# Calculation of Free-Atom Fractions in Hydrocarbon-Fueled Rocket Engine Plume

**Abstract**

Free atom fractions (β) of nine elements are calculated in the exhaust plume of $CH_4$-oxygen and RP-1-oxygen fueled rocket engines using free energy minimization method. The Chemical Equilibrium and Applications (CEA) computer program developed by the Glenn Research Center, NASA is used for this purpose. Data on variation of β in both fuels as a function of temperature (1600 K – 3100 K) and oxygen to fuel ratios (1.75 to 2.25 by weight) is presented in both tabular and graphical forms. Recommendation is made for the β value for a tenth element, Palladium. The CEA computer code was also run to compare with experimentally determined β values reported in literature for some of these elements. A reasonable agreement – within a factor of three - between the calculated and reported values is observed. Values reported in this work will be used as a first approximation for pilot rocket engine testing studies at the Stennis Space Center for at least six elements Al, Ca, Cr, Cu, Fe and Ni - until experimental values are generated. The current estimates will be improved when more complete thermodynamic data on the remaining four elements Ag, Co, Mn and Pd are added to the database. A critique of the CEA code is also included.

**Introduction**

Development and testing for flightworthiness of a rocket engine is critically dependent upon monitoring the exhaust plume. Ten elements (Ag, Al, Ca, Co, Cr, Cu, Fe, Mn, Ni and Pd) are spectroscopically peculiar to the materials used in rocket engines[1] and are of special interest to the plume diagnostic team at the John C. Stennis Space Center, Mississippi. Detection, identification and quantification of these elements is a part of rocket engine health monitoring program which can indicate the rate of progressive malfunction of specific components during the engine testing. Proper actions may then be initiated to avoid a disaster.

Real time detection of these elements is accomplished by monitoring and analyzing the spectral signatures from the atoms of these elements in the exhaust plume of a rocket engine. The total rate of discharge of each element in the plume is calculated by appropriately applying a quantity called β for each element. β is defined as the mole fraction of an element that is in the atomic form versus all its forms in the flame e.g. molecular, ionized, oxide, hydride, hydroxide etc. The spectroscopic data is regressed through several layers of computer codes to quantify the rate of wear and identify the particular engine components as the source of the discharge of a particular element.
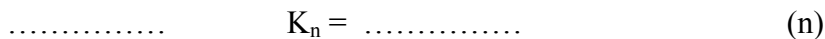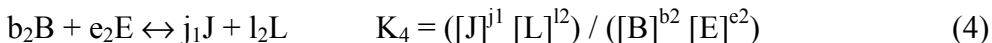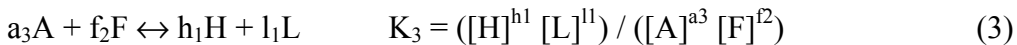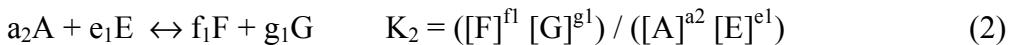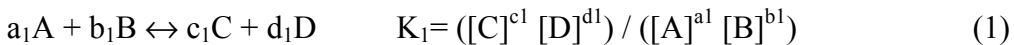
Details of the methodology of rocket engine health monitoring using spectral analysis, computer codes, scale model tests and ground tests for flightworthiness of the space shuttle main engines have been extensively published by Tejwani et.al.[2, 3, 4, 5]

NASA has been investigating the suitability of high energy density hydrocarbon fuels for the new generation reusable space shuttle engines. Two main hydrocarbons fuel candidates are $CH_4$ and RP-1. A comprehensive literature[6] search was conducted in summer 2005 and a compilation was made of the β values for the above mentioned ten elements in flame environments similar to the hydrocarbon-oxygen propelled rocket-engines. The environments reported in the literature were acetylene-oxygen, acetylene-nitrous oxide and hydrogen-nitrous oxide flames. β values generated from the current space shuttle engine tests using liquid hydrogen-liquid oxygen fuel system were also included in the above study for comparison purposes.

We concluded in that study that the reported β values could not be used for $CH_4$ or RP-1 flame conditions, because of the sensitivity of β values to flame composition, uncertainty in the details of experimental conditions and the large variations in the β values reported by different investigators. Alternative experimental and theoretical methods were recommended to generate β values for the $CH_4$ and RP-1 flames at oxygen / hydrocarbon ratios of interest to us. It was also recommended that because our primary interest is in the equilibrium composition, a thermodynamic approach rather than a kinetic approach should be used.

