NASA TECHNICAL NOTE

NASA TN D-5391

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NASA TN D-5391

CHEMICAL EQUILIBRIUM OF ABLATION MATERIALS INCLUDING CONDENSED SPECIES

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • AUGUST 1969

1. Report No. NASA TN D-5391	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle CHEMICAL EQUILIBRIUM OF ABLATION MATERIALS INCLUDING CONDENSED SPECIES		5. Report Date August 1969
		6. Performing Organization Code
7. Author(s) C. W. Stroud and Kay L. Brinkley		8. Performing Organization Report No. L-5957
9. Performing Organization Name and Address NASA Langley Research Center Hampton, Va. 23365		10. Work Unit No. 124-07-13-01-23
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Note
		14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

A computer program for calculating the multiphase chemical equilibrium of an arbitrary system is described and the complete program is included as an appendix. This program has been used to calculate the chemical equilibrium of low-density phenolic nylon over a wide range of conditions. The effects of including carbon in the condensed phase on equilibrium composition and ablative performance are discussed. Methods for incorporating the important effects of chemical equilibrium into ablation analyses are described.

17. Key Words Suggested by Author(s) Ablation materials Chemical equilibrium Phenolic nylon	18. Distribution Statement Unclassified – Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 41	22. Price* $3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

CHEMICAL EQUILIBRIUM OF ABLATION MATERIALS INCLUDING CONDENSED SPECIES

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SUMMARY

A method for computing the chemical equilibrium of complex systems including condensed species is described. The computer program developed to perform calculations based on this method is included as an appendix. This program is used to compute the chemical equilibrium composition of pyrolysis products of phenolic nylon over a temperature range from 500° K to 3500° K. The inclusion of condensed species as possible equilibrium products yielded a composition that had a simple form below 2700° K that can be applied to many ablation materials. The implications that these equilibrium results have on ablation analysis are discussed and ways to include the significant parts of these results in approximate ablation analyses are outlined.

INTRODUCTION

The gases that result from the pyrolysis of a charring ablator have a beneficial effect on ablator performance by influencing surface recession, by blocking energy at the external surface, and by absorbing energy in the char layer. In theory, a consideration of the kinetics of the reactions of the pyrolysis gases as they pass through the hot char to the external surface would result in the precise prediction of the chemical state of the gases and the most realistic appraisal of the influence of the gases on ablator performance. However, the chemical kinetics of the pyrolysis gases are not generally considered in detail because of the lack of information on reaction rates and the extensive computations that would be required.

Alternatives to a detailed study of the reaction kinetics of the gases are to assume that the gas composition is frozen in the initial pyrolysis state or to assume that the gases react to the equilibrium state corresponding to each temperature encountered during passage through the char layer. The frozen composition approximation is the simplest approximation, but leads to a conservative estimate of the ablator performance. On the other hand, the assumption of chemical equilibrium avoids the conservatism of frozen composition while providing a practical alternative to the detail of the kinetics case. However, previous calculations of the chemical equilibrium of pyrolysis gases have generally included only gaseous species and have neglected condensed species such as carbon. (For example, see ref. 1.)

The paper presents a computer program that was developed to include both gaseous and condensed species in the determination of equilibrium compositions by minimizing the Gibb's free energy. In addition, a technique for minimizing computer time and an approximate model based on the use of a few of the many possible species are described.

Example results are given from calculations for the pyrolysis gases of phenolic nylon for the temperature range of 500° K to 3500° K and pressures of 0.1, 1, and 10 atmospheres. The inclusion of the condensed carbon species is shown to have a significant effect on the surface-recession and heat-accommodating ability of a charring ablator.

SYMBOLS

The units used for the physical quantities defined in this section are given in cgs units and in the International System of Units (SI) (ref. 2).

a	elemental composition matrix
b	elemental total in mixture, moles
$\bar{c}_p$	effective specific heat, J/mole
f	free energy of individual species, J/mole
F	Gibb's free energy, J/mole
H_c	enthalpy plus chemical energy, J/mole
H	enthalpy, J/mole
i,j,k,l	integers
K_p	equilibrium constant
m	number of elements in mixture
N	number of gaseous species in mixture
n	mole fraction

p	partial pressure, atmospheres
p_t	total pressure, atmospheres
Q	number of condensed species in mixture
R	gas constant, 1.987 J/mole-$^{\circ}$K
T	temperature, $^{\circ}$K
x	number of moles
y	value of x at previous iteration
α	degree of dissociation
β	convergence criterion
ρ	density, kg/m^3

Superscripts:

g	denotes gaseous species
s	denotes condensed species

EQUILIBRIUM COMPOSITIONS BY MINIMIZATION OF FREE ENERGY

In a closed, chemically reacting system at constant pressure and temperature, the potential function which governs chemical changes is the Gibbs free energy. The condition for chemical equilibrium is that the free energy must be a minimum. (See ref. 3.) The technique used here to minimize the free energy was developed by modifying the well-known method of reference 4 to include condensed species. This modification is similar to that given in reference 5.

Formulation of Problem

The Gibbs free energy of a mixture of N gaseous species and Q condensed species can be written as:

$$F(x) = \sum_{i=1}^{N} f_i^g + \sum_{j=1}^{Q} f_j^s \tag{1}$$

where x is the set formed by the mole numbers of all the species, or

$$x = x\left(x_1^g, x_2^g, \ldots x_N^g; x_1^s, x_2^s, \ldots x_Q^s\right)$$

The free energy of an ideal gaseous species is

$$f_i^g = x_i^g \left[\left(\frac{F}{RT}\right)_i^g + \log_e p_t + \log_e \frac{x_i^g}{\sum_{i=1}^{N} x_i^g} \right] \tag{2}$$

where $\left(\frac{F}{RT}\right)_i^g$ is the molal standard free energy.

The free energy of a condensed species is

$$f_j^s = x_j^s \left(\frac{F}{RT}\right)_j^s \tag{3}$$

The equilibrium condition can be obtained by minimizing the free energy of the mixture (eq. (1)) subject to the mass balance constraints. These constraints are given by the following equations:

$$\sum_{i=1}^{N} a_{il} x_i^g + \sum_{j=1}^{Q} a_{jl} x_j^s = b_l \qquad (l = 1,2, \ldots m) \tag{4}$$

where m is the number of elements in the mixture.

Method of Solution

At a given temperature and total pressure, the free energies of all possible mixtures of a given set of species form a surface in the hyperspace the coordinates of which are the species. However, in practical cases some areas on this surface are not accessible because the mole fraction that a particular species may take on is constrained by the total amount of each element available for the mixture and by the fact that negative mole fractions are not realizable. Thus the objective is to find that location on the accessible areas where the free energy is a minimum. The set of coordinates, or mole fractions, that define the minimum point constitute the desired equilibrium composition.

The method used here to find the point of minimum free energy is the method of steepest descent (ref. 6) applied to a quadratic representation of the free-energy surface.

The solution is initiated by selecting an arbitrary set of mole fractions from which a point on the free-energy surface is computed. An n-dimensional parabola (where n equals the number of species) is fitted to the surface at the point corresponding to the initial selection of mole fractions and in the direction of steepest descent. The minimum of this parabola is obtained by using Lagrangian multipliers to deal with the mass balance constraints. The coordinates of the minimum, or the point on the parabola closest to the minimum but yielding a set of positive mole fractions, provides a new set of mole fractions from which a new point on the energy surface is calculated. A parabola is generated at the new point and the procedure is repeated until the change in the set of mole fractions is less than a prescribed value.

If the constraints are not preventing the minimum of the parabola from being reached, this procedure will quickly converge to the neighborhood of the minimum free-energy point. In this paper, convergence was judged to be sufficient if the sum of the absolute values of the changes in mole fractions from one iteration to another was less than a very small number; for example, 10^{-5}.

If the restriction to a positive set of mole numbers is causing the mole fractions to change very slowly, the solution can be expedited by removing the species that creates the constraint and continuing the calculations on a new free energy surface. When the minimum free energy point is reached, the species that was eliminated may again be included to determine whether it exists in the equilibrium mixture.

The question of uniqueness of solution has been considered in reference 7 where it is proven that all minima of the Gibbs free-energy function of multiphase mixtures are global minima.

The inherent advantage of this method for determining equilibrium compositions is that no prior knowledge of the reactions that take place in a mixture is required. As a matter of fact, experience has shown that a poor initial selection of the mole fractions does not change the final solution nor add greatly to the solution time. The method also affords the flexibility of changing the initial set of species as desired.

Computer Program

The computer program for the previously described solution was written in Fortran 6000 language and a listing of the program is included as appendix A. This listing is complete and contains all the subroutines necessary to run the program. Numerous comment cards are included in the listing to identify the various sections of the program. As compiled, the program can accept 90 gaseous species and 10 condensed species at one time.

These species may be composed of up to 10 elements. However, the dimension statements could be changed so that a larger number of species and elements could be accommodated.

The inputs required by the program are listed in appendix B. The program is, in general, self-contained. Once the thermodynamic data are obtained for all species, the only information required is related to the temperature and pressure involved and an elemental analysis of the mixture. In addition, the desired accuracy of iteration β must be specified. The iteration cycle is terminated when the sum of the absolute value of the changes in mole fraction is less than β from one iteration cycle to the next. A typical value used for β is 10^{-5}.

The equilibrium mole fraction and weight fraction of each species are printed as output. The standard output also includes the enthalpy of the mixture as inserted initially and at equilibrium conditions. The sum of the chemical energy and enthalpy is also calculated along with the molecular weight of the mixture. The enthalpy calculated is the sum of the partial enthalpies of the gaseous components. Thus,

$$H = \sum_{k=1}^{N} n_k H_k \tag{5}$$

Appendix C lists the species commonly found in ablation materials and sources of data on these materials. At present, there are 53 species for which reliable data have been found. Any of these species or new species can be added to a case merely by adding data cards to the input deck. The program will then include this species in the calculations and identify it whenever it appears.

The program consists of a framework of programed logic that has been built around the basic method of solution described in the previous section. This logical sequence makes possible the inclusion of all possible species (condensed and gaseous) in the initial mixture. The program automatically eliminates those species that exist in negligible quantities or attempt to take on negative mole fractions. The elimination process assures rapid convergence by removing the artificial constraint placed on the system initially by including those species in the mixture. Once the equilibrium condition is determined with the remaining species, the eliminated gaseous species are put back in the mixture. Thus, no species actually present in the mixture can be eliminated.

