes uniform, Ideal gas
- VSS Speed of Sound (Used when use of VS seemed precluded)
- W(47,15) Working Array
- X (RK4) Initial Value of Independent Variable (Prog. 4, DUMMY) Dummy Parameter
- X0 Far Upstream Dissociation for Calculation of Danckwerts Boundary Conditions
- X1 (RK4) Intermediate Value of Independent Variable
- XB Average Dissociation Between Stations, Used For Calculating Fluxes
- XC (RK4) Counter for Debugging Output
- XEQ(T,P) Equilibrium Dissociation at Temperature T and Pressure P
- XF (RK4) Final Value of Independent Variable (Progs. 1-3, RK4) Also Used as Flag for Divergent Integration
- XIT (Prog. 5) Dimensionless Value of change of controlling dependent variable
- XL (RK4) Dimensionless Value of Independent Variable
- XS Surface Dissociation
- XS1 Surface Dissociation To Sustain Mass Flux To Surface

- XSN(2) Array for Projection phase of Solution of Wall Boundary Conditions
- XSX(2) Array for Projection phase of Solution of Wall Boundary Conditions
- XTN(2,4) Array of XS and TS Values used for Simplex Method Search
- XWI Storage Variable for Wall Dissociation Value During Search
- XWO Storage Variable for Wall Dissociation Value During Search
- Y(47) Working Array: (Prog. 1) 1) X; 2) T; 3) P; 4) T_v.

(Prog. 2) 1) X; 2) T; 3) P; 4) T

(Prog. 3) 1) <X>; 2) <T>; 3) P; 4) T_c; 5 - 4+2n) odd elements X, even T.

(Prog. 4, ROCKET, DELTA2) 1) Z; 2) <X>; 3) <T>; 4) P; 5) T_c;

6 - 5+N) X; 6+N - 5+2N) T; 6+2N) dX/dZ; 7+2N - 6+3N) dX/dZ; 7+3N - 6+4N) dT/dZ; 7+4N) dT/dZ. (Prog. 4, DELTA), elements 2 through 5+2N, renumbers. (RK4, AVG, VS, EK, UB, TVSS, DUMMY, Prog. 5): Dummy Name for Submitted Array.

- YO(47) (Prog. 4) Y Array at initial location
- Y1(47) (Prog. 4) D2Y Array at previous print point.
- YMIN (Prog. 4) Minimum value for variables to invoke negative runaway. For dissociations = 0. Temperatures = coolant temperature
- YO Length at Call to Integrator routine
- Z (Progs. 1-3, DELTA, UB, EK, AR, DAR) Length Down Reactor.
 (Prog.4, ROCKET, DELTA2) Independent Variable for Arc-Length Method Integration.
- Z1 (AR) Length at start of Area Defining Function
- Z2 (ROCKET) Final Value of Independent Variable for Integration.(AR) Second defining length for Area Function.
- Z2D Length at Start of Integration Step
- Z3 (AR) Third Defining Length for Area Function
- Z4 (AR) Fourth Defining Length for Area Function
- ZA (AR) Dummy Variable for Area Computation

ZB	(AR) Dummy Variable for Area Computation
ZL	Total Reactor Length
ZP	Print Interval
ZPR	Print Length (Prog. 5) Target value for dependent variable Y(IT)
ZQ	(Prog. 4) $=$ -1., for early restarting procedure

APPENDIX B

APPENDIX B

COMPUTER PROGRAM LISTINGS

Contents

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Program 1

Vibrational Modelling

One-Dimensional, Plug Flow, Adiabatic, Gas-Phase Reaction, Inviscid Flow

```
PROGRAM ROCKET(INPUT, OUTPUT)
С
C PROGRAM TO MODEL HYDROGEN ATOM RECOMBINATION IN A PLUG-FLOW REACTOR
C ONE-DIMENSIONAL ADIABATIC MODEL WITH INTERNAL VIBRATIONAL
C ENERGY CONSIDERATION.
С
      COMMON/ALFA/A2,AK
      COMMON/BRAVD/AMO, FO, R
      COMMON/CHARLIE/DHO, DGO, TO, C(3,3), GAMMA
      DIMENSION Y(4), W(4,9)
      DATA R, TO/8314.34,298.15/
      DATA C/26880.,4.347,-2.645E-04,20786.,0.,0./
      DATA DHO. DGO/4.3141E08.4.0648E08/
      DATA AMO/2./
      DH(T)=DHO+T+CP(3,T)
      CP(I,T)=C(1,I)+T*(C(2,I)+T*C(3,I))
С
C VELOCITY OF SOUND COMPUTED FROM IDEAL GAS RELATIONSHIPS
С
      VS(Y) = SQRT((1, O+Y(1)) + R + Y(2) / AMO/(1, -R + (1, +Y(1))))
     +(2.*Y(1)*CP(2,Y(2))+(1.-Y(1))*CP(1,Y(2)))))
      VMACH(Y,Z)=UB(Y,Z)/VS(Y)
С
C INITIALIZATION INCLUDING EVALUATION OF DELTA CP OF REACTION
C AND STANDARD SET OF INITIAL CONDITIONS AND SYSTEM PARAMETERS.
С
      DO 5 I=1,3
      C(I,3)=(2.*C(I,2)-C(I,1))/I
5
      Z=0.
      Y(1)=0.1
      Y(2) = 1200.
      Y(3) = 3530.
      Y(4) = 1200.
      FO=3.82E-7
      ERR=1.E-6
      AK=A2=3.8E-4
      GAMMA=O.
103
      CONTINUE
      READ +, Z, Y, FO, GAMMA, ERR, AK, A2, ZL, ZP
      IF(Z.LT.O.)GO TO 102
      PRINT +, Z, Y, FO, GAMMA, ERR, AK, A2, ZL, ZP
      IF(Y(4),LT,O,)Y(4)=TVSS(Y)
      PRINT 20, Z, Y, UB(Y, Z), AR(Z), VS(Y), VMACH(Y, Z), TVSS(Y)
20
      FORMAT(3X, 10G12.5)
С
C INTEGRATION OF DIFFERENTIAL EQUATIONS VIA RUNGE-KUTTA 4 METHOD
С
      ZF=AMIN1(Z+ZP,ZL)
101
      CALL RK4(Z,ZF,Y,W,4,ERR)
      IF(ZF.LT.O.)G0 T0 103
      PRINT 20, Z, Y, UB(Y, Z), AR(Z), VS(Y), VMACH(Y, Z), TVSS(Y)
      IF(Z.LT.ZL)G0 T0 101
      GO TO 103
      CONTINUE
102
      END
      FUNCTION AR(Z)
C REACTOR CROSS-SECTIONAL AREA AS FUNCTION OF LENGTH
C MODEL USED HAS 2.5 CM STRAIGHT LENGTH OF AREA AK (USER SELECTED)
C STRAIGHT CONICAL CONVERGING SECTION 2.5 CM LONG TO AREA A2 (ALSO C USER SELECTED) AND STRAIGHT CONICAL DIVERGING SECTION 25 CM LONG
C BACK TO AREA A2. AK, A2 DEFAULTS ARE 3.8 E-4 SQ M.
C
```

```
COMMON/ALFA/A2,AK
      DATA Z1,Z2,Z3,Z4/.025..05..05..30/
      AR=AK
      IF(AK.EQ.A2)RETURN
      IF((Z.LE.Z1).OR.(Z.GE.Z4))RETURN
100
      IF(Z.LT.Z2)GO TO 101
      IF(Z.GT.Z3)G0 T0 102
      AR=A2
      RETURN
101
      ZA=Z1
      7R=72
      GO TO 103
102
      ZA=Z4
      ZB=Z3
103
      AR=(SQRT(AK)+(SQRT(AK)-SQRT(A2))+(Z-ZA)/(ZA-ZB))++2
      RETURN
      END
      FUNCTION DAR(Z)
С
C DERIVATIVE OF AREA VERSUS LENGTH BY FINITE DIFFERENCE METHOD
C STEP SIZE 1.E-6 M
С
      DY=1.E-6
      DAR=(AR(Z+DY)-AR(Z))/DY
      RETURN
      END
      FUNCTION UB(Y,Z)
С
C BULK VELOCITY BY IDEAL GAS LAW
С
      COMMON/BRAVO/AMO, FO, R
      DIMENSION Y(4)
      UB=FO*(1.+Y(1))*R*Y(2)/Y(3)/AR(Z)
      RETURN
      END
      SUBROUTINE DELTA(Z,N,Y,DY)
С
C COMPUTATION OF FIRST-ORDER DERIVATIVES OF CONCENTRATION
C TEMPERATURES AND PRESSURES FROM CONSERVATION RELATIONSHIPS
С
      IMPLICIT REAL (K)
      COMMON/BRAVO/AMO, FO, R
      COMMON/CHARLIE/DHO, DGO, TO, C(3,3), GAMMA
      COMMON/TANGO/THETA, A(3,2)
      DIMENSION Y(N), DY(N)
С
C RATE CONSTANTS DERIVED FROM SHUI AND APPLETON AND SHUI DATA
C LEAST-SQUARES FIT TO FORM OF A(I,1)+T**A(I,2)*EXP(A(I,3)/T)
С
      DATA A/2.014E11,-0.7497,-20.43,8.816E11,-0.7219,-92.09/
      DATA THETA/5990./
С
C RATE AND EQUILIBRIUM CONSTANT EXPRESSIONS
С
      K(I,T)=A(1,I)+T+A(2,I)+EXP(A(3,I)/T)
      KEQ(T)=1.01325E05+EXP((-DGO/TO+C(1,3)+ALOG(T/TO)+(DHO/T/TO+
     +C(2,3)+C(3,3)+(T+TO)/2.)+(T-TO))/R)
      DH(T)=DHO+T+CP(3,T)
      CP(I,T)=C(1,I)+T+(C(2,I)+T+C(3,I))
С
C KINETIC ENERGY OF FLOW AS FUNCTION OF X. T. P. AND Z
```

```
С
      EK(Y,Z)=1./(1./(AMO+UB(Y,Z)++2)-1./R/Y(2)/(1.+Y(1)))
С
C EXPRESSIONS FOR VIBRATIONAL ENERGY, HEAT CAPACTLY, RELAXATION
C RATE AND HEAT OF REACTION
С
      EV(T)=R+THETA/(EXP(THETA/T)-1.)
      CPV(T)=(EV(T)/T)++2+EXP(THETA/T)/R
      KVT(Y)=((1.-Y(1))+25300.+EXP(-100./(Y(2)++(1./3.)))+2+Y(1)+
     +6.60E09+EXP(-3800./Y(2))/Y(2))+Y(3)/(1.+Y(1))
      DHV=4.318852EO8+1.5*R*Y(2)-EV(Y(4))
С
C MATERIAL BALANCE EQUATION INCLUDING RATE EXPRESSION
С
      DY(1)=AR(Z)/FO+(K(2,Y(2))+2.+Y(1)+K(1,Y(2))+(1.-Y(1)))+(KEQ(Y(2))+
     +(1.-Y(1)++2)/Y(3)-4.+Y(1)+Y(1))+(Y(3)/R/Y(2)/(1.+Y(1)))++3
С
C ENERGY BALANCE EQUATIONS INCLUDING HEAT OF REACTION. KINETIC ENERGY
C AND VIBRATIONAL ENERGY TERMS
С
      DY4=-((1, -Y(1)) + KVT(Y) + (EV(Y(4)) - EV(Y(2)))/UB(Y, Z) +
     +DHV+GAMMA+DY(1))
      DY(2)=((EK(Y,Z)/(1.+Y(1))+DHV)+DY(1)-EK(Y,Z)+DAR(Z)/AR(Z)+
     +DY4)/(EK(Y,Z)/Y(2)+R+(7.+3.+Y(1))/2.)+(-1.)
      DY(3) = -EK(Y,Z) * (DY(2)/Y(2)+DY(1)/(1.+Y(1))-DAR(Z)/AR(Z))*
     +Y(3)/R/Y(2)/(1.+Y(1))
      DY(4)=(DY4)/(1.-Y(1))/CPV(Y(4))
      RETURN
      END
      SUBROUTINE RK4(X,XF,Y,W,N,TOL)
      DIMENSION Y(N).W(N.9)
С
C INTEGRATION OF DIFFERENTIAL EQUATIONS VIA RUNGE-KUTTA 4 METHOD
С
      DXO=XF-X
      DXL=1.
      DO 6 I=1,N
6
      W(I,9)=Y(I)
100
      XL=O.
      DO 5 I=1,N
      W(I, 1) = Y(I)
5
101
      CALL DELTA(X+XL+DXO,N,W(1,1),W(1,2))
С
C CHECKS FOR STEEP GRADIENTS, AND IF STEP SIZE BECOMES TOO SMALL
C RETURNS TO MAIN PROGRAM WITH NEGATIVE FINAL VALUE FOR INDEPENDENT
C VARIABLE
С
105
      IF(ABS(W(2,2)+DXL+DXD).GT.O.1+W(2,1))GO TO 106
      IF(ABS(W(4,2)+DXL+DXO).LE.O.1+W(4,1))GO TO 104
      DXL=DXL/2.
106
      GO TO 105
      IF(DXL.GT.2.**(-20))GO TO 114
PRINT *," INTEGRATION DIVERGED"
104
      XF = -XF
      RETURN
      XL=XL+DXL/2.
114
      X1=X+XL+DXO
      DX=DXL+DXO
      DO 10 I=1,N
      W(I,6)=W(I,1)+DX+W(I,2)/2.
10
      CALL DELTA(X1,N,W(1,6),W(1,3))
```

```
DO 20 I=1,N
      W(I,7)=W(I,1)+DX+W(I,3)/2.
20
      CALL DELTA(X1,N,W(1,7),W(1,4))
      DO 30 I=1,N
30
      W(I,8)=W(I,1)+DX+W(I,4)
      XI = XI + DXL
      XO=X+XL+DXD
      CALL DELTA(XO.N.W(1.8).W(1.5))
      DO 40 I=1,N
      W(I,1)=W(I,1)+(W(I,2)+2.+(W(I,3)+W(I,4))+W(I,5))+DX/6.
40
      IF(XL.LT.1.)G0 T0 101
      DXL=DXL/2.
      ERR=O.
      DO 50 I=1,N
      IF(ABS((W(I,1)-Y(I))/Y(I)).LT.TOL)GO TO 60
      ERR=ERR+((W(I,9)-W(I,1))/(W(I,1)-Y(I)))**2
      W(I,9) = W(I,1)
60
      CONTINUE
50
      IF(ERR.GT.TOL)GO TO 100
103
      X = XF
      DO 70 I=1,N
70
      Y(I) = W(I,9)
      RETURN
      END
      FUNCTION TVSS(Y)
С
C COMPUTATION OF STEADY-STATE VALUE OF VIBRATIONAL TEMPERATURE
C BALANCES EXCITATION AND RELAXATION RATES.
С
      IMPLICIT REAL (K)
      COMMON/BRAVD/AMO, FO, R
      COMMON/CHARLIE/DHO,DGO,TO,C(3,3),GAMMA
      COMMON/TANGO/THETA, A(3,2)
      DIMENSION Y(4)
С
C RATE AND EQUILIBRIUM CONSTANT EXPRESSIONS
C
      K(I,T)=A(1,I)+T++A(2,I)+EXP(A(3,I)/T)
      KEQ(T)=1.01325E05+EXP((-DG0/T0+C(1,3)+ALDG(T/T0)+(DH0/T/T0+
     +C(2,3)+C(3,3)+(T+TO)/2.)+(T-TO))/R)
      CP(I,T)=C(1,I)+T*(C(2,I)+T*C(3,I))
      EV(T)=R+THETA/(EXP(THETA/T)-1.)
      KVT(Y)=((1.-Y(1))+25300.+EXP(-100./(Y(2)++(1./3.)))+2+Y(1)+
     +6.60E09*EXP(-3800./Y(2))/Y(2))*Y(3)/(1.+Y(1))
      DHT=4.318852E08+1.5+R+Y(2)
      DX=(K(2,Y(2))+2.+Y(1)+K(1,Y(2))+(1.-Y(1)))+(KEQ(Y(2))+
     +(1, -Y(1)**2)/Y(3)-4.*Y(1)*Y(1))*(Y(3)/R/Y(2)/(1.+Y(1)))**2
      GOLF=GAMMA+DX/KVT(Y)/(1.-Y(1))
      EVTV=(EV(Y(2))-GOLF+DHT)/(1.-GOLF)
      TVSS=THETA/ALOG(1.+R+THETA/EVTV)
      RETURN
      END
```