**Kinetic Approach vs. Free Energy Minimization Approach**

Equilibrium composition of a reaction mixture may be calculated by both kinetic and thermodynamic methods. The kinetic approach utilizes the equilibrium constants of the various elementary reactions occurring in the mixture at equilibrium:

$$a_1A + b_1B \leftrightarrow c_1C + d_1D \qquad K_1 = ([C]^{c1} [D]^{d1}) / ([A]^{a1} [B]^{b1}) \qquad (1)$$

$$a_2A + e_1E \leftrightarrow f_1F + g_1G \qquad K_2 = ([F]^{f1} [G]^{g1}) / ([A]^{a2} [E]^{e1}) \qquad (2)$$

$$a_3A + f_2F \leftrightarrow h_1H + l_1L \qquad K_3 = ([H]^{h1} [L]^{l1}) / ([A]^{a3} [F]^{f2}) \qquad (3)$$

$$b_2B + e_2E \leftrightarrow j_1J + l_2L \qquad K_4 = ([J]^{j1} [L]^{l2}) / ([B]^{b2} [E]^{e2}) \qquad (4)$$

$$\ldots\ldots\ldots\ldots \qquad K_n = \ldots\ldots\ldots\ldots \qquad (n)$$

Where A, B, C etc. are the species generated from the starting compounds in the reaction mixture, a1, a2, b1, b2, etc. are their coefficients in the reactions, [A], [B], [C] etc. are their molar concentrations in the equilibrium mixture and $K_1$, $K_2$, $K_3$ etc. are the equilibrium constants for the reactions. Thus, a set of equations accounting for all possible interactions of all possible species may be considered, each with its own equilibrium constant at the appropriate reaction temperatures. The equilibrium concentrations of m species can be obtained by simultaneous solution of n equations in m species (where m ≤ n).

By comparison, free energy minimization (FEM) method utilizes the fact that the Gibbs free energy of a system is at a minimum when it is at equilibrium. The change in Gibbs free energy of a component is defined by:

$$G_i = H_i - T * S_i$$

Where,
$G_i$ = Gibbs free energy of component i.
$H_i$ = Enthalpy of component i.
$S_i$ = Entropy of component i.

The enthalpy and entropy of a component are functions of temperature and are defined in terms of specific heat at constant pressure $C_p^o$ by (component subscript i is not used to reduce clutter):

$$C_p^o/R = \sum^k a_{k*}T^{-k}$$

$$H^o/RT = \int C_p^o \, dT/ RT$$

$$S^o/R = \int (C_p^o / RT) \, dT$$

R is the Universal Gas Constant. Thus, if the temperature dependence of $C_p^o$ for a component can be described as a polynomial with seven terms (k = 7), the enthalpy and entropy can then be defined as follows:

$$C_p^o/R = a_{1*}T^{-2} + a_{2*}T^{-1} + a_3 + a_{4*}T + a_{5*}T^2 + a_{6*}T^3 + a_{7*}T^4$$

$$H^o/RT = -a_{1*}T^{-2} + a_{2*}T^{-1}*\ln T + a_3 + a_{4*}T/2 + a_{5*}T^2/3 + a_{6*}T^3/4 + a_{7*}T^4/5 + b_1/T$$

$$S^o/R = -a_{1*}T^{-2}/2 - a_{2*}T^{-1} + a_{3*}\ln T + a_{4*}T + a_{5*}T^2/2 + a_{6*}T_3/3 + a_{7*}T^4/4 + b_2$$

$b_1$ and $b_2$ are integration constants. Thermodynamic data on only those chemical species existing at equilibrium is needed to calculate the equilibrium composition. As a result, the need to know the exact composition of the initial fuel and the exact reactions between the numerous species is circumvented.

The free energy of a system or the change in free energy of a system starting from a standard state, which contains n species at molar concentration $c_i$ at equilibrium, can be calculated from the individual $\Delta G_i$ thus:

$$\Delta G = \sum^n c_i \, \Delta G_i$$

It is $c_i$, the molar concentration of species i at equilibrium, is the quantity we strive to estimate.

It should be pointed out here, that the kinetic and thermodynamic approaches should and must yield the same equilibrium composition provided the data base is complete. The equilibrium constant K and the change in the free energy ΔG of a system are related by the well known equation:

$$\Delta G = -RT \ln K$$

Thus if one is obtained from experimental or theoretical means, the other may be calculated.