The efficiency of the elimination process is typified by a calculation that required 6000 iterations before elimination, but only 10 iterations after the elimination process was adopted. With the modifications, as included, the program is capable of reasonable computing speed. The chief advantage of the program is its flexibility and the ease with which new species can be added. The speed of solution is more a function of the number of elements and condensed species involved than the number of gaseous species. For example, many ablation materials are limited to the four elements: carbon, hydrogen, oxygen, and nitrogen.

Since the number of equations equals the number of elements plus the number of condensed species plus one, there are only six simultaneous equations to solve at each iteration, and a large number of possible species may be included without undue expenditure of computing time.

Routine calculations of the type reported herein with 4 elements, 1 condensed specie, and approximately 40 gaseous species required about 1 second of computing time per temperature. Simpler systems, such as the check cases to be discussed later, require 300 to 400 milliseconds of computer time to complete a calculation. Since there is no great computing time penalty for including a large number of species, everything for which data are available can be included initially. After some experience is gained, those species that are never significant can be removed from subsequent calculations simply by removing data cards from the input deck.

Program Check Cases

In order to illustrate the accuracy of the computer program, results are compared with simple mixtures for which exact equilibrium compositions can be determined or experimental data exist. First, the decomposition of methane into solid carbon and hydrogen is considered. The equilibrium composition of these three species was calculated at 1273^{o} K with a total pressure of 7.1 atmospheres by using the computer program. The results indicate the following set of mole numbers: 0.1095 CH_4, 1.7810 H_2, and 0.8905 C(s) where (s) denotes the solid state.

The exact equilibrium composition may be computed by using the equilibrium constant K_p. Consider the reaction

$$CH_4 \rightarrow C(s) + 2H_2$$

for which by definition

$$K_p = \frac{{p_{H_2}}^2}{p_{CH_4}} \tag{6}$$

For ideal gases, the mole fraction n_k equals the partial pressure fraction p_k/p_t; therefore,

$$K_p = \frac{{n_{H_2}}^2 p_t}{n_{CH_4}} \tag{7}$$

The mixture of species that results from the dissociation of methane can be symbolized as follows:

$$CH_4 \rightarrow \alpha C(s) + 2\alpha H_2 + (1 - \alpha)CH_4 \tag{8}$$

From this relation, it can be seen that there are $1 + \alpha$ moles of gas species and that

$$\left.\begin{aligned} n_{H_2} &= \frac{2\alpha}{1 + \alpha} \\ n_{CH_4} &= \frac{1 - \alpha}{1 + \alpha} \end{aligned}\right\} \tag{9}$$

If equations (9) are substituted into equation (7) and solved for α, the result is

$$\alpha = \left(\frac{K_p}{4p_t + K_p}\right)^{1/2} \tag{10}$$

The equilibrium constant is related to the free energy as follows:

$$\log_e K_p = -\frac{\Delta F^0}{RT} \tag{11}$$

where

$$\Delta F^0 = \sum F^0_{products} - \sum F^0_{reactants}$$

and the superscript zero designates a standard pressure of 1 atmosphere. By using the free energies that were calculated in the computer program for the species

$$\log_e K_p = 4.6893$$

$$K_p = 108.7772$$

and with $p_t = 7.1$ atmospheres, from equation (10), $\alpha = 0.8905$. Thus, by referring to equations (9), the mole numbers are 0.1095 CH_4, 1.7810 H_2, and 0.8905 C(s) and compare exactly with those determined from the computer program. This agreement indicates that the program is accurate.

The second system considered was the dissociation of ammonia into nitrogen and hydrogen:

$$NH_3 \rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2$$

for which experimentally determined equilibrium compositions are given in reference 8. Calculated and experimental results at $T = 623^{\circ}$ K and $p_t = 10$ atmospheres are as follows:

Species	Mole fraction determined by –		
	Computer program	Equilibrium constant	Experiment
NH_3	0.0772	0.0772	0.0735
N_2	.2273	.2273	.2282
H_2	.6955	.6955	.6983

The comparison, which was made at the temperature and pressure for which the greatest difference existed between calculated and measured results, shows that the calculations do not predict the equilibrium composition within the maximum experimental error of 3 percent. (See ref. 8.) This difference apparently results from the free-energy values used in the calculations. Thus, as expected, the accuracy of the computer program is governed primarily by the free-energy input data.

EQUILIBRIUM COMPOSITIONS FOR PHENOLIC-NYLON

The equilibrium program was used to obtain the equilibrium compositions of the pyrolysis products of the low-density phenolic-nylon ablator described in reference 9. By the method of reference 10, the elemental composition of this material is by weight 69.9 percent carbon, 16.3 percent oxygen, 8.12 percent hydrogen, and 5.68 percent nitrogen. For the purpose of equilibrium calculations, this elemental composition completely specifies the material.

Pyrolysis Productions

Equilibrium compositions for the low-density phenolic-nylon ablator have been calculated for temperatures from 500° K to 3500° K when all the species shown in appendix C are considered. The results of these calculations, at each of three pressures (0.1, 1.0, and 10 atmospheres) are shown in figures 1(a), 1(b), and 1(c) when condensed carbon is included as a possible product of the thermal cracking of the pyrolysis gases. In figure 2, results are shown for a pressure of 1 atmosphere when the condensed species are not included.

A comparison of figures 1(b) and 2 shows that the inclusion of condensed carbon has a very significant effect on composition. The hydrocarbons dominate the composition at lower temperatures in the gaseous system of figure 2. However, when the solid carbon species is included, as in figure 1, these compounds do not occur until high temperatures are reached.

Above 3000° K, the compositions of figure 1 become complex because of the increasing number of carbon hydrogen and carbon nitrogen compounds. The presence of carbon hydrogen compounds at these higher temperatures indicates that hydrogen is combining with and removing condensed carbon. Thus, carbon is removed at a much greater rate than would be predicted by sublimation theory alone. Therefore, the use of sublimation data for pure carbon to predict the mass loss rates of charring ablators at higher heating rates and temperatures will result in unconservative estimates.

In the past, some investigators have attempted to compensate mathematically for the presence of condensed carbon by withholding some of the carbon from the original mixture, designating this carbon as solid or char, and proceeding with only the gas-phase reactions. Such an imposed constraint is somewhat arbitrary and can significantly affect the results. The present method eliminates the need for guessing by computing the amount of condensed carbon present at each equilibrium condition.

Char density from equilibrium calculations.- The char density is of fundamental importance in ablation calculations since the surface recession rate in an oxidizing atmosphere, with no mechanical removal, is explicitly inversely proportional to the char density at the surface. However, for quasi-steady ablation, the surface recession rate depends only on surface environmental conditions and free carbon density in the uncharred ablator, when free carbon is any carbon atoms for which no oxygen atoms exist in the ablator. The result assumes equilibrium between carbon and oxygen at the surface, but is completely independent of such factors as internal chemical reactions and char shrinkage. For this quasi-steady condition, equilibrium predicts the char density which will give the correct surface recession, at temperatures below the sublimation regime, without directly considering gas-phase reactions. Therefore, for conditions not far removed from quasi-steady conditions, the equilibrium approach is expected to provide a useful approximation, and this fact is substantiated by the experimental results of references 11 and 12.

By making use of this approximation, the equilibrium calculations such as shown in figure 1 can be used to predict char densities from the known virgin ablator densities. The equilibrium calculation procedure was used in conjunction with an ablation calculation program (ref. 13) to determine analytically the temperature distribution and char density of a tested ablator specimen. The specimen, which was made of low-density phenolic nylon (550 kg/m^3), was exposed for 100 seconds to an arc-heated airstream and experienced quasi-steady ablation. The environment of this specimen was as follows: cold wall, nonablating heating rate, 2.26 MW/m^2, enthalpy, 28 MJ/kg, and pressure, 0.03

atmosphere. The calculated equilibrium char density was about 318 kg/m^3 for all depths through the char layer, since the char density is relatively constant at 59 percent of virgin plastic density in the temperature range of this test (2200° K surface temperature).

The measured average density, for the entire thickness (6.3 mm) of char, was found to be 270 kg/m^3 by air-displacement pycnometer measurements. Pyrolysis measurements of this material with thermogravimetric techniques similar to those in reference 10 showed the residual char density to be 189 kg/m^3. The residual char density value should correspond to the frozen-flow case where there is no cracking of the pyrolysis gases and hence no deposition of carbon by the gases to increase density.

The pyrolysis gases are essentially frozen until they are heated to a certain temperature range. In this region, most of the gases react rapidly to equilibrium. If it is assumed that this region is very thin and essentially a plane, the location in the char of the instantaneous transition from the frozen state to equilibrium can be calculated so that the calculated average density would equal the measured average density. With an equilibrium char density of 318 kg/m^3 and a frozen flow char density of 189 kg/m^3, the instantaneous transition was determined to be at a location about 0.7 of the char-layer thickness from the exterior surface. The calculated temperature at this point was 1200° K; thus, the transition from frozen to equilibrium conditions likely occurs at a relatively low temperature.

The rate of surface recession is dependent on the char density at the surface. However, surface recessions are usually calculated by using an average char density rather than the surface density, and this procedure may lead to significant errors. For example, the surface recession calculated for the test case just described would be 18 percent greater if the measured average char density were used rather than the calculated equilibrium char surface density. Furthermore, the overprediction of surface recession by using average char density could be much greater than 18 percent if the thickness of char layer in which chemical equilibrium occurs is small compared with the thickness over which nonequilibrium conditions exist.

Pyrolysis gases.- The inclusion of solid carbon as a possible product in the pyrolysis gases equilibrium has a marked effect on the mean molecular weight of these gases. Figure 3 shows the mean molecular weights for pyrolysis gases in chemical equilibrium. When solid carbon is excluded as a possible product, the mean molecular weights of the gases are more than twice those in which the solid phase is considered. As expected, at higher temperatures where the solid phase cannot exist, the two mean molecular weights approach each other at a given pressure.

The aerodynamic blocking efficiency of a gas injected into the boundary layer is dependent on the mean molecular weight of the gas. For laminar flow, blocking is usually assumed to vary inversely as the 1/4 power of the molecular weight of the injected gas.

Thus, in the temperature range of interest (1000° K to 3000° K), the low molecular weight species, resulting from including solid carbon, would provide a 20-percent increase in blocking over that afforded by the high molecular weight gases that result when solid carbon is not included as a possible product.

The enthalpy of the pyrolysis gases in chemical equilibrium is shown in figure 4 as a function of temperature. The enthalpy that is plotted is the energy involved in chemical reactions plus the energy required to raise the gas temperatures. Thus, when moving from one temperature level to another, the chemical energy involved in the change in composition is taken into account. It is seen that at a pressure of 1 atmosphere the gases absorb approximately 50 percent more energy because of the chemical reactions that occur when solid or condensed carbon is included as a possible product. In addition, this energy is absorbed at a lower temperature level than when solid carbon is excluded and, consequently, could contribute an important increase in efficiency where surface temperatures were below 1500° K.

