AD-A089 405   AEROSPACE CORP EL SEGUNDO CA VEHICLE ENGINEERING DIV   F/G 7/4
AN IRREVERSIBLE THERMODYNAMICS MODEL FOR GRAPHITE SUBLIMATION I--ETC(U)
SEP 80 R L BAKER   F04701-79-C-0080
UNCLASSIFIED   TR-0080(5909-20)-1   SD-TR-80-62   NL

1 OF 1
AD A
089405

END
DATE
FILMED
10-80
DTIC

[illegible]

LEVEL ⑫

An Irreversible Thermodynamics Model For Graphite Sublimation in Intense Radiation Environments

R. L. BAKER
Vehicle Engineering Division
The Aerospace Corporation

15 September 1980

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

THE AEROSPACE CORPORATION

Prepared for

SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

This final report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract F04701-79-C-0080 with the Space Division, Deputy for Threat Analysis, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by E.G. Hertler of the Vehicle Engineering Division and W.P. Thompson of the Space Plans Directorate. The Air Force project officer was 1Lt James C. Garcia, SD/YLXT.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

James C. Garcia
JAMES C. GARCIA, 1Lt, USAF
Project Officer

Joseph J Cox
JOSEPH J. COX, Jr., LtCol, USAF
Chief, Advanced Technology Division

FOR THE COMMANDER

Burton H. Holaday
BURTON H. HOLADAY, Col, USAF
Director of Space Systems Planning
Deputy for Technology

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

19 **REPORT DOCUMENTATION PAGE**

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER 18 SD-TR-80-62

2. GOVT ACCESSION NO. AD-A089405

3. RECIPIENT'S CATALOG NUMBER 9

4. TITLE (*and Subtitle*) 6 AN IRREVERSIBLE THERMODYNAMICS MODEL FOR GRAPHITE SUBLIMATION IN INTENSE RADIATION ENVIRONMENTS.

5. ~~TYPE OF REPORT &~~ PERIOD COVERED Final rept.

6. ~~PERFORMING ORG. REPORT NUMBER~~ 14 TR-0080(5909-20)-1

7. AUTHOR(s) 10 R. L. Baker

8. ~~CONTRACT OR GRANT NUMBER(s)~~ 15 F04701-79-C-0080

9. PERFORMING ORGANIZATION NAME AND ADDRESS

The Aerospace Corporation
El Segundo, Calif. 90245

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

Space Division
Air Force Systems Command
Los Angeles, Calif. 90009

12. ~~REPORT DATE~~ 11 15 Sep~~tember 19~~80

13. ~~NUMBER OF PAGES~~ 33

14. MONITORING AGENCY NAME & ADDRESS (*if different from Controlling Office*) 12 37

15. SECURITY CLASS. (*of this report*) Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Carbon Ablation
Thermochemistry
Nonequilibrium Effects

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

A model for the phase change behavior of graphite when exposed to a high external radiation heat flux has been developed in order to examine solid-gas nonequilibrium effects. The usual Knudsen-Langmuir type model is extended to one which allows both pressure and temperature discontinuities at the ablating surface. Calculated results indicate a relatively constant effective heat of ablation. However, major uncertainties are shown to remain regarding individual carbon species concentrations and the input energy required for melting. A unique feature of the irreversible

DD FORM 1473 (FACSIMILE) 409369 DW

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

thermodynamics model is the prediction of gas phase supersaturation when JANNAF thermochemical data is utilized.

PREFACE

This work was supported by the Air Force Space and Missile Systems Organization under Contract No. F04701-77-C-0078. The helpful suggestions and stimulating discussions of this work through personal communications with Mr. Henry Hidalgo and Dr. Ron Bywater are acknowledged gratefully.

CONTENTS

FIGURES

TABLES

I. INTRODUCTION

The use of graphitic materials for thermal protection system applications involving high heat flux environments is based upon the fact that carbon possesses a rare combination of very desirable properties. Its thermal properties make graphitic materials good heat sinks with a very high melt temperature, while its thermochemical properties indicate a very large heat of sublimation. A considerable amount of ablation response modelling for graphite and graphitic materials has been reported (Ref. 1).

Until recently, the maximum heat flux environments encountered, in ballistic reentry vehicle applications and arc jet (Ref. 2) ground tests, have been about 10 kW/cm^2. At the present time, however, combined convective/radiative heat transfer up to 50 kW/cm^2 is predicted for the Jupiter entry probe (Ref. 3) which will probably have a graphitic material heat shield (Ref. 4) and laser/material interaction tests have exposed graphite to fluxes of 100-1000 kW/cm^2 (Ref. 5) and even as high as 10^4-10^5 kW/cm^2 (Ref. 6).

---

[1] Hurwirz, H., K.M. Kratsch, and J.E. Rogan, "Ablation," AGARDograph No. 161, March 1972.

[2] Lundell, J.H., and R.R. Dickey, "Ablation of ATJ Graphite at High Temperatures," AIAA Journal, 11, February 1973, pp. 216-222.

[3] Moss, J.N., E.E. Anderson, and C.W. Bolz, "Aerothermal Environment for Jovian Entry Probes," AIAA Paper 76-469, AIAA 11th Thermophysics Conference, San Diego, Calif., July 1976.

[4] Nunamaker, R.R., quoted in Aviation Week and Space Technology, April 3, 1978.

[5] Lundell, J.H., and R.R. Dickey, "Radiative Vaporization of Graphite in the Temperature Range of 4000° to 4500°K," Thermophysics of Spacecraft and Outer Planet Entry Probes, Progress in Astronautics and Aeronautics, 56, 1977.

[6] Stegman, R.L., J.T. Schriempf, and L.R. Hettche, "Experimental Studies of Laser-Supported Absorption Waves with 5 ms Pulses of 10.6μ Radiation," Journal of Applied Physics, 44(8), August 1973, pp. 3675-3681.

Ablation response models currently in use for graphite in these very high heat flux environments rely upon direct extension of the classical modelling (Ref. 1) which assumes solid-gas phase equilibrium. Baker (Ref. 7) has developed a nonequilibrium model for graphite sublimation in an air environment and concluded that, for relatively high heat flux at low pressures, nonequilibrium effects can become important.

The primary purpose of this work has been to model the nonequilibrium thermochemical response of graphite exposed to external radiation environments extending to 1000 kW/cm^2. Above this flux level, laser-supported absorption wave effects (Ref. 6) tend to significantly decouple the radiation input-material response behavior. The work has proceeded in two stages and is described in this manner. In the first stage, the Knudsen-Langmuir type model developed earlier (Ref. 7) was used. In the second stage, an irreversible thermodynamics phase change model developed by Bornhorst and Hatsopoulos (Ref. 8) was adapted to the present problem and extended to include multiple species with chemical reactions.

The problem formulation using these two models is given in the next section. Then, the model predictions are compared with available experimental data. Finally, some preliminary conclusions and recommendations for further work are given.

---

[7] Baker, R. L., "Graphite Sublimation Chemistry Nonequilibrium Effects," AIAA Journal, 15(10), pp. 1091-1097.

[8] Bornhorst, W. J., and G. N. Hatsopoulos, "Analysis of a Phase Change by the Methods of Irreversible Thermodynamics," Transactions of the ASME, J. Appl. Mech., 34(4), December 1967, pp. 840-846.

II. PROBLEM FORMULATION

A. KNUDSEN-LANGMUIR MODEL

The Knudsen-Langmuir equation is obtained from kinetic theory considerations and is given by Kennard (Ref. 9) as

$$\dot{m} = \alpha \sqrt{\frac{\mathcal{M}}{2\pi RT}} \left| p^{v} - p \right| \tag{1a}$$

where $\dot{m}$ is the mass flux between phases per unit wall area, $\mathcal{M}$ is the molecular weight, T_w is the wall temperature, p^v is the vapor pressure of the vaporizing material at the wall temperature, p is the partial pressure of vaporizing material at the surface, and α is the vaporization coefficient. For application to graphite ablation, Eq. (1a) has been assumed applicable to each carbon species (Refs. 7, 10), i.e.

$$\dot{m}_i = \alpha_i \sqrt{\frac{\mathcal{M}_i}{2\pi RT}} \left| p_i^{v} - p_i \right| \tag{1b}$$

The total mass loss is then obtained by summing over n species

$$\dot{m} = \sum_{i=1}^{n} \dot{m}_i \tag{1c}$$

---

[9] Kennard, E.H., Kinetic Theory of Gases, McGraw-Hill Book Company, Inc., New York, N.Y., 1938.

