

# THERMODYNAMIC PROPERTIES FOR ENGINE COMBUSTION SIMULATIONS

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The properties of gases in combustion environments are complex issues dealing with chemical kinetics and equilibrium. A large number of species are present and the detailed chemistry is not always known particularly for fuel rich mixtures. The following discussion presents a suitable approach to model compositions and properties of hydrocarbon fuel air mixtures and their combustion products for engine combustion simulations.

The most accurate and detailed analysis up to now is to use a full thermodynamic equilibrium model including a huge number of species and reactions. The NASA equilibrium programs [4] and [11] are readily available for this purpose and are well documented. But the complexities and the substantial computer time involved in such models make it prohibitive to use them in engine simulation models, where computational time limits are critical. On the other hand, even those detailed equilibrium programs cannot predict some kinetics controlled engine combustion phenomena such as knock, particulate formation and flame speed with a reasonable accuracy. For such processes a simpler equilibrium model coupled with the submodels describing those particular kinetics is preferred which presents a compromise between accuracy and simplicity.

The properties of premixed fuel air mixtures needed for gasoline engine simulations have been computed within a limited equivalence ratio range using simpler models as shown by Hires [7] and Olikara [10]. The simplest model is to assume a complete combustion for lean mixtures and include the consideration of equilibrium of the water gas reaction for rich mixtures. At higher temperatures effects of other dissociation reactions become important and they must therefore be included.

Non-homogeneous mixtures in spray combustion processes could have a wide range of fuel air ratio variations. It may change from pure vaporized fuel to pure air from one location to another. There may be over rich or lean mixtures beyond the combustible limits and partial burn is sometimes encountered. Soot formation often occurs in fuel rich regions. In order to cover all those possibilities, the present model extends the fuel

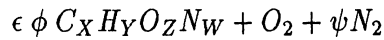
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air ratio to the full range of  $0 \leq \phi \leq \infty$  in contrast with the previous models [7] and [10]. The model also includes the consideration of combustion progress limit and allows partially burned mixtures to exist. These are done by a simplified model without going into detailed complex chemistry for fuel rich mixtures. It also includes the possibility to take into account of soot formation effects on the properties.

## 1 Hydrocarbon Air Combustions

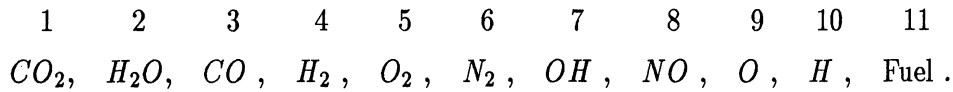
Mixtures of hydrocarbon fuels and air are considered as they are applicable for many combustion processes. The general reactant mixture can be described on the basis of one mole of oxygen



where the coefficients are

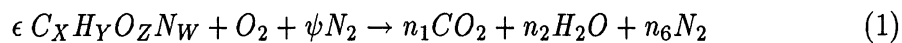
- $\psi$  The molar N:O ratio of the air.
- $\phi$  Equivalence ratio,  $(m_f/m_a)/(m_f/m_a)_o$ .
- $\epsilon$  Stoichiometric mole fuel oxygen ratio.
- $X$  The number of  $C$  atoms in fuel molecules.
- $Y$  The number of  $H$  atoms in fuel molecules.
- $Z$  The number of  $O$  atoms in fuel molecules.
- $W$  The number of  $N$  atoms in fuel molecules.

A limited number of species are considered for combustion products. According to the computation results [3] using the NASA program [11], the important species presented in products are listed as



provided the equivalence ratio  $\phi < 3$ . At low temperatures the list can be simplified further to neglect  $OH$ ,  $NO$ ,  $O$ ,  $H$  radicals since they would have significant effects only when  $T > 2000[K]$ . The list has been kept as small as possible in order to simplify the computation. A more comprehensive analysis must be done to include other radicals, soot and cracked fuels.

Assume a complete combustion for a stoichiometric mixture ( $\phi = 1$ ), the reaction is then can be described as



The mole fuel oxygen ratio  $\epsilon$  can be determined from the balances of  $C$ ,  $H$ ,  $O$  atoms

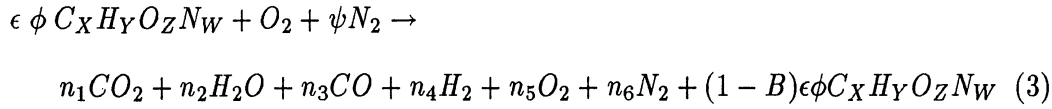
$$\epsilon = \frac{4}{4X + Y - 2Z} \quad (2)$$

The sections below discuss the models for low temperature range and high temperature range separately. Comparisons between them are also made to show their differences and the applicable range for each method.

## 2 Low Temperature Range

### 2.1 Chemistry at low temperature

At low temperature ( $T < 2000[K]$ ), chemical dissociation effects on the properties are small, only the water gas reaction will be considered. Combustion processes could be described as



where

- $n_i$  Moles of species  $i$  per mole of  $O_2$  reactant.
- $B$  The burned mass fraction of the fuel, or the progress variable.

Consider the burned and unburned gases separately,  $n_i$  can be determined by using following assumptions

- For lean mixtures ( $0 \leq \phi \leq 1$ ),  $CO, H_2$  can be neglected.
- For rich mixtures ( $1 < \phi \leq \phi_{max}$ ),  $O_2$  can be neglected. and  $n_3 = C$  will be determined from the water gas reaction.
- For over-rich mixtures ( $\phi > \phi_{max}$ ),  $CO_2$  and  $H_2O$  burn to form  $CO, H_2$ , extra fuel is left without burning.

The results for unburned gas  $B = 0$  and burned gas  $B = 1$  are listed in Table 1

For a mixture of the unburned and burned gases ( $0 \leq B \leq 1$ ), the mole fraction  $y_i$  can be expressed using the mass fraction  $x_i$  as

$$y_i = \frac{x_i/M_i}{\sum x_i/M_i} \quad (4)$$

where the  $M_i$  is the molecular weight of  $i$ th species.

Species <i>i</i>	<i>B</i> = 1			<i>B</i> = 0
	$0 \leq \phi \leq 1$	$1 \leq \phi \leq \phi_{max}$	$\phi_{max} \leq \phi$	$0 \leq \phi < \infty$
<i>CO</i> <sub>2</sub>	$\epsilon\phi X$	$\epsilon\phi X - C$	0	0
<i>H</i> <sub>2</sub> <i>O</i>	$\frac{1}{2}\epsilon\phi Y$	$\frac{1}{2}\epsilon\phi Y - 2(\phi - 1) + C$	0	0
<i>CO</i>	0	<i>C</i>	$\frac{2X}{X-Z}$	0
<i>H</i> <sub>2</sub>	0	$2(\phi - 1) - C$	$\frac{Y}{X-Z}$	0
<i>O</i> <sub>2</sub>	$1 - \phi$	0	0	1
<i>N</i> <sub>2</sub>	$\psi + \frac{1}{2}\epsilon\phi W$	$\psi + \frac{1}{2}\epsilon\phi W$	$\psi + \frac{W}{X-Z}$	$\psi$
Fuel	0	0	$\epsilon\phi - \frac{2}{X-Z}$	$\epsilon\phi$
Total <i>n</i> <sub><i>T</i></sub>	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon\phi + (1 - \phi) + \psi$	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon\phi + \psi$	$\frac{2X + Y + W - 2}{X - Z} + \epsilon\phi + \psi$	$1 + \epsilon\phi + \psi$

Table 1: Number of Moles  $n_i$  for Mixtures with  $B = 1$  and  $B = 0$

Let us consider a mixture composed of two components: unburned gas ‘*U*’ and burned gas ‘*B*’, the mole fraction of each component can be expressed as a function of burned fuel mass fraction  $B$

$$y_B = \frac{\frac{B}{M_B}}{\frac{1-B}{M_U} + \frac{B}{M_B}}; \quad y_U = \frac{\frac{1-B}{M_U}}{\frac{1-B}{M_U} + \frac{B}{M_B}} \quad (5)$$

The mole fraction of each species can be computed as

$$y_i = y_{i_U} y_U + y_{i_B} y_B = \frac{(1-B)(n_{i_U}) + B(n_{i_B})}{(1-B)(n_{T_U}) + B(n_{T_B})} = \frac{n_i}{n_T} \quad (6)$$

It can also be derived, from another point of view, by dividing the total reactant per mole of  $O_2$  in equation 3 into two parts. Let the amount  $B(\epsilon\phi C_X H_Y O_Z N_W + O_2 + \psi N_2)$  of reactant be completely burned, the remaining  $(1-B)(\epsilon\phi C_X H_Y O_Z N_W + O_2 + \psi N_2)$  stay completely unburned, then mix them as two non-reacting components.

The water gas reaction mentioned above is the reaction



Species	$0 \leq \phi \leq 1$	$1 \leq \phi \leq \phi_{max}$	$\phi_{max} \leq \phi$
$CO_2$	$\epsilon\phi XB$	$(\epsilon\phi X - C)B$	0
$H_2O$	$\frac{1}{2}\epsilon\phi YB$	$[\frac{1}{2}\epsilon\phi Y - 2(\phi - 1) + C]B$	0
$CO$	0	$CB$	$\frac{2XB}{X-Z}$
$H_2$	0	$[2(\phi - 1) - C]B$	$\frac{YB}{X-Z}$
$O_2$	$1 - B\phi$	$1 - B$	$1 - B$
$N_2$	$\psi + \frac{1}{2}\epsilon\phi WB$	$\psi + \frac{1}{2}\epsilon\phi WB$	$\psi + \frac{WB}{X-Z}$
Fuel	$\epsilon\phi(1 - B)$	$\epsilon\phi(1 - B)$	$\epsilon\phi - \frac{2B}{X-Z}$
Total	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon\phi B$	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon\phi B$	$\frac{2X+Y+W-2}{X-Z} B$
$n_T$	$+1 + [\epsilon - (1+\epsilon)B]\phi + \psi$	$+(1-B)(1+\epsilon\phi) + \psi$	$+1 - B + \epsilon\phi + \psi$

Table 2: Number of Moles  $n_i$  for a Mixture with  $0 \leq B \leq 1$

which is assumed to be in equilibrium at the given  $T$ . The equilibrium constant  $K$  is a function of temperature and it is approximated to fit the JANAF Table [9] as

$$K(T) = \exp(2.743 - 1.761Z - 1.611Z^2 + 0.2803Z^3); \quad Z = \frac{1000}{T} \quad (8)$$

The relation between the equilibrium constant and partial pressures of species

$$K(T) = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}} = \frac{C[\frac{1}{2}\epsilon\phi Y - 2(\phi - 1) + C]}{(\epsilon\phi X - C)[2(\phi - 1) - C]} \quad (9)$$

gives a quadratic equation for  $C$

$$(1 - K)C^2 + \left\{ \frac{1}{2}\epsilon\phi Y - 2(\phi - 1) + [2(\phi - 1) + \epsilon\phi X]K \right\} C - 2\epsilon\phi X(\phi - 1)K = 0 \quad (10)$$

Introducing following transformations for convenience

$$\begin{aligned} \delta &= \frac{1}{2}\epsilon\phi Y - 2(\phi - 1) \\ \sigma &= 2(\phi - 1) + \epsilon\phi X \\ \alpha &= 2(1 - K) \\ \beta &= \delta + \sigma K \\ \gamma &= 2\epsilon\phi X(\phi - 1) \end{aligned} \quad (11)$$

equation 10 can be simplified as

$$\frac{\alpha}{2}C^2 + \beta C - \gamma K = 0 \quad (12)$$

To be physically meaningful,  $C$  is solved by taking only the positive root as

$$C = \frac{-\beta + \sqrt{\beta^2 + 2\alpha\gamma K}}{\alpha} \quad (13)$$

In order to determine the maximum equivalence ratio  $\phi_{max}$  in the products, the physical constraint that the number of moles for each species cannot be negative is applied, which results following conditions for  $C$

$$\begin{aligned} C &\leq \epsilon\phi X && [CO_2] \\ C &\geq 2(\phi - 1) - \frac{1}{2}\epsilon\phi Y && [H_2O] \\ C &\geq 0 && [CO] \\ C &\leq 2(\phi - 1) && [H_2] \end{aligned} \quad (14)$$

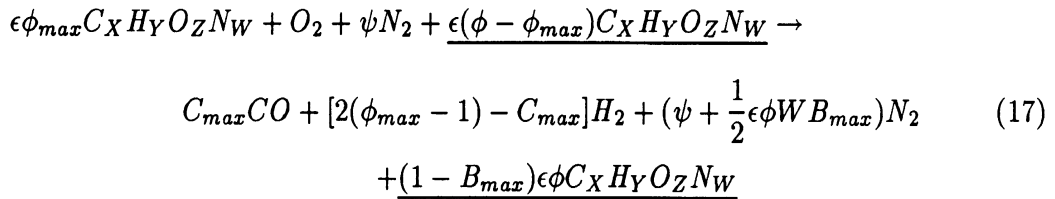
The results for octane  $C_8H_{18}$ , which has  $\epsilon = 0.08$ , are plotted in the Figure 1. The possible  $C - \phi$  solutions have to be located within the shaded area. When  $\phi$  approaches  $\phi_{max}$ ,  $C$  has to be under the  $[CO_2]$  line and above the  $[H_2O]$  line. In the limit, we have

$$\epsilon\phi_{max}X = C_{max} = (2X - Z)\epsilon\phi_{max} - 2 \quad (15)$$

which gives

$$\phi_{max} = \frac{2}{\epsilon(X - Z)}; \quad C_{max} = \frac{2X}{X - Z} \quad (16)$$

When  $\phi \geq \phi_{max}$ , the reaction can be described as



where the underlines denote the extra fuel left over. Noting the analysis also imposes a constraint for  $B$  at the large fuel-air ratio range

$$B_{max} = \begin{cases} 1 & \phi < \phi_{max} \\ \frac{\phi_{max}}{\phi} & \phi \geq \phi_{max} \end{cases} \quad (18)$$

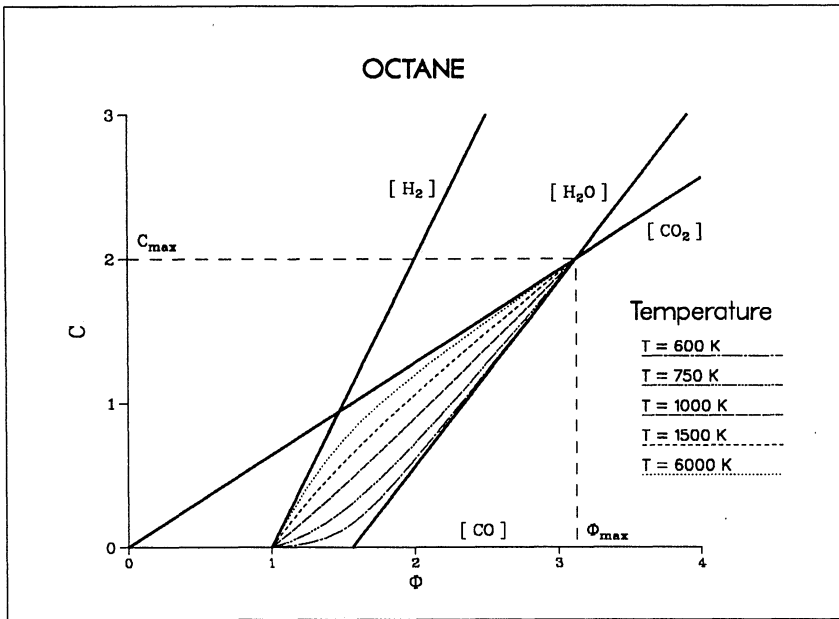


Figure 1: Physical Constraint for  $C$  and  $\phi$ .

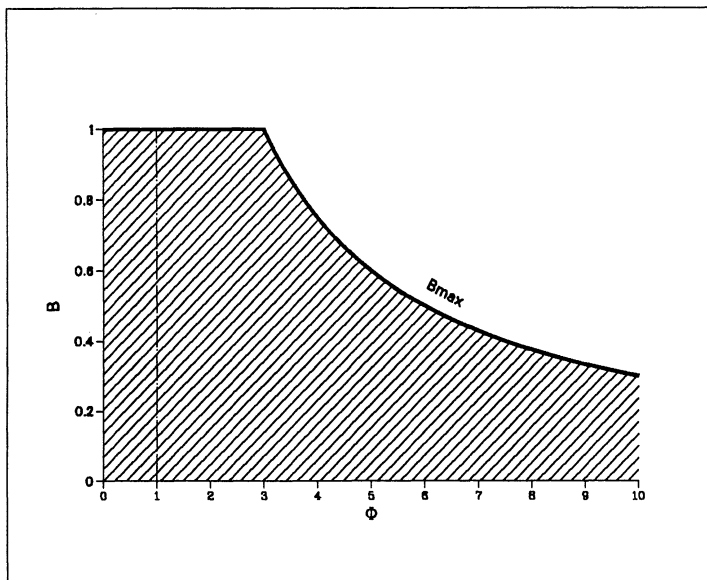


Figure 2: Valid  $B$  Range



$$B = \begin{cases} B & B < B_{max} \\ B_{max} & B \geq B_{max} \end{cases} \quad (19)$$

The valid  $B$  range is shown as the shaded area on Figure 2.