Program 2

Reactive Surface

One-Dimensional, Plug Flow, Cooled, Surface Reaction, Viscous Flow

```
PROGRAM ROCKET(INPUT, OUTPUT)
С
C PROGRAM TO MODEL HYDROGEN ATOM RECOMBINATION IN A PLUG-FLOW REACTOR
C ONE-DIMENSIONAL, COOLED REACTOR WITH VISCOUS DRAG OPTION
C INCLUDES OPTIONS FOR SURFACE REACTION
С
      COMMON/ALFA/A2,AK
      COMMON/BRAVO/AMO, FO, R
      COMMON/CHARLIE/DHO, TO, C(3,3), GAMMA
      COMMON/ECHO/TAIR.UO
      COMMON/POPPA/PI
      COMMON/FOXTROT/FR
      COMMON/MIKE/MODE, M2, TS
      DIMENSION Y(4), W(4,9)
      DATA R, TO/8314.34,298.15/
      DATA C/26880.,4.347,-2.645E-04,20786.,0.,0./
      DATA DHO, DGO/4.3141E08,4.0648E08/
      DATA AMO/2./
      DH(T)=DHO+T+CP(3,T)
      CP(I,T)=C(1,I)+T+(C(2,I)+T+C(3,I))
С
C VELOCITY OF SOUND BY IDEAL GAS RELATIONS
С
      VS(Y) = SQRT((1.0+Y(1))*R*Y(2)/AMO/(1.-R*(1.+Y(1))/(2.*Y(1)*))
     +CP(2,Y(2))+(1.-Y(1))*CP(1,Y(2))))
      VMACH(Y,Z)=UB(Y,Z)/VS(Y)
С
C INITIALIZATION INCLUDING EVALUATION OF DELTA CP OF REACTION
C AND STANDARD INITIAL CONDITIONS AND SYSTEM PARAMETERS.
С
      DO 5 I=1,3
5
      C(I,3)=(2.*C(I,2)-C(I,1))/I
      UO=1.6
      FR=O.
      PI=4. *ATAN(1.0)
      Z=0.
      Y(1)=0.1
      Y(2) = 1200.
      Y(3)=3530.
      Y(4)=400.
      FO=3.82E-7
      ERR=1.E-6
      AK=A2=3.8E-4
      TAIR=1.7E-4
103
      CONTINUE
      READ +,Z,Y,FO,ERR,AK,A2,ZL,ZP,TAIR,UO,MODE,M2,FR
      IF(Z.LT.O.)GD TO 102
      PRINT +,Z,Y,FO,ERR,AK,A2,ZL,ZP,TAIR,UO,MODE,M2,FR
С
C ESTIMATION OF THE GAS-DYNAMIC TEMPERATURE THAT THE EXPERIMENTAL
C ASSUMPTION OF ZERO DISSOCIATION WOULD REPORT UNDER THE CONDITIONS
C OF THE MODEL.
С
      TG=Y(2)+5.*(7.+3.*Y(1))*(1.+Y(1))/7./(5.+Y(1))
      TS=Y(2)
      PRINT 20, Z, Y, UB(Y, Z), AR(Z), VS(Y), TG
      FORMAT(3X, 10G12.5)
20
С
C INTEGRATION OF DIFFERENTIAL EQUATIONS VIA RUNGE-KUTTA 4 METHOD
С
101
      ZF=AMIN1(Z+ZP,ZL)
      DZ=ZP
104
      Z2=AMIN1(Z+DZ,ZF)
```

```
CALL RK4(Z,Z2,Y,W,4,ERR)
      IF (Z2.LT.O) DZ=DZ/16.
      IF (DZ.LT.1.E-7+ZP) GO TO 103
      IF (Z.LT.ZF) GO TO 104
С
C ESTIMATION OF THE GAS-DYNAMIC TEMPERATURE THAT THE EXPERIMENTAL
C ASSUMPTION OF ZERO DISSOCIATION WOULD REPORT UNDER THE CONDITIONS
C OF THE MODEL.
С
      TG=Y-(2)*5.*(7.+3.*Y(1))*(1.+Y(1))/7./(5.+Y(1))
      PRINT 20, Z, Y, UB(Y, Z), AR(Z), VS(Y), TG, TS
      IF(Z.LT.ZL)G0 T0 101
      GO TO 103
102
      CONTINUE
      END
      FUNCTION AR(Z)
С
C CROSS-SECTIONAL AREA OF REACTOR AS FUNCTION OF LENGTH
C MODEL USED WAS 2.5 CM LONG STRAIGHT TUBE OF AREA AK (USER SELECTED)
C THEN STRAIGHT CONICAL CONVERGING SECTION 2.5 CM LONG TO AREA A2
C (ALSO USER SELECTED) FOLLOWED BY A 25 CM LONG STRAIGHT CONE DIVERGING C SECTION BACK TO AREA AK. DEFAULTS AK, A2 3.8E-4 SQ M.
С
      COMMON/ALFA/A2,AK
      DATA Z1, Z2, Z3, Z4/.025,.05,.05,.30/
      AR=AK
      IF(AK.EQ.A2)RETURN
      IF((Z.LE.Z1).OR.(Z.GE.Z4))RETURN
      IF(Z.LT.Z2)G0 T0 101
100
      IF(Z.GT.Z3)G0 T0 102
      AR=A2
      RETURN
101
      ZA=Z1
      ZB=Z2
      GO TO 103
      ZA=74
102
      ZB=Z3
103
      AR=(SORT(AK)+(SORT(AK)-SORT(A2))+(Z-ZA)/(ZA-ZB))++2
      RETURN
      END
      FUNCTION DAR(Z)
С
C DERIVATIVE OF AREA WITH RESPECT TO LENGTH
C FINITE DIFFERENCE METHOD, STEP 1.E-6 M
С
      DY=1.E-06
      DAR=(AR(Z+DY)-AR(Z))/DY
      RETURN
      END
      FUNCTION UB(Y,Z)
С
C BULK VELOCITY BY IDEAL GAS LAW
С
      COMMON/BRAVO/AMO, FO, R
      DIMENSION Y(4)
      UB=FO+(1.+Y(1))+R+Y(2)/Y(3)/AR(Z)
      RETURN
      END
      SUBROUTINE DELTA(Z,N,Y,DY)
C
C COMPUTATION OF FIRST-ORDER DERIVATIVES BY CONSERVATION RELATIONS
```

```
С
      IMPLICIT REAL (K)
      COMMON/BRAVO/AMO, FO, R
      COMMON/CHARLIE/DHO, TO, C(3,3), GAMMA
      COMMON/ECHO/TAIR, UI
      COMMON/POPPA/PI
      COMMON/MIKE/MODE, M2, TS
      DIMENSION A(3,3), Y(N), DY(N)
      DATA DGO/4.0648E08/
С
C RATE CONSTANTS DERIVED FROM SHUI AND APPLETON AND SHUI DATA
C LEAST-SQUARES FIT TO FORM OF A(I,1)*T**A(I,2)*EXP(A(I,3)/T)
С
      DATA A/2.014E11,-0.7497,-20.43,8.816E11,-0.7219,-92.09,3.855E18,
     +-3.,-2900./
С
C RATE AND EQUILIBRIUM CONSTANT EXPRESSIONS
С
      K(I,T)=A(1,I)+T+A(2,I)+EXP(A(3,I)/T)
      KEQ(T)=1.01325E05*EXP((-DGO/TO+C(1,3)*ALOG(T/TO)+(DHO/
     +T/TO+C(2,3)+C(3,3)+(T+TO)/2.)+(T-TO))/R)
      DH(T)=DHO+T*CP(3,T)
      CP(I,T)=C(1,I)+T+(C(2,I)+T+C(3,I))
С
C KINETIC ENERGY OF FLOW AS FUNCTION OF X. T. P. AND Z
С
      EK(Y,Z)=1./(1./(AMO+UB(Y,Z)++2)-1./R/Y(2)/(1.+Y(1)))
С
C MATERIAL BALANCE EQUATION INCLUDING RATE EXPRESSION
C AND COMPUTATION OF SURFACE REACTION OPTIONS CONTROLLED BY
C PARAMETERS MODE AND M2. LINEAR INTER- AND EXTRAPOLATION TO
C FIND SURFACE CONDITIONS.
С
      A(1,3)=3.855E18
      LOOP = 1
С
C ASSUME CIRCULAR REACTOR CROSS SECTION TO RELATE SURFACE AREA AND
C CROSS-SECTIONAL AREA
С
      AS=2.*SQRT(PI*AR(Z))
      IF(MODE.EQ.1)A(1,3)=0.
      FD=FFF(Y,Z)+PI/AS
С
C DETERMINATION OF HEAT-TRANSFER COEFFICIENT
C IF UI LT O., USE ABSOLUTE VALUE IN SI UNITS
C IF UI = O., ADIABATIC
C IF UI GT O., MULTIPLY BY NUSSELT NUMBER COMPUTATION
С
      IF(UI)111,112,113
112
      HO=0.
      HI=1.
      GO TO 114
      HI=HO=ABS(UI)
111
      GO TO 110
113
      H0=UI+47.06
      HI=UI
      HI=HI+3.66+1.843E-3+Y(2)++.8+PI/AS
114
      TS1=TS=(HO+Y(4)+HI+Y(2))/(HO+HI)
110
      KW=3.66+PI+1.264E-3+Y(2)++0.72/(1.+Y(1))/R
C MATERIAL BALANCE BASED ON FLOW AND GAS-PHASE REACTION
```

```
С
      DXV=AR(Z)/FO*(K(2,Y(2))*2.*Y(1)+K(1,Y(2))*(1.-Y(1)))*
     +(KEQ(Y(2))*(1.-Y(1))/Y(3)*(1.+Y(1))-4.*Y(1)*Y(1))*
     +(Y(3)/R/Y(2)/(1.+Y(1)))**3
      DXSO=Y(1)
      XWO=O.
      XW=Y(1)
150
      XWI=XW
      TS=AMIN1(TS,Y(2)+10000.)
120
      TS=AMAX1(TS,Y(4)/2.)
      TS1=TW=TS
      IF(MODE.EQ.4)TW=Y(2)
      DXW=AS/FO+K(3,TW)+(KEQ(TW)/Y(3)+(1.-XW+XW)-
     +4.*XW**2)*(Y(3)/R/TW/(1.+XW))**2
      DY(1)=DXV+DXW
С
C ENERGY BALANCE EQUATION INCLUDING HEAT OF REACTION, KINETIC ENERGY
C AND THERMAL ENERGY TERMS
C ENERGY TRANSFER FROM SURFACE REACTION CONTROLLED BY PARAMETERS
C SURFACE CONDITIONS DETERMINED BY SOLUTION OF CONSERVATION LAWS
C BY LINEAR INTER- AND EXTRAPOLATIONS.
С
      DHS=DXW+DH(TS)+FO
      IF(MODE.GE.3)TS=TS1-DHS/AS/(HO+HI)
      DTS=TS-TSI
      IF(ABS(DTS).LE.1.)GO TO 130
      GO TO (121,122),LOOP
      IF(TSI.EQ.TSO)GO TO 130
122
      IF(DTS.EQ.DTSO)GO TO 130
      TS=TSI+DTS+(TSO-TSI)/(DTS-DTSO)
121
      LOOP=2
      TSO=TSI
      DTSO=DTS
      GO TO 120
      DXS=(Y(1)/(1.+Y(1))-XW/(1.+XW))+DXW+FO/KW+(1.+XW/(1.+XW))
130
      IF(M2.EQ.0)G0 TO 151
      IF(DXS.EQ.DXSO)GO TO 151
      XW=XW+DXS+(XWO-XW)/(DXS-DXSO)
      XW=AMAX1(XW,O.)
      IF(ABS(XWO-XW).LE.XW+O.1)GO TO 151
      XWO=XWI
      DXSO=DXS
      GO TO 150
151
      QI=(Y(2)-TS)+HI+AS
      IF(MODE.EQ.2)QI=QI+DHS
      00=0I-DHS
      DY(2)=((EK(Y,Z)/(1.+Y(1)))*DY(1)+DH(Y(2))*DXV-EK(Y,Z)*DAR(Z)/
     +AR(Z)+QI/FO+FD+UB(Y,Z)++4/R/Y(2)/(Y(1)+1.))/(EK(Y,Z)/Y(2)+
     +(1.-Y(1))+CP(1,Y(2))+2.+Y(1)+CP(2,Y(2)))+(-1.)
      DY(3) = -EK(Y,Z) * (DY(2)/Y(2)+DY(1)/(1.+Y(1))-DAR(Z)/
     +AR(Z)+UB(Y,Z)**2*FD)*Y(3)/R/Y(2)/(1.+Y(1))
С
C ENERGY BALANCE EQUATION ON COOLING AIR
C INCLUDES TERM FOR RADIATIVE-CONVECTIVE LOSS TO ENVIRONMENT
C USES DIATOMIC KINETIC THEORY VALUE FOR AIR HEAT CAPACITY
C
      DY(4) = (Q0+1.64 + (300. - Y(4)))/TAIR/3.5/R
      RETURN
      END
      SUBROUTINE RK4(X, XF, Y, W, N, TOL)
С
```

```
C INTEGRATION OF DIFFERENTIAL EQUATIONS VIA RUNGE-KUTTA 4 METHOD
С
      DIMENSION Y(N), W(N, 9)
      DXO=XF-X
      DXL=1.
      CALL DELTA(X,N,Y,W(1,8))
      KOUNT = -1
100
      KOUNT=KOUNT+1
      XC = .1
      XL=O.
      DO 5 I=1.N
      W(1,2)=W(1,8)
      W(I, 1) = Y(I)
5
      GO TO 105
101
      CONTINUE
      CALL DELTA(X+XL+DXO,N,W(1,1),W(1,2))
С
C CHECKS FOR STEEP GRADIENTS, REDUCES STEP SIZE IF FOUND
C IF STEP SIZE REDUCED TOO FAR, RETURNS, WITH NEGATIVE FINAL
C X-VALUE AS FLAG
C
105
      IF(ABS(W(2,2)+DXL+DXO).GT.O.1+W(2,1))GD TO 106
      IF(ABS(W(N,2)+DXL+DXO).LE.O.1+W(N,1))GO TO 104
106
      DXL=DXL/2.
      GO TO 105
      IF(DXL.GT.2.**(-20))G0 T0 110
104
      PRINT *, " INTEGRATION DIVERGED"
      XF = -XF
      RETURN
110
      XL=XL+DXL/2.
      X1=X+XL+DXO
      DO 10 I=1,N
      W(I,6)=W(I,1)+DXL+DXO+W(I,2)/2.
10
      CALL DELTA(X1,N,W(1,6),W(1,3))
      DO 20 I=1,N
20
      W(I,7)=W(I,1)+DXL+DXO+W(I,3)/2.
      CALL DELTA(X1, N, W(1,7), W(1,4))
      DO 30 I=1,N
30
      W(I,7)=W(I,1)+DXL+DXO+W(I,4)
      XL=XL+DXL/2.
      CALL DELTA(X+XL+DXO,N,W(1,7),W(1,5))
      DO 40 I=1,N
      W(I,1)=W(I,1)+(W(I,2)+2.*(W(I,3)+W(I,4))+W(I,5))*DXL*DXO/6.
40
      IF (XL-XC) 1001,1000,1000
     XC=XC+1./10.
1000
1001
      CONTINUE
      IF(XL.LT.1.)G0 T0 101
      DXL=DXL/2.
      IF(KOUNT.EQ.O)GO TO 102
      ERR=O.
      DO 50 I=1,N
      IF(ABS((W(I,9)-Y(I))/W(I,9)).LE.1.E-8)GO TO 51
      ERR=ERR+((W(I,9)-W(I,1))/(W(I,9)-Y(I)))**2
51
      CONTINUE
      CONTINUE
50
      IF(ERR.LE.TOL)GO TO 103
102
      DO 60 I=1,N
      W(I,9)=W(I,1)
60
      GO TO 100
103
      X=XF
      DO 70 I=1.N
```

```
70
      Y(I)=W(I,9)
      RETURN
      END
      FUNCTION FFF(Y,Z)
С
C COMPUTATION OF FANNING FRICTION FACTOR
C ITERATIVE SOLUTION OF RECURSIVE EQUATION FROM PERRY FOR
C SMOOTH PIPE TURBULENT FLOW
C LAMINAR FLOW USES F=64/RE
С
      COMMON/BRAVO/AMO, FO, R
      COMMON/CHARLIE/DHO, TO, C(3,3), GAMMA
      COMMON/POPPA/PI
      COMMON/FOXTROT/FR
      DIMENSION Y(4)
      CP(I,T)=C(1,I)+T*(C(2,I)+T*C(3,I))
      FFF=FR
      IF (FR.EQ.O.)RETURN
HI=1.843E-3+Y(2)++.8
      VIS=0.7*HI/(CP(1,Y(2))*(1.-Y(1))+2.*Y(1)*CP(2,Y(2)))*AMO
      RE=FO*AMO/VIS/SQRT(PI*AR(Z))
      FFF=FR+64./RE
      IF(RE.LT.2100.)RETURN
      FI=FFF/FR
101
      FFF=(2.*ALOG10(RE*SQRT(FI))-0.8)**(-2)
      IF(ABS((FFF-FI)/FFF).GT.1.E-6)GO TO 101
      RETURN
      END
```