The slope of the enthalpy curve is then an effective specific heat for the transpiring gases:

$$\bar{c}_p = \frac{\partial H}{\partial T} \tag{12}$$

The effective specific heat for the pyrolysis products of phenolic nylon is shown in figure 5. There are three peaks on each curve. The one at the lower temperature is a result of the decomposition of methane whereas the peaks above 3000° K are a result of the formation of carbon hydrogen and carbon nitrogen compounds. The values of $\bar{c}_p$ in figure 5 can be used in an approximate numerical analysis to account for the energy involved in the changes in composition as well as the energy involved when the pyrolysis gases move from one temperature level to the next.

There is considerable chemical energy which could have a marked effect on the temperature distribution through the char layer and on overall material performance. Calculations to determine material performance by using a transient analysis similar to the one described in reference 13 have shown that heat-shield weight requirements can be affected by as much as 30 percent by this chemical energy (ref. 14).

Simplified Equilibrium Determination

An inspection of figure 1 shows that in the temperature range of 1000° K to 2700° K, there are four main species (nitrogen, carbon monoxide, solid carbon, and hydrogen) and that the proportions of these species are essentially constant over that temperature range. These results and other calculations for different proportions of the four elements carbon, oxygen, nitrogen, and hydrogen indicated that within the temperature range of interest, the equilibrium composition is simply

(1) N_2 – all the nitrogen in the four-element system

(2) CO – in sufficient quantities to account for all oxygen in the system

(3) C_{solid} – all carbon in the virgin plastic not appearing in carbon monoxide

(4) H_2 – all the hydrogen in the four-element system

With one exception, this simple composition can be assumed to apply to all materials which are composed of the four-element system. The exception occurs when the number of moles of oxygen in the material exceeds the total number of moles of carbon in the material. However, this situation is unlikely to exist in a practical ablation material because of the undesirable effect of oxygen on ablative performance.

CONCLUDING REMARKS

A computer program based on minimization of the Gibbs free energy has been developed for computing multiphase equilibrium compositions of arbitrary mixtures of chemical compounds. The program has been shown to be accurate by the comparison of computer solutions to exact solutions for simple reacting systems. Furthermore, a computer programing logic has been used which results in reasonable computing speed.

The chemical equilibrium compositions of low-density phenolic-nylon ablative material have been computed for a wide range of temperature and pressure with the inclusion of solid carbon as a possible reaction product. Although not usually considered in determining ablation pyrolysis products, the formation of solid carbon was found to have a significant effect on many aspects of ablation analysis. The principal effects are:

(1) The formation of carbon-hydrogen and carbon-nitrogen compounds is delayed to higher temperatures.

(2) The average molecular weight of the pyrolysis gases was much less when solid carbon is a reaction product. The result is that the blocking of convective heating and diffusion of oxygen to the heated surface is increased by as much as 20 percent for surface temperatures up to 3000° K.

(3) The energy absorption by the pyrolysis gases due to chemical reactions is greater when solid carbon is included. Up to 1500° K, the energy absorption is increased by about 50 percent.

(4) Subject to certain conditions, the char surface density, which is important in recession calculations, can be computed on a rational basis with the developed program.

The results also indicate that a simple equilibrium composition model (including four species) can be defined for the phenolic-nylon ablator and can be used in ablation analysis without the need of further equilibrium calculations. It is expected that similar equilibrium composition models could be defined for other ablative materials.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., June 18, 1969.

APPENDIX A

CHEMICAL EQUILIBRIUM COMPUTER PROGRAM

The program listing is as follows:

```
      PROGRAM  CHEQ    (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C   CHEMICAL EQUILIBRIUM OF MULTIPHASE SYSTEMS BASED ON THE PRINCIPLE
C   OF MINIMIZATION OF THE FREE ENERGY OF THE MIXTURE
C
      EXTERNAL FOFX,AFOFX
      DIMENSION YG(90),YC(10),X(100),Y(100),SYM(100),DELT(100),ENT(100),
     1 CENT(100),DFHT(100),F0(100),BB(10),CP2(100),F(100),C(100),
     2 ALPHA(100),XLAM(100),FSUM(100),YSUM(100),PMW(100),WTPERC(100),
     3 BSUM(21,1),IPIVOT(21),INDEX(21,2),COEF(21,21),R(10,10),PI(21)
      COMMON/BLK1/I,AI(100),BI(100),CI(100),DI(100),EI(100)
      COMMON/BLK2/CP1(100),HINT(100),H0(100),FHTO(100),FORT(100),
     1 XMW(100),SYMB(100),PERC(100),AA(100,10),MM, DLT(100)
C
C   READ INPUT DATA - NOTE. READ ALL INPUTS FOR ALL GASEOUS SPECIES
C     FOLLOWED BY INPUTS FOR CONDENSED SPECIES. PROGRAM WILL ACCOMMODATE
C     90 GASEOUS SPECIES AND 10 CONDENSED SPECIES.  THE NUMBER OF
C     ELEMENTS CANNOT EXCEED 10.
C
    5 READ(5,2)XT,TFIN,TINC,TZERO,CRIT
      IF(EOF,5)1020,1030
 1030 READ(5,6)NG,NC,MM,NFREQ,IDEBUG
      NN=NC+NG
      DO 31 I=1,NN
      READ(5,8)HINT(I),H0(I),FHTO(I),XMW(I), Y(I),SYMB(I)
      READ(5,2)AI(I),BI(I),CI(I),DI(I),EI(I)
   31 READ(5,2)(AA(I,J),J=1,MM)
      READ(5,2)RR,P
    2 FORMAT(6E12.4)
    6 FORMAT(10I6)
    8 FORMAT(5F12.4,A6)
      MAXNT=50
      T=XT
      MC=NC
      MG=NG
      KX=0
      XBETA=CRIT
  500 NTEST=NFREQ
      NT=1
      DO 33 I=1,MG
      SYM(I)=SYMB(I)
   33 YG(I)=Y(I)
```

```
      MN=MG+1
      MMN=MN
      NNN=NN
      IF(MC.EQ.0)GO TO 37
      DO 34 I=MN,NN
      SYM(I)=SYMB(I)
   34 YC(I)=Y(I)
C
C   FREE ENERGY FUNCTION
C
   37 DO 41 I=1,NN
      CALL GAUSS(TZERO,T,50,SUM,FOFX)
      CP1(I)=SUM*RR
      CALL GAUSS(TZERO,T,50,ANS,AFOFX)
      CP2(I)=ANS*RR
      DFHT(I)=((1./T)-(1./TZERO))*HINT(I)+(1./T)*CP1(I)-CP2(I)
      FO(I)=FHT0(I)+DFHT(I)+HO(I)/T
   41 FORT(I)=FO(I)/(RR)
C
C   ENTHALPY OF INITIAL MIXTURE
C
      ENTMIX=0.
      CMIX=0.
      SUMYG=0.
      DO 35 I=1,MG
   35 SUMYG=SUMYG+YG(I)
      DO 36 I=1,MG
      ENT(I)=HINT(I)+CP1(I)
      CENT(I)=ENT(I)+HO(I)
      ENTMIX=ENTMIX+ENT(I)*YG(I)
   36 CMIX=CMIX+CENT(I)*YG(I)
      ENTMIX=ENTMIX/SUMYG
      CMIX=CMIX/SUMYG
C
C   WRITE OUTPUT FOR INITIAL MIXTURE
C
      WRITE(6,204)P,T
  204 FORMAT(1H1,9HPRESSURE=E13.5,5X,5HTEMP=E13.5)
      WRITE(6,4)
    4 FORMAT(///6X,1HI,19X,5HFO/RT,13X,12HINITIAL Y(I)/ )
      DO 42 I=1,NN
   42 WRITE(6,14)I,SYMB(I) ,FORT(I), Y(I)
   14 FORMAT(1X,I6,3X,A6,2E20.8)
```

APPENDIX A

```
      WRITE(6,18)ENTMIX
      WRITE(6,21)CMIX
   18 FORMAT(///34H SENSIBLE ENTHALPY OF GAS MIXTURE=E16.8)
   21 FORMAT(/1X,36HCHEM + SENS ENTHALPY OF GAS MIXTURE=E16.8)
C
C    MASS BALANCE CONSTRAINT
C
 1000 DO 320 J=1,MM
      BB(J)=0.0
      DO 320 I=1,MG
  320 BB(J)=BB(J)+AA(I,J)*Y(I)
      IF(MC.EQ.0)GO TO 300
      DO 321 J=1,MM
      L=NG
      DO 321 I=MN,NN
      L=L+1
  321 BB(J)=BB(J)+AA(L,J)*Y(I)
  300 YBAR=0.
      DO 50 I=1,MG
   50 YBAR=YBAR+YG(I)
C
C    SET UP AND SOLVE MATRIX
C
      DO 10 I=1,MG
      C(I)=FORT(I)+ALOG(P)
      FAC=YG(I)/YBAR
      IF(FAC.LT.1.E-38)FAC=1.E-38
   10 F(I)=YG(I)*(C(I)+ALOG(FAC))
      IF(MC.EQ.0)GO TO 13
      J=NG
      DO 11 I=MN,NN
      J=J+1
      C(I)=FORT(J)
   11 F(I)=Y (I)*C(I)
   13 FESUM=0.
      DO 43 I=1,NN
   43 FESUM=FESUM+F(I)
      IF(NT.NE.1)GO TO 51
      WRITE(6,61)FESUM
   61 FORMAT(1H 27HFREE ENERGY SUM OF MIXTURE=E16.8)
   51 DO 30 J=1,MM
      DO 30 K=1,MM
      ASUM=0.0
```