To recapitulate, if all reactions occurring in the flame and their equilibrium constants are known, one can calculate the equilibrium concentration of species in the flame. For simple flames this approach is suitable, however, for complicated systems, this approach is not efficient because all flame reactions may not be sufficiently characterized in terms of the species involved, and activation energies and temperature dependent reaction rate coefficients for all these reactions may not be available. Consequently, most investigators limit the consideration to the interaction of a handful of species of highest concentrations. For example, a kinetic model for combustion of acetylene considers thirty two species and one hundred and six reactions[7]! Another review article[8] on combustion of various hydrocarbons reports fifty three species, three hundred twenty five elementary reactions and associated rate coefficient expressions and thermochemical parameters for combustion of $CH_4$ and twelve hundred reactions and one hundred twenty seven species for ethane and propane combustions. Given the computing power available now-a-days, numbers of species and reactions may no longer be an issue, however, the problem becomes significantly more complex in the case of mixed fuels such as kerosene, jet fuels such as RP-1 and rocket propellants where the fuel compositions is variable. The presence of non-ideal species and condensed phase introduces further difficulty in the kinetic approach. By contrast, in the FEM method, thermodynamic data on only those species existing at equilibrium is needed to calculate the equilibrium composition. As a result the need to know the exact composition of the initial fuel and the exact reactions between the species is circumvented. A surrogate formula may be used for mixed fuels in the FEM approach and the presence of ionized and condensed species at equilibrium conditions does not pose any problem.

The free energy minimization method has been used in the past for combustion reactions[9-13]. Some authors have used the classical thermodynamic approach[9, 10, 11] and some others have suggested a statistical mechanical approach[12, 13]. In this report we have used a computerized method known as the Chemical Equilibrium and Application (CEA). This FORTRAN based computer code was developed and refined by Gordon and McBride at the Glenn Research Center NASA[14, 15, 16] over a number of years and has been used extensively since then. The CEA program requires the following information on the species: heat of formation at 298.15 K, phase (gas / condensed) of the specie, its molecular weight, temperature coefficients ($a_1$ through $a_7$) in the equation for heat capacity at constant pressure $C_p^o$ and the temperature intervals over which they are valid, assigned enthalpy $H^o(T)$ at a reference temperature T to correct for non-ideality, and

integration constants ($b_1$, $b_2$) in the expressions of enthalpy and entropy (expressed as dimensionless quantities $H^o/RT$ and $S^o/R$ respectively).

A brief comment on whether equilibrium is actually achieved in the flame reactions is as follows. The presumption of thermodynamic equilibrium implies that the rate of reaction between various species is fast compared to the residence time of these species in the flame. Attainment of equilibrium requires that the particles in the system have undergone a sufficient number of collisions with each other. According to Alkemade[17], calculations show that the translational and rotational energies of particles equilibrate very quickly - within $10^{-8}$ sec at atmospheric pressure. Although, vibrational energy equilibration is slower in comparison with translational and rotational energies, any serious lag in equipartition of energy is not expected in this time frame. It is, therefore, safe to assume that local thermodynamic equilibrium is achieved in the flame reactions.

An interesting feature of the CEA code, and indeed equilibrium compositions at specified temperature and pressure should be pointed out here. If the oxygen/carbon and oxygen/hydrogen molar ratio in the feed are kept constant, the equilibrium distribution of species does not change whether the starting compound is $C_2H_4$ or $C_3H_6$ or $C_4H_8$ and so on – because these compounds also have a constant hydrogen/carbon molar ratio. Stated in general terms, all reactions characterized as

$C_nH_m + p\ O_2$ = various C, H, O species
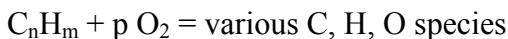
will yield the same equilibrium composition for all feed compositions that have the same n/p and m/p ratios. The coefficients n, m and p may be fractions.

The two determining factors for making this statement are: the relative thermal stability of species at the specified temperature and pressure and the mass balance on elements. Different heats of combustion for different reactants does not affect the equilibrium composition because temperature and pressure are specified. This is also the basis for using a surrogate formula for RP-1 in the absence of a "true" formula.