Program 3

Two-Dimensional Model

Two-Dimensional, Plug Flow, Cooled, Surface Reaction, Inviscid Flow

```
PROGRAM ROCKET(INPUT, OUTPUT)
С
C PROGRAM TO MODEL HYDROGEN ATOM RECOMBINATION IN A PLUG-FLOW REACTOR
C TWO-DIMENSIONAL PLUG-FLOW MODEL
C
      COMMON/ALFA/A2.AK
      COMMON/BRAVO/AMO.FO.R
      COMMON/CHARLIE/DHO, TO, C(3,3), GAMMA
      COMMON/ECHO/TAIR, UO
      COMMON/POPPA/PI
      DIMENSION Y(24), W(24,9)
      EXTERNAL DELTA
      DATA R, TO/8314.34,298.15/
      DATA C/26880.,4.347,-2.645E-04,20786.,0.,0./
      DATA DHO, DGO/4.3141EO8, 4.0648EO8/
      DATA AMO/2./
      DH(T)=DHO+T+CP(3,T)
      CP(I,T)=C(1,I)+T+(C(2,I)+T+C(3,I))
С
C VELOCITY OF SOUND FROM IDEAL GAS RELATIONS
С
      VS(Y)=SQRT((1.0+Y(1))*R*Y(2)/AMO/(1.-R*(1.+Y(1))/(2.*Y(1)*
     +CP(2,Y(2))+(1,-Y(1))+CP(1,Y(2))))
      VMACH(Y,Z)=UB(Y,Z)/VS(Y)
С
C INITIALIZATION INCLUDING EVALUATION OF DELTA CP OF REACTION
C AND STANDARD SET OF INITIAL CONDITIONS AND SYSTEM PARAMETERS.
С
      DO 5 I=1,3
5
      C(I,3)=(2.*C(I,2)-C(I,1))/I
      Z=0.
      Y(1)=0.1
      Y(2) = 1200.
      Y(3)=3530.
      Y(4) = 400.
      FO=3.82E-7
      ERR=1.E-6
      AK=A2=3.8E-4
      TAIR=1.7E-4
      PI=4. *ATAN(1.0)
      UO=1.6
      CONTINUE
103
С
C INPUT OF INITIAL CONDITIONS AND SYSTEM PARAMETERS
C
      READ *,Z,(Y(L),L=1,4),FO,ERR,AK,A2,ZL,ZP,TAIR,UO,INPRO,N1
      IF(Z.LT.O.)G0 T0 102
      PRINT +,Z,(Y(L),L=1,4),FO,ERR,AK,A2,ZL,ZP,TAIR,UO,INPRO,N1
      N2=N1+2+4
      GO TO (111,112,113,111), INPRO
С
C IF INPRO = 1, INITIAL PROFILES ARE UNIFORM ACROSS REACTOR
С
      DO 110 I=5,N2,2
111
      Y(I) = Y(1)
      Y(I+1)=Y(2)
110
      GO TO (150,150,150,114), INPRO
С
C IF INPRO = 4, INITIAL PROFILES ARE UNIFORM EXCEPT THAT OUTER-MOST
C STATION IS AT CODLANT TEMPERATURE AND ZERO DISSOCIATION
С
114
      Y(N2-1)=0.
      Y(N2) = Y(4)
```

```
GO TO 150
С
C IF INPRO = 2, INITIAL PROFILE IS ZERO-DISSOCIATION AND COOLANT
C TEMPERATURE ACROSS REACTOR EXCEPT FOR CENTRAL STATION, WHICH IS AT
C INPUT TEMPERATURE AND DISSOCIATION.
С
112
       Y(5)=Y(1)
      Y(6) = Y(2)
      DO 120 I=7,N2,2
       Y(I)=0.
120
      Y(I+1)=Y(4)
       GO TO 150
С
C IF INPRO=3, PROGRAM PROMPTS FOR ARBITRARY INITIAL PROFILES.
C IF CONTINUATION OF A PREVIOUS RUN IS DESIRES, DEFAULTS TO LAST
C PROFILE, SO STRING OF ", "'S WILL CONTINUE RUN. NO DEFAULT ON
C INITIALIZATION FOR FIRST RUN.
С
113
      PRINT +, " X PROFILE"
      READ *, (Y(L), L=5, N2, 2)
       PRINT +, (Y(L), L=5, N2, 2)
      PRINT *. " T PROFILE"
       READ *, (Y(L), L=6, N2, 2)
      PRINT +, (Y(L), L=6, N2, 2)
150
      N3=N2-5
       Y(1) = AVG(Y(5), N3)
       Y(2) = AVG(Y(6).N3)
С
C ESTIMATION OF THE GAS-DYNAMIC TEMPERATURE THAT THE EXPERIMENTAL
C ASSUMPTION OF ZERO DISSOCIATION WOULD REPORT UNDER THE CONDITIONS
C PREDICTED BY THE MODEL
С
       TG=Y(2)*5.*(7.+3.*Y(1))*(1.+Y(1))/7./(5.+Y(1))
       PRINT 20, Z, (Y(L), L=1, 4), UB(Y, Z), AR(Z), VS(Y). TG
       PRINT 30, (Y(L), L=5, N2, 2)
      PRINT 30, (Y(L), L=6, N2, 2)
       FORMAT(8X, 10G11.4)
30
       FORMAT(3X, 10G12.5)
20
С
C INTEGRATION OF DIFFERENTIAL EQUATIONS VIA RUNGE-KUTTA 4 METHOD
С
101
      ZF=AMIN1(Z+ZP,ZL)
      DZ=ZP
104
       Z2=AMIN1(Z+DZ,ZF)
       CALL RK4(DELTA,Z,Z2,Y,W,N2,ERR)
C WHEN THE INTEGRATION SUBROUTINE REPORTED THAT IT DIVERGED,
C THIS VERSION WOULD CUT THE INITIAL STEP SIZE BY A FACTOR OF 16 AND C REPEAT, UNTIL IT WAS REDUCED BY A FACTOR OF 10 MILLION
С
       IF (Z2.LT.O) DZ=DZ/16.
       IF (DZ.LT.1.E-7+ZP) GO TO 103
       IF (Z.LT.ZF) GO TO 104
С
C ESTIMATION OF THE GAS-DYNAMIC TEMPERATURE THAT THE EXPERIMENTAL
C ASSUMPTION OF ZERO DISSOCIATION WOULD REPORT UNDER THE CONDITIONS
C PREDICTED BY THE MODEL
С
       TG=Y(2)+5.+(7.+3.+Y(1))+(1.+Y(1))/7./(5.+Y(1))
       PRINT 20, Z, (Y(L), L=1,4), UB(Y, Z), AR(Z), VS(Y), TG
       PRINT 30, (Y(L), L=5, N2, 2)
```

```
PRINT 30, (Y(L), L=6, N2, 2)
      IF(Z.LT.ZL)GO TO 101
      GO TO 103
102
      CONTINUE
      END
      FUNCTION AR(Z)
С
C REACTOR AREA FLOW PROFILE SUBROUTINE
C PRESENTLY CONSISTS OF A 25 MM. STRAIGHT LENGTH OF TUBE WITH
C CROSS-SECTIONAL AREA AK (OPERATOR INPUT, DEFAULT 3.8E-4 SQ. M.)
C FOLLOWED BY A STRAIGHT CONICAL TAPER OVER ANOTHER 25 MM. TO
C A THROAT WITH AREA A2 (ALSO INPUT, SAME DEFAULT) WHICH IS FOLLOWED
C BY ANOTHER STRAIGHT CONICAL DIVERGENT TAPER OVER 25 CM. LENGTH
C BACK TO AREA AK.
С
      COMMON/ALFA/A2, AK
      DATA Z1, Z2, Z3, Z4/0.,.025,.05,.30/
      AR=AK
      IF (AK.EQ.A2) RETURN
      IF((Z.LE.Z1).OR.(Z.GE.Z4))RETURN
      IF(Z.LT.Z2)GO TO 101
IF(Z.GT.Z3)GO TO 102
100
      AR=A2
      RETURN
101
      ZA = Z1
      ZB≠Z2
      GO TO 103
102
      ZA = Z4
      ZB≠Z3
      AR=(SQRT(AK)+(SQRT(AK)-SQRT(A2))+(Z-ZA)/(ZA-ZB))++2
103
      RETURN
      END
      FUNCTION DAR(Z)
С
C COMPUTATION OF DERIVATIVE OF CROSS-SECTIONAL AREA WITH LENGTH
C USED IN INVISCID FLOW RELATIONS
C FINITE DIFFERENCE CALCULATION, WITH STEP-SIZE 1 MICRON.
С
      DY=1.E-06
      DAR=(AR(Z+DY)-AR(Z))/DY
      RETURN
      END
      FUNCTION UB(Y,Z)
С
C CALCULATION OF BULK VELOCITY BASED ON IDEAL GAS LAW
С
      COMMON/BRAVD/AMO, FO, R
      DIMENSION Y(4)
      UB=FO*(1.+Y(1))*R*Y(2)/Y(3)/AR(Z)
      RETURN
      END
      SUBROUTINE DELTA(Z.N.Y.DY)
С
C CALCULATION OF MATERIAL AND ENERGY BALANCES FOR FIRST DERIVATIVES
C
      IMPLICIT REAL (K)
      COMMON/BRAVD/AMO, FO, R
      COMMON/CHARLIE/DHO, TO, C(3, 3), GAMMA
      COMMON/ECHO/TAIR,UI
      COMMON/POPPA/PI
      DIMENSION A(3,3), Y(N), DY(N)
```

```
DATA DGO/4.0648E08/
С
C RATE CONSTANTS DERIVED FROM SHUI AND APPLETON, SHUI, AND WOOD AND WISE
C DATA
C LEAST-SQUARES FIT TO FORM OF EXPRESSION K = A*(T**B)*EXP(C/T)
С
      DATA A/2.014E11,-0.7497,-20.43,8.816E11,-0.7219,-92.09,3.855E18,
     +-3.,-2900./
С
C RATE AND EQUILIBRIUM CONSTANT EXPRESSIONS
С
      K(I,T)=A(1,I)+T++A(2,I)+EXP(A(3,I)/T)
      KEQ(T)=1.01325E05+EXP((-DGO/TO+C(1,3)+ALOG(T/TO)+(DHO/
     +T/TO+C(2,3)+C(3,3)*(T+TO)/2.)*(T-TO))/R)
      DH(T)=DHO+T+CP(3,T)
      CP(I,T)=C(1,I)+T*(C(2,I)+T*C(3,I))
      DH2HP(T)=1.264E-3+T++1.72
      KTH(T)=1.843E-3+T++.8
С
C KINETIC ENERGY OF FLOW AS FUNCTION OF X, T, P, AND Z
С
      EK(Y,Z)=1./(1./(AMO+UB(Y,Z)++2)-1./R/Y(2)/(1.+Y(1)))
      AS=2.*SQRT(PI*AR(Z))
      IF(UI)111,112,113
112
      HO=0.
      GO TO 110
      HO=ABS(UI)
111
      GO TO 110
      HO = UI + 47.06
113
      CONTINUE
110
      DR=2./(N-6.)
      N3=N-3
      DO 160 J=5,N3,2
      R2=DR*(J-4.)/2.
      R1=AMAX1(R2-DR,O.)
С
C MATERIAL BALANCE EQUATION INCLUDING RATE EXPRESSION
C AND RADIAL DIFFUSION TERM
С
      DXR=AR(Z)/FO*((K(2,Y(J+1))*2.*Y(J)+K(1,Y(J+1))*(1.-Y(J)))*
     +(KEQ(Y(J+1))*(1.-Y(J))/Y(3)*(1.+Y(J))-4.*Y(J)*Y(J))*
     +(Y(3)/R/Y(J+1)/(1.+Y(J)))**3)/(2.-(R2*R2+R1*R1))
      DY(J)=DXR-PI/FO/R/DR*(DH2HP((Y(J+1)+Y(J-1))/2.)*R1*
     +(Y(J)/(Y(J)+1.)/Y(J+1)-Y(J-2)/(Y(J-2)+1.)/Y(J-1))+
     +DH2HP((Y(J+1)+Y(J+3))/2.)*R2*
     +(Y(J)/(Y(J)+1.)/Y(J+1)-Y(J+2)/(Y(J+2)+1.)/Y(J+3)))*
     +(1.+Y(J))/(1.+2.+Y(J))/(2.-R1+R1-R2+R2)
С
C ENERGY BALANCE EQUATION INCLUDING HEAT OF REACTION, KINETIC ENERGY
C AND THERMAL ENERGY TERMS
С
      DY(J+1)=(((EK(Y,Z)/(1.+Y(J)))*DY(J)+DH(Y(J+1))*DXR-EK(Y,Z)*
     +DAR(Z)/AR(Z))+2.*PI/DR/FO/(R2*R2-R1*R1)/(2.-R2*R2-R1*R1)*
     +(KTH((Y(J+1)+Y(J-1))/2.0)*R1*(Y(J+1)-Y(J-1))+KTH((Y(J+1)+Y(J+3))/
     +2.)*(R2+Y(J+1)-R2+Y(J+3))))/(EK(Y,Z)/Y(J+1)+
     +(1.-Y(J))*CP(1,Y(J+1))+2.*Y(J)*CP(2,Y(J+1)))*(-1.)
160
      CONTINUE
С
C COMPUTATION OF BOUNDARY CONDITIONS AT OUTERMOST STATION
С
      QO=(Y(N)-Y(4))+HO+AS
```

```
DXR=AR(Z)/FO+(AS/AR(Z)+K(3,Y(N))+(1.-R2+R2)+Y(3)/R/Y(N)/
           +(1.+Y(N-1))*(K(2,Y(N))*2.*Y(N-1)+K(1,Y(N))*(1.-Y(N-1))))*
           +(KEQ(Y(N))+(1.-Y(N-1)++2)/Y(3)-4.+Y(N-1)+Y(N-1))+
           ++(Y(3)/R/Y(N)/(1.+Y(N-1)))++2/(1.-R2+R2+(2.-R2+R2))
             DY(N-1)=DXR-PI/FO+DH2HP((Y(N)+Y(N-2))/2.)/R/DR/(1.+Y(N-1)/
           +(Y(N-1)+1.))+(R2+Y(N-1)/(1.+Y(N-1))/Y(N)-R2+Y(N-3)/
           +(1.-Y(N-3))/(N-2))/(1.-R2*R2)
С
C ENERGY BALANCE EQUATION INCLUDING HEAT OF REACTION, KINETIC ENERGY
C AND THERMAL ENERGY TERMS
С
             DY(N) = (((EK(Y,Z)/(1.+Y(N-1))) + DY(N-1) + DH(Y(N)) + DXR - EK(Y,Z) + DY(N-1) + DY(N-1
           +DAR(Z)/AR(Z))+(KTH((Y(N)+Y(N-2))/2.)/DR*(R2*Y(N)-R2*
           +Y(N-2))+2.+PI+Q0)/FO/(1.-R2+R2)++2)/(EK(Y,Z)/Y(N)+
           +(1.-Y(N-1))*CP(1,Y(N))+2.*Y(N-1)*CP(2,Y(N)))*(-1.)
             DY(1)=AVG(DY(5),N-5)
             DY(2)=AVG(DY(6),N-5)
             DY(3) = -EK(Y,Z) + (DY(2)/Y(2)+DY(1)/(1.+Y(1))-DAR(Z)/AR(Z)) +
           +Y(3)/R/Y(2)/(1.+Y(1))
             DY(4)=(Q0+1.64*(300.-Y(4)))/TAIR/3.5/R
             RETURN
             END
             SUBROUTINE RK4(DELTA,X,XF,Y,W,N,TOL)
С
C INTEGRATION OF DIFFERENTIAL EQUATIONS VIA RUNGE-KUTTA 4 METHOD
С
             DIMENSION Y(N), W(N,9)
             DXO=XF-X
             DXL=1.
             KOUNT=-1
100
             KOUNT=KOUNT+1
             XC=.1
             XL=O.
             DO 5 I=1,N
5
             W(I, 1) = Y(I)
101
             CONTINUE
             CALL DELTA(X+XL+DXO, N, W(1, 1), W(1, 2))
С
C PROVIDES CHECK AGAINST STIFF EQUATIONS. IF CHANGE OVER INTEGRATION STE
C STEP IS TOO LARGE, REDUCES STEP SIZE. IF STEP SIZE REACHES FLOOR
C RETURNS WITH FLAG SET TO TELL THAT THE INTEGRATION DIVERGED.
             DO 120 K=2,N,2
105
             IF(ABS(W(K,2)*DXL*DXO).LE.O.1*W(K,1))GO TO 114
             DXL=DXL/2.
             GO TO 105
114
             CONTINUE
120
             CONTINUE
             IF(DXL.GT.2.**(-20))G0 T0 110
             PRINT *, " INTEGRATION DIVERGED"
             XF = -XF
             RETURN
110
             XL=XL+DXL/2.
             X1=X+XL+DXO
             DO 10 I=1,N
             W(I,6)=W(I,1)+DXL+DXO+W(I,2)/2.
10
             CALL DELTA(X1,N,W(1,6),W(1,3))
             DO 20 I=1.N
             W(I,7)=W(I,1)+DXL+DXO+W(I,3)/2.
20
             CALL DELTA(X1,N,W(1,7),W(1,4))
            DO 30 I=1,N
```

```
30
      W(I,8)=W(I,1)+DXL+DXO+W(I,4)
      XL=XL+DXL/2.
      CALL DELTA(X+XL+DXO, N, W(1,8), W(1,5))
      DO 40 I=1,N
      W(I,1)=W(I,1)+(W(I,2)+2.*(W(I,3)+W(I,4))+W(I,5))*DXL*DXO/6.
40
      IF (XL-XC) 1001, 1000, 1000
1000 XC=XC+1./10.
1001
      CONTINUE
      IF(XL.LT.1.)G0 T0 101
      DXL=DXL/2.
      IF (KOUNT.EQ.O)GO TO 102
      ERR=0.
      DO 50 I=1.N
      IF(ABS((W(I,9)-Y(I))/W(I,9)).LE.1.E-8)GO TO 51
      ERR=ERR+((W(I,9)-W(I,1))/(W(I,9)-Y(I)))**2
51
      CONTINUE
50
      CONTINUE
      IF(ERR.LE.TOL)GO TO 103
102
      DO 60 I=1,N
60
      W(I,9)=W(I,1)
      GO TO 100
103
      X=XF
      DO 70 I=1,N
70
      Y(I) = W(I, 9)
      RETURN
      END
      FUNCTION AVG(Y,N)
С
C COMPUTES BULK AVERAGES BASED ON PARABOLIC MASS FLOW PROFILE
С
      DIMENSION Y(N)
      A1=N-1
      N2=N-2
      A3=A1/2
      AVG=Y(1)/A1**2*(2.-1./A1**2)+Y(N)*(1.-(N2/A1)**2*(2.-(N2/A1)**2))
      DO 10 I=3,N2,2
      A=I/A1
      B=A-1./A3
10
       AVG=AVG+Y(I)*(A*A*(2.-A*A)-B*B*(2.-B*B))
      RETURN
      END
```