APPENDIX A

```
      DO 20 I=1,MG
      SUM=AA(I,J)*AA(I,K)*YG(I)
   20 ASUM=ASUM+SUM
   30 R(J,K)=ASUM
      DO 330 J=1,MM
      ALPHA(J)=0.
      DO 330 I=1,MG
  330 ALPHA(J)=ALPHA(J)+AA(I,J)*YG(I)
      KM=MM+MC
      NM=MM+MC+1
      MMM=MM+1
      DO 360 J=MMM,NM
  360 ALPHA(J)=0.
      DO 401 I=1,NM
      DO 401 J=1,1
  401 COEF(I,J)=ALPHA(I)
      MMC=MC+1
      IF(MC.EQ.0)GO TO 406
      K=NG
      DO 402 J=2,MMC
      K=K+1
      DO 402 I=1,MM
  402 COEF(I,J)=AA(K,I)
  406 MCC=MMC+1
      DO 403 I=1,MM
      DO 403 J=MCC,NM
      K=J-MMC
  403 COEF(I,J)=R(I,K)
      DO 407 I=MMM,NM
      DO 407 J=2,MMC
  407 COEF(I,J)=0.
      IF(MC.EQ.0)GO TO 408
      L=NG
      DO 404 I=MMM,KM
      K=0
      L=L+1
      DO 404 J=MCC,NM
      K=K+1
  404 COEF(I,J)=AA(L,K)
  408  DO 405 I=NM,NM
      K=0
      DO 405 J=MCC,NM
      K=K+1
```

```
  405 COEF(I,J)=ALPHA(K)
      DO 361 K=1,1
      DO 361 J=1,MM
      BSUM(J,K)=0.
      DO 362 I=1,MG
  362 BSUM(J,K)=BSUM(J,K)+AA(I,J)*F(I)
  361 BSUM(J,K)=BSUM(J,K)+BB(J)
      IF(MC.EQ.0)GO TO 409
      DO 363 K=1,1
      L=MG
      DO 363 J=MMM,KM
      L=L+1
  363 BSUM(J,K)=C(L)
  409 DO 364 K=1,1
      DO 364 J=NM,NM
      BSUM(J,K)=0.
      DO 364 I=1,MG
  364 BSUM(J,K)=BSUM(J,K)+F(I)
      CALL SIMEQ(COEF,NM,BSUM,1,DETERM,IPIVOT,21,ISCALE)
      XYBAR=BSUM(1,1)
      IF(MC.EQ.0)GO TO 103
C
C     NEW X-S FOR CONDENSED SPECIES
C
      J=MG
      DO 101 I=2,MMC
      J=J+1
  101 X (J)=BSUM(I,1)
C
C     NEW X-S FOR GASEOUS SPECIES
C
  103 J=0
      DO 102 I=MCC,NM
      J=J+1
  102 PI(J)=BSUM(I,1)
      DO 60 I=1,MG
   60 FSUM(I)=-F(I)+YG(I)*XYBAR
      DO 110 I=1,MG
      PSUM=0.
      DO 120 J=1,MM
  120 PSUM=PSUM+PI(J)*AA(I,J)
      YSUM(I)=PSUM*YG(I)
  110 X (I)=FSUM(I)+YSUM(I)
```

APPENDIX A

```
C
C   LAMBDA AND DIRECTIONAL DERIVATIVE
C
      XLAMBD =1.
  310 DO 86 I=1,NN
      DELT(I)=X(I)-Y(I)
      IF(IDEBUG.NE.0)PRINT 1005,DELT(I)
 1005 FORMAT(1X,E15.5)
      IF(DELT(I).GE.0.)GO TO 86
      XLAM(I)=Y(I)/(-DELT(I))
      XLAMBD=AMIN1(XLAMBD,XLAM(I))
   86 CONTINUE
      DEBAR=0.
      DO 87 I=1,MG
   87 DEBAR=DEBAR+DELT(I)
   93 DFDL=0.
      DO 88 I=1,MG
   96 FAC=(YG(I)+XLAMBD*DELT(I))/(YBAR+XLAMBD*DEBAR)
      IF(FAC.GT.0.)GO TO 82
      XLAMBD=.5*XLAMBD
      GO TO 96
   82 DFDL=DFDL+DELT(I)*(C(I)+ALOG((YG(I)+XLAMBD*DELT(I))/
     1 (YBAR+XLAMBD*DEBAR)))
   88 CONTINUE
      IF(MC.EQ.0)GO TO 84
      DO 83 I=MN,NN
   83 DFDL=DFDL+C(I)*DELT(I)
   84 IF(DFDL.LT.0.)GO TO 89
      IF(XLAMBD.GT.0.E-38)GO TO 91
      KX=KX+1
      GO TO 94
   91 XLAMBD=.5*XLAMBD
      GO TO 93
   89 IF(IDEBUG.NE.0)PRINT 1021,XLAMBD
 1021 FORMAT(//1X,7HLAMBDA=E15.5//)
C
C   NEW Y-S FOR GASEOUS AND CONDENSED SPECIES
C
   94 DO 76 I=1,NN
      Y(I) =Y(I)+XLAMBD*DELT(I)
      IF(IDEBUG.NE.0)PRINT 1031,SYM(I),Y(I)
 1031 FORMAT(1X,A6,E15.5)
   76 CONTINUE
```

```
      DO 77 I=1,MG
   77 YG(I)=Y(I)
      IF(MC.EQ.0)GO TO 78
      J=NG
      DO 74 I=MN,NN
      J=J+1
   74 YC(J)=Y(I)
C
C    MOLE PERCENT
C
   78 SUMY=0.
      DO 370 I=1,NN
  370 SUMY=SUMY+Y(I)
      DO 340 I=1,NN
  340 PERC(I)=(Y(I)/SUMY)*100.
      IF(MC.EQ.0)GO TO 351
      J=NG
      DO 350 I=MN,NN
      J=J+1
  350 PERC(J)=PERC(I)
C
C    TEST FOR CONVERGENCE
C
  351 BETA=0.
      DO 85 I=1,NN
   85 BETA=BETA+ABS(DELT(I))
      IF(BETA.LT.XBETA)GO TO 800
      IF(KX.GT.0)GO TO 560
      IF(NT.EQ.NTEST)GO TO 570
      GO TO 560
C
C    TEST FOR SIGNIFICANCE OF SPECIES
C
  570 NTEST=NTEST+NFREQ
  590 IF(MG.EQ.0)GO TO 48
      CALL TEST(YG,1,MG,NMG)
   48 IF(MC.EQ.0)GO TO 47
      CALL TEST(YC,MMN,NNN,MNN)
      MC=MNN-NG
   47 MG=NMG
      MN=MG+1
      NN=MC+MG
      NNN=NG+MC
```

```
      DO 561 I=1,MG
      SYM(I)=SYMB(I)
  561 Y(I)=YG(I)
      IF(MC.EQ.0)GO TO 560
      J=NG
      DO 562 I=MN,NN
      J=J+1
      SYM(I)=SYMB(J)
  562 Y(I)=YC(J)
  560 IF(NT.GE.MAXNT)GO TO 600
      NT=NT+1
      IF(KX.GT.0)GO TO 300
      GO TO 1000
  600 XBETA=XBETA+CRIT
      MAXNT=MAXNT+50
      NT=NT+1
      GO TO 1000
  800 NN=MC+NG
      KX=KX+1
      MG=NG
      MN=MG+1
      DO 563 I=1,MG
      SYM(I)=SYMB(I)
  563 Y(I)=YG(I)
      IF(MC.EQ.0)GO TO 567
      DO 564 I=MN,NN
      SYM(I)=SYMB(I)
  564 Y(I)=YC(I)
  567 IF(KX.LT.2)NT=NT+1
      IF(KX.LT.2)GO TO 1000
C
C   WEIGHT PERCENT
C
  801 TPMW=0.
      DO 80 I=1,NN
      PMW(I)=PERC(I)*XMW(I)
   80 TPMW=TPMW+PMW(I)
      DO 70 I=1,NN
   70 WTPERC(I)=(PMW(I)/TPMW)*100.
      KKLB=NN+1
C
C   ENTHALPY OF EQUILIBRIUM MIXTURE
C
```

APPENDIX A

```
      CMIX=0.
      ENTMIX=0.
      XSUMY=0.
      DO 580 I=1,MG
  580 XSUMY=XSUMY+YG(I)
      DO 73 I=1,NN
      ENT(I)=HINT(I)+CP1(I)
   73 CENT(I)=ENT(I)+HO(I)
      DO 75 I=1,MG
      ENTMIX=ENTMIX+ENT(I)*YG(I)
   75 CMIX=CMIX+CENT(I)*YG(I)
      ENTMIX=ENTMIX/XSUMY
      CMIX=CMIX/XSUMY
C
C    MOLECULAR WEIGHT OF EQUILIBRIUM MIXTURE
C
      XMWMIX=0.
      DO 81 I=1,MG
   81 XMWMIX=XMWMIX+XMW(I)*YG(I)
      XMWMIX=XMWMIX/XSUMY
C
C    WRITE OUTPUT FOR EQUILIBRIUM MIXTURE
C
      WRITE(6,16)NT
   16 FORMAT( /1X,27HNT=NO. ITERATIONS REQUIRED=I5/ )
      WRITE(6,201)XBETA
  201 FORMAT( /1X,5HBETA=E12.4/)
      WRITE(6,29)
   29 FORMAT(//47X,4HMOLE,17X,6HWEIGHT)
      WRITE(6,32)
   32 FORMAT(6X,1HI,21X,4HY(I),14X,7HPERCENT,14X,7HPERCENT/)
      DO 44 I=1,NN
   44 WRITE(6,19)I,SYMB(I),Y(I),PERC(I),WTPERC(I)
   19 FORMAT(1X,I6,3X,A6,3E20.8)
      WRITE(6,12)
   12 FORMAT(///12X,17HSENSIBLE ENTHALPY,3X,20HCHEM + SENS ENTHALPY/)
      DO 79 I=1,NN
   79 WRITE(6,24)SYMB(I),ENT(I),CENT(I)
   24 FORMAT(1X,A6,2E20.8)
      WRITE(6,18)ENTMIX
      WRITE(6,21)CMIX
      WRITE(6,17)XMWMIX
   17 FORMAT(/1X,32HMOLECULAR WEIGHT OF GAS MIXTURE=E16.8//)
```

APPENDIX A

```
      WRITE(6,61)FESUM
C
C    INCREMENT TEMPERATURE AND START NEW CASE
C
      IF(T.LE.TFIN)GO TO 5
      T=T-TINC
      XBETA=CRIT
      KX=0
      MC=NC
      NN=NC+NG
      IF(MC.EQ.0)GO TO 500
      DO 52 I=KKLB,NN
   52 YC(I)=1.E-03
      DO 53 I=KKLB,NN
   53 Y(I)=YC(I)
      GO TO 500
 1020 STOP
      END
```

```
      FUNCTION FOFX(TEMP)
      COMMON/BLK1/I,AI(100),BI(100),CI(100),DI(100),EI(100)
      FOFX=AI(I)+BI(I)*TEMP+CI(I)*TEMP**2+DI(I)*TEMP**3+EI(I)*TEMP**4
      RETURN
      END
```

```
      FUNCTION AFOFX(TEMP)
      COMMON/BLK1/I,AI(100),BI(100),CI(100),DI(100),EI(100)
      AFOFX=(AI(I)+BI(I)*TEMP+CI(I)*TEMP**2+DI(I)*TEMP**3+EI(I)*TEMP**4)
     1/TEMP
      RETURN
      END
```