[10] Dolton, J.A., R.E. Mauer, and H.E. Goldstein, "Thermodynamic Performance of Carbon in Hyperthermal Environments," AIAA Paper No. 68-754, AIAA Third Thermophysics Conference, Los Angeles, Calif., June 1968.

Since the primary interest of the present work is high external radiation environments, diffusive (boundary layer) heat transfer effects will be assumed to be negligible and not retained in the surface energy balance. It is further assumed that the surface mass addition rates are sufficiently high so that only carbon species are present at the ablating surface. With these simplifying assumptions, the surface energy balance becomes simply

$$\dot{q}_{cond} = \dot{q}_{rad} - \epsilon\sigma T_w^4 - \dot{m}[H_w - H_s] \tag{2a}$$

where $\dot{q}_{cond}$ is the heat conducted into the ablating material, $\dot{q}_{rad}$ and $\epsilon\sigma T_w^4$ are the net heat radiated to and away from the surface, and $\dot{m}[H_w - H_s]$ is the net heat convected away from the surface by the mass loss. Assuming the heat conducted into the material is given by the steady-state approximation, which is

$$\dot{q}_{cond} = \dot{m}\, c_p[T_w - T_b] \tag{2b}$$

the surface energy balance equation becomes, with $H_s = c_p T_w$

$$\dot{q}_{rad} - \epsilon\sigma T_w^4 - \dot{m}[H_w - H_b] = 0 \tag{2c}$$

For the multiple species case, the wall enthalpy H_w is given in terms of the partial specific enthalpies h_i and the mass fractions K_i by

$$H_w = \sum_{i=1}^{n} K_i h_i \tag{3}$$

Also, the mass fraction K_i is represented by

$$K_i = \frac{p_i \mathcal{M}_i}{p_e \bar{\mathcal{M}}} \tag{4a}$$

and the average molecular weight is

$$\bar{\mathcal{M}} = \sum_{i=1}^{n} p_i \mathcal{M}_i \Big/ \sum_{i=1}^{n} p_i = \sum_{i=1}^{n} [K_i/\mathcal{M}_i]^{-1} \tag{4b}$$

The Mach number of the flow from the ablating surface is defined by

$$M = \frac{V}{\sqrt{\frac{\gamma R T}{\bar{\mathcal{M}}}}} = \frac{\dot{m}}{p_e} \sqrt{\frac{RT}{\gamma \bar{\mathcal{M}}}} \tag{5}$$

To determine the partial pressure of species i at the surface, it is necessary to assume either frozen or equilibrium chemistry in the gas phase. If the chemistry is assumed to be frozen, then

$$\dot{m}_i = \dot{m} K_i \tag{6a}$$

By combining Eqs. (1b), (1c), (4a), (5) and (6a) we obtain for this case

$$p_i = \left[1 + \frac{M}{\alpha_i} \sqrt{\frac{2\pi \mathcal{M}_i}{\bar{\mathcal{M}}}} \right]^{-1} p_i^v \tag{6b}$$

if the chemistry is assumed to be equilibrium in the gas phase, then the partial pressures p_i are given by

$$p_i = [p_1/p_1^v]^i \, p_i^v \tag{6c}$$

The equilibrium vapor pressure p_i^v and the partial specific enthalpies h_i of species i at the wall temperature are represented by

$$p_i^v \text{ (atm)} = \frac{A_i}{T(^oK)} + B_i \tag{7a}$$

$$h_i = h_i^o + \int_{2500}^{T} \left[a_i + b_i T' + \frac{C_i}{T'} \right] dT' + d_i \tag{7b}$$

The values of the constants in Eqs. (7a) and (7b) for the three thermochemical data bases (Refs. 10-12) used in the present study are given by Baker (Ref. 13).

Equations (1) through (7) provide (5n + 7) equations in the same number of unknowns to be solved simultaneously to obtain mass loss rate $\dot{m}$ as a function of $\dot{q}_{rad}$ and the external pressure p_e. If the Mach number calculated from Eq. (5) is supersonic, then p_e is increased in accordance with the requirement

$$M = \frac{\dot{m}}{p_e} \sqrt{\frac{RT}{\gamma \bar{\mathcal{M}}}} = 1.0 \tag{8}$$

Laser/material interaction flows of this type have recently been reported by Covington, et al. (Ref. 14), who observed a plume flowfield away from the ablating surface with a barrel shock and a Mach disk.

---

[11] "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Michigan, 1969.

[12] Palmer, H. B., and M. Shelef, "Vaporization of Carbon," Chemistry and Physics of Carbon, 4, ed. P. L. Walker, Jr., Marcel Dekker, Inc., New York, N. Y., 1968.

[13] Baker, R. L., "The Thermochemical Response of Graphitic Materials Subjected to High External Radiation Environments," Report No. TOR-0078 (3701)-2, The Aerospace Corporation, El Segundo, Calif., April 1978.

[14] Covington, M. A., G. N. Liu, and K. A. Lincoln, "Free-Jet Expansions from Laser-Vaporized Planar Surfaces," AIAA Paper No. 76-22, AIAA 14th Aerospace Sciences Meeting, Washington, D. C., 26-28 January 1976.

B. IRREVERSIBLE THERMODYNAMICS MODEL--SINGLE COMPONENT (C_3)

The Knudsen-Langmuir model discussed above considers the pressure discontinuity $\Delta p = p - p^v$ but neglects the possible existence of a temperature discontinuity $\Delta T = T_g - T_w$. It also neglects potential coupling between the mass flux $\dot{m}$ and the energy flux j_u, where $j_u = H_w \dot{m}$. Irreversible thermodynamics provides a methodology whereby these effects can be modelled.*

The first application of this methodology to phase change modelling was apparently the work of Bornhorst and Hatsopoulos (Ref. 8). In the following paragraphs, the salient features of their development are given. The relationship of this type of formulation to the Knudsen-Langmuir representation and the groundwork for extension of the irreversible thermodynamics model to the multiple species chemically reacting case are then discussed.

In order to model the discontinuous behavior of intensive properties at the subliming graphite surface, the discontinuous system is envisioned as shown in Fig. 1. Two equilibrium regions I and II are connected by a region of vanishingly small thickness, III. The pressure and temperature in regions I and II are considered to be held constant by pistons and heat reservoirs. These quantities are highly nonuniform in the communicating region III.

The total entropy production σ_{tot} for the system depicted in Fig. 1 is (Refs. 8, 15)

$$\sigma_{tot} = -j_u x_u - j_m x_m \tag{9}$$

---

[15] DeGroot, S. R., and P. Mazur, Non-equilibrium Thermodynamics, North Holland Publishing Co., Amsterdam, 1962.

[*] The entire methodology is based upon the validity of linear flux-force relationships [see Eqs. (11a, b)].