## 2.2 Partial derivatives of composition at low temperature

The partial derivative of  $\frac{\partial n_i}{\partial T}$  is nonzero when  $1 \leq \phi \leq \phi_{max}$ , where it is

$$\frac{\partial n_i}{\partial T} = \text{TAB}[i] \left( \frac{\partial C}{\partial T} \right) B \quad (20)$$

with  $\text{TAB} = [ -1, 1, 1, -1, 0, 0, 0 ]$

The partial derivative of  $C$  with respect to  $T$  can be obtained from equation 8 and equation 13 using the chain rule

$$\frac{\partial C}{\partial T} = \frac{\partial C}{\partial K} \frac{dK}{dT} \quad (21)$$

The first partial derivative on the right hand side is

$$\frac{\partial C}{\partial K} = \frac{C^2 - \sigma C + \gamma}{\alpha C + \beta} \quad (22)$$

noting  $\frac{d\alpha}{dK} = -2$ ,  $\frac{d\beta}{dK} = \sigma$ ,  $\frac{d\gamma}{dK} = 0$  and equation 12 have been used to simplify the result.

Getting the second part is straight forward

$$\frac{dK}{dT} = K(-1.761 - 3.222Z + 0.8409Z^2) \frac{dZ}{dT} \quad (23)$$

And also using equation 13 and  $\frac{d\alpha}{d\phi} = 0$ ,  $\frac{d\beta}{d\phi} = (2 + \epsilon X)K - (2 - \frac{1}{2}\epsilon Y)$ ,  $\frac{d\gamma}{d\phi} = 2\epsilon X(2\phi - 1)$

$$\frac{\partial C}{\partial \phi} = \frac{2K\epsilon X(2\phi - 1) - [(2 + \epsilon X)K - (2 - \frac{1}{2}\epsilon Y)]C}{\alpha C + \beta} \quad (24)$$

The other partial derivatives needed in the computation are listed in Tables 3 and 4. Obviously, these tables are obtained by operating on Table 2.

The derivative of  $B$  with respect to  $\phi$  in Table 3 can be derived from equations 18 and 19

$$\frac{\partial B}{\partial \phi} = \begin{cases} -\frac{\phi_{max}}{\phi^2} & B \geq B_{max} \text{ and } \phi \geq \phi_{max} \\ 0 & \text{otherwise} \end{cases} \quad (25)$$

Species	$0 \leq \phi \leq 1$	$1 \leq \phi \leq \phi_{max}$	$\phi_{max} \leq \phi$
$CO_2$	$\epsilon XB$	$(\epsilon X - \frac{\partial C}{\partial \phi})B$	0
$H_2O$	$\frac{1}{2}\epsilon YB$	$(\frac{1}{2}\epsilon Y - 2 + \frac{\partial C}{\partial \phi})B$	0
$CO$	0	$\frac{\partial C}{\partial \phi}B$	$(\frac{2X}{X-Z})\frac{\partial B}{\partial \phi}$
$H_2$	0	$(2 - \frac{\partial C}{\partial \phi})B$	$(\frac{Y}{X-Z})\frac{\partial B}{\partial \phi}$
$O_2$	$-B$	0	$-\frac{\partial B}{\partial \phi}$
$N_2$	$\frac{1}{2}\epsilon WB$	$\frac{1}{2}\epsilon WB$	$(\frac{W}{X-Z})\frac{\partial B}{\partial \phi}$
Fuel	$\epsilon(1-B)$	$\epsilon(1-B)$	$\epsilon - (\frac{2}{X-Z})\frac{\partial B}{\partial \phi}$
$\partial n_T$	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon B$	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon B$	$(\frac{2X+Y+W-2}{X-Z})\frac{\partial B}{\partial \phi}$
$\partial \phi$	$+\epsilon - (1+\epsilon)B$	$+\epsilon(1-B)$	$+\epsilon - \frac{\partial B}{\partial \phi}$

Table 3: Partial Derivative of  $n$  with respect to  $\phi$

Species	$0 \leq \phi \leq 1$	$1 \leq \phi \leq \phi_{max}$	$\phi_{max} \leq \phi$
$CO_2$	$\epsilon\phi X$	$\epsilon\phi X - C$	0
$H_2O$	$\frac{1}{2}\epsilon\phi Y$	$\frac{1}{2}\epsilon\phi Y - 2(\phi-1) + C$	0
$CO$	0	$C$	$\frac{2X}{X-Z}$
$H_2$	0	$2(\phi-1) - C$	$\frac{Y}{X-Z}$
$O_2$	$-\phi$	-1	-1
$N_2$	$\frac{1}{2}\epsilon\phi W$	$\frac{1}{2}\epsilon\phi W$	$\frac{W}{X-Z}$
Fuel	$-\epsilon\phi$	$-\epsilon\phi$	$-\frac{2}{X-Z}$
$\partial n_T$	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon\phi$	$(X + \frac{1}{2}Y + \frac{1}{2}W)\epsilon\phi$	$\frac{2X+Y+W-2}{X-Z} - 1$
$\partial B$	$-(1+\epsilon)\phi$	$-(1+\epsilon\phi)$	

Table 4: Partial Derivative of  $n$  with respect to  $B$

### 2.3 Basic thermodynamic properties at low temperature

Combustible mixtures and their products inside engine combustion chambers could be treated as an ideal gas.

On a mole basis (denoted by an over-bar)

$$\bar{R} = 8.31434 \quad [\text{kJ/kmol K}] \quad (26)$$

$$\bar{h} = \sum(y_i \bar{h}_i) \quad [\text{kJ/kmol}] \quad (27)$$

$$\bar{s} = \sum(y_i \bar{s}_i) \quad [\text{kJ/kmol K}] \quad (28)$$

On a mass basis

$$R = \frac{\bar{R}}{M} = \left(\frac{n_T}{m_T}\right) \bar{R} \quad [\text{kJ/kg K}] \quad (29)$$

$$h = \frac{\bar{h}}{M} = \frac{\sum[(\frac{n_i}{n_T}) \bar{h}_i]}{(\frac{m_T}{n_T})} = \frac{1}{m_T} \sum(n_i \bar{h}_i) \quad [\text{kJ/kg}] \quad (30)$$

$$s = \frac{\bar{s}}{M} = \frac{1}{m_T} \sum(n_i \bar{s}_i) = \frac{1}{m_T} \sum[n_i (\bar{s}_i^o - \bar{R} \ln \frac{P_i}{P_o})] \quad [\text{kJ/kg K}] \quad (31)$$

where  $m_T$  is the total mass per mole of  $O_2$ .

$$m_T = \epsilon \phi M_f + M_{O_2} + \psi M_{N_2} \quad (32)$$

It is a conserved quantity for both reactant and product and is a function of  $\phi$  only for given fuel and air compositions. It has a derivative

$$\frac{\partial m_T}{\partial \phi} = \epsilon M_f \quad (33)$$

The molecular weight of a fuel in above equations is

$$M_f = 12.01X + 1.008Y + 16.00Z + 14.007W \quad (34)$$

## 2.4 Partial derivatives of properties at low temperature

From expressions in section 2.3 it is easy to show

$$\begin{aligned}
\frac{1}{R} \frac{\partial R}{\partial T} &= 0 \\
\frac{1}{R} \frac{\partial R}{\partial P} &= 0 \\
\frac{1}{R} \frac{\partial R}{\partial \phi} &= \frac{1}{n_T} \left( \frac{\partial n_T}{\partial \phi} \right) - \frac{1}{m_T} \left( \frac{\partial m_T}{\partial \phi} \right) \\
\frac{1}{R} \frac{\partial R}{\partial B} &= \frac{1}{n_T} \left( \frac{\partial n_T}{\partial B} \right)
\end{aligned} \tag{35}$$

$$\begin{aligned}
\frac{\partial h}{\partial T} &= \frac{1}{m_T} \sum \left[ \left( \frac{\partial n_i}{\partial T} \right) \bar{h}_i \right] + \frac{1}{m_T} \sum \left[ n_i \left( \frac{\partial \bar{h}_i}{\partial T} \right) \right] \\
\frac{\partial h}{\partial P} &= 0 \\
\frac{\partial h}{\partial \phi} &= \frac{1}{m_T} \sum \left[ \left( \frac{\partial n_i}{\partial \phi} \right) \bar{h}_i \right] - \frac{h}{m_T} \left( \frac{\partial m_T}{\partial \phi} \right) \\
\frac{\partial h}{\partial B} &= \frac{1}{m_T} \sum \left[ \left( \frac{\partial n_i}{\partial B} \right) \bar{h}_i \right]
\end{aligned} \tag{36}$$

and

$$\begin{aligned}
\frac{\partial S}{\partial T} &= \frac{1}{m_T} \sum \left\{ \left( \frac{\partial n_i}{\partial T} \right) \left[ \bar{s}_i^o - \bar{R} \ln \left( y_i \frac{P}{P_o} \right) \right] \right\} + \frac{1}{m_T} \sum \left[ n_i \left( \frac{\partial \bar{S}_i^o}{\partial T} \right) \right] \\
\frac{\partial S}{\partial P} &= -\frac{R}{P} \\
\frac{\partial S}{\partial \phi} &= \frac{1}{m_T} \sum \left\{ \left( \frac{\partial n_i}{\partial \phi} \right) \left[ \bar{s}_i^o - \bar{R} \ln \left( y_i \frac{P}{P_o} \right) \right] \right\} - \frac{S}{m_T} \left( \frac{\partial m_T}{\partial \phi} \right) \\
\frac{\partial S}{\partial B} &= \frac{1}{m_T} \sum \left\{ \left( \frac{\partial n_i}{\partial B} \right) \left[ \bar{s}_i^o - \bar{R} \ln \left( y_i \frac{P}{P_o} \right) \right] \right\}
\end{aligned} \tag{37}$$

The last terms in equations 36.1 and 37.1 are related to the frozen specific heat which will be given in equation 84.1. The first terms in those equations are nonzero only when  $1 \leq \phi \leq \phi_{max}$  and  $\frac{\partial n_i}{\partial T}$  are given in equation 20. The other required partial derivatives can be found in section 2.2.

Proceeding up to now, we have had all necessary information to calculate the required thermodynamic properties and their derivatives at low temperature for computations. The calculated results from the low temperature model are given later together with the results from the high temperature model and comparisons are made there.

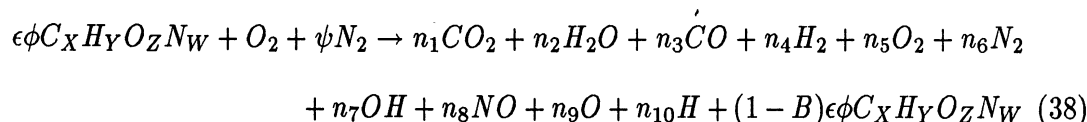
## 3 High Temperature Range

### 3.1 Chemistry at high temperature

At high temperature ( $T > 2000[K]$ ), chemical dissociation effects have to be taken into account. The basic approach is based on the method developed by Olikara and Borman [10] where a rapid means for thermodynamic property calculation is presented compared to the extensive NASA program [4] in which a large number of species are considered. In order to simplify the matter further, only the species of importance because of dissociation are included. These species are  $OH$ ,  $NO$ ,  $O$ ,  $H$  (see [3]), provided

the equivalence ratio  $\phi < 3$ , beyond which solid carbon will be formed in the products. Thus the species list in the program is terminated at  $i = 11$ .

The hydrocarbon-air combustion process described in equation 3 could be expanded as



where the nomenclature is the same as before and the stoichiometric fuel oxygen mole ratio  $\epsilon$  is given in equation 2.

Atom balancing yields

$$\begin{aligned} \text{C: } B\epsilon\phi X &= (y_1 + y_3)n_T \\ \text{H: } B\epsilon\phi Y &= (2y_2 + 2y_4 + y_7 + y_{10})n_T \\ \text{O: } 2 + B\epsilon\phi Z &= (2y_1 + y_2 + y_3 + 2y_5 + y_7 + y_8 + y_9)n_T \\ \text{N: } 2\psi + B\epsilon\phi W &= (2y_6 + y_8)n_T \end{aligned} \quad (39)$$

Also the constraint that the mole fractions of all species add up to unity must be satisfied

$$(B - 1)\epsilon\phi = \left( \sum_{i=1}^{10} y_i - 1 \right) n_T \quad (40)$$

In order to solve for the 11 unknowns (  $n_T, y_i, i = 1, \dots, 10$  ), 6 more equations are needed which may be derived from the consideration of equilibriums among the products.

Following 6 major dissociation reactions are considered in the program

$$\begin{aligned} \frac{1}{2} H_2 &\rightleftharpoons H & K_1 &= \frac{y_{10} P^{1/2}}{y_4^{1/2}} \\ \frac{1}{2} O_2 &\rightleftharpoons O & K_2 &= \frac{y_9 P^{1/2}}{y_5^{1/2}} \\ \frac{1}{2} N_2 + \frac{1}{2} O_2 &\rightleftharpoons NO & K_3 &= \frac{y_8}{y_6^{1/2} y_5^{1/2}} \\ \frac{1}{2} H_2 + \frac{1}{2} O_2 &\rightleftharpoons OH & K_4 &= \frac{y_7}{y_4^{1/2} y_5^{1/2}} \\ H_2 + \frac{1}{2} O_2 &\rightleftharpoons H_2O & K_5 &= \frac{y_2}{y_4 y_5^{1/2} P^{1/2}} \\ CO + \frac{1}{2} O_2 &\rightleftharpoons CO_2 & K_6 &= \frac{y_1}{y_3 y_5^{1/2} P^{1/2}} \end{aligned} \quad (41)$$

Equilibrium constants in equation 41 are curve fitted to the JANAF Thermochemical Table [9] in the form

$$\log K_i = A_i \ln \frac{T}{1000} + \frac{B_i}{T} + C_i + D_i T + E_i T^2 \quad (42)$$

where  $T$  is in [K],  $P$  in equation 41 is in [atm]. The coefficients  $A_i, B_i, C_i, D_i$ , and  $E_i$  are listed in Table 7 for the temperature range  $300 \leq T \leq 5000K$ .

Rearranging the expressions for equilibrium constants, the mole fractions of the species  $i = 1, 2, 7, 8, 9, 10$  can be expressed as functions of the mole fractions of the species  $i = 3, 4, 5, 6$

$$\begin{aligned}
y_1 &= C_1 y_3 y_5^{1/2} & C_1 &= K_6 P^{1/2} \\
y_2 &= C_2 y_4 y_5^{1/2} & C_2 &= K_5 P^{1/2} \\
y_7 &= C_3 y_4^{1/2} y_5^{1/2} & C_3 &= K_4 \\
y_8 &= C_4 y_6^{1/2} y_5^{1/2} & C_4 &= K_3 \\
y_9 &= C_5 y_5^{1/2} & C_5 &= K_2 P^{-1/2} \\
y_{10} &= C_6 y_4^{1/2} & C_6 &= K_1 P^{-1/2}
\end{aligned} \tag{43}$$

fining

$$\begin{aligned}
D &= B\epsilon\phi \\
d_1 &= 2\psi + DW \\
d_2 &= 2 + DZ \\
d_3 &= DX \\
d_4 &= 1 + B(X - 1) \\
d_5 &= BX
\end{aligned} \tag{44}$$

equation 39 and equation 40 can be manipulated into a homogeneous form so that the  $n_T$  term is cancelled out

$$\begin{aligned}
Y(y_1 + y_3) - X(2y_2 + 2y_4 + y_7 + y_{10}) &= 0 \\
d_1(2y_1 + y_2 + y_3 + 2y_5 + y_7 + y_8 + y_9) - d_2(2y_6 + y_8) &= 0 \\
d_1(y_1 + y_3) - d_3(2y_6 + y_8) &= 0 \\
d_4(y_1 + y_3) + d_5(y_2 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9 + y_{10} - 1) &= 0
\end{aligned} \tag{45}$$

Utilizing equation 43, equation 45 can be expressed symbolically as functions of  $y_3, y_4, y_5, y_6$  only

$$f_j(y_3, y_4, y_5, y_6) = 0, \quad (j = 1, 2, 3, 4) \tag{46}$$

If we have an approximate solution  $[y_3^n, y_4^n, y_5^n, y_6^n]$ , where  $n$  denotes the approximation after the  $n$ th correction, reasonably close to the real solution of equation 46, a further correction can be made by

$$y_i^{n+1} = y_i^n + \Delta y_i^n, \quad (i = 3, 4, 5, 6) \tag{47}$$

until the correction terms are smaller than a prescribed error allowance, which is the so called Newton Raphson iteration scheme.