**RP-1 surrogate formula**

The hydrogen to carbon (H/C) ratio for RP-1 reported in literature has varied over a wide range[18, 19, 20]. Latest RP-1 specification[21] indicates a minimum hydrogen content of 13.8 % by mass. This would correspond to an H/C ratio of 1.91. RP-1 in the CEA data base has the elemental formula $CH_{1.95}$. Wang[22] used a surrogate formula of $C_{12}H_{24}$ for RP-1 (C/H ratio of 2.0) for fluid dynamic modeling of the combustion process. We expect that efforts to decrease the aromatic fraction, (H/C ratio =1) in RP-1 to avoid soot formation tendency[19], and increase naphthalene (H/C ratio =2) and paraffin fractions (H/C ratio >2) will move the desired RP-1 formulation toward an H/C ratio of two. Using an H/C ratio of two or a surrogate formula of $C_{12}H_{24}$ keeps our results in conformity with the fluid modeling efforts.

A further point is noted here regarding the formulation of RP-1. Refinery processes such as catalytic cracking, alkylation etc, are very corrosive and it is likely that the RP-1 fuel may contain Fe, Cr in trace quantities. Also, Ni, Co, Ag are commonly used as catalysts in the oil refining process, therefore, these elements may also be present at parts per million level concentrations. Therefore, it is necessary to establish a base line concentration of these elements in RP-1. The CR-101 thruster tests[5] with RP-1 will provide an opportunity to make such determination. The thruster will operate on pressure feed without the aid of any rocket engine turbomachinery.

**Case Studies Run**

Two cases reported in literature were chosen to run on CEA so that a comparison with the reported results can be made. Then $CH_4$ and RP-1 cases of interest to us were run using the CEA code.

The combustion of CH4 and RP-1 is represented thus:

$CH_4 + 2 O_2 = CO_2 + 2 H_2O$   O/F ratio = 4.0 for complete combustion ($\varphi = 1$)

$C_{12}H_{24} + 18 O_2 = 12 CO_2 + 12 H_2O$    O/F ratio = 3.43 for complete combustion ($\varphi = 1$)
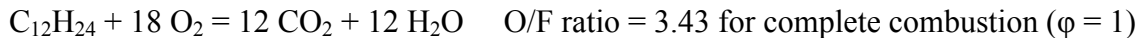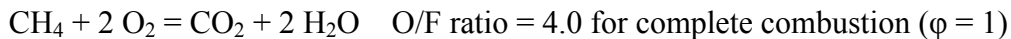
The choice of oxygen / fuel ratios (O/F ratios) for $CH_4$, $O_2$ system was made to include the ratios of 2.0 and 2.5 used in initial studies on $CH_4$ thruster currently being conducted

**Table -1 Case Studies Run on the CEA Code**

| Comparison with cases reported in literature | | | | |
|---|---|---|---|---|
| | O/F ratios by weight (Equivalence ratios) | Temperatures K | Pressure atm | Elements [#] |
| $C_2H_2$, $O_2$ | 1.368, 1.758 (0.445, 0.571) | 2750 | 1.0 | Ca, Cr, Cu, Fe |
| $H_2$, $O_2$ | 6.0** | 3097 | 2.455 | Cr, Cu, Fe, Mn, Ni |
| Cases in the current study | | | | |
| $CH_4$, $O_2$ | 2.0, 2.25, 2.5 (0.5, 0.563, 0.625) | 1600, 2000, 2400, 2600, 2800, 3000, 31000 | 2.0 | Ag, Al, Ca, Co, Cr, Cu, Fe, Mn, Ni |
| RP-1, $O_2$ | 1.75, 2.0, 2.25 (0.51, 0.583, 0.656) | 1600, 2000, 2400, 2600, 2800, 3000, 31000 | 2.0 | Ag, Al, Ca, Co, Cr, Cu, Fe, Mn, Ni |
| RP-1, S*, $O_2$ | 1.75, 2.0, 2.25 (0.51, 0.583, 0.656) | 1600, 2000, 2400, 2600, 2800, 3000, 31000 | 2.0 | Ag, Al, Ca, Co, Cr, Cu, Fe, Mn, Ni |

# All elements were present at 1 ppm by mole concentration
* 30 ppm Sulfur by weight
**Space shuttle main engine test conditions

at the Stennis Space Center. These correspond to equivalence ratios $\varphi = 0.5$ and $0.625$ respectively. The O/F ratios for RP-1 were chosen arbitrarily in the vicinity.