APPENDIX A

```
      SUBROUTINE TEST(VAR,IN,N,M)
      COMMON/BLK1/I,AI(100),BI(100),CI(100),DI(100),EI(100)
      COMMON/BLK2/CP1(100),HINT(100),HO(100),FHTO(100),FORT(100),
     1 XMW(100),SYMB(100),PERC(100),AA(100,10),MM,DELT(100)
      DIMENSION VAR(100),YX(100),XY(100),XAI(100),XBI(100),XCI(100),
     1 XDI(100),XEI(100),XCP1(100),XHINT(100),XHO(100),XFHTO(100),
     2 XFORT(100),XXMw(100),XSYMB(100),XPERC(100),XAA(100,10)
      CORR=1.E-50
      DO 531 I=IN,N
      IF(VAR(I).NE.0.)GO TO 531
      VAR(I)=CORR
      CORR=CORR+1.E-50
  531 CONTINUE
      DO 540 J=IN,N
      YMAX=0.
      DO 520 L=IN,N
  520 YMAX=AMAX1(YMAX,VAR(L))
      DO 530 K=IN,N
      YX(K)=VAR(K)/YMAX
      IF(ABS(YX(K)-1.).GT.1.E-7)GO TO 530
      VAR(K)=0.
      XY(J)=YMAX
      XAI(J)=AI(K)
      XBI(J)=BI(K)
      XCI(J)=CI(K)
      XDI(J)=DI(K)
      XEI(J)=EI(K)
      XCP1(J)=CP1(K)
      XHINT(J)=HINT(K)
      XHO(J)=HO(K)
      XFHTO(J)=FHTO(K)
      XFORT(J)=FORT(K)
      XXMW(J)=XMw(K)
      XSYMB(J)=SYMB(K)
      XPERC(J)=PERC(K)
      XDELT(J)=DELT(K)
      DO 532 I=1,MM
  532 XAA(J,I)=AA(K,I)
      GO TO 540
  530 CONTINUE
  540 CONTINUE
      DO 510 I=IN,N
      AI(I)=XAI(I)
```

APPENDIX A

```
      DELT(I)=XDELT(I)
      BI(I)=XBI(I)
      CI(I)=XCI(I)
      DI(I)=XDI(I)
      EI(I)=XEI(I)
      SYMB(I)=XSYMB(I)
      FORT(I)=XFORT(I)
      CP1(I)=XCP1(I)
      HINT(I)=XHINT(I)
      HO(I)=XHO(I)
      FHTO(I)=XFHTO(I)
      XMW(I)=XXMW(I)
      PERC(I)=XPERC(I)
      DO 590 J=1,MM
  590 AA(I,J)=XAA(I,J)
  510 VAR(I)=XY(I)
      M=N
      DO 550 I=IN,N
      IF(PERC(I).GT.1.E-5.OR.DELT(I).GT.0.)GO TO 550
      M=M-1
  550 CONTINUE
      RETURN
      END



      SUBROUTINE GAUSS (A,B,N,SUM,FOFX)
      DIMENSION  U(5),R(5)
      U(1)=.425562830509184
      U(2)=.283302302985376
      U(3)=.160295215550488
      U(4)=.067460316655508
      U(5)=.013046735741414
      R(1)=.147762112357376
      R(2)=.134633359654998
      R(3)=.109543181257991
      R(4)=.074725674575290
      R(5)=.033335672154344
      SUM=0.0
      IF(A.EQ.B) RETURN
      FINE=N
      DELTA=FINE/(B-A)
      DO 3 K=1,N
      XI=K-1
      FINE=A+XI/DELTA
      DO 2 II= 1,5
      UU=U(II)/DELTA+FINE
    2    SUM=R(II)*FOFX(UU)+SUM
      DO 3 L=1,5
      UU=(1.0-U(L))/DELTA+FINE
    3 SUM=R(L)*FOFX(UU)+SUM
      SUM=SUM/DELTA
      RETURN
      END
```

APPENDIX A

```
C     SOLUTION OF SIMULTANEOUS LINEAR EQUATIONS
********* DOCUMENT DATE 08-01-68   SUBROUTINE REVISED 08-01-68 *******
      SUBROUTINE SIMEQ(A,N,B,M,DETERM,IPIVOT,NMAX,ISCALE)
C
      DIMENSION IPIVOT(N),A(NMAX,N),B(NMAX,M)
      EQUIVALENCE (IROW,JROW),(ICOLUM,JCOLUM),(AMAX,T,SWAP)
C
C     INITIALIZATION
C
    5 ISCALE=0
    6 R1=10.0**100
    7 R2=1.0/R1
   10 DETERM=1.0
   15 DO 20 J=1,N
   20 IPIVOT(J)=0
   30 DO 550 I=1,N
C
C     SEARCH FOR PIVOT ELEMENT
C
   40 AMAX=0.0
   45 DO 105 J=1,N
   50 IF (IPIVOT(J)-1) 60,105,60
   60 DO 100 K=1,N
   70 IF (IPIVOT(K)-1) 80,100,740
   80 IF (ABS(AMAX)-ABS(A(J,K))) 85,100,100
   85 IROW=J
   90 ICOLUM=K
   95 AMAX=A(J,K)
  100 CONTINUE
  105 CONTINUE
      IF (AMAX) 110,106,110
  106 DETERM=0.0
      ISCALE=0
      GO TO 740
  110 IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1
C
C     INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
C
  130 IF (IROW-ICOLUM) 140,260,140
  140 DETERM=-DETERM
  150 DO 200 L=1,N
  160 SWAP=A(IROW,L)
  170 A(IROW,L)=A(ICOLUM,L)
  200 A(ICOLUM,L)=SWAP
  205 IF (M) 260,260,210
  210 DO 250 L=1,M
  220 SWAP=B(IROW,L)
  230 B(IROW,L)=B(ICOLUM,L)
  250 B(ICOLUM,L)=SWAP
  260 PIVOT=A(ICOLUM,ICOLUM)
      IF (PIVOT) 1000,106,1000
```

APPENDIX A

```
C
C      SCALE THE DETERMINANT
C
 1000 PIVOTI=PIVOT
 1005 IF(ABS(DETERM)-R1)1030,1010,1010
 1010 DETERM=DETERM/R1
      ISCALE=ISCALE+1
      IF(ABS(DETERM)-R1)1060,1020,1020
 1020 DETERM=DETERM/R1
      ISCALE=ISCALE+1
      GO TO 1060
 1030 IF(ABS(DETERM)-R2)1040,1040,1060
 1040 DETERM=DETERM*R1
      ISCALE=ISCALE-1
      IF(ABS(DETERM)-R2)1050,1050,1060
 1050 DETERM=DETERM*R1
      ISCALE=ISCALE-1
 1060 IF(ABS(PIVOTI)-R1)1090,1070,1070
 1070 PIVOTI=PIVOTI/R1
      ISCALE=ISCALE+1
      IF(ABS(PIVOTI)-R1)320,1080,1080
 1080 PIVOTI=PIVOTI/R1
      ISCALE=ISCALE+1
      GO TO 320
 1090 IF(ABS(PIVOTI)-R2)2000,2000,320
 2000 PIVOTI=PIVOTI*R1
      ISCALE=ISCALE-1
      IF(ABS(PIVOTI)-R2)2010,2010,320
 2010 PIVOTI=PIVOTI*R1
      ISCALE=ISCALE-1
  320 DETERM=DETERM*PIVOTI
C
C      DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
  340 DO 351 L=1,N
  341 IF (IPIVOT(L)-1) 350,351,740
  350 A(ICOLUM,L)=A(ICOLUM,L)/PIVOT
  351 CONTINUE
  355 IF (M) 380,380,360
  360 DO 370 L=1,M
  370 B(ICOLUM,L)=B(ICOLUM,L)/PIVOT
C
C      REDUCE NON-PIVOT ROWS
C
  380 DO 550 L1=1,N
  390 IF (L1-ICOLUM) 400,550,400
  400 T=A(L1,ICOLUM)
  430 DO 451 L=1,N
  431 IF (IPIVOT(L)-1) 450,451,740
  450 A(L1,L)=A(L1,L)-A(ICOLUM,L)*T
  451 CONTINUE
  455 IF (M) 550,550,460
  460 DO 500 L=1,M
  500 B(L1,L)=B(L1,L)-B(ICOLUM,L)*T
  550 CONTINUE
  740 RETURN
      END
```

APPENDIX B

INPUTS FOR EQUILIBRIUM PROGRAM

The inputs for an equilibrium program are as follows:

XT	initial temperature at which equilibrium is to be calculated, $^{\circ}$K
TFIN	final temperature at which equilibrium is to be calculated, $^{\circ}$K (XT $\geqq$ TFIN)
TINC	temperature increment at which equilibrium is to be calculated, $^{\circ}$K
TZERO	298.2° K
CRIT	convergence criterion $\sum_{i=1}^{N} \lvert x_i - y_i \rvert < \mathrm{CRIT}$
NG	number of gaseous species
NC	number of condensed species
MM	number of elements
NFREQ	frequency of test for negligible species
IDEBUG	trigger for printing debug information; IDEBUG not equal to 0 prints this information
HINT(I)	sensible enthalpy for standard state of ith species, cal/mole
HO(I)	chemical energy at 0° K for standard state of ith species, cal/mole
FHTO(I)	sensible free energy for standard state of ith species at 298.2° K, cal/mole
XMW(I)	molecular weight of ith species
Y(I)	initial guess for the mole number of ith species
SYMB(I)	alphameric name of ith species

APPENDIX B

AI(I), BI(I), CI(I), DI(I), EI(I)	coefficients of equation for specific heat of ith species. The equation has the form: $c_p = A + BT + CT^2 + DT^3 + ET^4$
AA(I,J)	formula number indicating number of atoms of elements j in a molecule of species i
RR	universal gas constant, 1.987 cal/mole-°K
P	pressure, atmospheres

APPENDIX C

LIST OF SPECIES

A list of species for which data cards have been prepared is presented herein. Data for the following species are contained in reference 15:

Gases

C
C_2
C_3
CH
CH_2
CH_3
CH_4
C_2H_2
C_2H_4
CN
C_2N_2
CO
CO_2
H
H_2
HCN
HCO
H_2O

Gases

N
N_2
NH
NH_3
NO
NO_2
N_2O_2
O
O_2
OH
Si
Si_2
Si_3
SiH
SiH_4
SiN
SiO
SiO_2

Solids

C
Si solid
Si liquid

The species from reference 16 are:

C_2H_6
C_3H_8
CHO
CH_3OH
C_3O_2
COH_2
H_2O_2
O_3

APPENDIX C

The following species were obtained from reference 17:

C_2H

C_3H

C_4H

C_4H_2

The species from reference 18 (solids) are:

SiC

SiO_2

REFERENCES

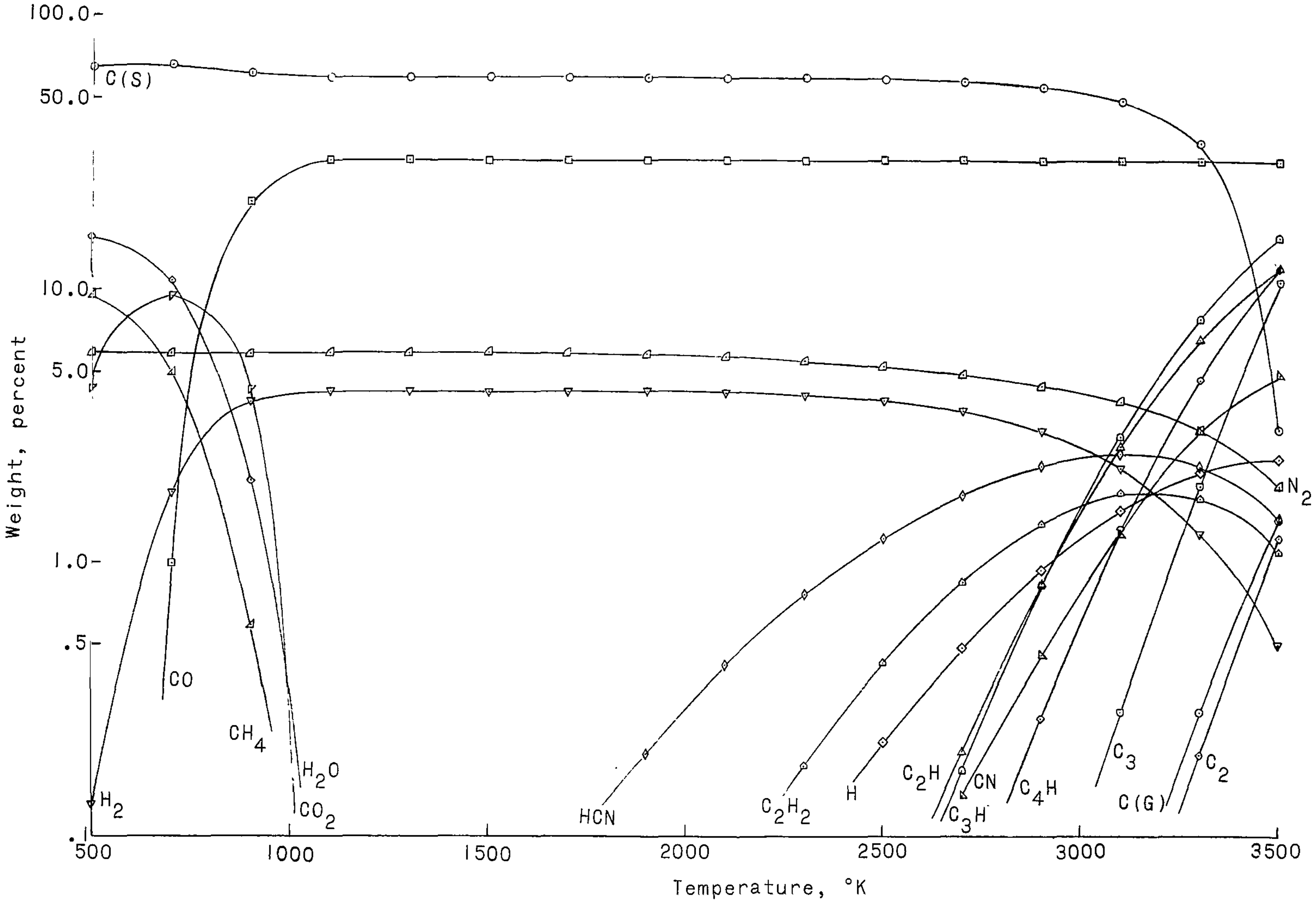
1. Kratsch, K. M.; Hearne, L. F.; and McChesney, H. R.: Thermal Performance of Heat Shield Composites during Planetary Entry. Presented at AIAA-NASA National Meeting (Palo Alto, Calif.), Sept. 30 – Oct. 1, 1963.
2. Comm. on Metric Pract.: ASTM Metric Practice Guide. NBS Handbook 102, U.S. Dep. Com., Mar. 10, 1967.
3. Daniels, Farrington; and Alberty, Robert A.: Physical Chemistry. Third ed., John Wiley & Sons, c.1966.
4. White, W. B.; Johnson, S. M.; and Dantzig, G. B.: Chemical Equilibrium in Complex Mixtures. J. Chem. Phys., vol. 28, no. 5, May 1958, pp. 751-755.
5. Bahn, Gilbert S.: Hand Calculation of Equilibrium Compositions as a Learned Habit, and Speed-Up Effected With the IBM 610 Computer. Kinetics, Equilibria and Performance of High Temperature Systems, Gilbert S. Bahn and Edward E. Zukoski, eds., Butterworths, 1960, pp. 137-140.
6. Wilde, Douglass J.: Optimum Seeking Methods. Prentice-Hall, Inc., c.1964.
7. Shapiro, N. Z.; and Shapley, L. S.: Mass Action Laws and the Gibbs Free Energy Function. J. Soc. Indust. Appl. Math., vol. 13, no. 2, June 1965, pp. 353-375.
8. Larson, A. T.; and Dodge, R. L.: The Ammonia Equilibrium. J. Am. Chem. Soc., vol. 45, 1923, pp. 2918-2930.
9. Sykes, George F.; and Nelson, James B.: Thermoanalysis of Ablation Materials. Paper presented at American Institute Chemical Engineers Meeting (Houston, Tex.), Feb. 1967.
10. Sykes, George F.: Decomposition Characteristics of a Char-Forming Phenolic Polymer Used for Ablative Composites. NASA TN D-3810, 1967.
11. Dow, Marvin B.; and Swann, Robert T.: Determination of Effects of Oxidation of Performance of Charring Ablators. NASA TR R-196, 1964.
12. Wakefield, Roy M.; Lundell, John H.; and Dickey, Robert R.: The Effects of Oxygen Depletion in Gas-Phase Chemical Reactions on the Surface Recession of Charring Ablators. AIAA Paper No. 68-302, Apr. 1968.
13. Swann, Robert T.; Pittman, Claud M.; and Smith, James C.: One-Dimensional Numerical Analysis of the Transient Response of Thermal Protection Systems. NASA TN D-2976, 1965.
14. Brewer, William D.; Stroud, C. W.; and Clark, Ronald K.: Effect of the Chemical State of Pyrolysis Gases on Heat-Shield Mass. NASA TN D-4975, 1968.

15. McBride, Bonnie J.; Heimel, Sheldon; Ehlers, Janet G.; and Gordon, Sanford: Thermodynamic Properties to 6000° K for 210 Substances Involving the First 18 Elements. NASA SP-3001, 1963.

16. Wolfson, Bernard T.; and Dunn, Robert G.: Thermodynamic Properties of Selected Species Containing Carbon, Hydrogen, Oxygen, Helium and Argon. ARL 62-390, U.S. Air Force, Aug. 1962.

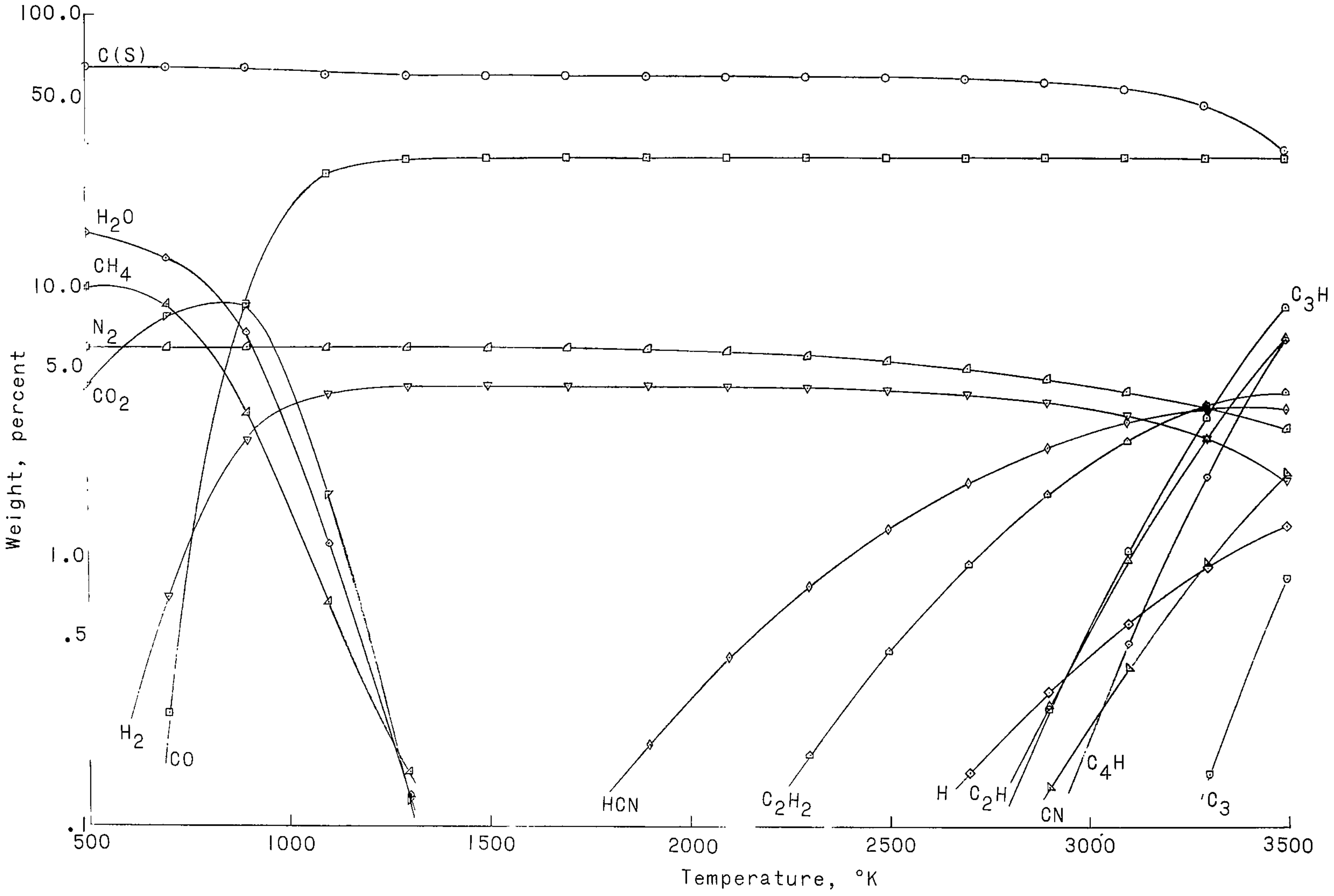
17. Bauer, S. H.; and Assistants: Kinetics of Reactions in Shock Tubes. ARL 100, U.S. Air Force, Dec. 1961.