The correction terms could be generated by a Taylor expansion of equation 46 about a known vector. Neglecting the second and higher order partial derivatives we get a set of linear equations for  $\Delta y$

$$f_j + \left(\frac{\partial f_j}{\partial y_3}\right)\Delta y_3 + \left(\frac{\partial f_j}{\partial y_4}\right)\Delta y_4 + \left(\frac{\partial f_j}{\partial y_5}\right)\Delta y_5 + \left(\frac{\partial f_j}{\partial y_6}\right)\Delta y_6 \approx 0, \quad (j = 1, 2, 3, 4) \quad (48)$$

Or writing in matrix notation

$$[A] [Y] = [F] \quad (49)$$

where  $[F] = [-f]$ ,  $[Y] = [\Delta y]$  and  $[A] = \left[\frac{\partial f}{\partial y}\right]$ .

For convenience, defining following partial derivatives

$$D_{ij} = \frac{\partial y_i}{\partial y_j}; \quad (i = 1, 2, 7, 8, 9, 10; j = 3, 4, 5, 6)$$

so that

$$\begin{aligned} D_{13} &= C_1 y_5^{1/2} & D_{15} &= \frac{1}{2} C_1 y_3 y_5^{-1/2} \\ D_{24} &= C_2 y_5^{1/2} & D_{25} &= \frac{1}{2} C_2 y_4 y_5^{-1/2} \\ D_{74} &= \frac{1}{2} C_3 y_4^{-1/2} y_5^{1/2} & D_{75} &= \frac{1}{2} C_3 y_4^{1/2} y_5^{-1/2} \\ D_{86} &= \frac{1}{2} C_4 y_6^{-1/2} y_5^{1/2} & D_{85} &= \frac{1}{2} C_4 y_6^{1/2} y_5^{-1/2} \\ D_{95} &= \frac{1}{2} C_5 y_5^{-1/2} & D_{104} &= \frac{1}{2} C_6 y_4^{-1/2} \end{aligned} \quad (50)$$

Elements in the  $[A]$  matrix can then be expressed as

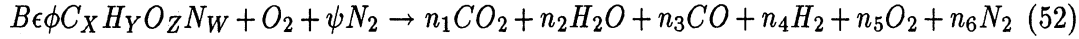
$$\begin{aligned} A_{11} &= Y(D_{13} + 1) \\ A_{12} &= -X(2D_{24} + 2 + D_{74} + D_{104}) \\ A_{13} &= YD_{15} - X(2D_{25} + D_{75}) \\ A_{14} &= 0 \\ A_{21} &= d_1(2D_{13} + 1) \\ A_{22} &= d_1(D_{24} + D_{74}) \\ A_{23} &= d_1(2D_{15} + D_{25} + 2 + D_{75} + D_{85} + D_{95}) - d_2 D_{85} \\ A_{24} &= d_1 D_{86} - d_2(2 + D_{86}) \\ A_{31} &= d_1(D_{13} + 1) \\ A_{32} &= 0 \\ A_{33} &= d_1 D_{15} - d_3 D_{85} \\ A_{34} &= -d_3(2 + D_{86}) \\ A_{41} &= d_4(D_{13} + 1) \\ A_{42} &= d_5(D_{24} + 1 + D_{74} + D_{104}) \\ A_{43} &= d_4 D_{15} + d_5(D_{25} + 1 + D_{75} + D_{85} + D_{95}) \\ A_{44} &= d_5(1 + D_{86}) \end{aligned} \quad 1)$$

The solution of the matrix equation 49 by means of the Gaussian elimination gives the  $\Delta y$  required in equation 47. After the independent variables  $y_3, y_4, y_5, y_6$  in the iteration are corrected, the dependent variables are updated using equation 43 at every step until the convergence criteria are satisfied.

### 3.2 Initial estimate

It is necessary to make an initial estimation for the iteration described above since it is not self starting. A low temperature model, where only the 6 species  $CO_2, H_2O, CO, H_2, O_2, N_2$  are considered, is found to give a remarkably good initial estimation.

The simplified equation reads



The  $C$  balance  $B\epsilon\phi X = (y_1 + y_3)n_T$  with equations 43 and 44 give

$$y_3 = \frac{DX}{(1 + C_1 y_5^{1/2})n_T} \quad (53)$$

The  $H$  balance  $B\epsilon\phi Y = (2y_2 + 2y_4)n_T$  with equations 43 and 44 give

$$y_4 = \frac{DY}{2(1 + C_2 y_5^{1/2})n_T} \quad (54)$$

Insert above relations into the  $O$  balance  $B\epsilon\phi Z + 2 = (2y_1 + y_2 + y_3 + 2y_5)n_T$ , a nonlinear equation for  $y_5$  is derived

$$f_5 = D[X(1 + g_1) + \frac{1}{2}Yg_2 - Z] + 2(y_5 n_T - 1) = 0 \quad (55)$$

with

$$f'_5 = \frac{1}{2}D\left[\frac{X}{C_1}g_1^2 + \frac{Y}{2C_2}g_2^2\right]\frac{1}{y_5^{3/2}} + 2n_T \quad (56)$$

so that  $y_5$  can be iterated to a given accuracy

$$y_5^{n+1} = y_5^n - \left(\frac{f_5}{f'_5}\right)^n \quad (57)$$

The function  $g$  is defined as

$$g_i = \frac{C_i y_5^{1/2}}{1 + C_i y_5^{1/2}}; \quad g'_i = \frac{g_i^2}{2C_i y_5^{3/2}} \quad (58)$$

and the total mole number  $n_T$  can be taken from Table 2 as a first approximation.



The mole fraction for nitrogen  $y_6$  can be estimated as

$$y_6 = \frac{\psi + \frac{1}{2}DW}{n_T} \quad (59)$$

The results of computed composition are shown in Figures 3 - 6. Having the composition available, we pursue further to calculate the partial derivatives of mole fractions.

### 3.3 Partial derivatives of composition with respect to $T$ and $P$ at high temperature

The independent derivatives are obtained by solution of the matrix equation that results from differentiating equation 48

$$\frac{\partial f_j}{\partial \xi} + \left(\frac{\partial f_j}{\partial y_3}\right)\frac{\partial y_3}{\partial \xi} + \left(\frac{\partial f_j}{\partial y_4}\right)\frac{\partial y_4}{\partial \xi} + \left(\frac{\partial f_j}{\partial y_5}\right)\frac{\partial y_5}{\partial \xi} + \left(\frac{\partial f_j}{\partial y_6}\right)\frac{\partial y_6}{\partial \xi} = 0, \quad (j = 1, 2, 3, 4) \quad (60)$$

In matrix notation

$$[A] [Y, \xi] = [F, \xi] \quad (61)$$

where  $\xi$  could be  $T, P, \phi$ , or  $B$ ,  $[F, \xi] = [-\frac{\partial f}{\partial \xi}]$ ,  $[Y, \xi] = [\frac{\partial y}{\partial \xi}]$  and  $[A]$  is identical to that used in equation 49. The elements  $\frac{\partial f}{\partial \xi}$  on the right hand side can be evaluated from differentiating equation 45

$$\begin{aligned} \frac{\partial f_1}{\partial T} &= Y \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial T}\right) - X \left[ 2 \frac{y_2}{C_2} \left(\frac{\partial C_2}{\partial T}\right) + \frac{y_7}{C_3} \left(\frac{\partial C_3}{\partial T}\right) + \frac{y_{10}}{C_6} \left(\frac{\partial C_6}{\partial T}\right) \right] \\ \frac{\partial f_2}{\partial T} &= d_1 \left[ 2 \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial T}\right) + \frac{y_2}{C_2} \left(\frac{\partial C_2}{\partial T}\right) + \frac{y_7}{C_3} \left(\frac{\partial C_3}{\partial T}\right) + \frac{y_8}{C_4} \left(\frac{\partial C_4}{\partial T}\right) + \frac{y_9}{C_5} \left(\frac{\partial C_5}{\partial T}\right) \right] \\ &\quad - d_2 \frac{y_8}{C_4} \left(\frac{\partial C_4}{\partial T}\right) \\ \frac{\partial f_3}{\partial T} &= d_1 \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial T}\right) - d_3 \frac{y_8}{C_4} \left(\frac{\partial C_4}{\partial T}\right) \\ \frac{\partial f_4}{\partial T} &= d_4 \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial T}\right) \\ &\quad + d_5 \left[ \frac{y_2}{C_2} \left(\frac{\partial C_2}{\partial T}\right) + \frac{y_7}{C_3} \left(\frac{\partial C_3}{\partial T}\right) + \frac{y_8}{C_4} \left(\frac{\partial C_4}{\partial T}\right) + \frac{y_9}{C_5} \left(\frac{\partial C_5}{\partial T}\right) + \frac{y_{10}}{C_6} \left(\frac{\partial C_6}{\partial T}\right) \right] \end{aligned} \quad (62)$$

$$\begin{aligned} \frac{\partial f_1}{\partial P} &= Y \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial P}\right) - X \left[ 2 \frac{y_2}{C_2} \left(\frac{\partial C_2}{\partial P}\right) + \frac{y_{10}}{C_6} \left(\frac{\partial C_6}{\partial P}\right) \right] \\ \frac{\partial f_2}{\partial P} &= d_1 \left[ 2 \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial P}\right) + \frac{y_2}{C_2} \left(\frac{\partial C_2}{\partial P}\right) + \frac{y_9}{C_5} \left(\frac{\partial C_5}{\partial P}\right) \right] \\ \frac{\partial f_3}{\partial P} &= d_1 \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial P}\right) \\ \frac{\partial f_4}{\partial P} &= d_4 \frac{y_1}{C_1} \left(\frac{\partial C_1}{\partial P}\right) + d_5 \left[ \frac{y_2}{C_2} \left(\frac{\partial C_2}{\partial P}\right) + \frac{y_9}{C_5} \left(\frac{\partial C_5}{\partial P}\right) + \frac{y_{10}}{C_6} \left(\frac{\partial C_6}{\partial P}\right) \right] \end{aligned}$$

The required partial derivatives of  $C$  with respect to  $T$  and  $P$  are

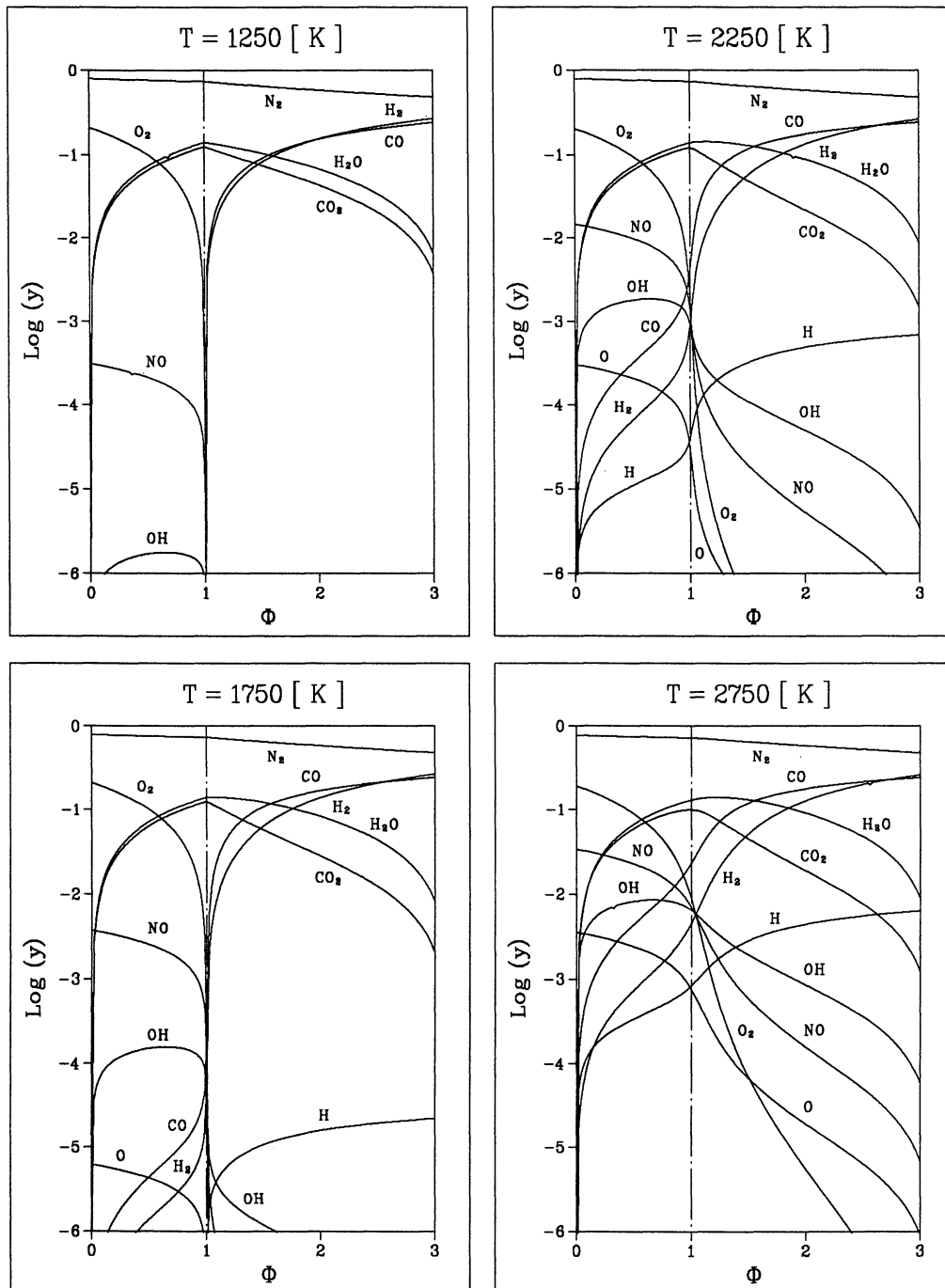


Figure 3: Combustion Product Compositions as Functions of  $\Phi$  ( $P = 30 \text{ [atm]}$ )