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Program 4

Axial Dispersion Model

Two-Dimensional, Axial Dispersion, Cooled, Surface Reaction, Inviscid

Flow

PROGRAM MODEL C C DUMMY MASTER PROGRAM THAT CALLS MAIN SUBROUTINE C CALL ROCKET STOP END

```
SUBROUTINE ROCKET
       IMPLICIT REAL+8 (A-H,K,O-Z)
С
C PROGRAM TO MODEL HYDROGEN ATOM RECOMBINATION IN AN AXIALLY DISPERSED-
C FLOW REACTOR
C TWO-DIMENSIONAL MODEL WITH IMSL DGEAR INTEGRATOR
C SEARCH TO FIND INITIAL DERIVATIVES FOR DISPERSION MODEL
C MODIFICATION BEGUN 5-27-86
C MODIFIED INTO SUBROUTINE TO PERMIT ERROR RECOVERY TRANSFER VIA CALL OF
C SECOND ENTRY POINT
Ċ
       COMMON/ALFA/A2,AK
       COMMON/BRAVO/AMO.FO.R
       COMMON/CHARLIE/DH0,DG0,T0,C(3,3)
       COMMON/ECHO/ERR.TS.XS.TAIR.UO
       COMMON/GOLF/GAMMA
       COMMON/HOTEL/DISP(2)
       COMMON/POPPA/PI
         COMMON /INDIA/IF1, IF2
         EXTERNAL DELTA2, DUMMY
       DIMENSION Y(47), W(47,75), IWK(47)
       DIMENSION V0(47), V1(47), D2V(47), D3V(47)
       DIMENSION SRC(20,3), IS(20), IB(20), HMAT(20,20)
DATA R, T0/8314.34D0,298.15D0/
       DATA C/26880.D0,4.347D0,-2.645D-04,20786.D0,0.D0,0.D0,
      +0.D0,0.D0,0.D0/
       DATA DH0, DG0/4.3141D08,4.0648D08/
       DATA AMO/2.DO/
       DH(T)=DHO+T*CP(3,T)
      KEQ(T)=1.01325D05*DEXP((-DG0/T0+C(1,3)*DLOG(T/T0)+(DH0/
+T/T0+C(2,3)+C(3,3)*(T+T0)/2.D0)*(T-T0))/R)
       XEQ(T,P)=1.D0/DSQRT(1.D0+4.D0+P/KEQ(T))
       VMACH(Y,Z)=UB(Y,Z)/VS(Y)
       DH2HP(T)=1.264D-3*T**1.72D0
       KTH(T)=1.843D-3*T**.8D0
С
C INITIALIZATION INCLUDING EVALUATION OF DELTA CP OF REACTION
  AND STANDARD SET OF INITIAL CONDITIONS AND SYSTEM PARAMETERS
С
С
         OPEN (UNIT=34,FILE='STARTG.DAT',STATUS='OLD')
OPEN (UNIT=44,FILE='SYS$OUTPUT',STATUS='NEW')
OPEN (UNIT=45,FILE='SAVES.DAT',STATUS='OLD')
OPEN (UNIT=55,FILE='SEARCH.DAT',STATUS='OLD')
         OPEN (UNIT=65, FILE='HMAT.DAT', STATUS='OLD')
         INPR=3
         ZQ=-1.D0
         INPRO=INPR
       DO 5 I=1,3
       C(I,3)=(2.D0*C(I,2)-C(I,1))/I
5
       Y(1)=0.00
       Y(2) = 0.100
       Y(3) = 1200.D0
       Y(4) = 3530.00
       Y(5)=400.D0
       F0=3.82D-7
       ERR=1.D-6
       AK=3.8D-4
       A2=3.8D-4
       TAIR=1.70-4
       PI=4.D0*DATAN(1.D00)
         ICON=0
       U0=1.6D0
         DO 555 I=1,47
         DO 555 J=1,75
555
         W(I,J)=0.D0
103
       CONTINUE
```

```
WRITE (44,*), ' ENTER INITIAL CONDITIONS AND SYSTEM PARAMETERS'
      READ (34, +), (Y(L), L=1,5), FO, ERR, AK, A2, ZL, ZP, TAIR, UO, INPRO, N1,
      +METH, MITER, DISP, GAMMA
      IF(Y(1).LT.0.D0)G0 T0 102
      WRITE (44,*),(Y(L),L=1,5),F0,ERR,AK,A2,ZL,ZP,TAIR,U0,INPRO,N1,
      +METH, MITER, DISP, GAMMA
      N2=N1+2+5
        N7=2*N1
      N3=4*N1+7
      GO TO (111,112,113,111,115), INPRO
С
  IF INPRO=1, INITIAL PROFILE IS UNIFORM ACROSS REACTOR
С
С
      DO 110 I=1,N1
111
      V(I+5)=V(2)
      Y(I+N1+5)=Y(3)
110
      IF(INPRO.NE.4)GO TO 150
C
C IF INPRO=4, UNIFORM PROFILE EXCEPT THAT OUTERMOST STATION IS AT
  COOLANT TEMPERATURE AND ZERO DISSOCIATION
С
C
      V(N2-N1)=0.D0
      V(N2) = V(5)
      GO TO 150
С
C IF INPRO=2, INITIAL PROFILE IS UNIFORM AT ZERO DISSOCIATION AND C COOLANT TEMPERATURE EXCEPT FOR CENTRAL SEGMENT, WHICH IS AT INPUT
 CONDITIONS (Y(2) AND Y(3)).
С
С
      Y(6) = Y(2)
112
      Y(6+N1)=Y(3)
      DO 120 I=2.N1
      Y(I+5)=0.D0
      V(I+N1+5)=V(5)
120
      GO TO 150
С
C IF INPRO = 5, INITIAL PROFILE MUST BE INPUT, DERIVATIVES CALCULATED
C FROM DANCKWERTS BOUNDARY CONDITIONS BASED ON UNIFORM TO AND XO.
С
      X0=V(2)
115
      TOO=V(3)
С
C IF INPRO = 3, INITIAL PROFILES MUST BE ENTERED AT PROGRAM PROMPTS.
С
      WRITE (44,*),' X PROFILE'
113
      READ (34,*), (Y(5+L), L=1,N1)
      WRITE (44,*), (Y(5+L),L=1,N1)
WRITE (44,*), 'T PROFILE'
READ (34,*), (Y(L+N1+5),L=1,N1)
      WRITE (44,*), (V(L+N1+5), L=1, N1)
150
      CONTINUE
С
C Y(2) AND Y(3) ARE THE BULK (MASS AVERAGE) DISSOCIATION AND TEMPERATURE
C RESPECTIVELY. EXCEPT WHEN INPRO=1, THEY MUST BE COMPUTED INITIALLY FROM
  THE ACTUAL INITIAL PROFILES
С
C
      Y(2) = AVG(Y(6), N1)
      Y(3) = AVG(Y(6+N1), N1)
С
С
  READ IN SEARCH PARAMETERS AND CONTROL VALUES
С
      READ (55,*),(((SRC(I,J),J=1,3),IS(I),IB(I)),I=1,N7)
         READ (55, *), ICON
С
C READS IN MATRIX FOR TRANSFORMED SEARCH COORDINATES
C DEFAULT IS UNTRANSFORMED
```

```
С
        DO 932 I=1,N7
        DO 931 J=1,N7
        HMAT(I,J)=0.D0
931
932
        HMAT(I,I)=1.D0
        READ (65, *), ((HMAT(I, J), J=1, N7), I=1, N7)
        DO 901 I=1,N7
         Y(I+N2+1)=0.D0
        DO 902 J=1,N7
        V(I+N2+1)=V(I+N2+1)+HMAT(I,J)*SRC(J,3)
902
        CONTINUE
901
      Y(N2+1) = AVG(Y(N2+2), N1)
      Y(N3) = AVG(Y(N3-N1), N1)
        DO 1001 I=1,N3
        VO(I)=V(I)
1001
      TS=Y(N2)
      XS=V(N2-N1)
        IF1=0
        IF2=0
С
C ENTRY POINT FOR ERROR RECOVERY RESTART
С
        ENTRY EGRESS
С
C IF TWO ERRORS WITHOUT REACHING NEW PRINT POINT, RESET TO INPUT
C START POSITION
С
        IF(IF1.GE.2) GO TO 401
С
C READ IN SAVED LAST PRINT POSITION FOR RESTART
С
        REWIND 45
        READ (45,*), (Y(I), I=1,N3), TS, XS
С
C ESTIMATION OF THE GAS-DYNAMIC TEMPERATURE THAT THE EXPERIMENTAL
C ASSUMPTION OF ZERO DISSOCIATION WOULD REPORT UNDER THE CONDITIONS
C PREDICTED BY THE MODEL
С
      TG=Y(3)*5.D0*(7.D0+3.D0*Y(2))*(1.D0+Y(2))/7.D0/(5.D0+Y(2))
119
      WRITE (44,*), (Y0(6+2*N1+L), L=1, N1)
      WRITE (44,*), (VO(L+3*N1+6), L=1, N1)
        IF2=1
        CALL DELTA2(N3,0.D0,Y,D2Y)
        IF(IF1.GT.0)THEN
      TS=V(N2)
      XS=Y(N2-N1)
        IF1=0
        GO TO 119
        ENDIF
        IF2=0
        DO 701 I=2,N3
        D2Y(I) = D2Y(I) / D2Y(1)
701
        D2Y(1)=1.D0
      Z2D=Y(1)
      VB=UB(Y(2),Y(1))
      VSS=VS(Y(2))
      IF (ICON.EQ.0)GO TO 1200
      WRITE (44,20),(V(L),L=1,5),VB,AR(Y(1)),VSS,TG
WRITE (44,30),(Y(5+L),L=1,N1),XS
      WRITE (44,30), (D2Y(5+L), L=1,N1)
      IF(DISP(1).NE.O.DO)WRITE (44,30),(D2Y(6+2*N1+L),L=1,N1)
      WRITE (44,30), (V(L+N1+5), L=1,N1), TS
      WRITE (44,30), (D2Y(L+N1+5), L=1,N1)
      IF(DISP(2).NE.0.D0)WRITE (44,30),(D2Y(L+3*N1+6),L=1,N1)