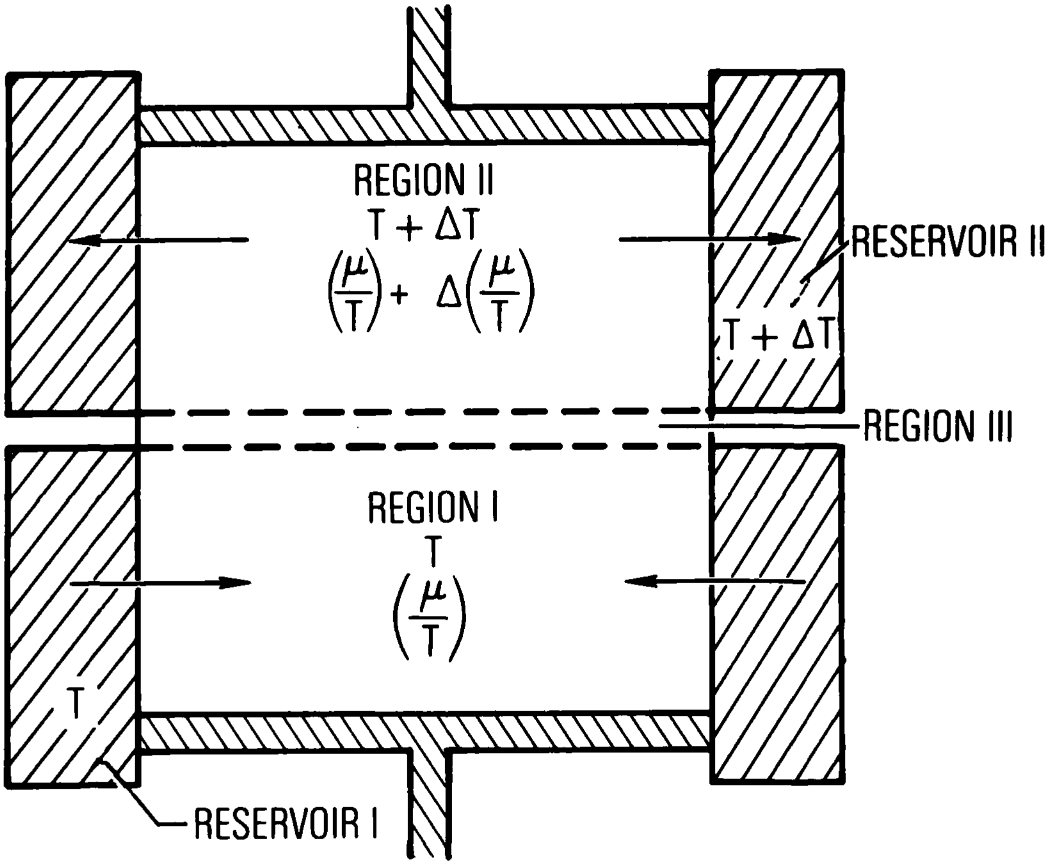


Fig. 1. Representation of Phase Change Problem as a Discontinuous System

where j_u and j_m are the net interphase energy and mass transport rates ($j_m \equiv \dot{m}$), and x_u and x_m are the driving potentials or affinities for energy and mass transfer, respectively, and are given by

$$x_u = \Delta\left(\frac{1}{T}\right) \tag{10a}$$

$$x_m = \Delta\left(\frac{\mu}{T}\right) \tag{10b}$$

where μ is the chemical potential.

The phenomenological equations relate the transport rates and driving potentials in terms of the transport coefficients L. Thus

$$j_u = - L_{uu}\Delta\left(\frac{1}{T}\right) - L_{ui}\Delta\left(\frac{\mu}{T}\right) \tag{11a}$$

$$j_m = - L_{iu}\Delta\left(\frac{1}{T}\right) - L_{ii}\Delta\left(\frac{\mu}{T}\right) \tag{11b}$$

The chemical potential for a homogeneous system is related to the temperature and pressure by (Ref. 16)

$$\frac{\mu}{T} = R\left|\varphi(T) + \ln p\right| \tag{12a}$$

It can easily be shown that

$$\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right)_p = - \frac{h}{T^2} \tag{12b}$$

$$\frac{\partial}{\partial p}\left(\frac{\mu}{T}\right)_T = \frac{R}{p} = \frac{v}{T} \tag{12c}$$

---

[16] Callen, H. G., Thermodynamics, John Wiley & Sons, Inc., New York, N. Y., 1960.

Thus

$$\Delta\left(\frac{\mu}{T}\right) = h\Delta\left(\frac{1}{T}\right) + \frac{v}{T}\,\Delta p \tag{12d}$$

In Ref. 8 the transport coefficients L are evaluated by considering various limiting cases of j_m or ΔT going to zero and comparing the resultant form of Eqs. (11a) and (11b) with kinetic theory expressions for that particular limiting case. By combining the transport coefficient expressions obtained in this way with Eqs. (11a), (11b), (12d), and the Onsager reciprocity condition $L_{ui} = L_{iu}$, Bornhorst and Hatsopoulos obtain

$$j_u = \left(h - \frac{1}{2}\frac{RT}{\mathcal{M}}\right) j_m - L_k \frac{\Delta T}{T^2} \tag{13a}$$

$$j_m = L_{ii}\left\{\frac{pv\Delta T}{2T^2} - \frac{v\Delta p}{T}\right\} \tag{13b}$$

where

$$L_k = \sqrt{\frac{\mathcal{M}}{2\pi RT}}\,(\gamma+1)\,pC_vT^2 \tag{14a}$$

$$L_{ii} = \frac{T}{v}\left(\frac{2\alpha}{2-\alpha}\right)\sqrt{\frac{\mathcal{M}}{2\pi RT}} \tag{14b}$$

and v is the specific volume which is the reciprocal of the mass density.

Of particular interest is the limit of j_m for $\Delta T = 0$.

$$(\text{For } \Delta T = 0)\ j_m = -\left(\frac{2\alpha}{2-\alpha}\right)\sqrt{\frac{\mathcal{M}}{2\pi RT}}\,\Delta p \tag{15}$$

Comparing this expression with the Knudsen-Langmuir expression given by Eq. (1a), we see that they are equivalent except that the vaporization coefficient (Ref. 12) appears as α in Eq. (1a) and in the term $[(2\alpha/2-\alpha)]$ in Eq. (15).

The reason for this was first recognized by Schrage (Ref. 17) who demonstrated, using kinetic theory arguments, that by accounting for the gas phase bulk flow velocity in the velocity distribution function at the surface, one obtains, for small j_m, Eq. (15) in place of Eq. (1a). Physically, this indicates that the bulk flow velocity at the surface gives rise to an effective vaporization coefficient $[(2\alpha/2-\alpha)]$. The basic definition of α (Ref. 12), however, has not been changed.

Two alternate forms of Eqs. (13a) and (13b) are useful as an aid in understanding the relationships of the irreversible thermodynamics formulation to the Knudsen-Langmuir representation and of the single component model to the multiple species chemically reacting model. Thus, following DeGroot and Mazur (Ref. 15) if we require the entropy production, as given by Eq. (9), to be constant and define a new energy flux j_q and a volumetric flux j_v by

$$j_q = j_u - H_w j_m \qquad (16a)$$

$$j_v = v j_m \qquad (16b)$$

then a symmetric set of equations entirely equivalent to Eqs. (13a) and (13b) is

$$j_q = - \Lambda_{qq} \frac{\Delta T}{T^2} - \Lambda_{qv} \frac{\Delta p}{T} \qquad (17a)$$

$$j_v = - \Lambda_{vq} \frac{\Delta T}{T^2} - \Lambda_{vv} \frac{\Delta p}{T} \qquad (17b)$$

---

[17] Schrage, R. W., A Theoretical Study of Interphase Mass Transfer, Columbia University Press, New York, N. Y., 1953.

where

$$\Lambda_{qq} = L_k + \frac{1}{4}(pv)^2 L_{ii} \tag{18a}$$

$$\Lambda_{qv} = \Lambda_{vq} = -\frac{1}{2} pv^2 L_{ii} \tag{18b}$$

$$\Lambda_{vv} = v^2 L_{ii} \tag{18c}$$

The entropy production then becomes, in place of Eq. (9)

$$\sigma_{tot} = -j_q \Delta\left(\frac{1}{T}\right) - j_v \frac{\Delta p}{T} \tag{19}$$

Now, if we consider the steady-state phase change problem to be defined by *fixing Δp, then the steady state is characterized* by *minimum entropy* production for this constraint (Refs. 15, 18) which requires

$$j_q = 0 \tag{20a}$$

or

$$\frac{\Delta T}{\Delta p} = -\frac{\Lambda_{qv}}{\Lambda_{qq}} T \tag{20b}$$

Substituting from Eqs. (14a), (14b), (18a), and (18b)

$$\frac{p}{T}\frac{\Delta T}{\Delta p} = 2\left\{1 + \frac{C_v}{R}\left[\frac{2(2-\alpha)(\gamma+1)}{\alpha}\right]\right\}^{-1} \tag{21a}$$

---

[18] Prigogine, J., Thermodynamics of Irreversible Processes, Interscience Publishers, Division of John Wiley & Sons, Inc., New York, N.Y., 1961.

If Eqs. (21a) and (16b) are used to eliminate ΔT and j_v, respectively, in Eq. (17b), it can be shown that

$$j_m = \frac{\frac{2\alpha}{2-\alpha}\sqrt{\frac{\mathcal{M}}{2\pi RT}}\left|p^v - p\right|}{\left[1 + \frac{R}{C_v}\left[\frac{\alpha}{2(2-\alpha)(\gamma+1)}\right]\right]} \qquad (21b)$$

Equations (13a) and (13b), (17a) and (17b) and (21a) and (21b) are alternate expressions relating the mass and energy fluxes, allowing for both a temperature and a pressure discontinuity as well as accounting for cross-coupling effects through the transport coefficients L_{iu} or Λ_{qv}. Equation (21b) explicitly shows the relationship of the irreversible thermodynamics model to the Knudsen-Langmuir model. Equations (17a) and (17b) are in the form to be extended to the case of multiple species with chemical reactions.