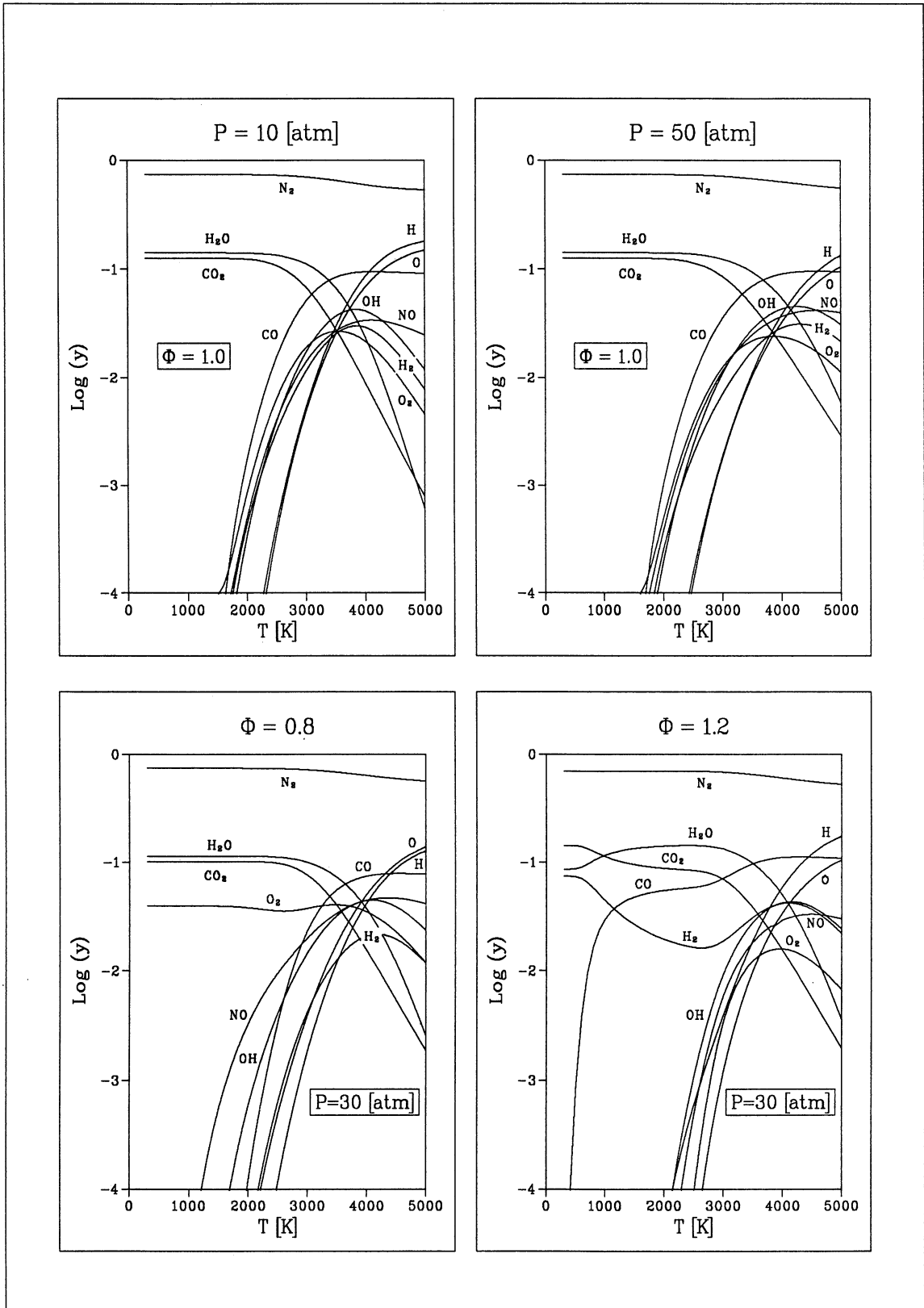


Figure 4: Combustion Product Equilibrium Compositions as Functions of  $T$

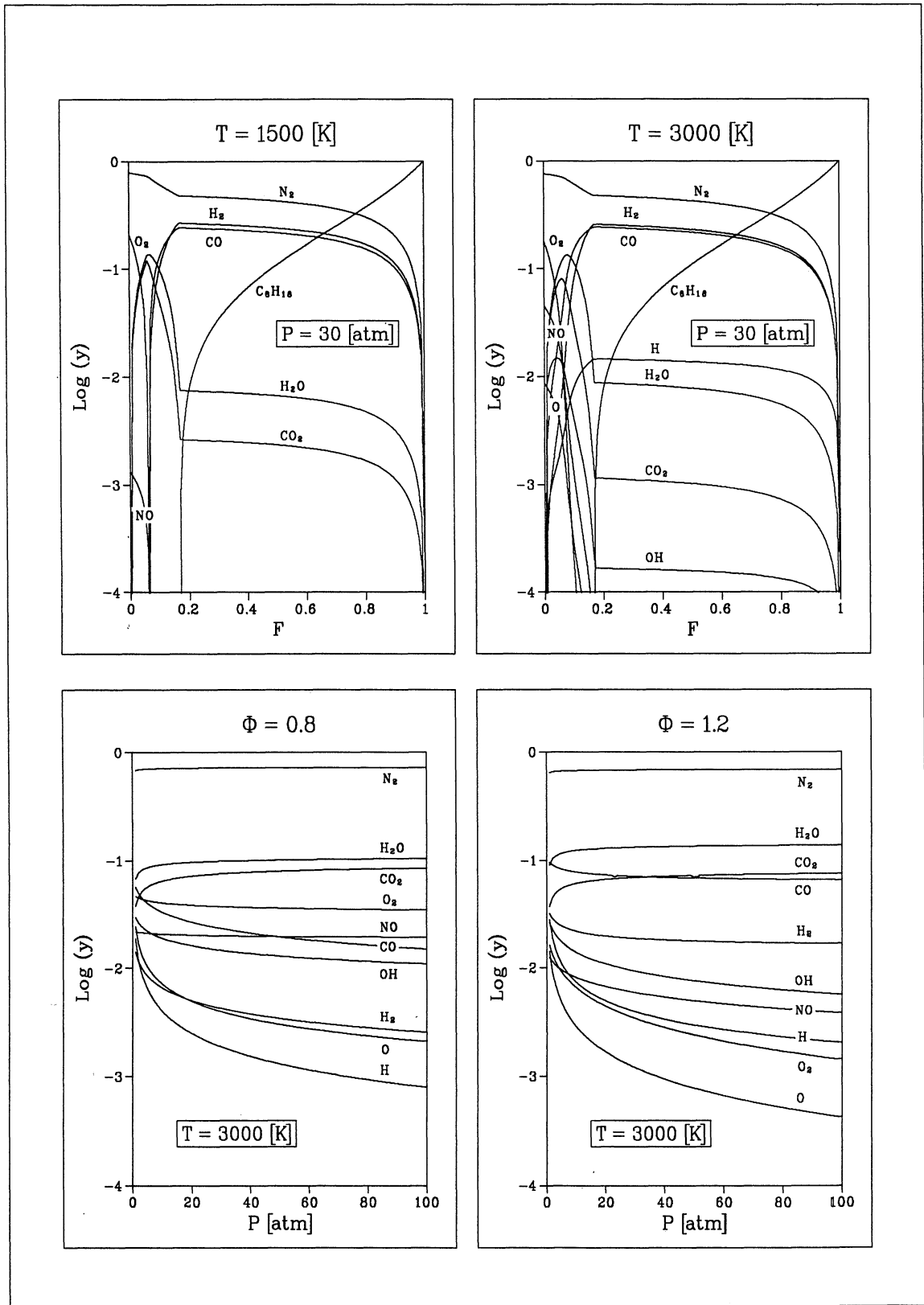


Figure 5: Combustion Product Equilibrium Compositions as Functions of  $F$  and  $P$

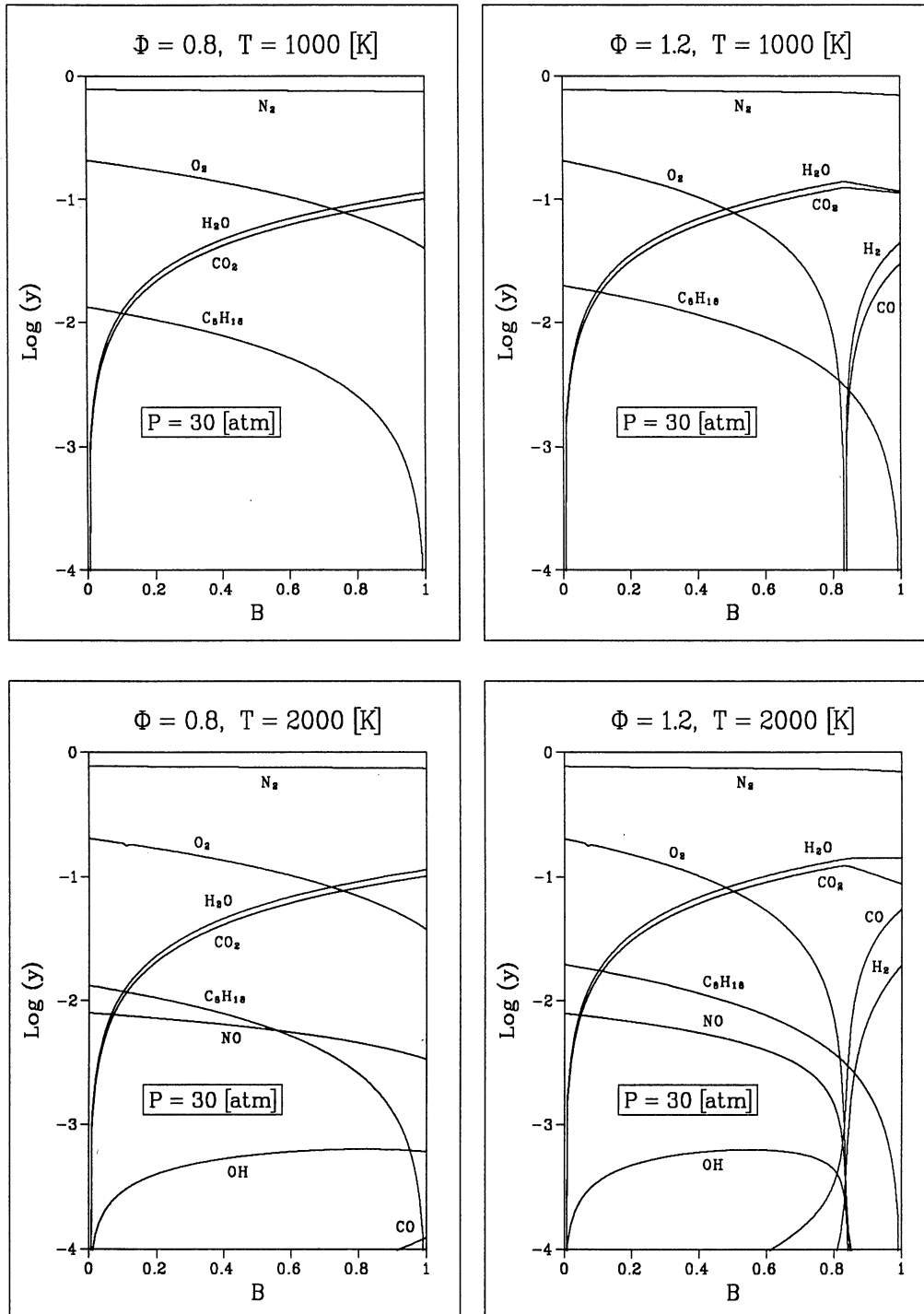


Figure 6: Combustion Product Equilibrium Compositions as Functions of  $B$

$$\begin{aligned}
\frac{\partial C_1}{\partial T} &= \frac{dK_6}{dT} P^{\frac{1}{2}} & \frac{\partial C_1}{\partial P} &= \frac{1}{2} \frac{C_1}{P} \\
\frac{\partial C_2}{\partial T} &= \frac{dK_5}{dT} P^{\frac{1}{2}} & \frac{\partial C_2}{\partial P} &= \frac{1}{2} \frac{C_2}{P} \\
\frac{\partial C_3}{\partial T} &= \frac{dK_4}{dT} & \frac{\partial C_3}{\partial P} &= 0 \\
\frac{\partial C_4}{\partial T} &= \frac{dK_3}{dT} & \frac{\partial C_4}{\partial P} &= 0 \\
\frac{\partial C_5}{\partial T} &= \frac{dK_2}{dT} P^{-\frac{1}{2}} & \frac{\partial C_5}{\partial P} &= -\frac{1}{2} \frac{C_5}{P} \\
\frac{\partial C_6}{\partial T} &= \frac{dK_1}{dT} P^{-\frac{1}{2}} & \frac{\partial C_6}{\partial P} &= -\frac{1}{2} \frac{C_6}{P}
\end{aligned} \tag{63}$$

where

$$\frac{dK_i}{dT} = 2.302585 K_i \left( \frac{A_i}{T} - \frac{B_i}{T^2} + D_i + 2E_i T \right) \tag{64}$$

The remaining derivatives can be obtained in terms of the independent ones

$$\begin{aligned}
\frac{\partial y_1}{\partial T} &= \frac{y_1}{C_1} \left( \frac{\partial C_1}{\partial T} \right) + D_{13} \left( \frac{\partial y_3}{\partial T} \right) + D_{15} \left( \frac{\partial y_5}{\partial T} \right) & \frac{\partial y_1}{\partial P} &= \frac{y_1}{C_1} \left( \frac{\partial C_1}{\partial P} \right) + D_{13} \left( \frac{\partial y_3}{\partial P} \right) + D_{15} \left( \frac{\partial y_5}{\partial P} \right) \\
\frac{\partial y_2}{\partial T} &= \frac{y_2}{C_2} \left( \frac{\partial C_2}{\partial T} \right) + D_{24} \left( \frac{\partial y_4}{\partial T} \right) + D_{25} \left( \frac{\partial y_5}{\partial T} \right) & \frac{\partial y_2}{\partial P} &= \frac{y_2}{C_2} \left( \frac{\partial C_2}{\partial P} \right) + D_{24} \left( \frac{\partial y_4}{\partial P} \right) + D_{25} \left( \frac{\partial y_5}{\partial P} \right) \\
\frac{\partial y_7}{\partial T} &= \frac{y_7}{C_3} \left( \frac{\partial C_3}{\partial T} \right) + D_{74} \left( \frac{\partial y_4}{\partial T} \right) + D_{75} \left( \frac{\partial y_5}{\partial T} \right) & \frac{\partial y_7}{\partial P} &= D_{74} \left( \frac{\partial y_4}{\partial P} \right) + D_{75} \left( \frac{\partial y_5}{\partial P} \right) \\
\frac{\partial y_8}{\partial T} &= \frac{y_8}{C_4} \left( \frac{\partial C_4}{\partial T} \right) + D_{86} \left( \frac{\partial y_6}{\partial T} \right) + D_{85} \left( \frac{\partial y_5}{\partial T} \right) & \frac{\partial y_8}{\partial P} &= D_{86} \left( \frac{\partial y_6}{\partial P} \right) + D_{85} \left( \frac{\partial y_5}{\partial P} \right) \\
\frac{\partial y_9}{\partial T} &= \frac{y_9}{C_5} \left( \frac{\partial C_5}{\partial T} \right) + D_{95} \left( \frac{\partial y_5}{\partial T} \right) & \frac{\partial y_9}{\partial P} &= \frac{y_9}{C_5} \left( \frac{\partial C_5}{\partial P} \right) + D_{95} \left( \frac{\partial y_5}{\partial P} \right) \\
\frac{\partial y_{10}}{\partial T} &= \frac{y_{10}}{C_6} \left( \frac{\partial C_6}{\partial T} \right) + D_{104} \left( \frac{\partial y_4}{\partial T} \right) & \frac{\partial y_{10}}{\partial P} &= \frac{y_{10}}{C_6} \left( \frac{\partial C_6}{\partial P} \right) + D_{104} \left( \frac{\partial y_4}{\partial P} \right)
\end{aligned} \tag{65}$$

### 3.4 Partial derivatives of composition with respect to $\phi$ and $B$ at high temperature

The partial derivatives of the mole fractions with respect to  $\phi$  and  $B$  are similar, except with  $\partial/\partial\phi, \partial/\partial B$  replacing  $\partial/\partial T, \partial/\partial P$ . Noticing only the parameter  $D$  is a function of  $\phi$  but none of  $C_i$  is, the expressions are therefore much simpler

$$\begin{aligned}
\frac{\partial f_1}{\partial \phi} &= 0 \\
\frac{\partial f_2}{\partial \phi} &= \left(\frac{\partial D}{\partial \phi}\right)[W(2y_1 + y_2 + y_3 + 2y_5 + y_7 + y_8 + y_9) - Z(2y_6 + Y_8)] \\
\frac{\partial f_3}{\partial \phi} &= \left(\frac{\partial D}{\partial \phi}\right)[W(y_1 + y_3) - X(2y_6 + y_8)] \\
\frac{\partial f_4}{\partial \phi} &= \left(\frac{\partial B}{\partial \phi}\right)(-y_1 - y_3 - Xy_{11})
\end{aligned} \tag{66}$$

$$\begin{aligned}
\frac{\partial f_1}{\partial B} &= 0 \\
\frac{\partial f_2}{\partial B} &= \left(\frac{\partial D}{\partial B}\right)[W(2y_1 + y_2 + y_3 + 2y_5 + y_7 + y_8 + y_9) - Z(2y_6 + Y_8)] \\
\frac{\partial f_3}{\partial B} &= \left(\frac{\partial D}{\partial B}\right)[W(y_1 + y_3) - X(2y_6 + y_8)] \\
\frac{\partial f_4}{\partial B} &= -y_1 - y_3 - Xy_{11}
\end{aligned}$$

where

$$\frac{\partial D}{\partial \phi} = \epsilon(B + \phi \frac{\partial B}{\partial \phi}); \quad \frac{\partial D}{\partial B} = \epsilon\phi \tag{67}$$

and the partial derivative  $\frac{\partial B}{\partial \phi}$  is given in equation 25, where the equivalence ratio limit  $\phi_{max}$  is set to be approximately equal to 3 to prevent the presence of negative mole fractions.