18. Anon.: JANAF Thermochemical Tables. Quart. Suppl. no. 8 (Contract No. AF04(611)7554(1)), Thermal Res. Lab., The Dow Chem. Co., Dec. 31, 1962.



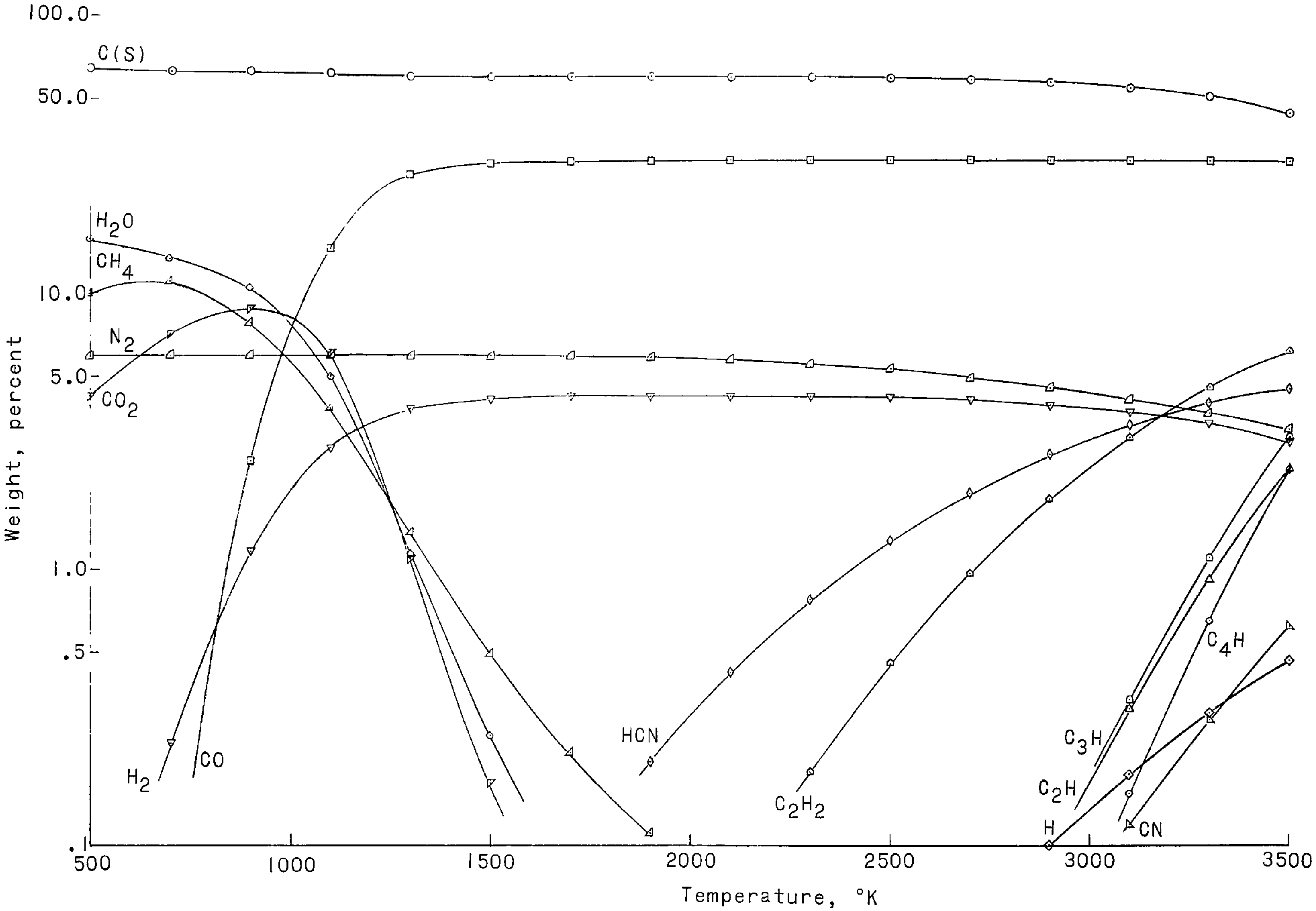
(a) Pressure, 0.1 atmosphere.

Figure 1.- Equilibrium composition of pyrolysis products of phenolic nylon. (S) and (G) after material denote solid and gaseous states, respectively.



(b) Pressure, 1.0 atmosphere.

Figure 1.- Continued.



(c) Pressure, 10.0 atmospheres.

Figure 1.- Concluded.

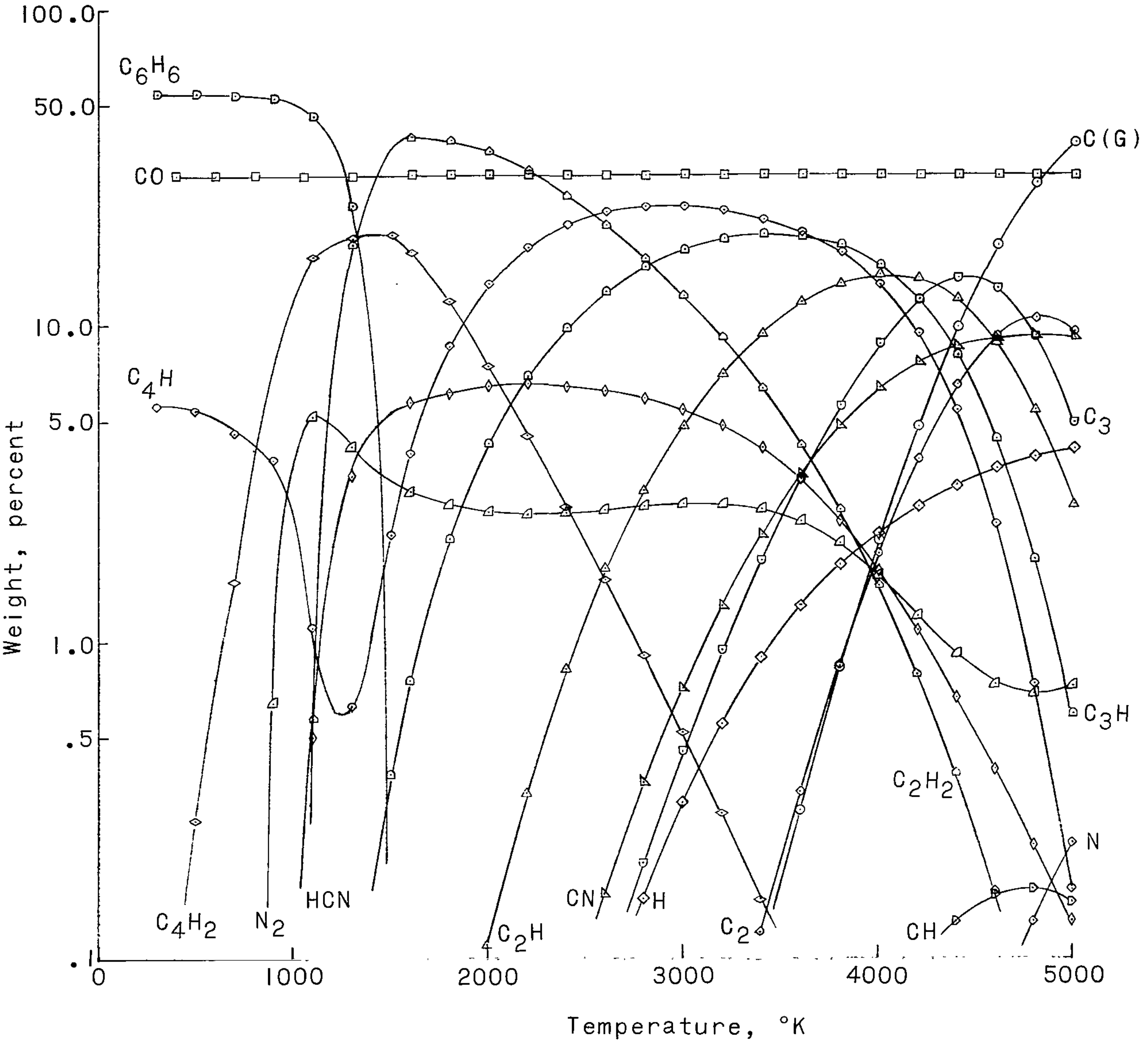


Figure 2.- Equilibrium composition when only the gaseous phase is allowed. Pressure, 1 atmosphere.