To employ the formulation developed in this section in place of the Knudsen-Langmuir model, one replaces Eq. (1a) with Eq. (21b) and then carries along Eq. (21a) which defines the additional unknown for this model, i.e., the gas phase temperature $T_g = T_w + \Delta T$. Since C_3 is the dominant species in the gas phase, the restrictions to C_3-only is a reasonable first approximation.

C. IRREVERSIBLE THERMODYNAMICS MODEL--MULTIPLE SPECIES WITH CHEMICAL REACTIONS

The development of the model for this case is largely analogous to the model development outlined above for the single component case. In place of Eqs. (17a) and (17b), which define a 2 × 2 matrix for j_q and j_v, one obtains in the case of frozen gas phase chemistry for n species an n × n matrix that defines j_q and (n-1) independent species mass fluxes j_i in terms of ΔT and (n-1) independent discontinuities of species chemical potential $\Delta\mu_i$. For the case of n species with gas phase chemical reactions, one obtains a (2n-1) × (2n-1) matrix in terms of the above frozen case fluxes and driving potentials plus (n-1) independent chemical reaction rates j_j and (n-1) chemical affinities A_j. A report describing this work is being prepared (Ref. 19). However, except for the discussion of the effective heat of ablation, all the results presented in this paper were obtained either with the Knudsen-Langmuir multiple species model or the irreversible thermodynamics single component model.

---

[19] Baker, R. L., "An Irreversible Thermodynamics Model for Graphite Sublimation Including Multiple Species with Chemical Reactions," (In preparation), The Aerospace Corporation, El Segundo, Calif.

III. RESULTS AND DISCUSSION

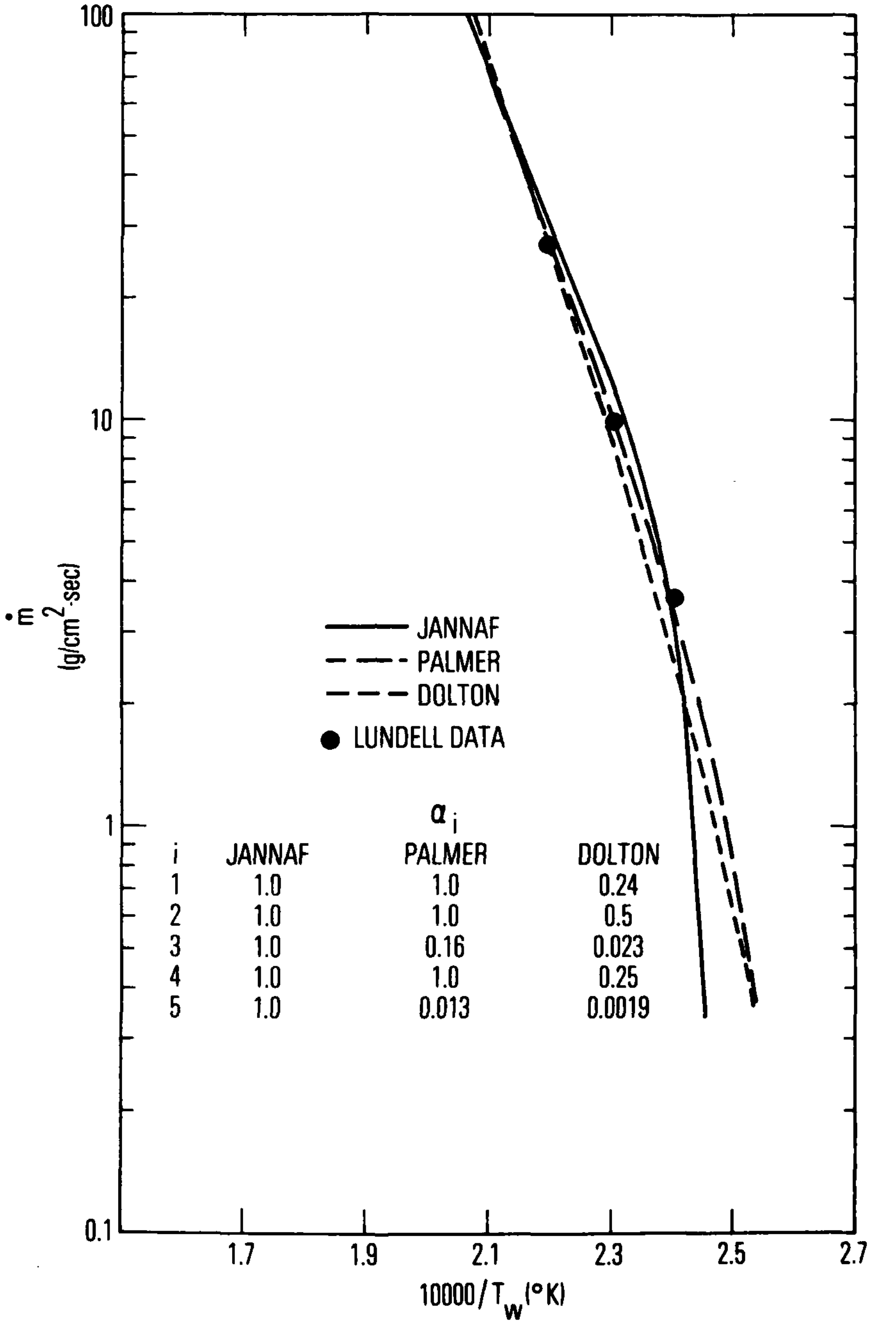
A. KNUDSEN-LANGMUIR MODEL

A complete description of results calculated with this representation is given in Ref. 13. In this section, a summary of the results is given, emphasizing the basis for the need of a more complete model.

The initial calculations performed were for an external pressure of one atmosphere using the 1969 JANNAF thermochemical property data (Ref. 11) for carbon species C_1-C_5. Equations (1) through (7) were solved simultaneously for mass loss $\dot{m}$ and wall temperature T_w as a function of the external radiation heat flux. The experimental data of Lundell and Dickey (Ref. 5) was used to select vaporization coefficients that allowed the calculated results to simultaneously match both the experimental mass loss rate as well as the surface temperature. Other thermochemical data bases (Refs. 10, 12) were then employed, and it was found that different values of the species vaporization coefficients were required to obtain agreement of the calculated results with the experimental data.

The results of these calculations are shown in Fig. 2 along with the species vaporization coefficient values deduced for each thermochemistry model. The α_i values used with the Dolton, et al., thermochemical data are the "nominal" values selected in Ref. 10. The unit vaporization coefficients deduced for the JANNAF thermochemical data are in agreement with a prior conclusion of Lundell and Dickey (Ref. 5). We see from Fig. 2 that resolution of a unique set of thermochemical data and vaporization coefficients cannot easily be accomplished using the Knudsen-Langmuir model.

The major reason for this nonuniqueness is illustrated in Fig. 3. The sum of the species partial pressures and the sum of the species vapor pressures are shown for a wide range of radiation heat flux and an ambient pressure of one atmosphere. The pressure discontinuity $(\Sigma p_i^v - \Sigma p_i)$ increases dramatically, moving from the JANNAF to the Palmer and then to



		α_i	
i	JANNAF	PALMER	DOLTON
1	1.0	1.0	0.24
2	1.0	1.0	0.5
3	1.0	0.16	0.023
4	1.0	1.0	0.25
5	1.0	0.013	0.0019

Fig. 2. The Effect of Assumed Chemistry on Predicted Mass Loss Rates, Knudsen-Langmuir Model