The other partial derivatives of mole fractions are

$$\begin{aligned}
\frac{\partial y_1}{\partial \phi} &= D_{13}\left(\frac{\partial y_3}{\partial \phi}\right) + D_{15}\left(\frac{\partial y_5}{\partial \phi}\right) & \frac{\partial y_1}{\partial B} &= D_{13}\left(\frac{\partial y_3}{\partial B}\right) + D_{15}\left(\frac{\partial y_5}{\partial B}\right) \\
\frac{\partial y_2}{\partial \phi} &= D_{24}\left(\frac{\partial y_4}{\partial \phi}\right) + D_{25}\left(\frac{\partial y_5}{\partial \phi}\right) & \frac{\partial y_2}{\partial B} &= D_{24}\left(\frac{\partial y_4}{\partial B}\right) + D_{25}\left(\frac{\partial y_5}{\partial B}\right) \\
\frac{\partial y_7}{\partial \phi} &= D_{74}\left(\frac{\partial y_4}{\partial \phi}\right) + D_{75}\left(\frac{\partial y_5}{\partial \phi}\right) & \frac{\partial y_7}{\partial B} &= D_{74}\left(\frac{\partial y_4}{\partial B}\right) + D_{75}\left(\frac{\partial y_5}{\partial B}\right) \\
\frac{\partial y_8}{\partial \phi} &= D_{86}\left(\frac{\partial y_6}{\partial \phi}\right) + D_{85}\left(\frac{\partial y_5}{\partial \phi}\right) & \frac{\partial y_8}{\partial B} &= D_{86}\left(\frac{\partial y_6}{\partial B}\right) + D_{85}\left(\frac{\partial y_5}{\partial B}\right) \\
\frac{\partial y_9}{\partial \phi} &= D_{95}\left(\frac{\partial y_5}{\partial \phi}\right) & \frac{\partial y_9}{\partial B} &= D_{95}\left(\frac{\partial y_5}{\partial B}\right) \\
\frac{\partial y_{10}}{\partial \phi} &= D_{104}\left(\frac{\partial y_4}{\partial \phi}\right) & \frac{\partial y_{10}}{\partial B} &= D_{104}\left(\frac{\partial y_4}{\partial B}\right)
\end{aligned} \tag{68}$$

### 3.5 Basic thermodynamic properties at high temperature

The required thermodynamic properties in engine combustion simulations are

$$R = \frac{\bar{R}}{M} \quad [\text{kJ/kg.K}] \tag{69}$$

$$h = \frac{1}{M} \sum (y_i \bar{h}_i) \quad [\text{kJ/kg}] \tag{70}$$

$$s = \frac{1}{M} \sum (y_i \bar{s}_i) \quad [\text{kJ/kg K}] \quad (71)$$

The equivalent molecular weight  $M$  of the mixture in above equations is

$$M = \sum (y_i M_i) \quad (72)$$

and it has derivatives

$$\frac{\partial M}{\partial \xi} = \sum \left[ \left( \frac{\partial y_i}{\partial \xi} \right) M_i \right] \quad (73)$$

The entropy  $\bar{s}_i$  in equation 71 should include both temperature contribution and pressure contribution under the partial pressure  $P_i = y_i P$  of the species “ $i$ ”.

$$\bar{s}_i = \bar{s}_i^o - \bar{R} \ln \left( \frac{P_i}{P_o} \right) \quad (74)$$

So that equation 71 can be written as

$$s = \frac{1}{M} \sum [y_i (\bar{s}_i^o - \bar{R} \ln y_i)] - R \ln \left( \frac{P}{P_o} \right) \quad (75)$$

### 3.6 Partial derivatives of properties at high temperature

The partial derivatives of properties can be derived from section 3.5 as

$$\frac{1}{R} \frac{\partial R}{\partial \xi} = -\frac{1}{M} \left( \frac{\partial M}{\partial \xi} \right) \quad (76)$$

$$\frac{\partial h}{\partial \xi} = -\frac{h}{M} \left( \frac{\partial M}{\partial \xi} \right) + \frac{1}{M} \sum \left[ \left( \frac{\partial y_i}{\partial \xi} \right) \bar{h}_i + y_i \left( \frac{\partial \bar{h}_i}{\partial \xi} \right) \right] \quad (77)$$

$$\frac{\partial s}{\partial \xi} = -\frac{s}{M} \left( \frac{\partial M}{\partial \xi} \right) + \frac{1}{M} \sum \left[ \left( \frac{\partial y_i}{\partial \xi} \right) (\bar{s}_i^o - \bar{R} \ln y_i) \right] + \frac{1}{M} \sum y_i \left( \frac{\partial \bar{s}_i^o}{\partial \xi} \right) - \frac{R}{P} \left( \frac{\partial P}{\partial \xi} \right) \quad (78)$$

Enthalpy  $\bar{h}_i$  and entropy  $\bar{s}_i^o$  are only functions of  $T$  and they can be found from equation 84 as  $\bar{C}_p$  and  $\frac{\bar{C}_p}{T}$ . Therefore, the last term in equation 77 and the third term in equation 78 will vanish except when  $\xi = T$ . The last term in equation 78 is finite only when  $\xi = P$ .



### 3.7 Relations between $F$ and $\phi$

The representations of the fuel mass fraction  $F$  and the equivalence ratio  $\phi$  are exchangeable. Their relations can be derived from the definitions

$$F = \frac{m_f}{m_a + m_f}; \quad \phi = \frac{\left(\frac{m_f}{m_a}\right)}{\left(\frac{m_f}{m_a}\right)_o} \quad (79)$$

A simple manipulation gives

$$\phi = \frac{\frac{F}{1-F}}{\frac{F_o}{1-F_o}} \quad (80)$$

and

$$F = \frac{F_o\phi}{(1-F_o) + F_o\phi} \quad (81)$$

where  $F_o$  is the stoichiometric fuel mass fraction

$$F_o = \frac{\epsilon M_f}{\epsilon M_f + M_{O_2} + \psi M_{N_2}} \quad (82)$$

The derivatives have a correlation

$$\frac{\partial}{\partial F} = \left(\frac{1-F_o}{F_o}\right) \frac{1}{(1-F)^2} \frac{\partial}{\partial \phi} \quad (83)$$

## 4 Results and Discussion

The calculated results for properties using the both methods are shown in Figures 7-12.

1. Unlike other available programs which will predict a unrealistic negative species concentration when the equivalence ratio  $\phi > 3$ , the present program is capable of covering the entire fuel mass fraction range  $0 \leq F \leq 1$  ( $0 \leq \phi \leq \infty$ ) at an expense of neglecting the solid carbon formation under fuel rich conditions (Figure 10 and 11). It preserves the original fuel structure in order to simplify the calculation. If one is interested in modeling fuel cracking or soot formation, an additional subroutine is needed to carry out the calculations of corresponding reaction equations. This capability is crucial in stochastic Diesel combustion modeling since we are often confronted with computing the properties of fuel rich elements due to the heterogeneous nature of the combustion process. Suppose a pure air element could always be found to mix with, the sequence of the resulting equivalence ratio from a pure octane fuel element would be  $\phi = \infty, 15.03, 5.01, 2.15, 1.00, \dots$ .

2. The dissociation effects on properties become important starting about  $T = 2000$  [K], (Figure 7, 8) The rapid increases in  $h$  and  $C_P$  are mainly due to the shifting of composition from  $CO_2, H_2O$  to high enthalpy containing radicals, such as  $OH, NO, O, H$  (Figure 4, 13.b). The maximum deviation of the calculated specific heat from the simple routine happens at around  $T = 4000$ [K]. Beyond which, the effect of the decrease of  $CO_2, H_2O$  (Figure 4), which have large specific heats (Figure 13.a), dominates, that is, the decrease of the frozen specific heat dominates, although the concentrations of radicals  $O, H$  still keep increasing. This provides us an opportunity to save some computer time by using the simple routine if one is only interested in energy balance with the exception of near the TDC range where the peak temperature is too high to neglect the dissociation effects. Also, because of the lacking of the initial conditions to start calculation, simulation programs usually run for several cycles using guessed initial conditions until some convergence criteria are reached. The convergence process can be sped up by using the simple routine in pre-convergence cycles.
3. The pressure effects are small compared with effects of the other three independent variables  $T, F, B$ . Increasing the pressure actually reduces the effects of dissociation reactions (Figure 7, 8). It helps in some degree when the simple routine is used in pre-convergence cycle calculations because high gas temperature near the TDC is always associated with the peak pressure. The simple routine is totally independent of pressure since the pressure does not appear in the water-gas reaction equilibrium equation, and all derivatives with respect to pressure therefore vanish in the simple routine.
4. In some range of fuel rich region, increasing the progress variable  $B$  gives an endothermic reaction instead of a exothermic one (Figure 9.b, 11.a). The reason for those phenomena is that the maximum utilization of the oxidizer is allowed in the program. The definition of the  $B$  is the mass fraction of the burned fuel over the total available fuel, and there is no restriction on the available oxidizer. Therefore in a fuel rich case, small  $B$  allows fuel to find more oxidizer and the actual air fuel ratio of the products will be closer to the stoichiometry until the oxidizer is used up. This in turn gives more energy release. As the  $B$  increases, more and more fuel is put into reaction, this will cause a shift of the actual air fuel ratio towards to the richer input value, the reaction will be endothermic. If a totally unmixed model is desirable, such as in SI engine simulations, multizone modeling, the program can be called twice setting  $B = 1$  and  $B = 0$ , then combining the results using the mixing rule according to the fractions of the both burned and unburned gases. The corresponding results are shown in Figure 12.

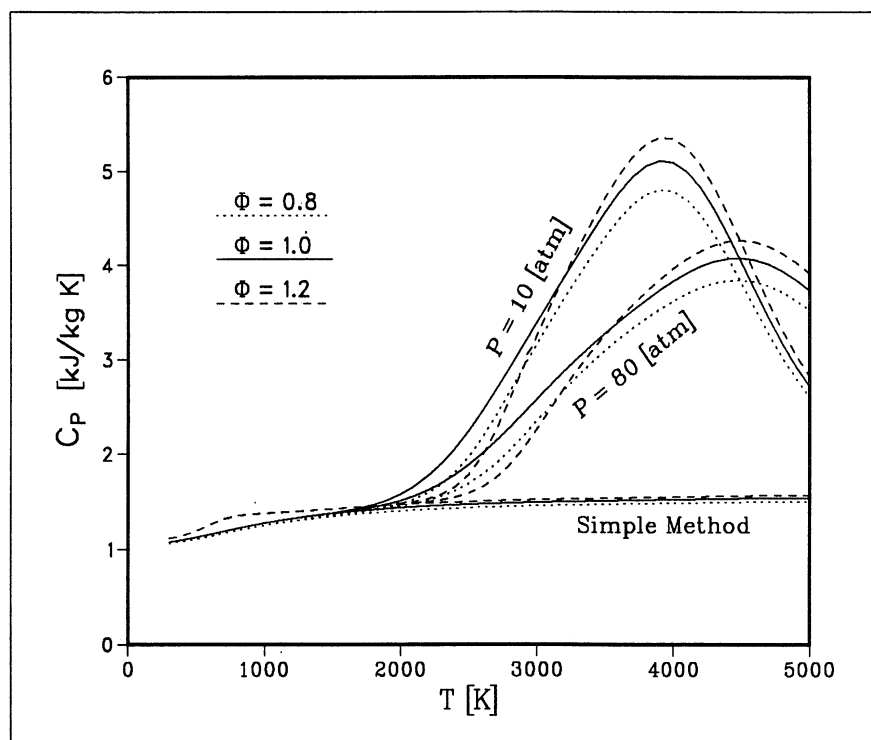
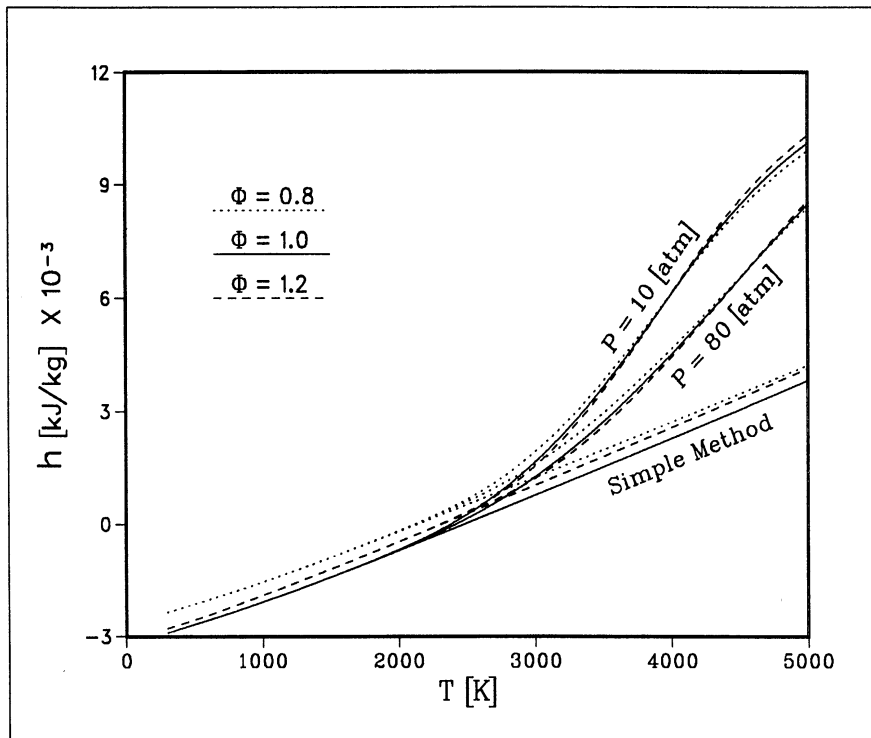


Figure 7: Enthalpies and Specific Heats of Combustion products as Functions of  $T$

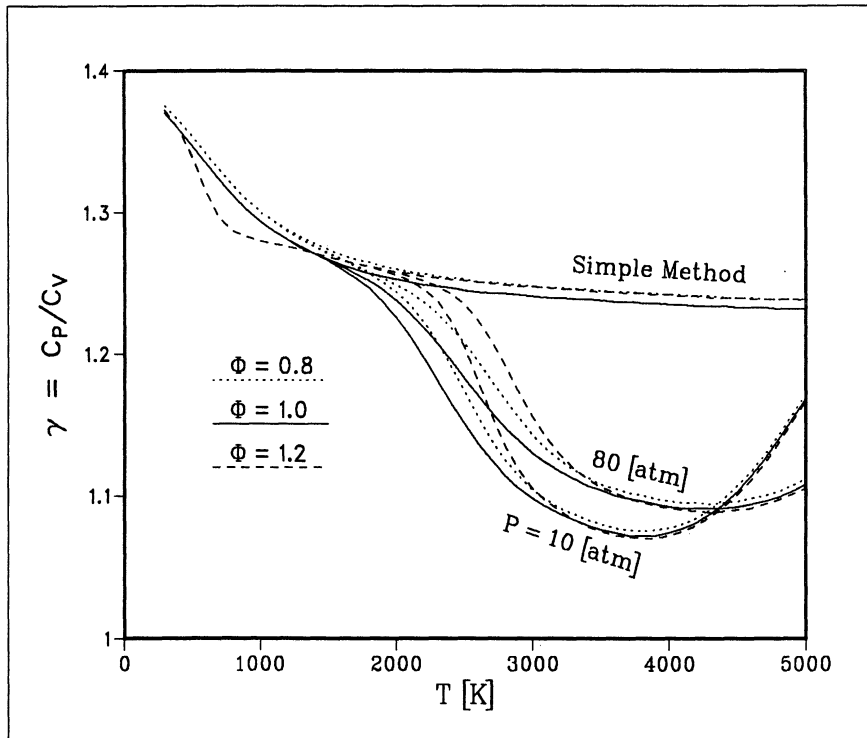
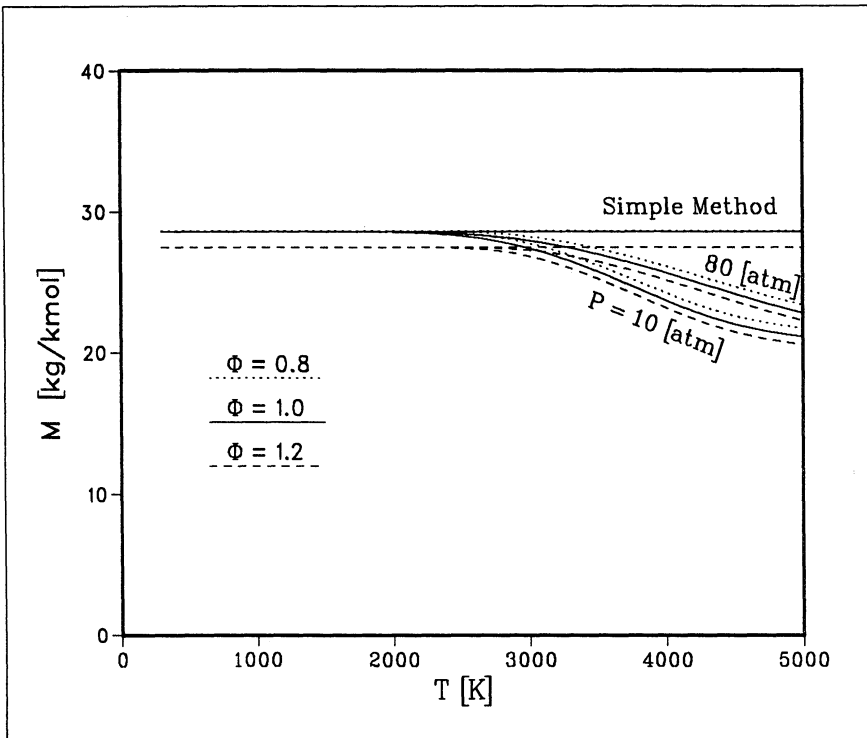