30
      FORMAT(8X, 10G11.4)
20
      FORMAT(3X,5G12.5)
```

```
C INTEGRATION OF DIFFERENTIAL EQUATIONS VIA IMSL DEEAR SUBROUTINE
C
       Z=0.D0
1200
       ZPR=Z2D
         INDEX=1
       ZPR=DMIN1(ZPR+ZP,ZL)
101
       YO=Y(1)
         DO 601 I=1,N3
         V1(I)=D2V(I)
601
105
       DZ=ZP
Č IN ARC-LENGTH INTEGRATION, USES VARIABLE STEP SIZE AS INPUT TO
C INTEGRATOR TO CONSERVE COMPUTATIONAL TIME (MIGHT NEGATE ADVANTAGES
C OF ARC-LENGTH METHOD)
C
       IF(V0.NE.Y(1))DZ=DMAX1(DABS((ZPR-Y(1))/(Y(1)-Y0))*DZ/16.D0,ZP)
       YO=Y(1)
       DX0=DZ
104
       Z2=Z+DZ
         H=DZ
       CALL DGEAR(N3, DELTA2, DUMMY, Z, H, Y, Z2, ERR, METH, MITER, INDEX, IWK, W,
      +IER)
         IF (IER.LE.127) GO TO 106
         WRITE (44,*) 'INTEGRATION DIVERGED'
         GO TO 103
IF (Y(1).LT.ZPR) GO TO 105
106
         CALL DELTA2(N3,Z,Y,D2Y)
         DO 702 I=2,N3
         D2Y(I) = D2Y(I) / D2Y(1)
702
         D2Y(1)=1.D0
         DO 602 I=1,N3
         D3Y(I) = (D2Y(I) - Y1(I))/ZP
602
       TG=V(3)*5.D0*(7.D0+3.D0*V(2))*(1.D0+V(2))/7.D0/(5.D0+V(2))
         IF1=0
       IF (ICON.NE.0)THEN
         WRITE (44,20),(Y(L),L=1,5),UB(Y(2),Y(1)),AR(Y(1)),
      +VS(V(2)).TG
       WRITE (44,30), (Y(L+5), L=1,N1),XS
WRITE (44,30), (D2Y(5+1), L=1,N1)
       IF(DISP(1).NE.0.D0)WRITE (44,30),(D2V(N2+1+1),L=1,N1)
WRITE (44,30),(V(L+N1+5),L=1,N1),TS
WRITE (44,30),(D2V(L+N1+5),L=1,N1)
       IF(DISP(2).NE.O.DO)WRITE (44,30), (D2Y(L+3*N1+6), L=1, N1)
         ENDIF
С
C SAVE DATA FOR RESTART
С
         REWIND 45
       WRITE (45,*), (Y(L), L=1,N3), TS, XS
С
C SERIES OF CHECKS FOR RUNAWAY CONDITIONS
C USABLE IN SEARCH TECHNIQUE TO ESTABLISH CORRECT VALUES FOR
C INITIAL DERIVATIVES
С
         DO 595 IN=6,N2
         IN1=IN-5
         IN2=IN+2*N1+1
С
C IF PLUG-FLOW ON EITHER MASS OR ENERGY, DOES NOT SEARCH
C
         ID=1
         VMIN=0.D0
         IF(Y(IN).GT.XS)YMIN=XS
IF(IN1.GT.N1)ID=2
         IF(IN1.GT.N1)YMIN=Y(5)
```

```
IF(DISP(ID).NE.0.D0)THEN
С
C DIRECT CHECK FOR NEGATIVE RUNAWAY
С
         IF(Y(IN)+ZP*Y(IN2).LT.YMIN)GO TO 123
С
C INDIRECT CHECK FOR POSITIVE RUNAWAY BASED ON FIRST, SECOND, AND
C THIRD DERIVATIVES BEING POSITIVE IMPLYING RUNAWAY
С
         IF(Y(IN2).GT.0.D0.AND.D3Y(IN2).GT.0.D0.AND.
     +D2Y(IN2).GT.0.D0)G0 T0 133
         ENDIF
595
         CONTINUE
      IF (Y(1).LT.ZL) GO TO 101
IF (ICON.EQ.1)GO TO 103
         ICON=1
         GO TO 400
C
C SEARCH ALGORITHM TO FIND NEXT GUESS FOR INITIAL DERIVATIVES
С
123
         ISN=IS(IN1)
         DO 125 I=1,N7
IS(I)=IB(I)
125
         IS(IN1)=1
         IF(SRC(IN1,1).EQ.SRC(IN1,2))THEN
         SRC(IN1,1)=SRC(IN1,1)-DMIN1(.01D0,.01D0+DABS(SRC(IN1,1)))
         SRC(IN1,2)=SRC(IN1,2)+DMIN1(.01D0,.01D0*DABS(SRC(IN1,2)))
         ENDIF
         IF(SRC(IN1,3).EQ.SRC(IN1,2))GO TO 126
         IF(ISN.NE.0)G0 TO 124
         SRC(IN1,1)=SRC(IN1,3)
         SRC(IN1,3)=SRC(IN1,2)
         GO TO 400
124
         SRC(IN1,1)=SRC(IN1,3)
         SRC(IN1,3)=(SRC(IN1,1)+SRC(IN1,2))/2.DO
154
         GO TO 400
126
         SRC(IN1,3)=2.D0*SRC(IN1,2)-SRC(IN1,1)
         SRC(IN1,1)=SRC(IN1,2)
SRC(IN1,2)=SRC(IN1,3)
         GO TO 400
         ISN=IS(IN1)
133
         DO 135 I=1.N7
135
         IS(I)=IB(I)
         IS(IN1)=1
         IF(SRC(IN1,1).EQ.SRC(IN1,2))THEN
         SRC(IN1,1)=SRC(IN1,1)-DMIN1(.01D0,.01D0*DABS(SRC(IN1,1)))
SRC(IN1,2)=SRC(IN1,2)+DMIN1(.01D0,.01D0*DABS(SRC(IN1,2)))
         ENDIF
         IF(SRC(IN1,3).EQ.SRC(IN1,1))GO TO 136
         IF(ISN.NE.0)G0 TO 134
         SRC(IN1,2)=SRC(IN1,3)
         SRC(IN1,3)=SRC(IN1,1)
         GO TO 400
         SRC(IN1,2)=SRC(IN1,3)
134
         GO TO 154
         SRC(IN1,3)=2.DO*SRC(IN1,1)-SRC(IN1,2)
136
         SRC(IN1,2)=SRC(IN1,1)
         SRC(IN1,1)=SRC(IN1,3)
         REWIND 55
400
         WRITE (55,*),(((SRC(I,J),J=1,3),IS(I),IB(I)),I=1,N7)
WRITE (55,*),ICON
         DO 911 I=1,N7
         YO(I+N2+1)=0.D0
         DO 912 J=1,N7
         YO(I+N2+1)=YO(I+N2+1)+HMAT(I,J)*SRC(J,3)
912
911
         CONTINUE
```
	VO(N2+1)=AVG(YO(N2+2),N1)
	VO(N3) = AVG(VO(N3-N1), N1)
401	DO 1002 I=1,N3
1002	Y(I)=YO(I)
	GO TO 119
102	CONTINUE
	IF(IF1.EQ.0)STOP
	RETURN
	END

```
SUBROUTINE DELTA2(N,Z,Y,DY)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      COMMON/BRAVO/AMO, FO, R
      COMMON/CHARLIE/DH0,DG0,T0,C(3,3)
      COMMON/HOTEL/DISPM, EDISP
        COMMON /INDIA/IF1, IF2
      DIMENSION V(N), DV(N)
      DH2HP(T)=1.264D-3*T**1.72D0
      KTH(T)=1.843D-3*T**.8D0
      N2=(N-7)/4
      NF=N-2*N2-3
      A1=N2
      CALL DELTA (NF, V(1), V(2), DV(2))
C PROVISION FOR CASCADING ERROR RECOVERY RETURN IF USING OWN
 INTEGRATOR SUBROUTINE
С
С
        IF(IF1#IF2.NE.0)RETURN
С
C IF DISPERSION COEFFICIENTS SET TO 0., CIRCUMVENT DISPERSION
 CALCULATION TO AVOID INFINITIES
С
С
      IF(EDISP.EQ.O.DO.AND.DISPM.EQ.O.DO0)GO TO 130
      R2=0.D0
      DO 100 I=1,N2
      I1=I+5
      I2=I+N2+5
      I3=NF+N2+2+I
      A2=I
      R1=R2
      R2=DMIN1(1.D0,A2/A1)
      IF(EDISP)140,141,142
      KTHV=DABS(EDISP)
140
      GO TO 143
      KTHY=EDISP*KTH(Y(I2))
142
      DY(I3)=(Y(I3)-DY(I2))*(EK(Y(2),Y(1))/Y(I2)+CPM(Y(I1),Y(I2)))*F0*
143
     +(2.D0-R2*R2-R1*R1)/AR(Y(1))/KTHY
      DY(I2)=Y(I3)
      I4=NF+2+I
141
      IF(DISPM) 150, 151, 152
      DHH2P=DABS(DISPM)
150
      GO TO 153
      DHH2P=DISPM+DH2HP(V(I2))
152
      DY(I4)=Y(I1)*(Y(I1)+1.D0)*((Y(I4)-DY(I1))*R*Y(I2)*(Y(I1)+1.D0)*
153
     +F0*(2.D0-R2*R2-R1*R1)/V(I1)/AR(V(1))/DHH2P+DV(I3)/V(I2)+
     +2.D0*(Y(I4)**2/(Y(I1)+1.D0)**2/Y(I1)+DY(4)*DY(I2)/Y(4)/Y(I2)+
     +Y(I4) +DY(I2)/Y(I2)/Y(I1)/(Y(I1)+1.D0)-DY(4)+Y(I4)/Y(4)/Y(I1)/
     +(Y(I1)+1.D0)))
      DY(I1)=Y(I4)
151
      CONTINUE
100
      CONTINUE
      IF(EDISP.EQ.0.D0)G0 T0 131
      DY(N) = AVG(DY(N-N2), N2)
      DY(3)=Y(N)
      IF(DISPM.EQ.0.D0)G0 TO 130
131
      DV(N-2*N2-1) = AVG(DV(N-N2*2), N2)
      DY(2) = Y(N-2*N2-1)
      DY(1)=1.D0
130
С
С
 COMPUTATION OF TERMS FOR ARC-LENGTH METHOD INTEGRATION
С
      DS=0.D0
      DO 110 I=1,N
      DS=DS+DY(I)*DY(I)
110
      DS=SQRT(DS)
      DO 120 I=1,N
```