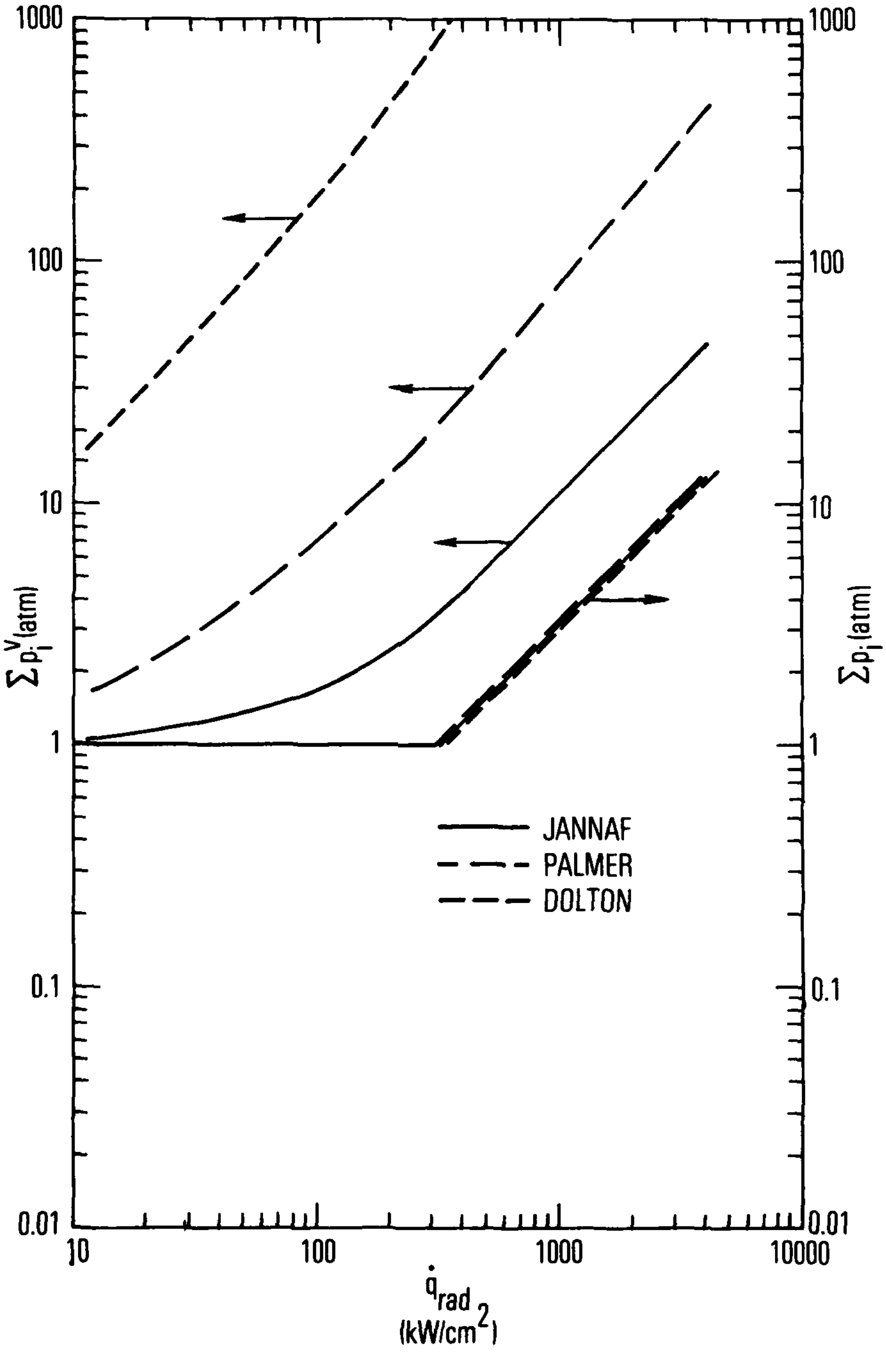


Fig. 3. Calculated Partial Pressures and Vapor Pressures, $p_e = 1$ atm

the Dolton thermochemical data predictions. However, since the mass loss, as given by the Knudsen-Langmuir equation (1b), is proportional to both α_i and $(p_i^v - p_i)$, smaller vaporization coefficient values with large pressure differences can compensate for unit vaporization coefficients with small pressure differences.

The inability to select a unique set of thermochemical data and vaporization coefficients, while disturbing from a theoretical viewpoint, appears from Fig. 2 to be not too serious from a practical viewpoint since all three data sets reasonably predict the experimental data. However, the calculations performed have assumed that the radiation heat flux reaching the surface is known. In actuality, the flux reaching the surface depends upon radiation transport phenomena occurring in the gas phase in the path of the input radiation flux. These phenomena in turn depend on carbon species concentrations which are shown for different thermochemical models in Fig. 4.

The species mole fractions predicted using JANNAF data when compared with the Dolton data predictions differ by a factor of at least two for all species in some range of $\dot{q}_{rad}$, and the difference may be as much as a factor of thirty. These uncertainties provided the major impetus for development of the irreversible thermodynamics model. Comparison of species concentration data with the predicted results in Fig. 4 could potentially allow selection of a unique data set using the Knudsen-Langmuir representation. However, as shown below, the irreversible thermodynamics formulation provides additional useful information.

B. IRREVERSIBLE THERMODYNAMICS MODEL

The results discussed, using this model, in the present report are limited to those in which the carbon vapor phase is assumed to be homogeneous and composed only of carbon species C_3 molecules. Because of this, predicted species concentration results cannot be given. However, the general nature of results calculated using this extended model can be

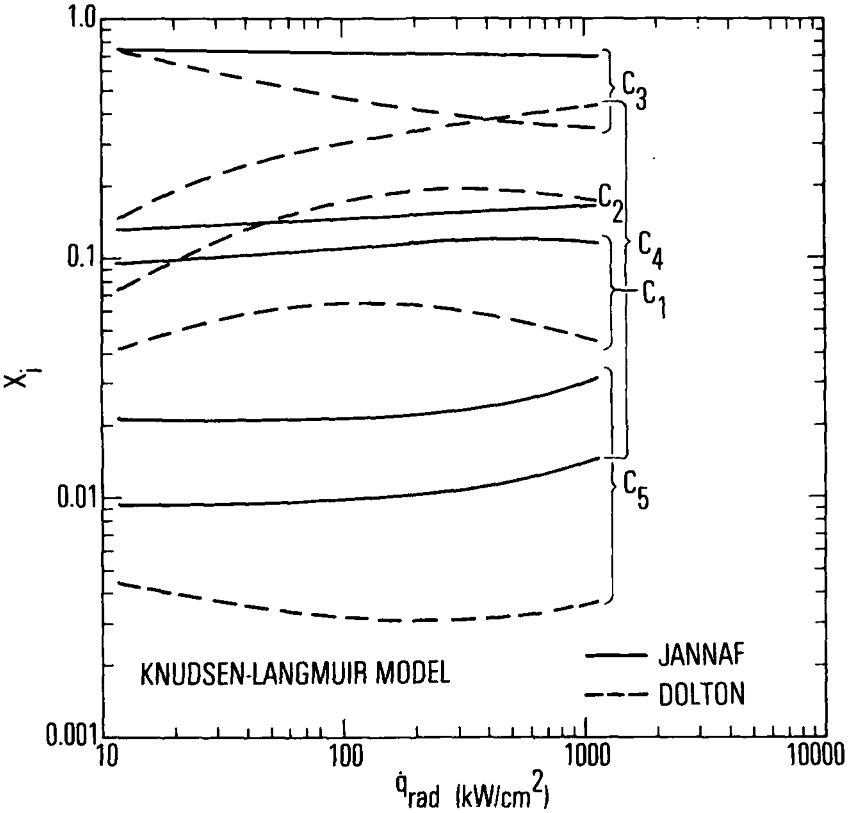


Fig. 4. Species Mole Fractions, JANNAF versus Dolton, Frozen Chemistry

presented. In particular, new and unique results obtainable only with the irreversible thermodynamics model can be illustrated.

Following the procedure established with the Knudsen-Langmuir model, vaporization coefficient values for α_3 were determined for each of the three thermochemical data sets previously considered, by again matching the Lundell and Dickey mass loss rate-surface temperature data. Appropriate values of α_3 were found to be 1.0, 0.21 and 0.062 for the JANNAF, Palmer and Dolton data, respectively. The predicted pressure discontinuities Δp were found to be similar to those shown in Fig. 3. The new variable calculated with the present formulation is the gas phase temperature T_g. The predicted temperature discontinuities $\Delta T = T_g - T_w$ are shown as a function of the calculated T_w for an ambient pressure of one atmosphere in Fig. 5. The absolute magnitude of ΔT is largest for the JANNAF data for which $\alpha_3 = 1.0$ and smallest for the Dolton data for which $\alpha_3 = 0.062$ [see Eq. (21a)].