Figure 8:  $M$  and  $\gamma$  as Functions of  $T$  for Combustion Products

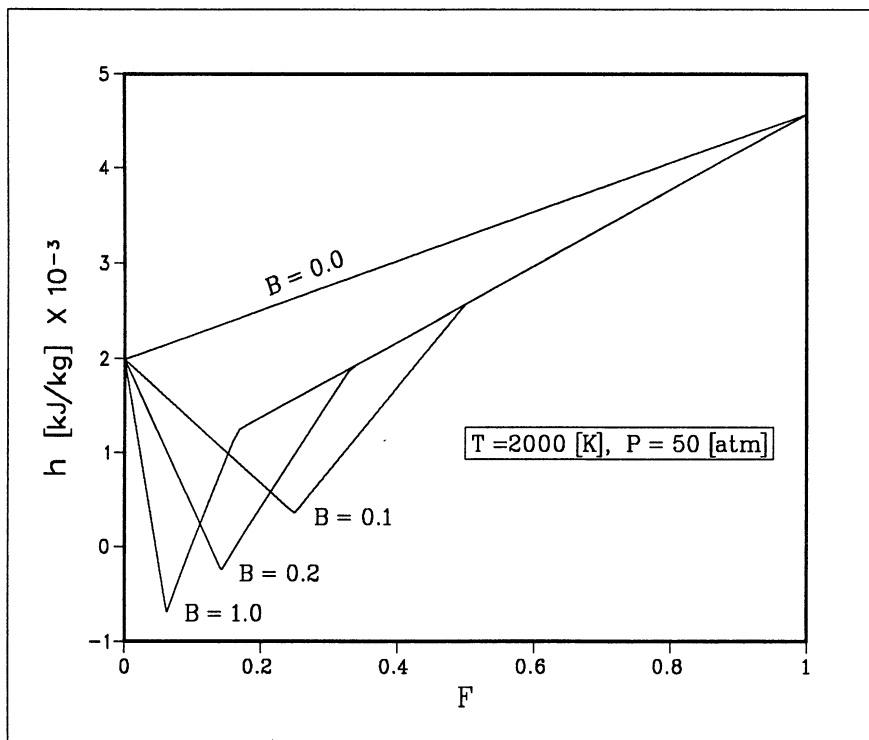
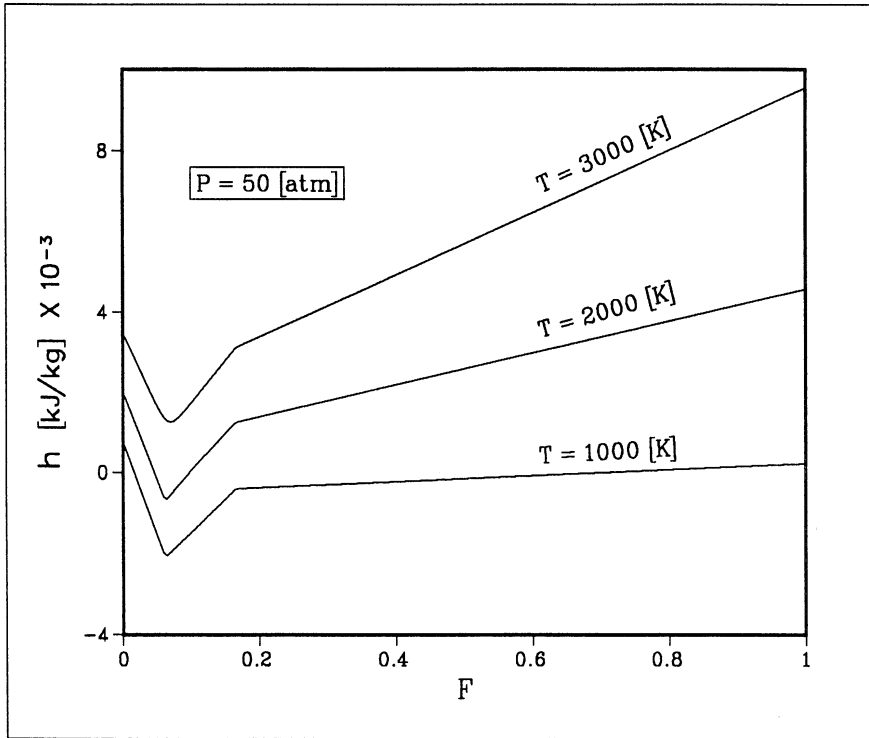


Figure 9:  $h$  as Functions of  $F$  for Combustion products

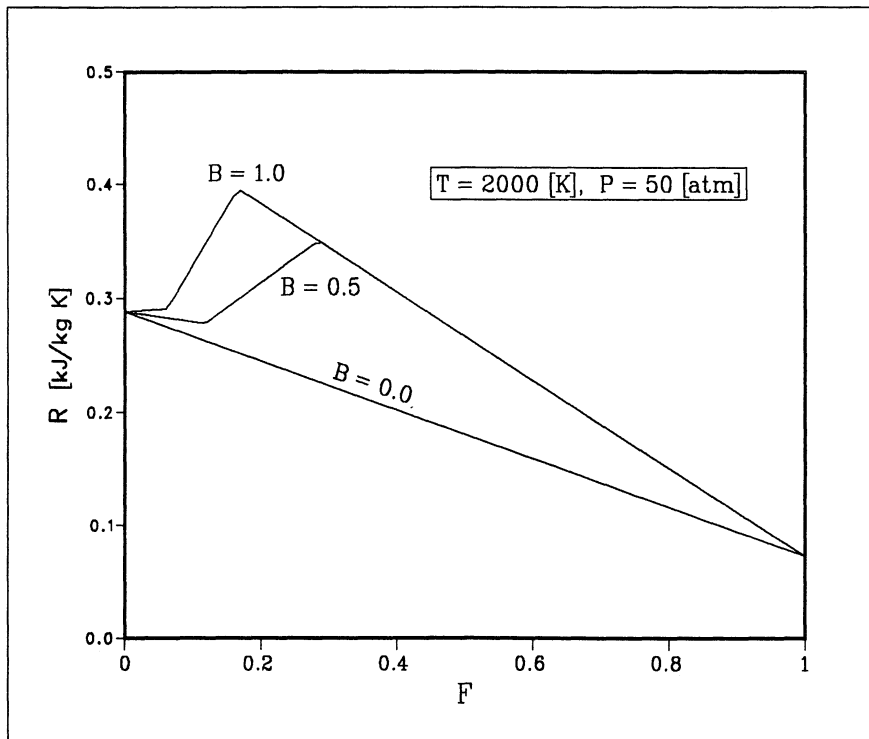
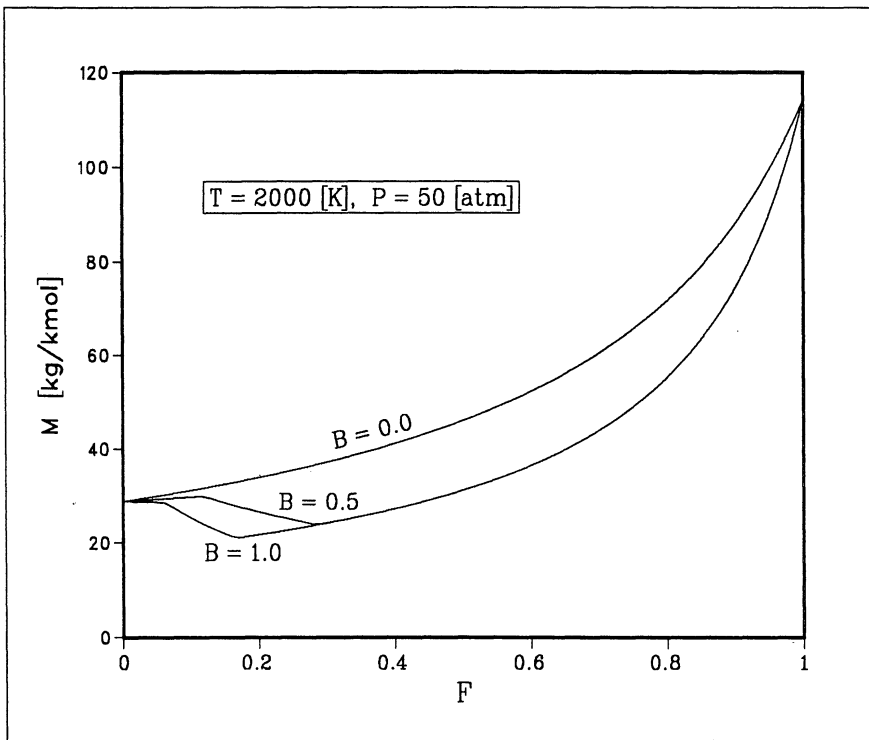


Figure 10:  $M$  and  $R$  as Functions of  $F$  for Combustion products

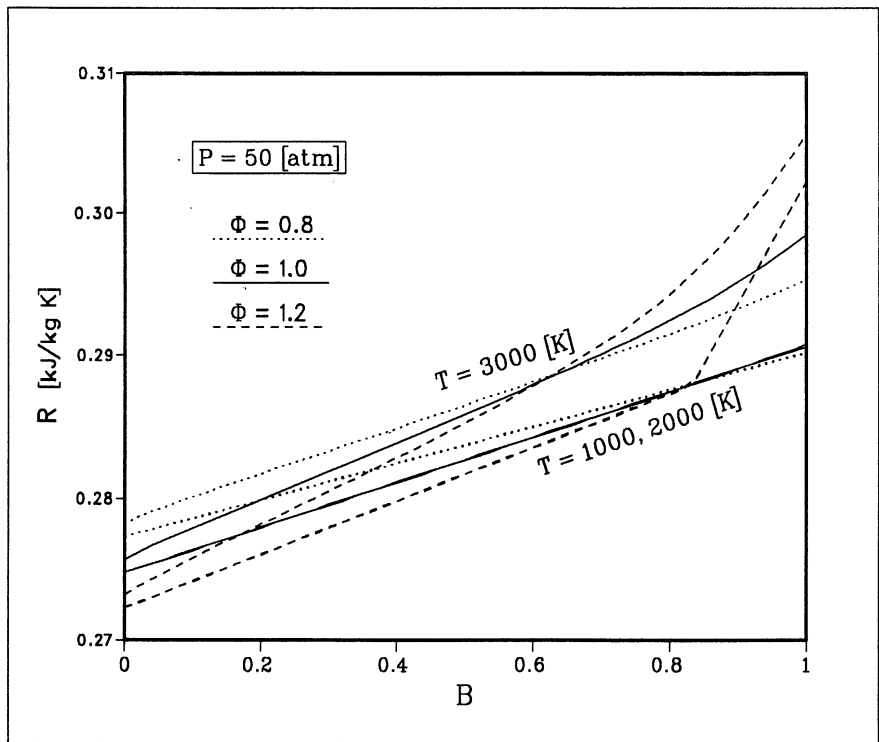
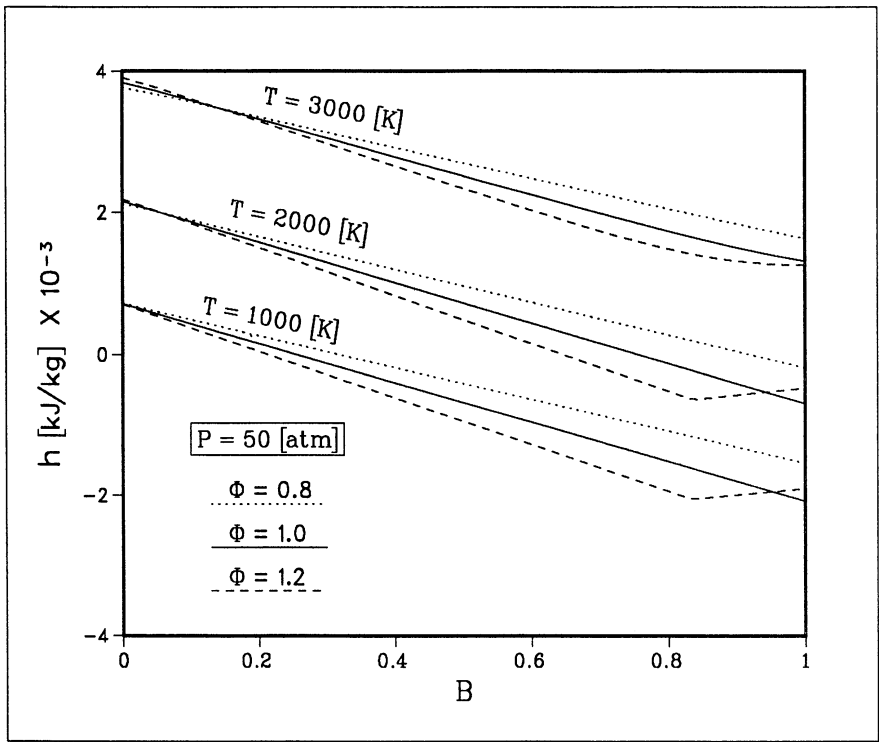


Figure 11:  $h$  and  $R$  as Functions of  $B$

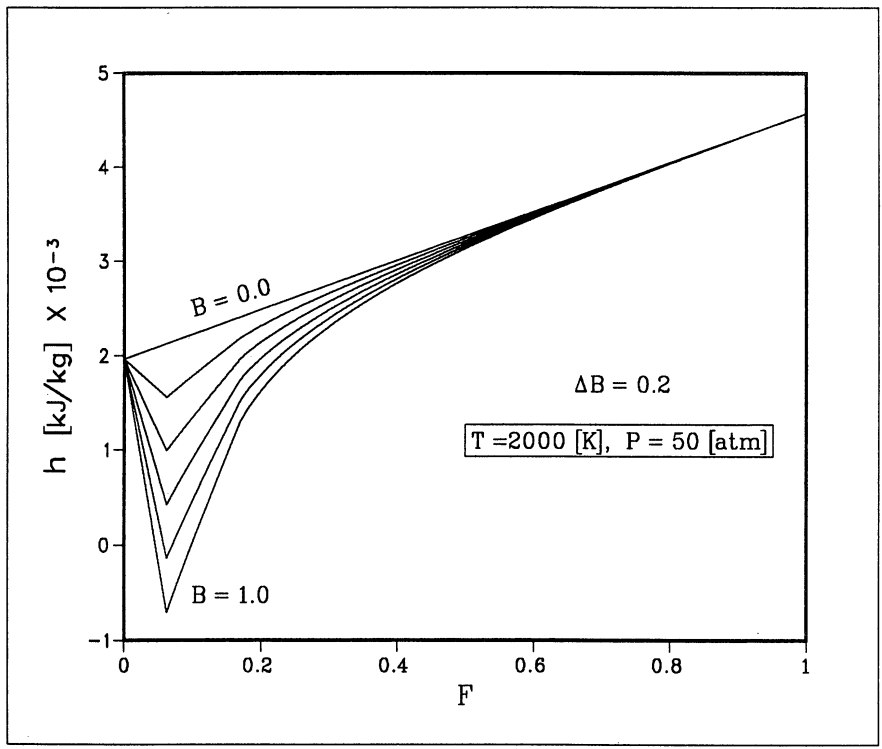
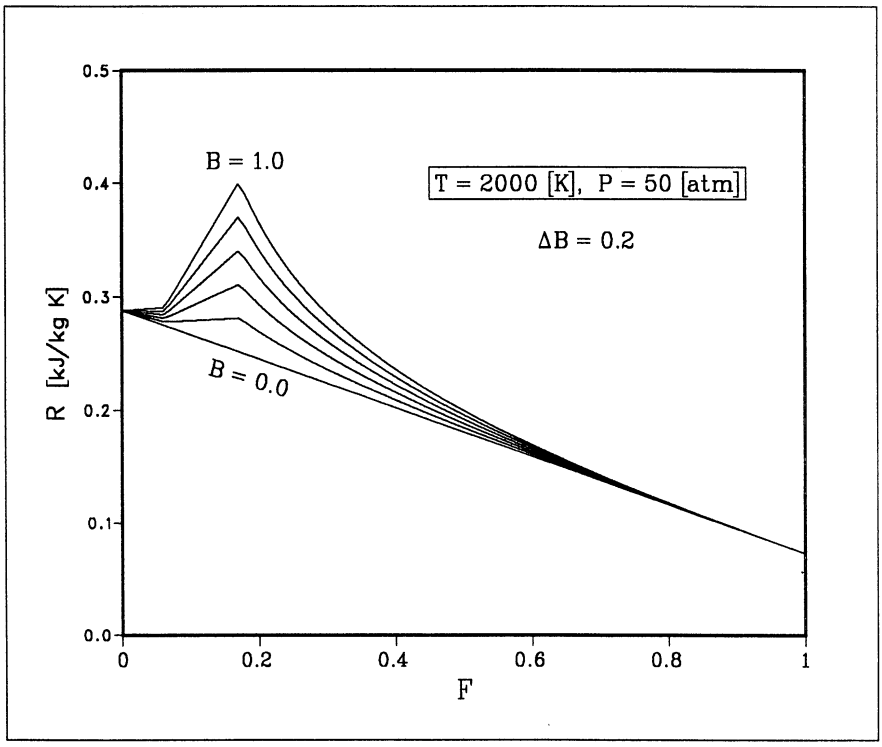