120 DY(I)=DY(I)/DS RETURN END

SUBROUTINE DUMMY(N,X,Y,PD) C DUMMY SUBROUTINE REQUIRED FOR IMSL DGEAR COMPUTATION C DIMENSION Y(N),PD(N,N) RETURN END

```
SUBROUTINE DELTA(N,Z,Y,DY)
С
C COMPUTES FIRST-ORDER DERIVATIVES OF TEMPERATURE, CONCENTRATION,
C COOLANT TEMPERATURE, AND PRESSURE FROM MATERIAL AND ENERGY
C BALANCES.
С
       IMPLICIT REAL*8 (A-H,K,O-Z)
       COMMON/BRAVO/AMO, FO, R
       COMMON/CHARLIE/DH0,DG0,T0,C(3,3)
       COMMON/ECHO/ERR, TS, XS, TAIR, UI
       COMMON/GOLF/GAMMA
       COMMON/POPPA/PI
         COMMON /INDIA/IF1, IF2
      DIMENSION A(3,3),Y(N),DY(N)
DIMENSION XSN(2),TSN(2),XSX(2),TSX(2),DXN(2)
      DIMENSION XTN(2,4), FXT(4), SUM(2)
С
C RATE CONSTANTS DERIVED FROM SHUI, APPLETON AND SHUI, AND SANCIER AND C WISE DATA. LEAST-SQUARES FIT TO FORM OF A*T**B*EXP(C/T)
С
       DATA A/2.014D11,-0.7497D0,-20.43D0,8.816D11,-0.7219D0,-92.09D0,
      +3.855D18,-3.D0,-2900.D0/
С
C RATE AND EQUILIBRIUM CONSTANT EXPRESSIONS
С
       K(I,T)=A(1,I)*T**A(2,I)*DEXP(A(3,I)/T)
     KEQ(T)=1.01325D05*DEXP((-DG0/T0+C(1,3)*DLOG(T/T0)+(DH0/
+T/T0+C(2,3)+C(3,3)*(T+T0)/2.D0)*(T-T0))/R)
       XEQ(T,P)=1.D0/DSQRT(1.D0+4.D0*P/KEQ(T))
       DH(T)=DHO+T*CP(3,T)
       DH2HP(T)=1.264D-3*T**1.72D0
       KTH(T)=1.843D-3*T**.8D0
С
C DEBUGGING PRINT STATEMENT
С
       IF(GAMMA.NE.O.DO)WRITE (44,*),Z,Y
       G2=GAMMA
       AS=2.DO*DSQRT(PI*AR(Z))
      IF(UI)111,112,113
112
      H0=0.D0
       GO TO 110
111
      HO=DABS(UI)
       GO TO 110
      H0=UI+47.06D0
113
110
       CONTINUE
       DR=2.D0/(N-4.D0)
      N2=(N-4)/2
       N3=N2+5
       N4=N2-1
С
C CENTRAL BOUNDARY CONDITIONS
С
       R2=0.D0
      RQ2=0.D0
      RNH2=0.D0
       L5=1
       NCOUNT=1
         LCOUNT=0
С
C OUTERMOST STATION WITH WALL BOUNDARY CONDITIONS COMPUTED SEPARATELY
C SINGLE STATION COMPUTATION PSEUDO-ONE-DIMENSIONAL
С
       IF(N4.EQ.0)GO TO 170
      DO 160 J=1.N4
С
C THIS SAVES COMPUTATION AND ENSURES CONSERVATION
```

R1=R2RQ1=RQ2 RNH1=RNH2 R2=DR*J J1=J+4 J2=J1+N2 C ERROR BAILOUT. IF OWN INTEGRATOR SUBROUTINE, CASCADING RETURNS. C IF LIBRARY INTEGRATOR, CALL TO RECOVERY ENTRY POINT IN MAIN C SUBROUTINE. C IF(V(J2).LE.0.D0.OR.V(J2+1).LE.0.D0)THEN IF1=1+IF1 IF(IF2.NE.O)RETURN WRITE (44,*), 'ILLEGAL TEMPERATURE' CALL EGRESS ENDIF С C RADIAL FLUXES BASED ON TRANSPORT PROPERTIES COMPUTED AT AVERAGE C CONDITIONS С TB=(Y(J2)+Y(J2+1))/2.D0XB = (Y(J1) + Y(J1 + 1))/2.D0RQ2=R2*(-KTH(TB)*(Y(J2+1)-Y(J2))/DR)RNH2=R2*(-DH2HP(TB)*(V(J1+1)/(V(J1+1)+1.D0)/V(J2+1)-V(J1)/ +(Y(J1)+1)/Y(J2))*2.D0/R/DR)*(1.D0-XB/(1.D0+XB)) С C MATERIAL BALANCE BASED ON AXIAL FLOW AND REACTION ALONE С DXR=AR(Z)/F0*((K(2,Y(J2))*2.D0*Y(J1)+K(1,Y(J2))*(1.D0-Y(J1)))*+(KEQ(Y(J2))*(1.D0-Y(J1))/Y(3)*(1.D0+Y(J1))-4.D0*Y(J1)*Y(J1))* +(Y(3)/R/Y(J2)/(1.D0+Y(J1)))**3)/(2.D0-(R2*R2+R1*R1)) С C MATERIAL BALANCE INCLUDING RADIAL MASS FLUX С DY(J1)=DXR-2.D0*PI/F0*(RNH2-RNH1)/(2.D0-R2*R2-R1*R1) DY(J2)=(((EK(Y,Z)/(1.D0+Y(J1)))*DY(J1)+DH(Y(J2))*DXR-EK(Y.Z)* +DAR(Z)/AR(Z))+2.D0*PI/F0/(R2*R2-R1*R1)/(2.D0-R2*R2-R1*R1)* +(RQ2-RQ1))/(EK(Y,Z)/Y(J2)+ +(1.D0-Y(J1))*CP(1,Y(J2))+2.D0*Y(J1)*CP(2,Y(J2)))*(-1.D0) 160 CONTINUE С C SOLUTION OF WALL BOUNDARY CONDITIONS BY (1) BOUNDED LINEAR INTER- AND C EXTRAPOLATIONS (2) PROJECTING ALONG LINEARIZED ZERO CURVE OF ONE C BOUNDARY CONDITION TO FIND NEW POINT TO RESTART INTER- AND EXTRA-C POLATIONS (3) SIMPLEX METHOD IF PROJECTION TAKES PAST BOUNDARY С 170 LX=1 LT=1 TSMIN=Y(4) *0.1D0 L7=1 J5=1 LAST=4 J6=1 L5=1 150 XWI=XS TS=DMIN1(TS,Y(N)+10000.D0)120 TS = DMAX1(TS, TSMIN) С

```
C ERROR BAILOUT. IF OWN INTEGRATOR SUBROUTINE, CASCADING RETURNS.
C IF LIBRARY INTEGRATOR, CALL TO RECOVERY ENTRY POINT IN MAIN
C SUBROUTINE.
C
IF(Y(N).LE.O.DO.OR.TS.LE.O.DO)THEN
```

```
IF1=1+IF1
```