Due to the reduction in T_g below T_w, it is possible in some cases for the partial pressure of C_3 at the ablating surface to be greater than the vapor pressure of C_3 at the gas phase temperature, i.e., the vapor is supersaturated. Calculated supersaturation ratios are shown as a function of wall temperature and ambient pressure for the JANNAF data set in Fig. 6. Corresponding values of $\dot{q}_{rad}$ can be obtained from Fig. 7.

It cannot be easily determined theoretically if a supersaturation ratio of 2-3 is great enough to cause condensation to solid carbon. It appears that from the standpoint of the homogeneous nucleation theory, carbon species supersaturation levels much greater than this are required (Ref. 20). However, nucleation sites such as free electrons could considerably reduce the required supersaturation level. The point is that the present model predicts that condensation may occur, and the presence of solid carbon particles in

---

[20] Donn, B., N.C. Wickramasinghe, J.P. Hudson, and T.P. Stecher, "On the Formation of Graphite Grains in Cool Stars," Astrophysical J., 153, August 1968, pp. 451-464.

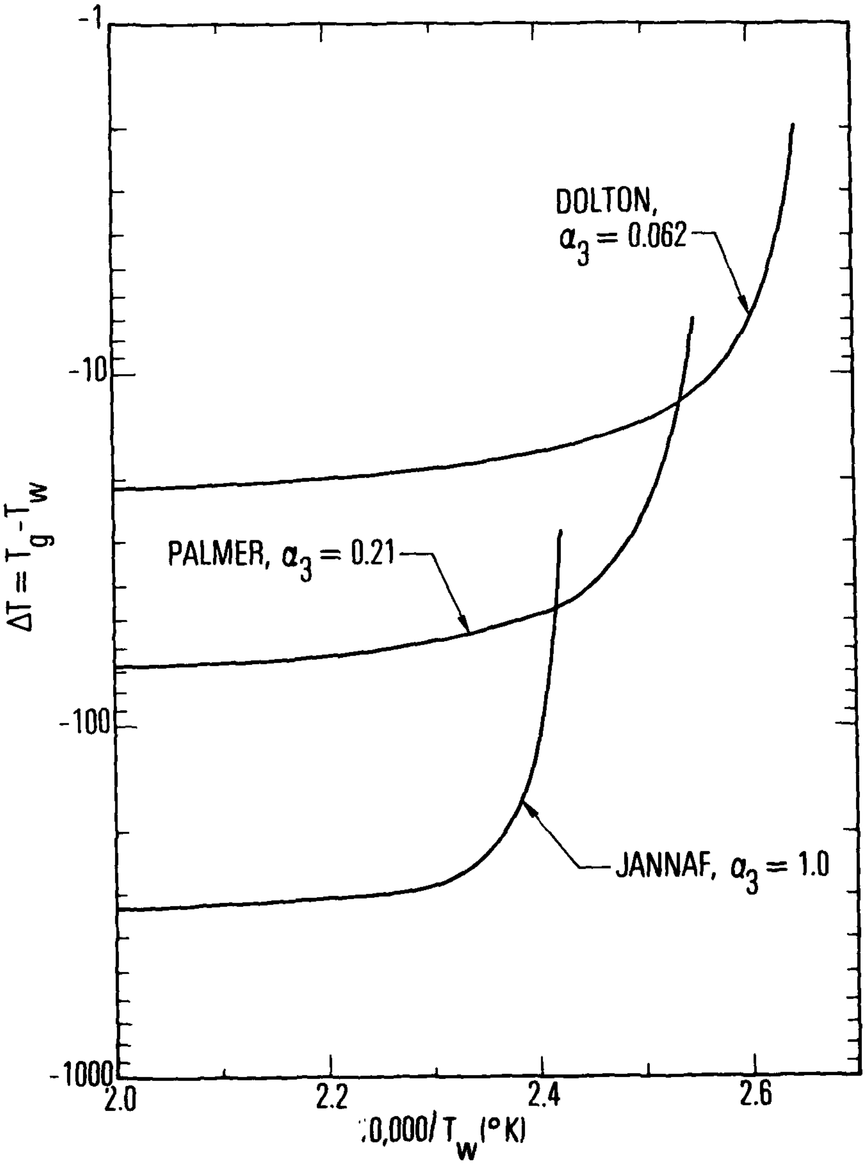


Fig. 5. Predicted Temperature Discontinuities, Irreversible Thermodynamics Model

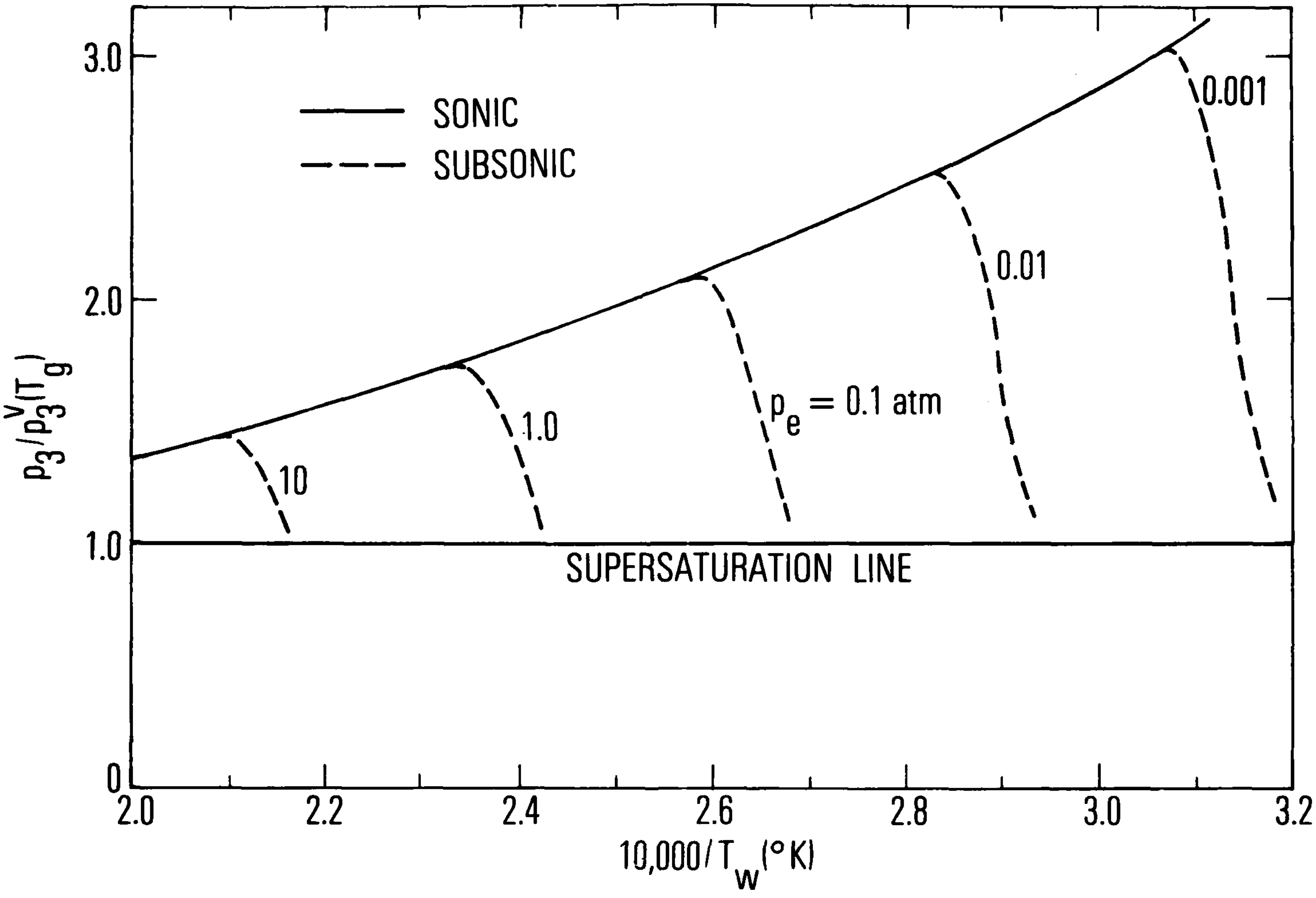


Fig. 6. Predicted Supersaturation Ratios for JANNAF Chemistry, $\alpha_3 = 1.0$

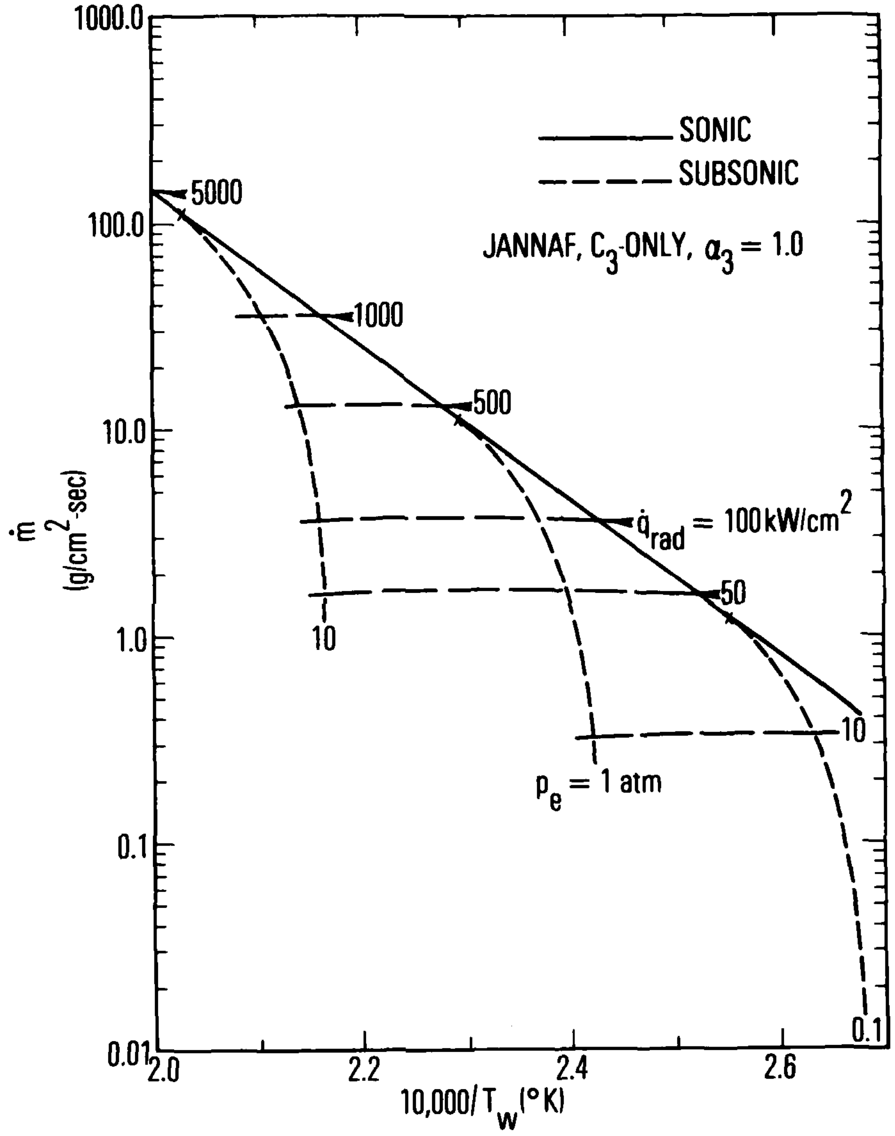


Fig. 7. Mass Loss as a Function of $\dot{q}_{rad}$ and p_e, Irreversible Thermodynamics Model

the flow would further complicate the gas phase radiation transport prediction problem. An additional important point is that supersaturation is predicted to occur only for the JANNAF data set which exhibits the largest reduction in T_g below T_w.

C. GENERAL RESULTS

The above calculated results are unique to the irreversible thermodynamics formulation. Predicted mass loss as a function of ambient pressure and $\dot{q}_{rad}$ for the JANNAF C_3-only irreversible thermodynamics model is shown in Fig. 7. For given $\dot{q}_{rad}$, $\dot{m}$ is relatively insensitive to the ambient pressure