Figure 12: Results of the Unmixed Model



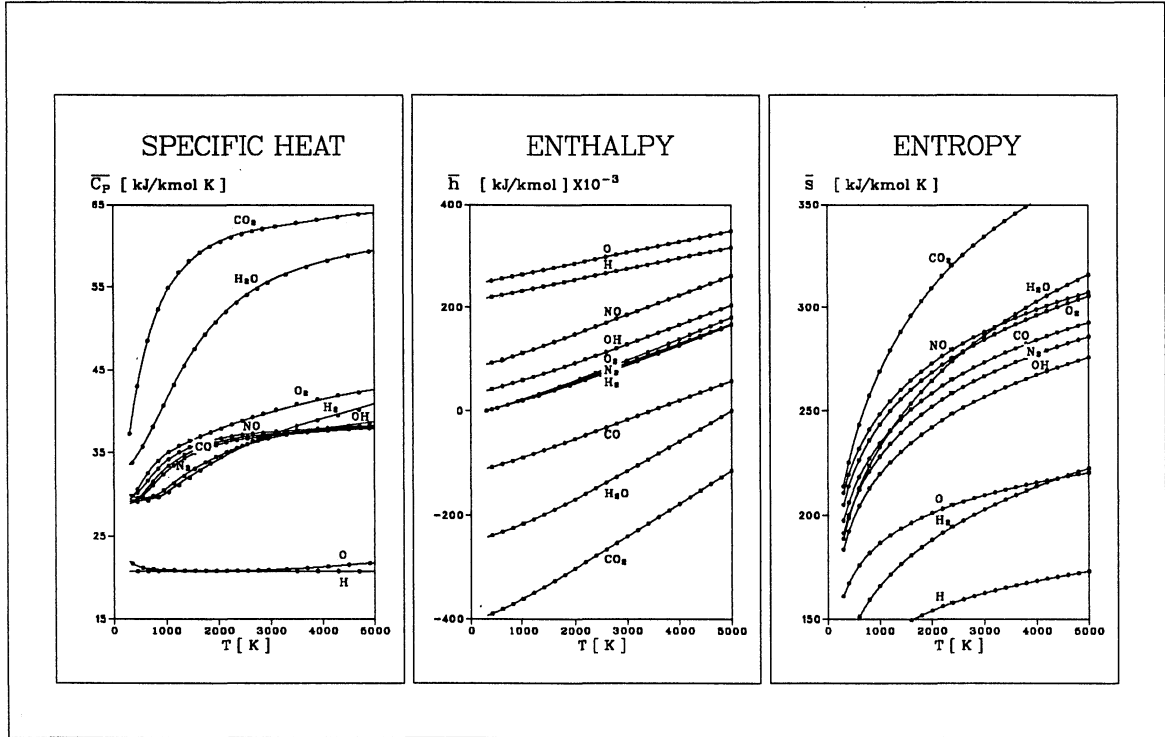


Figure 13: Curve Fitting of the JANAF Table Data

## 5 Thermodynamic Properties for Elements

A simultaneous polynomial fitting of the specific heat  $\bar{C}_p$ , enthalpy  $\bar{h}$  and entropy  $\bar{s}^\circ$  to the JANAF Table [9] data is used to evaluate those thermodynamic properties as functions of temperature at the reference pressure  $P_o = 1$  [atm]. The functions employed are

$$\begin{aligned} \frac{\bar{C}_p}{R} &= a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \\ \frac{\bar{h}}{RT} &= a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T} \\ \frac{\bar{s}^\circ}{R} &= a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \end{aligned} \quad (84)$$

the enthalpy  $\bar{h}$  and entropy  $\bar{s}^\circ$  are related to  $\bar{C}_p$  as

$$\bar{h} = \int \bar{C}_p dT; \quad \bar{s}^\circ = \int \frac{\bar{C}_p}{T} dT$$

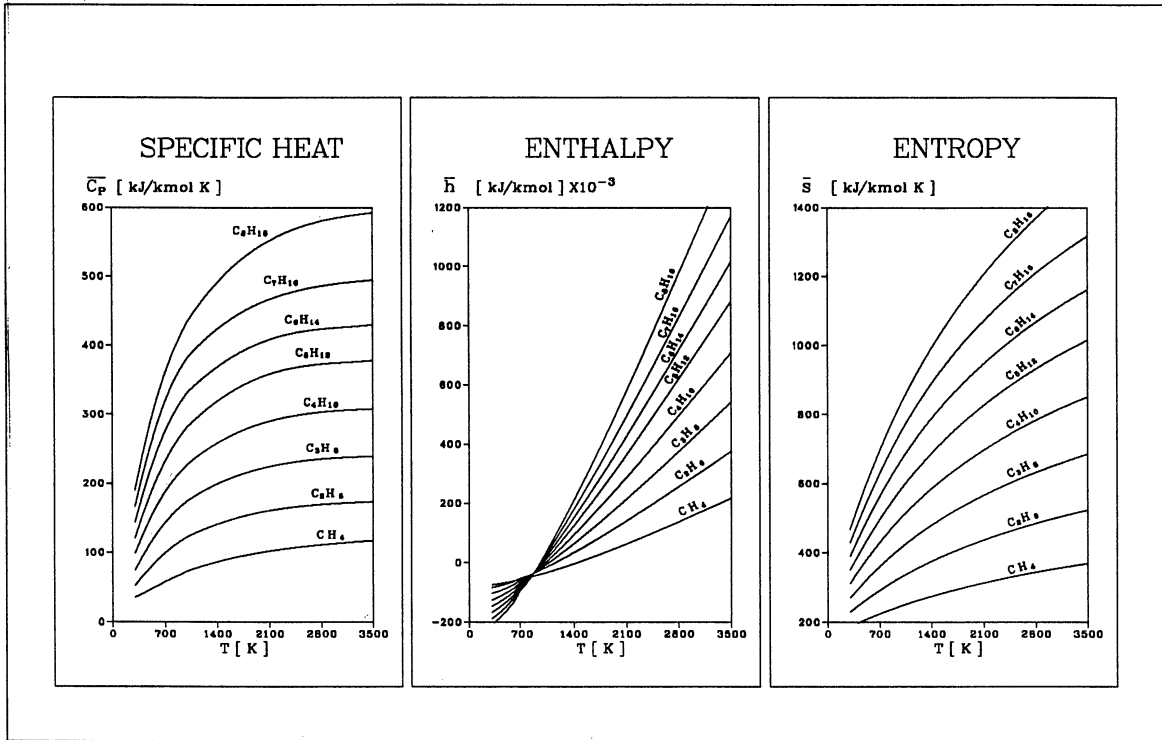


Figure 14: Fuel Thermodynamic Properties

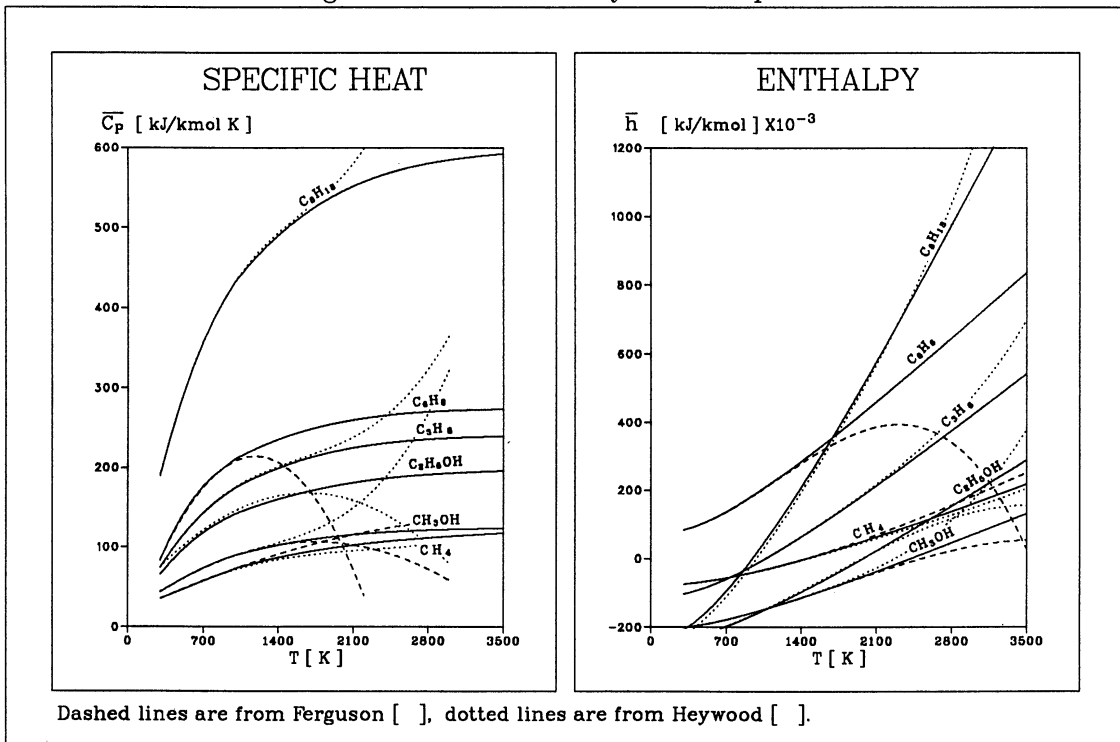


Figure 15: Comparison between Different Polynomials

The coefficients are listed in Tables 5 and 6. There are two sets of coefficients to cover both low temperature range (300–1000[K]) and high temperature range (1000–5000[K]) because it was found long ago that the thermal properties tend to have characteristic knees around 1000 [K]. Thus a single polynomial fit may not give a good reproduction of the original data, the pinned polynomials used here give relative low deviations. The results of the fitting are shown in the Figure 13.

Other alternate polynomials for fuel properties are found in Ferguson [3] or Heywood [6]. Since most thermodynamic data tables cover temperature ranges too low for combustion calculations, those polynomials, when extrapolated to higher temperatures, will give improper results, especially for  $\overline{C}_p$  curves (see Figure 15). To overcome this inconvenience, the coefficients in the Table 6 were calculated using the Woihoit's method [13] which forces  $\overline{C}_p$  curves to approach asymptotically the correct classical upper values at  $T_\infty$ .

## 6 Transport Properties

A simple approach for computing transport properties for working fluids is assume that they can be represented by the values for air. Approximate correlations fitted to air data could be used

$$\mu = 1.468 \times 10^{-6} \frac{T^{1.5}}{T + 110.4} \quad [\text{Pa s}] \quad (85)$$

$$\lambda = 3.65 \times 10^{-7} T^{0.748} \quad \left[\frac{\text{kW}}{\text{m K}}\right] \quad (86)$$

The principal advantage of these correlations is computation speed. For such approximations the properties vary as function of temperature only, but not vary with gas composition and pressure. The measured property dependence can only be explained by more sophisticated models.

A more rigorous treatment of gas transport properties based on more realistic intermolecular potential energy models can be found in Hirschfelder *et al.* [8], which also presents methods for computing the transport properties of mixtures of gases. The procedures used in our program to compute the transport properties are basically based on those techniques.

According to the Chapman-Enskog theory [1], the viscosity and thermal conductivity of a pure monatomic gas may be written as

$$\mu_i = 2.6693 \times 10^{-6} \frac{\sqrt{TM_i}}{\sigma_i^2 \Omega_i} \quad [\text{Pa s}] \quad (87)$$

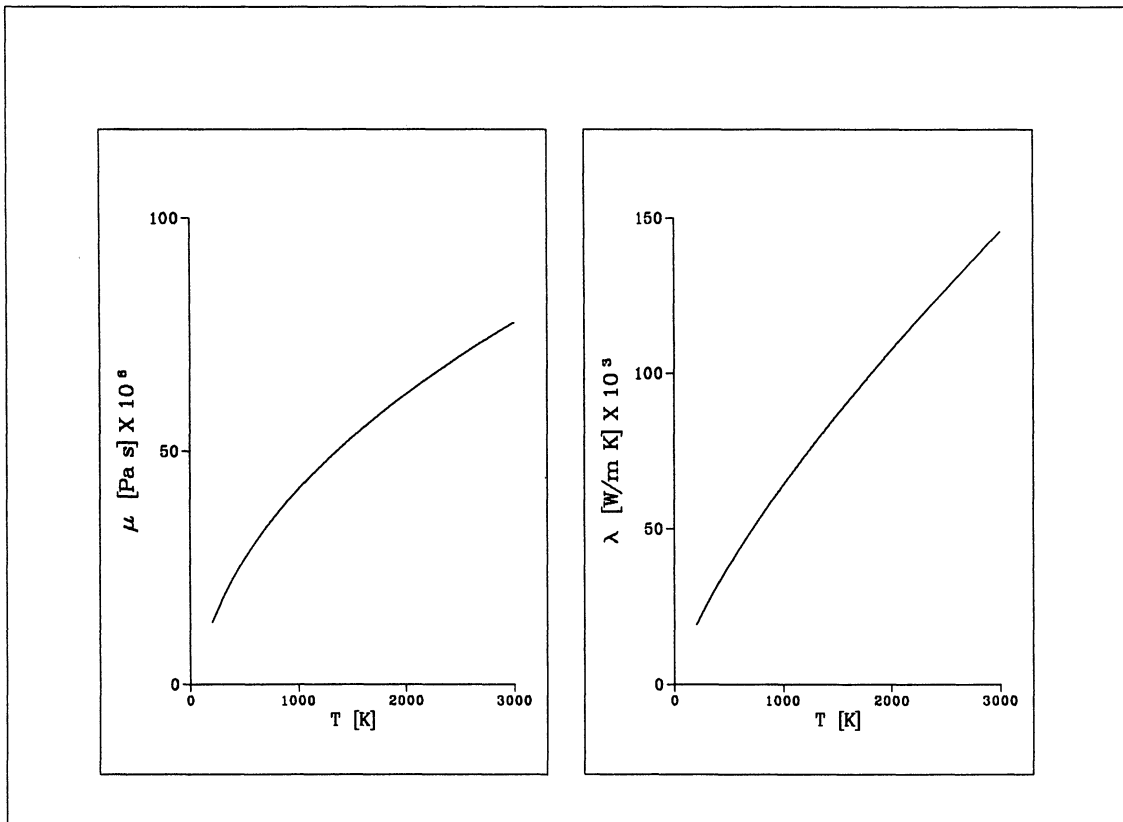


Figure 16: Transport Properties of Air

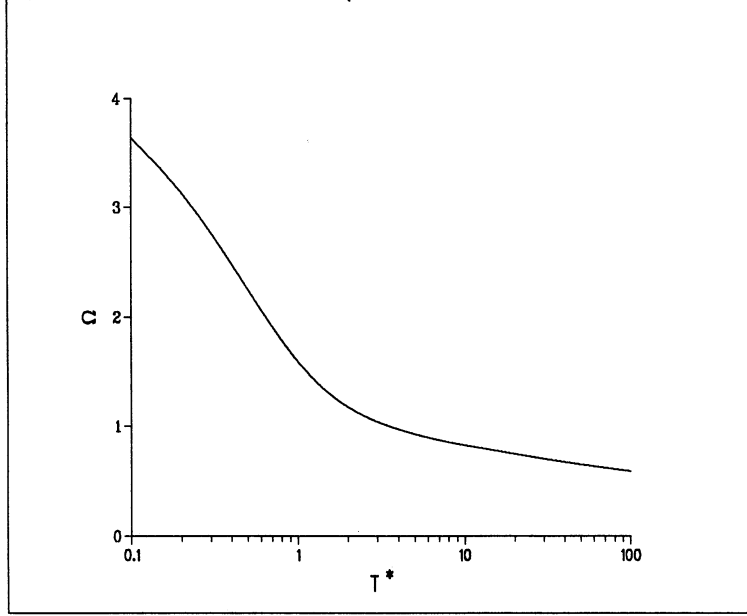


Figure 17: Integral Function for Transport Properties

$$\lambda_i = 8.3224 \times 10^{-5} \frac{\sqrt{T/M_i}}{\sigma_i^2 \Omega_i} \quad \left[ \frac{\text{kW}}{\text{m K}} \right] \quad (88)$$

where  $M$  is the molecular weight,  $\sigma$  is the molecular diameter in [ $\text{\AA}$ ], and  $\Omega$  is the dimensionless integral of order unity dependent on the details of the force interaction during a collision. For the Lennard-Jones interaction, which assumes the potential energy  $\phi$  is a function of the distance  $r$  separating two molecules,  $\phi_i = 4 \epsilon_i [(\frac{\sigma_i}{r})^{12} - (\frac{\sigma_i}{r})^6]$ , the integral function is given by Hattikudur [5] and may be curve fitted as

$$\Omega_i = 1.155T_i^{*-0.1462} + 0.3945e^{-0.6672T_i^*} + 2.05e^{-2.168T_i^*} \quad (89)$$

where  $T^*$  is a dimensionless temperature scaled by the Boltzmann's constant  $k$  and the maximum energy of interaction during the collision  $\epsilon$

$$T_i^* = \frac{kT}{\epsilon_i} \quad (90)$$

A partial list of the interaction parameters is given in Table 8. When values of  $\sigma$  and  $\epsilon$  are not known, they may be estimated from the properties of the fluid at the critical point

$$\frac{\epsilon}{k} \approx 0.77T_c; \quad \sigma \approx 8.41\bar{v}_c^{\frac{1}{3}} \approx 113.75\left(\frac{T_c}{P_c}\right)^{\frac{1}{3}}$$