С

```
IF(IF2.NE.0)RETURN
        WRITE (44,*),'ILLEGAL TEMPERATURE'
        CALL EGRESS
        ENDIF
        ERRX=ERR*DMAX1(ERR,XS)
      HI=4.D0*KTH((TS+Y(N))/2.D0)*PI/AS/DR
      KW=4.D0*DH2HP((TS+V(N))/2.D0)*PI/V(3)/AS/DR
      TS1=(HO*Y(4)+HI*Y(N))/(HO+HI)
      TSI=TS
      DXW=AS/(1.D0-R2*R2)**2*K(3,TS)*(KEQ(TS)/Y(3)*(1.D0-XS*XS)-
     +4.D0*X$*X$)*(Y(3)/R/T$/(1.D0+X$))**2
DHS=DXW*DH(T$)*(1.D0-R2*R2)**2
      DXS = (Y(N-N2)/Y(N)/(1.D0+Y(N-N2))+
130
     +DXW*(1.D0-R2*R2)**2/KW*(1.D0-XS/(1.D0+XS))/AS*R/Y(3))*TS
      XS1=DXS/(1.DO-DXS)
      DXS=XS1-XWI
      XS1=DMAX1(XS1,0.D0)
      XS1=DMIN1(XS1,1.D0)
      TSA=TS1-DHS/AS/(HO+HI)
      DTS=TSA-TSI
      IF(G2.GT.2.D0)WRITE (44,*),TSI,DTS,XS,DXS,' L5=',L5,' L7=',L7,
        L8=',L8
     + '
      IF(NCOUNT.LT.1000)G0 TO 300
        G2=GAMMA+1.D0
        NCOUNT=0
С
C ERROR BAILOUT. IF OWN INTEGRATOR SUBROUTINE, CASCADING RETURNS.
C IF LIBRARY INTEGRATOR, CALL TO RECOVERY ENTRY POINT IN MAIN
C SUBROUTINE.
С
        IF (LCOUNT.LT.10)G0 TO 310
        IF1=1+IF1
        IF(IF2.NE.O)RETURN
        WRITE (44,*), 'BOUNDARY CONDITIONS HUNG UP'
        CALL EGRESS
        LCOUNT=LCOUNT+1
310
300
      NCOUNT=NCOUNT+1
      IF(DABS(DTS).LT.ERR*TS.AND.DABS(DXS).LE.ERRX) GO TO 151
      IF(L7.NE.1)GO TO 250
IF(L5.NE.2)GO TO 134
      IF(DABS(DXS).GT.ERRX)GO TO 131
        IF(J5.GT.2)G0 TO 134
      IF(G2.GE.2.D0)WRITE (44.*), 'J5=', J5, TS, XS
      XSX(J5)=XS
      TSX(J5)=TSI
      XTN(1,2+J5)=XS
      XTN(2,2+J5)=TSI
      FXT(2*J5-1)=(DTS/Y(N))**2
      IF(Y(N-N2).NE.O.D0)FXT(2*J5-1)=FXT(2*J5-1)+(DXS/Y(N-N2))**2
       J5=J5+1
      IF(J6.GE.3)G0 T0 180
      CONTINUE
134
      IF(L5.EQ.2)LT=1
      L5=1
      IF(LT.EQ.1)GO TO 124
      IF(LT.EQ.2)GO TO 122
      IF(DTS*DTS0.LT.0.D0)G0 T0 122
      IF(DTS*DTS2.LT.0.D0)G0 T0 122
      IF(DABS(DTS).LT.DABS(DTSO))GO TO 122
      IF(DABS(DTS).LT.DABS(DTS2))GO TO 122
C IF TEMPERATURE BOUNDARY CONDITION GENERATES MINIMUM WITHOUT CROSSING
C ZERO, FITS QUADRATIC CURVE AND FINDS MINIMUM FOR NEW VALUE
C
      AQ=((DTS2-DTS)/(TS2-TSI)-(DTS0-DTS)/(TS0-TSI))/(TS2-TS0)
      BQ=(DTSO-DTS)/(TSO-TSI)-AQ*(TSO+TSI)
```

```
TS=-BQ/AQ/2.D0
      IF(DABS(TS-TSI).LT.ERR.OR.DABS(TS-TSO).LT.ERR.OR.DABS(TS-TS2).LT.
     +ERR)GO TO 131
     GO TO 133
IF(TSI.EQ.TSO) GO TO 131
122
      IF(DTS.EQ.DTSO) GO TO 131
      IF(DABS(DXS).LT.ERRX)GO TO 131
      TS=TSI+DTS*(TSO-TSI)/(DTS-DTSO)
      IF(G2.GE.2.D0)WRITE (44,*),TS,XS
      IF(TS.LT.TSMIN.AND.(TSI-TSMIN)*(TSO-TSMIN).EQ.0.D0)G0 TO 131
      IF(L5.EQ.1.AND.DABS(DTS).GT.ERR*TS)GO TO 133
      IF(J6.GT.2)GO TO 131
      IF(G2.GE.2.DO)WRITE (44,*),'J6=',J6,TS,XS
      XSN(J6)=XS
      TSN(J6)=TSI
      XTN(1,2*J6-1)=XS
      XTN(2,2*J6-1)=TSI
      FXT(2*J6-1)=(DTS/Y(N))**2
      IF(Y(N-N2).NE.0.D0)FXT(2+J6-1)=FXT(2+J6-1)+(DXS/Y(N-N2))+2
      DXN(J6)=DXS
      J6=J6+1
      IF(J6.GE.3)GO TO 180
131
      L5=2
      TS=TSI
      IF(LX.EQ.1)GO TO 121
      IF(DXS,EQ.DXSO)GO TO 132
        IF(DABS(DXS-DXO).LT.DABS(DXS*(XWO-XWI)))THEN
        XS=0.D0
        IF(DXS*(XWO-XWI)*(DXS-DXSO).GT.0.D0)XS=1.D0
        ELSE
      XS=DMAX1(0.D0,XWI+DXS*(XWO-XWI)/(DXS-DXSO))
        ENDIF
      IF(XS.EQ.0.D0.AND.XWO*XWI.EQ.0.D0)G0 T0 132
      XS=DMIN1(1.D0,XS)
      LX=2
      IF(XWO-XS)121,132,121
132
      XS=XS1
      LT=1
      L5=1
      GO TO 125
      IF(LX.EQ.1)XS=XS1
121
      GO TO 125
124
      LT=2
        TS=TSA
      IF(LX.NE.1)GO TO 123
125
      XWO=XWI
      DXSO=DXS
      IF(LX.NE.1)G0 T0 150
      1 X=2
133
      LT=3
      TS2=TSO
      DTS2=DTS0
123
      TSO=TSI
      DTSO=DTS
      GO TO 150
С
C PROJECTS TO NEW START POINT BY TAKING ONE LINEARIZED ZERO LINE AND
C LINEAR EXTRAPOLATION OF OTHER FUNCTION ALONG LINE
С
180
      CONTINUE
      IF(G2.GE.2.DO)WRITE (44,*), 'PROJECTING', TSX, XSX, TSN, XSN
      IF(XSN(2), EQ.XSN(1))GO TO 170
      IF(DXN(1).NE.DXN(2))XS=XSN(1)+DXN(1)*(XSN(2)-XSN(1))/
     +(DXN(1)-DXN(2))
      TS=TSN(2)+(TSN(2)-TSN(1))*(XS-XSN(2))/(XSN(2)-XSN(1))
181
      IF(G2.GE.2.DO)WRITE (44,*), 'PROJECTION', TS, XS
```

```
IF(XS.LT.O.DO.AND.TS.LT.TSMIN)GO TO 251
       XS=DMAX1(XS,0.D0)
       XS=DMIN1(XS,1.D0)
       L5=1
       IF(XS.EQ.0.D0)L5=2
       GO TO 170
С
C FINDS MINIMUM OF SUM OF SQUARES OF EQUATIONS BY SIMPLEX METHOD
С
250
       FXT(LAST)=(DTS/Y(N))**2
       IF(Y(N-N2).NE.0.D0)FXT(LAST)=FXT(LAST)+(DXS/Y(N-N2))**2
       IF(L8.NE.1)GO TO 251
       LAST=MINO(4,LAST+1)
       XS=XTN(1,LAST)
       TS=XTN(2,LAST)
       IF(LAST.LE.3)GO TO 150
251
       L7=2
       L8=2
       IMIN=1
       IMAX=1
       DO 252 L=2,3
IF(FXT(L).GT.FXT(IMAX))IMAX=L
       IF(FXT(L).LT.FXT(IMIN))IMIN=L
       CONTINUE
252
       IF(IMAX.NE.LAST.AND.IMAX.NE.IMIN)GO TO 260
       DO 525 L=1,3
       DO 525 J=1,2
       XTN(J,L) = (XTN(J,L) + XTN(J,IMIN))/2.D0
525
       LAST=1
       L8=1
       GO TO 280
260
       CONTINUE
       IF(G2.GE.2.DO)WRITE (44,*),XTN,FXT
       DO 261 L1=1,2
       SUM(L1)=0.D0
       DO 262 L2=1.3
       SUM(L1)=SUM(L1)+XTN(L1,L2)
262
261
       CONTINUE
       LAST=IMAX
       DO 263 L3=1,2
       XTN(L3, IMAX)=SUM(L3)-2.D0*XTN(L3, IMAX)
263
       IF(DABS(SUM(1)-3.DO*XTN(1,IMAX)).LT.ERR.AND.
      +DABS(SUM(2)-3.DO*XTN(2,IMAX)).LT.ERR*Y(N))GO TO 281
       XTN(2,IMAX)=DMIN1(XTN(2,IMAX),Y(N)+10000.D0)
      XTN(2, IMAX)=DMAX1(XTN(2, IMAX), TSMIN)
XTN(1, IMAX)=DMIN1(XTN(1, IMAX), 1.DO)
       XTN(1,IMAX)=DMAX1(XTN(1,IMAX),0.D0)
       XS=XTN(1,LAST)
       TS=XTN(2,LAST)
       IF(DABS(XTN(2,1)-XTN(2,2)).GT.ERR*Y(N).OR.
280
      +DABS(XTN(2,1)-XTN(2,3)).GT.ERR*Y(N).OR.
      +DABS(XTN(1,1)-XTN(1,2)).GT.ERR.OR.DABS(XTN(1,1)-XTN(1,3)).GT.ERR)
      +GO TO 150
281
      XS=XTN(1,IMIN)
       TS=XTN(2, IMIN)
       GO TO 170
       QI = (V(N) - TS) + HI + AS
151
       QO=QI-DHS
С
  MATERIAL BALANCE BASED ON AXIAL FLOW AND GAS-PHASE REACION ONLY
С
С
      \begin{aligned} DXR=&AR(Z)/FO*(K(2,Y(N))*2.DO*Y(N-N2)+K(1,Y(N))*(1.DO-Y(N-N2)))*\\ &+(KEQ(Y(N))*(1.DO-Y(N-N2))/Y(3)*(1.DO+Y(N-N2))-4.DO*Y(N-N2)**2)* \end{aligned} 
     +(Y(3)/R/Y(N)/(1.D0+Y(N-N2)))**3/(1.D0-R2*R2)
C
C MATERIAL BALANCE INCLUDING RADIAL FLUX AND SURFACE REACTION
```

```
С
      DV(N-N2) = DXR + (DXW+2, DO \neq PI \neq (RNH2) / (1, DO - R2 \neq R2)) / FO
С
C ENERGY BALANCE EQUATION INCLUDING HEAT OF REACTION, KINETIC ENERGY
C AND THERMAL ENERGY TERMS
Ċ
      DY(N)=(((EK(Y,Z)/(1.D0+Y(N-N2)))*DY(N-N2)+DH(Y(N))*DXR-EK(Y,Z)*
     +DAR(Z)/AR(Z))+(-RQ2*2.DO*PI+QI)/FO/(1-R2*R2)**2)/(EK(Y,Z)/Y(N)+
     +(1.D0-Y(N-N2))*CP(1,Y(N))+2.D0*Y(N-N2)*CP(2,Y(N)))*(-1.D0)
      DV(1) = AVG(DV(5), N2)
      DY(2) = AVG(DY(N3), N2)
С
C MECHANICAL ENERGY BALANCE FOR NON-VISCOUS FLOW
С
      DY(3) = -EK(Y,Z) + (DY(2)/Y(2)+DY(1)/(1,D0+Y(1))-DAR(Z)/AR(Z)) +
     +Y(3)/R/Y(2)/(1.D0+Y(1))
С
C ENERGY BALANCE ON COOLANT, INCLUDING RADIATIVE AND CONVECTIVE LOSSES
Ĉ
 TO ENVIRONMENT
С
      DY(4)=(Q0+1.64D0*(300.D0-Y(4)))/TAIR/3.5D0/R
      IF(GAMMA.NE.O.DO)WRITE (44,*),ts,xs
      RETURN
      END
      REAL FUNCTION AVG+8(Y,N)
C COMPUTATION OF BULK (MASS-) AVERAGES BASED ON PARABOLIC FLOW
C PROFILE
С
        IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(N)
      AVG=V(1)
      IF(N.EQ.1)RETURN
      A1=N
      AVG=0.D0
      A=0.D0
      DO 10 I=1,N
      B=A
      A=DMIN1(1.D0/A1*I,1.D00)
       AVG=AVG+Y(I)*(A*A*(2.D0-A*A)-B*B*(2.D0-B*B))
10
      RETURN
      END
      REAL FUNCTION VS*8(Y)
С
C COMPUTATION OF SPEED OF SOUND BASED ON IDEAL GAS
С
      IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(2)
      COMMON/BRAVO/AMO, FO, R
      VS=DSQRT((1.D0+Y(1))*R*Y(2)/AM0/(1.D0-R*(1.D0+Y(1))/
     +CPM(Y(1),Y(2)))
      RETURN
      END
      REAL FUNCTION EK+8(Y,Z)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(4)
      COMMON/BRAVO/AMO, FO, R
C KINETIC ENERGY OF FLOW AS FUNCTION OF X, T, P, AND Z
С
      EK=1.D0/(1.D0/(AMO*UB(Y,Z)**2)-1.D0/R/Y(2)/(1.D0+Y(1)))
      RETURN
      END
      REAL FUNCTION CP+8(I,T)
С
C HEAT CAPACITY COMPUTATION FOR PURE GASES BASED ON QUADRATIC
```

```
C FIT DATA
С
       IMPLICIT REAL*8 (A-H,K,O-Z)
       COMMON/CHARLIE/DH0,DG0,T0,C(3,3)
CP=C(1,I)+T*(C(2,I)+T*C(3,I))
       RETURN
        END
       REAL FUNCTION CPM+8(X,T)
С
C HEAT CAPACITY BASED ON IDEAL MIXTURES
С
       IMPLICIT REAL*8 (A-H,K,O-Z)
CPM=(1.DO-X)*CP(1,T)+2.DO*X*CP(2,T)
        RETURN
       END
       REAL FUNCTION AR*8(Z)
С
C CROSS-SECTIONAL AREA OF TUBE AS FUNCTION OF LENGTH.
C GRUSS-SECTIONAL AREA OF TODE AS FUNCTION OF LENGTH.
C STRAIGHT TUBE OF AREA AK (USER INPUT, DEFAULT 3.8E-4 SQ. M.) FOR
C .025 M, THEN STRAIGHT CONICAL CONVERGENCE TO THROAT OF AREA A2
C (USER INPUT, SAME DEFAULT), AT .05 M, THEN STRAIGHT CONICAL DIVERGING
C SECTION OF .25 M LENGTH TO AK.
С
          IMPLICIT REAL*8 (A-H,K,O-Z)
        COMMON/ALFA/A2,AK
       DATA Z1,Z2,Z3,Z4/0.025D0,.05D0,.05D0,.30D0/
       AR=AK
        IF(AK.EQ.A2)RETURN
        IF((Z.LE.Z1).OR.(Z.GE.Z4))RETURN
100
        IF(Z.LT.Z2)G0 T0 101
        IF(Z.GT.Z3)G0 T0 102
        AR = A2
       RETURN
101
       ZA=Z1
        ZB=Z2
        GO TO 103
102
       ZA=Z4
       ZB=Z3
       AR=(DSQRT(AK)+(DSQRT(AK)-DSQRT(A2))*(Z-ZA)/(ZA-ZB))**2
103
       RETURN
       END
       REAL FUNCTION DAR+8(Z)
С
C COMPUTES DERIVATIVE OF AREA WITH LENGTH BY FINITE DIFFERENCE METHOD
C STEP SIZE 1.E-6 M
C
          IMPLICIT REAL*8 (A-H,K,O-Z)
       DY=1.D-06
       DAR=(AR(Z+DY)-AR(Z))/DY
       RETURN
       END
       REAL FUNCTION UB*8(Y,Z)
С
C COMPUTES BULK VELOCITY BASED ON AVERAGE CONDITIONS AND IDEAL GAS LAW
C
          IMPLICIT REAL*8 (A-H,K,O-Z)
        COMMON/BRAVO/AMO, FO, R
        DIMENSION Y(4)
       UB=F0*(1.D0+V(1))*R*V(2)/V(3)/AR(Z)
       RETURN
        END
```