level. This indicates that the effective heat of ablation $Q^* = \dot{q}_{rad}/\dot{m}$ does not vary significantly. As p_e decreases, for $\dot{q}_{rad}$ constant, the flow from the surface eventually becomes sonic. This means that further reductions in p_e have no effect. Therefore, a given point on the solid line in Fig. 7 at a particular value of p_e should be interpreted as representing all pressures less than p_e also.

A given surface temperature can be attained at many values of p_e and $\dot{q}_{rad}$. Generally, to reach a specified temperature, the highest $\dot{q}_{rad}$ required occurs when the flow from the surface is sonic. As the pressure increases and the flow becomes subsonic (constant T_w), the required $\dot{q}_{rad}$ decreases significantly. This behavior is illustrated more clearly in Fig. 8. Figure 8 shows that if the melt temperature is low, i.e., 3800°K (Ref. 21), then the $\dot{q}_{rad}$ required for melting to occur may be nearly an order of magnitude below that required to reach the more commonly accepted melt temperature of 4200°K (Ref. 22).

---

[21] Whittaker, A.G., and P. L. Kintner, "Laser-Heating Studies of Carbon Melting and Vaporization," American Ceramic Society 27th Pacific Coast Regional Meeting, North Hollywood, Calif., Oct. 23-26, 1974.

[22] Diaconis, N. W., E. R. Stove, J. Hook, and G. J. Catalano, "Graphite Melting Behavior," Re-Entry and Environmental Systems Division, General Electric Company, AFML-TR-71-119, July 1971.

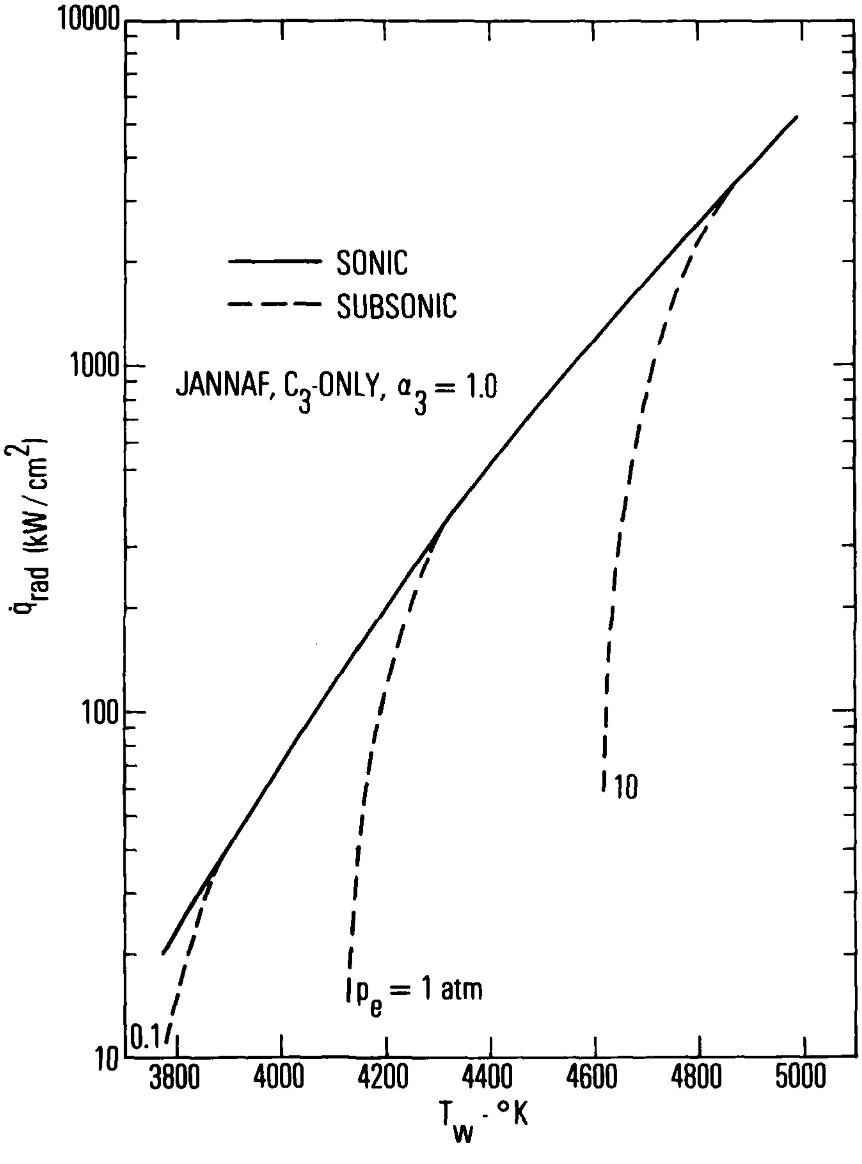


Fig. 8. Relationship of T_w to $\dot{q}_{rad}$ at Several Pressures, Irreversible Thermodynamics Model

The question of melt temperature remains open at the present time (Refs. 23, 24). If melting does not occur, the variation in the effective heat of ablation Q^*, predicted by all of the various models considered in this report, is relatively small. This is seen in Table 1 which includes results predicted by the 5-species *irreversible thermodynamics* model. If melting does occur, the Q^* value could be decreased an order of magnitude by mechanical removal of liquid carbon (Ref. 21).