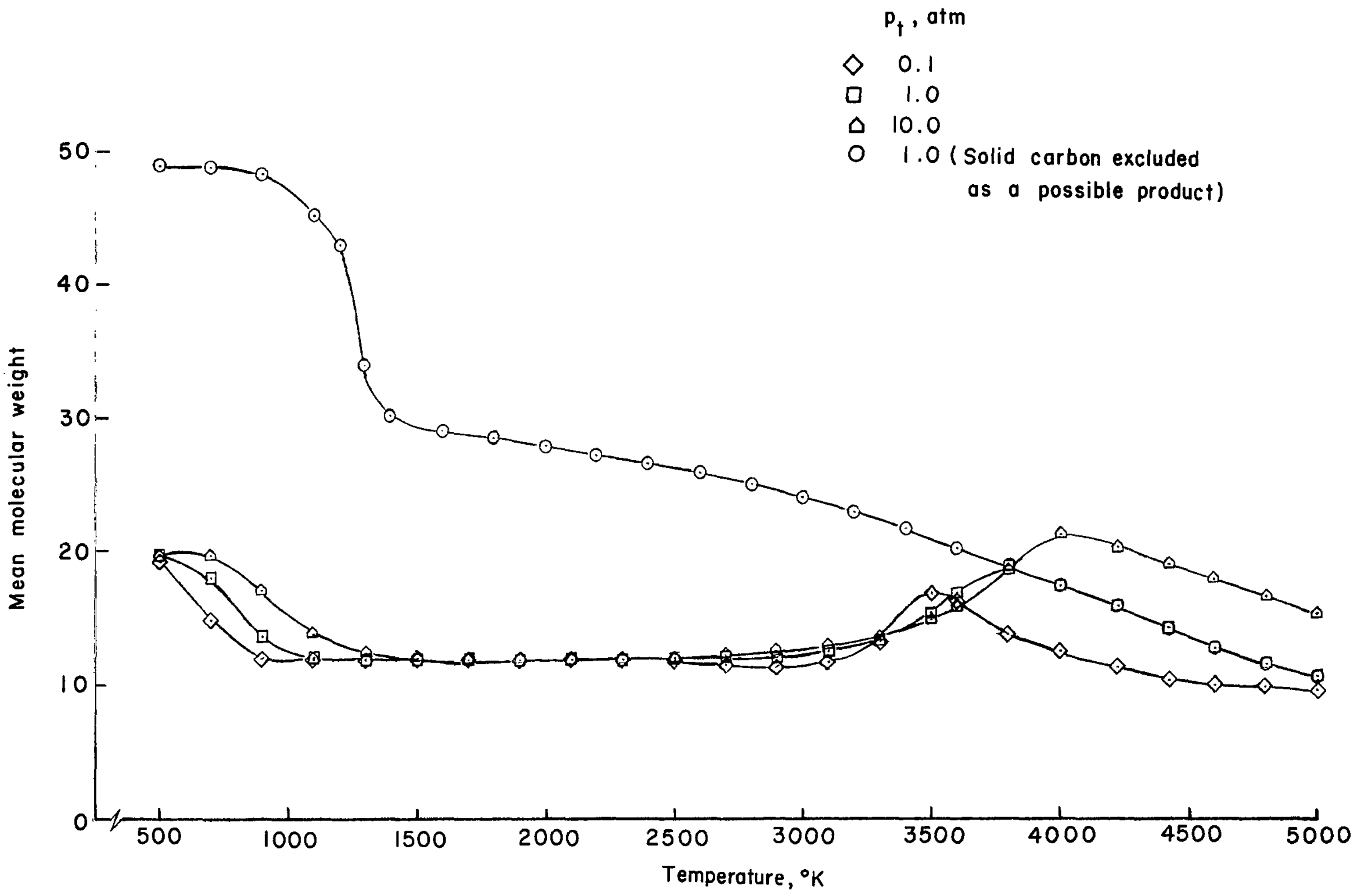


Figure 3.- Mean molecular weights of the pyrolysis gases of phenolic nylon in chemical equilibrium.

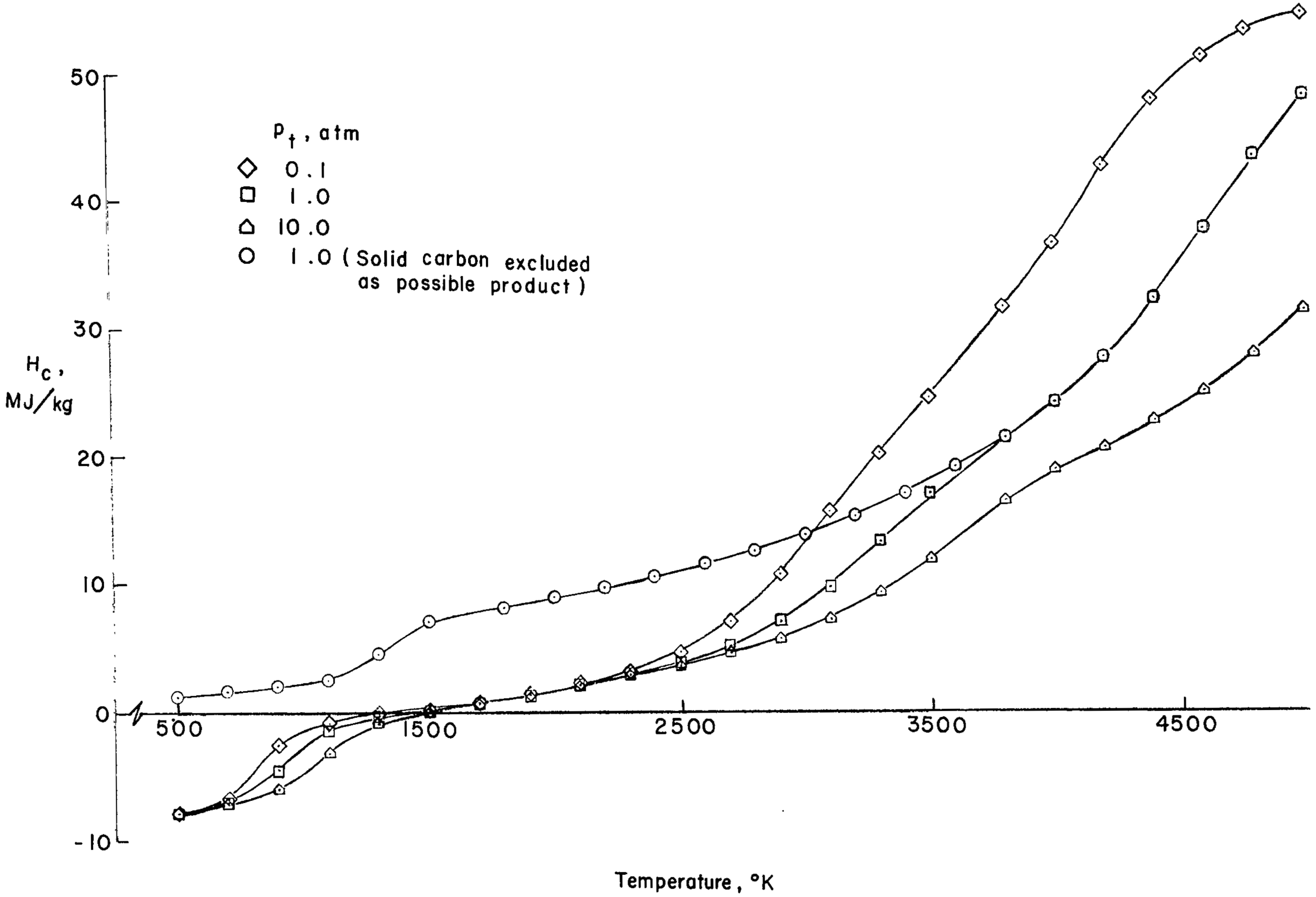


Figure 4.- Total enthalpy of pyrolysis gases of phenolic nylon in chemical equilibrium.

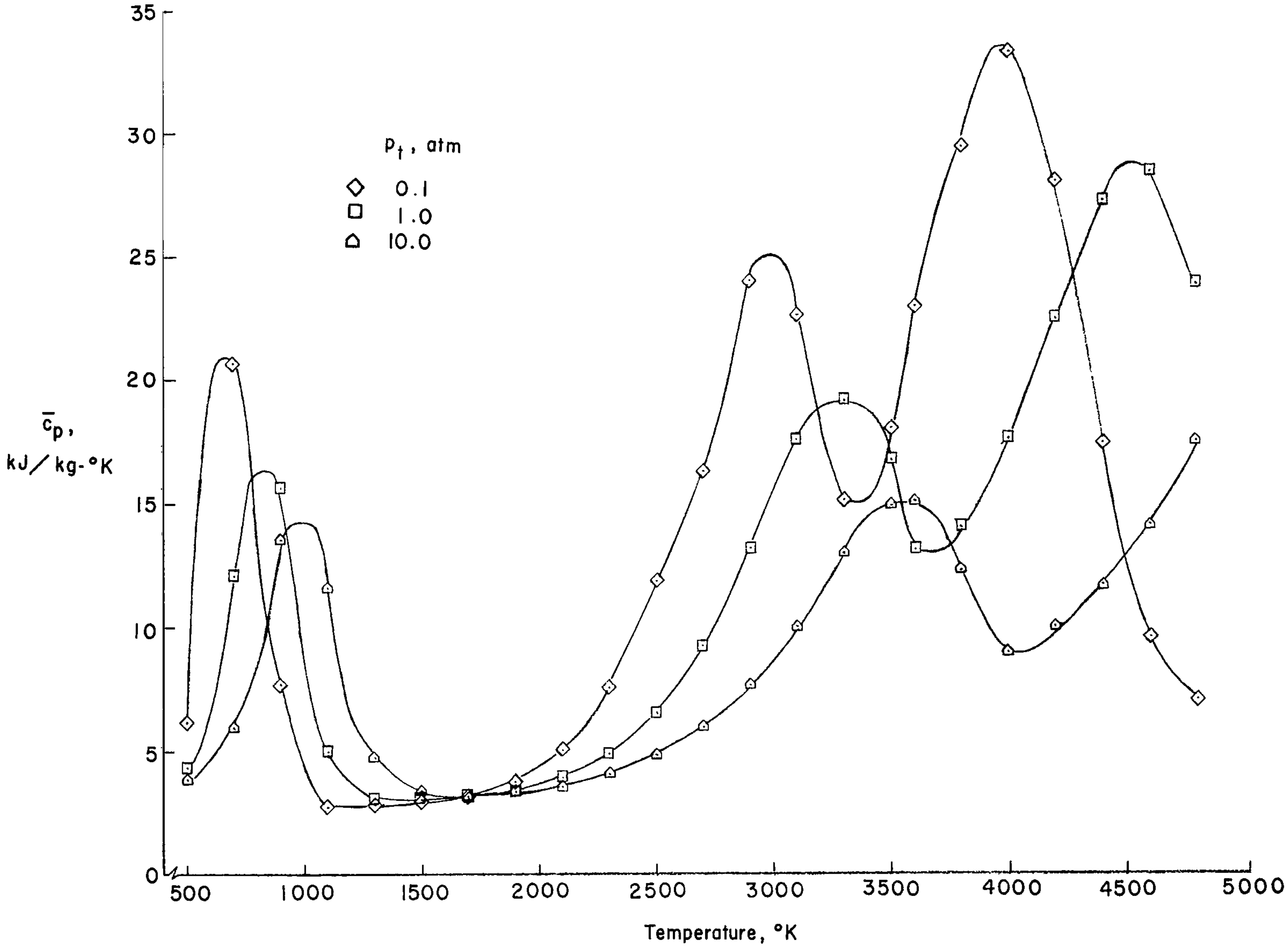


Figure 5.- Effective specific heat of pyrolysis gases of phenolic nylon in chemical equilibrium.

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