Program 5

Runge-Kutta-4 Integrator

Stiff Equations Control, Cascade Error Return, Dependent Variable

Control

•

```
SUBROUTINE RK4(FCN,X,XF,Y,W,N,TOL,IF2,IT,ZPR)
С
C INTEGRATION OF DIFFERENTIAL EQUATIONS BY RUNGE-KUTTA 4 METHOD
C
        IMPLICIT REAL*8 (A-H, 0-Z)
      DIMENSION V(N),W(N,9)
      DX0=XF-X
      DXL=1.DO
      N1 = (N-7)/4
      N2=N1+6
      N3=2*N1+5
      CALL FCN(N.X.Y.W(1.8))
        IF(IF2.NE.O)RETURN
      KOUNT=-1
100
      KOUNT=KOUNT+1
      XC = .1D0
      XL=0.D0
      DO 5 I=1,N
      W(I,2)=W(I,8)
      W(I,1)=Y(I)
5
      GO TO 130
101
      CONTINUE
      CALL FCN(N,X+XL*DX0,W(1,1),W(1,2),DXL*DX0)
        IF(IF2.NE.O)RETURN
      CONTINUE
130
      DO 120 K=N2,N3
      IF(DABS(W(K,2)*DXL*DX0).LE.0.1D0*DABS(W(K,1)))G0 T0 114
105
      DXL=DXL/2.DO
      GO TO 105
114
      CONTINUE
      CONTINUE
120
      IF(DXL.GT.2.DO**(-20))GO TO 110
WRITE (44,*),' INTEGRATION DIVERGED'
        IF2=1
      RETURN
      XL=XL+DXL/2.D0
110
      X1=X+XL*DX0
      DO 10 I=1,N
10
      W(I,6)=W(I,1)+DXL*DXO*W(I,2)/2.DO
      CALL FCN(N,X1,W(1,6),W(1,3))
        IF(IF2.NE.O)RETURN
      DO 20 I=1.N
      W(I,7)=W(I,1)+DXL*DXO*W(I,3)/2.DO
CALL FCN(N,X1,W(1,7),W(1,4))
20
        IF(IF2.NE.O)RETURN
      DO 30 I=1.N
      W(I,7)=W(I,1)+DXL*DXO*W(I,4)
30
      XL=XL+DXL/2.D0
      CALL FCN(N,X+XL*DX0,W(1,7),W(1,5))
        IF(IF2.NE.O)RETURN
      DO 40 I=1,N
      W(I,1)=W(I,1)+(W(I,2)+2.DO*(W(I,3)+W(I,4))+W(I,5))*DXL*DXO/
     +6.D0
40
      CONTINUE
      IF (XL-XC) 1001,1000,1000
1000 XC=XC+.1D0
1001
      CONTINUE
        XIT=0.D0
        IF(IT.EQ.0.)GO TO 901
      IF(Y(IT).NE.ZPR)XIT=(W(IT,1)-Y(IT))/(ZPR-Y(IT))
      IF(XL.LT.1.DO.AND.XIT.LT.1.DO)GO TO 101
901
      DXL=DXL/2.D0
      IF(KOUNT.EQ.0)GO TO 102
      ERR=0.D0
      DO 50 I=1,N
      IF(W(I,9).NE.Y(I).AND.I.NE.IT)ERR=ERR+
```

```
+((W(I,9)-W(I,1))/(W(I,9)-Y(I)))**2

50 CONTINUE

IF(ERR.LE.TOL)GO TO 103

102 DO 60 I=1,N

60 W(I,9)=W(I,1)

GO TO 100

103 X=X+XL*DX0

DO 70 I=1,N

70 Y(I)=W(I,9)

RETURN

END
```

APPENDIX C

APPENDIX C: Relations For Physical Properties, Transport Properties, and Rate Constants

Physical Properties

The reacting gas was assumed to be an ideal mixture of ideal gases.

Heat Capacity (Cp, CP):

For atomic hydrogen - $C_{\rm p}$ = 5/2 R = 20786 J / kg-mol K

For molecular hydrogen - $C_p = 26880 + 4.347 \text{ T} - 0.0002645 \text{ T}^2 \text{ J} / \text{kg-mol K}$ (T in K)

For vibrationally equilibrated hydrogen. Correlation taken from Balzhiser, <u>et al</u>. [1972].

For vibrationally excited hydrogen -

$$C_{PT} = 7/2 R = 29,100 J / kg-mol K$$

 $C_{PV}(T) = (E_V(T) / T) e^{h \nu / k T} / R$
 $E_V(T) = N_{Av} h \nu / (e^{h \nu / k T} - 1)$

using h ν / k = 5990 K based on the ground-state vibrational frequency for molecular hydrogen $\omega_e = \nu$ / c = 4395.24 cm⁻¹ (Herzberg [1950]).

For mixture, based on mole fractions:

$$C_{PM} = [(1 - X) C_{PH_2} + 2 X C_{PH}] / (1 + X)$$

<u>Heat of Reaction</u> (DH_R, DH):

For vibrationally equilibrated system, computed by integrating the $\Delta C_{\rm P}$ from 0 K to the temperature. DH_R(0) = 431.41 MJ / kg-mol. Extrapolated from Balzhiser, <u>et al</u>. [1972] using C_P correlation.

In vibrationally excited case, use

$$DH_R(T,T_V) - DH_R(0.,0.) + 3/2 R T - E (T_V)$$

with $DH_R(0.,0.) = 431.885 \text{ MJ} / \text{kg-mol}$, extrapolated from Balzhiser, <u>et</u> <u>al</u>. (<u>Ibid</u>.) value at T = T_V = 298.15 K.

Equilibrium Constant (K, KEQ):

Computed using standard relationships;

 $\ln K_0 - DG_0 / R T_0$ $d \ln K / d T - DH_R / R T^2$

and above relationships for DH_R , based on equilibrium vibrational excitation. $DG_0 = 406.48$ MJ / kg-mol, at $T_0 = 298.15$ K, taken from Balzhiser, et al., (Ibid.).

Transport Properties

Thermal Conductivity: $\lambda = KTH = 1.843 \times 10^{-3} T^{0.8} W / m K (T in K)$

Fitted to Perry and Chilton [1973] (p. 3-215) corrected for apparent two order of magnitude error in table, discovered by Prandtl number calculations. Assumed independent of atom concentration from Prandtl number argument. Under ideal gas conditions, the Prandtl number, the ratio of the product of the constant-pressure heat capacity and the viscosity to the thermal conductivity is roughly the same for all simple gases, around 0.7, from the kinetic theory, supported by experiment. At low temperatures, this heat capacity for atomic hydrogen is 5/2 R, and that for molecular hydrogen is 7/2 R, on the same bases. When corrected for the molecular weights, on the mass basis appropriate for Prandtl number calculations, the heat capacity at constant pressure for atomic hydrogen is 10/7 that of the molecular gas. Similarly, kinetic theory predicts that the viscosity, to a first, very rough, approximation, should be proportional to the square root of the molecular weight. Browning and Fox [1964] verified this experimentally, measuring a viscosity for atomic hydrogen 0.7 times that of the molecular gas. Hence, the product of the heat capacity and the viscosity is roughly the same for molecular and atomic hydrogen, and, to give the same Prandtl number, the thermal conductivity should also be roughly the same, and independent of composition, in a mixture of atomic and molecular hydrogen, such as a partially dissociated hydrogen gas. This

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is probably only rigorous at low temperatures, though it was used for all temperatures, and the tabulated values extrapolated freely.

Diffusion Coefficient:
$$D_{H-H_2} P = DH2HP = 1.264 \times 10^{-3} T^{1.72} Pa m^2/s$$

Taken from Lede and Villermaux [1976], extrapolated freely beyond the range reported, 270-320 K. Fits well high temperature dependence of Sancier and Wise [1969]. Assumed constant over all dissociations.

<u>Viscosity</u>: μ - VISC (For one-dimensional model, friction factor calculation)

For mixture, computed from simple mixture heat capacity and conductivity relations (vide supra), assuming Prandtl number of 0.7.

Rate Constants

- 1. Recombination Reaction Rates
 - a. Gas Phase Reaction
 - i. Hydrogen Molecule as third body

k = 2.014 x 10¹¹ T^{-0.7497} $e^{-20.43/T}$ m⁶ / kg-mol² / s (T in K) Fit to curve in Shui and Appleton [1971]

ii. Hydrogen Atom as third body

k = 8.816 x 10¹¹ T^{-0.7219}
$$e^{-92.09/T}$$
 m⁶ / kg-mol² / s
(T in K)

Fit to curve in Shui [1973]

b. Surface Reaction

k =
$$3.855 \times 10^{18} \text{ T}^{-3} e^{-2900/\text{T}} \text{ m}^4 / \text{kg-mol} / \text{s}$$

(T in K)

Fit to data for quartz in Wood and Wise [1962]. Assumes second-order surface reaction, and adjusts low-temperature values to give pseudo-second order rate constant. Neglects high-temperature 0. rate constant. Extrapolated freely, assuming temperature reported is surface temperature.

- 2. Collisional Relaxation Rates
 - a. Hydrogen molecule as collision partner

$$k_{\rm VT} = 25300 \ e^{-100/T^{1/3}} \ P \ s^{-1}$$
 (T in K, P in Pa)
From Kiefer and Lutz [1966] extrapolated freely to lower
temperatures, after Heidner and Kaspar [1972].

b. Hydrogen atom collision partner / exchange relaxation

 $k_{\rm VT} = 6.6 \times 10^9 e^{-3800/T} P / T s^{-1}$ (T in K, P in Pa) From Cohen [1978]. BIBLIOGRAPHY

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