Table 1. Q^* Values

Model	Range of Q^* (MJ/kg)
Knudsen-Langmuir/JANNAF	31.0 - 33.1
Knudsen-Langmuir/Palmer	28.4 - 31.3
Knudsen-Langmuir/Dolton	26.9 - 32.3
Present-C_3 Only/JANNAF	27.4 - 28.1
Present-C_3 Only/Palmer	27.4 - 28.4
Present-C_3 Only/Dolton	29.3 - 30.3
Present-5 Species/JANNAF	30.5 - 32.5

---

[23] Gokcen, N.A., E.T. Chang, T.M. Poston, and D.J. Spencer, "Determination of Graphite/Liquid/Vapor Triple Point by Laser Heating," <u>High Temperature Science</u>, <u>8</u>, 1976, pp. 81-97.

[24] Whittaker, A. Greenville, and P.K. Kinter, "Comments on the Solid-Liquid-Vapor Triple Point of Carbon," <u>High Temperature Science</u>, <u>9</u>(1), March 1977.

The results presented herein are preliminary in many respects. It is anticipated that further comparisons of the complete 5-species irreversible thermodynamics model predictions with experimental data will help facilitate the selection of a unique set of thermochemical property data and the correct melt temperature. The following experimental data would aid considerably in this work: (1) carbon species concentration measurements above radiation heated graphite surfaces, (2) measurements of the reduction in the gas phase temperature below the surface temperature, (3) detection of condensation to solid carbon particles, and (4) detection of surface melting.

IV. SUMMARY AND CONCLUSIONS

It has been demonstrated by comparing predicted results with experimental data that a unique set of vaporization coefficients and species thermochemical data cannot be readily selected using a Knudsen-Langmuir type multiple species model. Because of this, a large uncertainty presently remains regarding the concentration of carbon species C_1-C_5 above a carbon surface exposed to a high radiation heat flux. This uncertainty will be very important to consider if gas phase radiation transport predictions are required.

In an attempt to help resolve this uncertainty, an irreversible thermodynamics phase change model has been adapted to this problem in order to incorporate effects neglected by the Knudsen-Langmuir representation.

Preliminary results calculated with the new model, assuming gaseous carbon to be composed of C_3 molecules only, indicate significant differences in the predicted temperature discontinuity between the subliming surface and the gas phase, depending on the thermochemical data used. The largest temperature differences are predicted for the JANNAF data, and the reduced gas temperatures in this case result in predicted gas phase supersaturation ratios of as much as 2-3. For the other thermochemical data considered, no supersaturation is predicted.

Assuming that the graphite does not melt with subsequent liquid removal, the predicted effective heat of ablation Q^* is 30 ± 3 MJ/kg for all the different model types and thermochemical data sets used. However, if melting with liquid removal occurs, this could be reduced considerably. The predicted radiation flux required to reach various postulated melt temperatures is given as a function of ambient pressure in Fig. 8.

Additional work employing the irreversible thermodynamics phase change model considering multiple species with chemical reactions is in progress.

REFERENCES

1. Hurwirz, H., K.M. Kratsch, and J.E. Rogan, "Ablation," AGARDograph No. 161, March 1972.

2. Lundell, J.H., and R.R. Dickey, "Ablation of ATJ Graphite at High Temperature," AIAA Journal, 11, February 1973, pp. 216-222.

3. Moss, J.N., E.E. Anderson, and C.W. Bolz, "Aerothermal Environment for Jovian Entry Probes," AIAA Paper 76-469, AIAA 11th Thermophysics Conference, San Diego, Calif., July 1976.

4. Nunamaker, R.R., quoted in Aviation Week and Space Technology, April 3, 1978.

5. Lundell, J.H., and R.R. Dickey, "Radiative Vaporization of Graphite in the Temperature Range of 4000° to 4500°K," Thermophysics of Spacecraft and Outer Planet Entry Probes, Progress in Astronautics and Aeronautics, 56, 1977.

6. Stegman, R.L., J.T. Schriempf, and L.R. Hettche, "Experimental Studies of Laser-Supported Absorption Waves with 5 ms Pulses of 10.6μ Radiation," Journal of Applied Physics, 44(8), August 1973, pp. 3675-3681.

7. Baker, R.L., "Graphite Sublimation Chemistry Nonequilibrium Effects," AIAA Journal, 15(10), pp. 1091-1097.

8. Bornhorst, W.J., and G.N. Hatsopoulos, "Analysis of a Phase Change by the Methods of Irreversible Thermodynamics," Transactions of the ASME, J. Appl. Mech., 34(4), December 1967, pp. 840-846.

9. Kennard, E.H., Kinetic Theory of Gases, McGraw-Hill Book Company, Inc., New York, N.Y., 1938.

10. Dolton, J.A., R.E. Mauer, and H.E. Goldstein, "Thermodynamic Performance of Carbon in Hyperthermal Environments," AIAA Paper No. 68-754, AIAA 3rd Thermophysics Conference, Los Angeles, Calif., June 1968.

11. "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich., 1969.

12. Palmer, H.B., and M. Shelef, "Vaporization of Carbon," Chemistry and Physics of Carbon, 4, ed. P.L. Walker, Jr., Marcel Dekker, Inc., New York, N.Y., 1968.

REFERENCES (Continued)

13. Baker, R. L., "The Thermochemical Reponse of Graphitic Materials Subjected to High External Radiation Environments," Report No. TOR-0078(3701)-2, The Aerospace Corporation, El Segundo, Calif., April 1978.

14. Covington, M.A., G.N. Liu, and K.A. Lincoln, "Free-Jet Expansions from Laser-Vaporized Planar Surfaces," AIAA Paper No. 76-22, AIAA 14th Aerospace Sciences Meeting, Washington, D.C., 26-28 January 1976.

15. DeGroot, S. R., and P. Mazur, Non-equilibrium Thermodynamics, North Holland Publishing Co., Amsterdam, 1962.

16. Callen, H.G., Thermodynamics, John Wiley & Sons, Inc., New York, N. Y., 1960.

17. Schrage, R. W., A Theoretical Study of Interphase Mass Transfer, Columbia University Press, New York, N. Y., 1953.

18. Prigogine, J., Thermodynamics of Irreversible Processes, Interscience Publishers, Division of John Wiley & Sons, Inc., New York, N. Y., 1961.

19. Baker, R. L., "An Irreversible Thermodynamics Model for Graphite Sublimation Including Multiple Species with Chemical Reactions," (In preparation), The Aerospace Corporation, El Segundo, Calif.

20. Donn, B., N.C. Wickramasinghe, J.P. Hudson, and T.P. Stecher, "On the Formation of Graphite Grains in Cool Stars," Astrophysical J., 153, August 1968, pp. 451-464.

21. Whittaker, A.G., and P. L. Kintner, "Laser-Heating Studies of Carbon Melting and Vaporization," American Ceramic Society 27th Pacific Coast Regional Meeting, North Hollywood, Calif., Oct. 23-26, 1974.

22. Diaconis, N.W., E.R. Stove, J. Hook, and G.J. Catalano, "Graphite Melting Behavior," Re-entry and Environmental Systems Division, General Electric Company, AFML-TR-71-119, July 1971.

23. Gokcen, N.A., E.T. Chang, T.M. Poston, and D.J. Spencer, "Determination of Graphite/Liquid/Vapor Triple Point by Laser Heating," High Temperature Science, 8, 1976, pp. 81-97.

24. Whittaker, A. Greenville, and P.K. Kinter, "Comments on the Solid-Liquid-Vapor Triple Point of Carbon," High Temperature Science, 9(1), March 1977.