From equation 87 and 88, the monatomic gas relation between  $\lambda$  and  $\mu$  is

$$\lambda_i = \frac{15}{4} R_i \mu_i = \frac{5}{2} C_{v_i} \mu_i \quad (91)$$

Although the viscosity formula was derived for monatomic gases, measurements show it is remarkably good for polyatomic gases as well. The thermal conductivity model does not take into account the vibrational and rotational energy exchange in collisions between polyatomic molecules which contribute to energy transport in gases of interest in engines. Comparisons with experimental data show some discrepancy for polyatomic gases. Eucken [2] proposed an empirical correction expression

$$\lambda_i = (C_{p_i} + \frac{5}{4} R_i) \mu_i \quad (92)$$

The monatomic formula is a special case of equation 92 because  $C_p = \frac{5}{2} R$  for monatomic gases. Equation 92 also gives a simple method of estimating the Prandtl number

$$\text{Pr} = \frac{C_p \mu}{\lambda} = \frac{C_p}{C_p + 1.25 R} \quad (93)$$

which is in good agreement for monatomic and diatomic gases but less satisfactory for more complex gases.

A semiempirical formula for the viscosity of a multicomponent gas mixture was proposed by Wilke [14]

$$\mu \approx \sum_{i=1}^n \frac{y_i \mu_i}{\sum_{j=1}^n y_j \Phi_{ij}}; \quad \lambda \approx \sum_{i=1}^n \frac{y_i \lambda_i}{\sum_{j=1}^n y_j \Phi_{ij}} \quad (94)$$

in which

$$\Phi_{ij} = \frac{[1 + (\frac{\mu_i}{\mu_j})^{\frac{1}{2}} (\frac{M_j}{M_i})^{\frac{1}{4}}]^2}{2\sqrt{2}(1 + \frac{M_i}{M_j})^{\frac{1}{2}}} \quad (95)$$

In the case of reacting mixtures, that are mixtures in which, compositions shift with temperature and pressure, as opposed to frozen mixtures, there is also a contribution due to the dissociation and recombination as molecules fluctuate back and forth in the temperature gradient driving the heat flux. In order to take into account this effect following approximation could be used

$$\lambda_e = \lambda \frac{C_p}{C_{p_f}} \quad (96)$$

where  $C_p$  is the equilibrium specific heat and  $C_{p_f}$  is the frozen specific heat. The results are given in Figures 18 and 19.

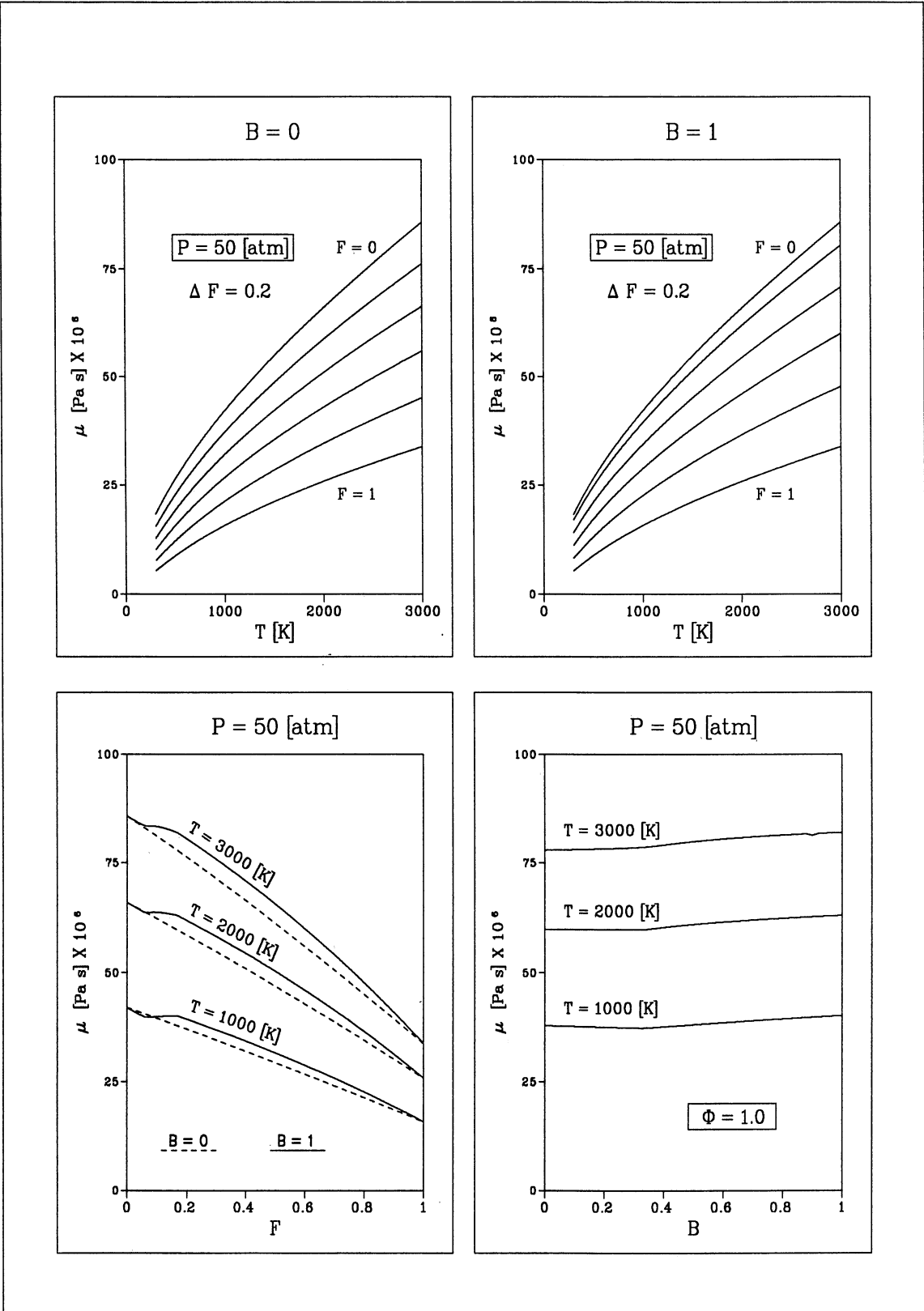


Figure 18: Calculated Viscosity

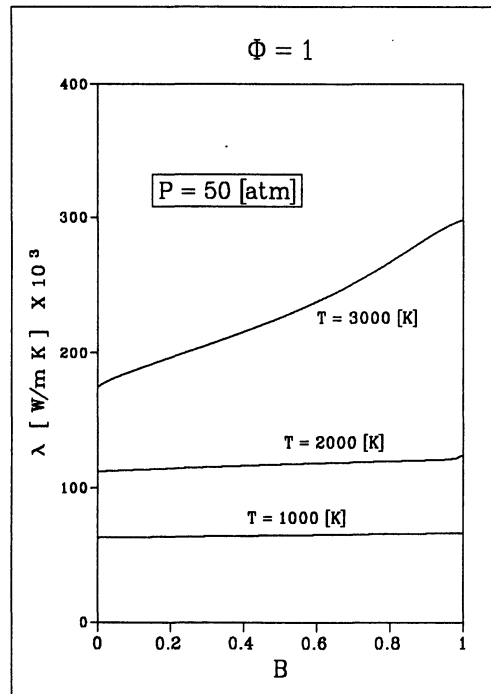
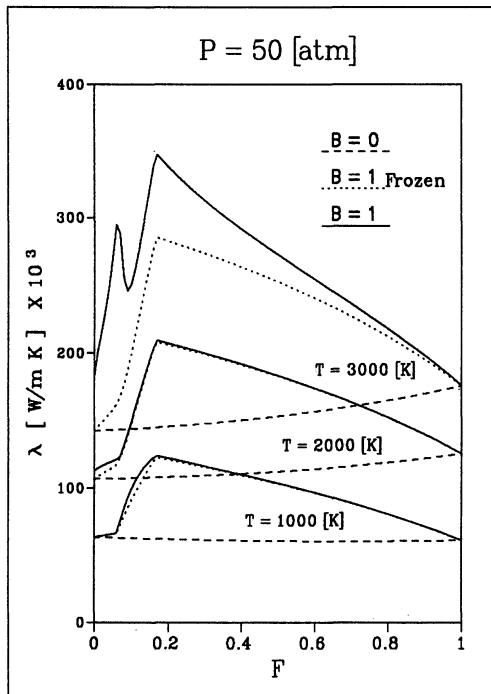
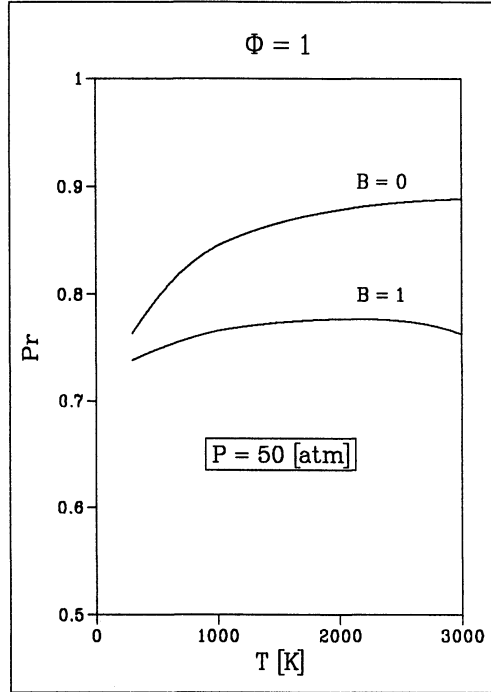
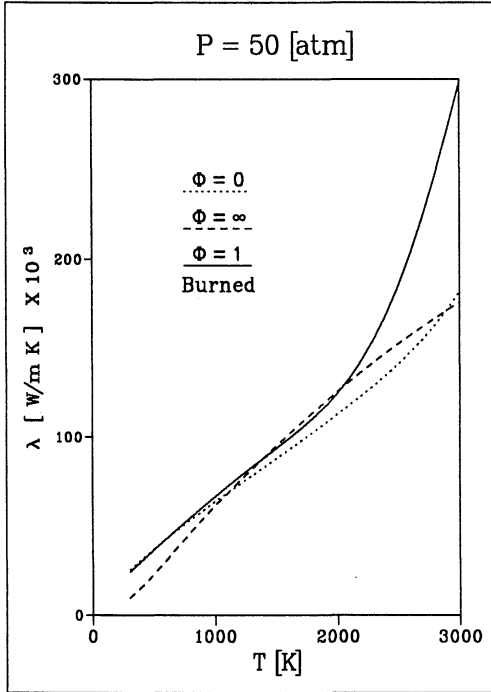


Figure 19: Calculated Thermal Conductivity



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## A APPENDIX: COEFFICIENTS



Temperature Range $300 \leq T \leq 1000$ [ K ]					
	$a_3$	$a_4$	$a_5$	$a_6$	$a_7$
2	.83465E-05	-.48251E-08	.83841E-13	-.10027E+05	.44047E+01
1	.57805E-05	-.12578E-07	.45863E-11	-.11239E+05	.14432E+02
1	.54314E-05	-.21260E-07	.92433E-11	-.13955E+05	.19355E+02
1	.81007E-05	-.29215E-07	.12673E-10	-.17126E+05	.18349E+02
1	.12532E-04	-.37015E-07	.15256E-10	-.20038E+05	.18773E+02
1	.12596E-04	-.44284E-07	.18722E-10	-.22927E+05	.20881E+02
1	.21813E-04	-.54234E-07	.20809E-10	-.26003E+05	.17509E+02
1	.13469E-04	-.58321E-07	.26347E-10	-.28873E+05	.21120E+02
2	.71701E-05	-.87932E-08	.23906E-11	-.25353E+05	.11233E+02
1	.32672E-05	-.16375E-07	.73522E-11	-.29674E+05	.18271E+02
1	-.21823E-05	-.34845E-07	.18421E-10	.89179E+04	.37036E+02
Temperature Range $1000 \leq T \leq 5000$ [ K ]					
	$a_3$	$a_4$	$a_5$	$a_6$	$a_7$
2	-.27888E-05	.40232E-09	-.20206E-13	-.10162E+05	.75069E+01
1	-.45573E-05	.67250E-09	-.35982E-13	-.12718E+05	-.52395E+01
1	-.62839E-05	.91794E-09	-.48124E-13	-.16465E+05	-.17844E+02
1	-.78760E-05	.11502E-08	-.60251E-13	-.20519E+05	-.32140E+02
1	-.35333E-05	-.57422E-09	.15159E-12	-.25537E+05	-.63729E+02
1	-.35307E-05	-.54662E-09	.14789E-12	-.30738E+05	-.95832E+02
1	-.11120E-04	.17132E-08	-.96212E-13	-.33679E+05	-.94335E+02
1	-.12878E-04	.17911E-08	-.88109E-13	-.36113E+05	-.89323E+02
2	-.30503E-05	.43588E-09	-.22247E-13	-.26158E+05	.23782E+01
1	-.35144E-05	.42572E-09	-.15468E-13	-.31944E+05	-.16427E+02
1	-.65489E-05	.98388E-09	-.53417E-13	.40879E+04	-.43938E+02

Coefficients for Fuel Thermodynamic Properties

<i>i</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
$K_1$	.432168E+00	-.112464E+05	.267269E+01	-.745744E-04	.242484E-08
$K_2$	.310805E+00	-.129540E+05	.321779E+01	-.738336E-04	.344645E-08
$K_3$	.150879E-01	-.470959E+04	.646096E+00	.272805E-05	-.154444E-08
$K_4$	-.141784E+00	-.213308E+04	.853461E+00	.355015E-04	-.310227E-08
$K_5$	-.752364E+00	.124210E+05	-.260286E+01	.259556E-03	-.162687E-07
$K_6$	-.415302E-02	.148627E+05	-.475746E+01	.124699E-03	-.900227E-08

Table 7: Coefficients for the Equilibrium Constants

Species	$\sigma$ [ $\text{\AA}$ ]	$\epsilon/k$ [K]	Species	$\sigma$ [ $\text{\AA}$ ]	$\epsilon/k$ [K]
$CO_2$	3.996	190.0	$CH_4$	3.822	137.0
$H_2O$	2.641	809.1	$C_2H_6$	4.418	230.0
$CO$	3.590	110.0	$C_3H_8$	5.061	254.0
$H_2$	2.915	38.0	$C_4H_{10}$	5.341	313.0
$O_2$	3.433	113.0	$C_5H_{12}$	5.769	345.0
$N_2$	3.681	91.5	$C_6H_{14}$	5.909	413.0
$OH$	3.147	79.8	$C_8H_{18}$	7.451	320.0
$NO$	3.470	119.0	$C_6H_6$	5.270	440.0
$O$	3.050	106.7			
$H$	2.708	37.0			

Table 8: Collision Parameters

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