The CEA program was run as a constant temperature, constant pressure (t, p) problem. Pd could not be included in these calculations because it is not in the CEA data base. In the case of $CH_4$ and RP-1 feeds without sulfur, the mole fraction of each of nine elements in the hydrocarbon feed was $1.0 \times 10^{-6}$, and that of the hydrocarbon fuel itself was 99.9991. In the case of RP-1 fuel with sulfur, the mole fraction of sulfur was 0.0157 corresponding to 30 ppm by weight in the fuel of formula $C_{12}H_{24}$. Consequently, the mole fraction of the RP-1 fuel was 99.9834. Oxygen was input as 100% pure oxygen. The input compositions for various cases are presented in Table-2.

Ions, electron gas and all possible species combinations of C, H and the elements in the

### Table – 2  Input File for CEA Program for Various Case Studies

| Case | $C_2H_2$, $O_2$ | $H_2$, $O_2$ | $CH_4$, $O_2$ | RP-1, $O_2$ | RP-1, S, $O_2$ |
|---|---|---|---|---|---|
| O/F ratio | Variable, see Table 1 | | | | |
| $O_2$ | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| $CH_4$ | 99.9996 | 99.9995 | 99.9991 | | |
| RP-1 | | | | 99.9991 | 99.9834 |
| S | | | | | .0157 |
| Ag | | | .0001 | .0001 | .0001 |
| Al | | | .0001 | .0001 | .0001 |
| Ca | .0001 | | .0001 | .0001 | .0001 |
| Co | | | .0001 | .0001 | .0001 |
| Cr | .0001 | .0001 | .0001 | .0001 | .0001 |
| Cu | .0001 | .0001 | .0001 | .0001 | .0001 |
| Fe | .0001 | .0001 | .0001 | .0001 | .0001 |
| Mn | | .0001 | .0001 | .0001 | .0001 |
| Ni | | .0001 | .0001 | .0001 | .0001 |

data base were included in the equilibrium mixture. The program output was in terms of mole fraction of various species in the equilibrium mixture. The lower limit on the concentration of species reported in the output was reduced to $1 \times 10^{-15}$ mole fraction from the default value of $1 \times 10^{-5}$. $\beta$ for each element was calculated using the following equation:

$$\beta = (\text{mole fraction in atomic form}) / \Sigma (\text{mole fractions of the element in all forms})$$

Air entrainment in the plume was not taken into consideration. Therefore, no nitrogen species were assumed to be present in the equilibrium mixture. The calculated $\beta$ values for all cases are presented in Tables 4 through 7 and Figures 1 and 2.

**Discussion**

**a. Critique of the CEA Program**
The CEA program, especially with its current graphical user interface, is an excellent tool for calculations of equilibrium composition. The program is essentially a mass balance on atoms of all elements in the feed distributed among the various species containing these elements in the data base, while seeking the minimum of the free energy for the whole system at the same time. Any computational program, including CEA, is completely dependent upon the quality and comprehensiveness of its data base. If all relevant forms of an elements e.g. ions, radicals and compounds with other elements, are not included in the data base, an erroneous mass fraction for free atoms of that element will result. Further error may be introduced if the temperature dependence of enthalpy and entropy for each species is not available for rigorous energy minimization calculations.

Table 3 lists the species that are in the data base for each element of interest to us in the hydrocarbon combustion environment. Most species in the data base have temperature dependent data up to 6000 K, and some up to 20000 K. Data on remaining species is valid for temperatures less than 2500 K, they are crystals forms and are not expected to exist above their melting temperatures.

The data in CEA is taken from the JANAF tables[23] and other reputed sources, therefore, it is considered to be of good quality. Pd is absent from the database. Also as noted in a later section, some species of interest to us, such as Pd species (e.g. Pd+, $Pd_2H$, $PdH_2$, PdO), Ag species (AgOH, $Ag_2O$, $Ag_2O_2$, $Ag_2O_3$, $Ag_3O_4$, $Ag_3O$, $Ag_2S$), Co species (CoO, $Co_3O_4$, and $CoSO_4$) and Ni species (NiH and $Ni_2O_3$) are not in the data base. Similarly a limited number of Mn species are present in the data base. The extent, to which inclusion or absence of these species would affect the equilibrium distribution of an element in various forms at temperatures of interest to us, is unknown. There is a provision to add data on new compounds to the database. However, data on all possible species of interest to us is not yet available in the literature. The data base on Al, Ca, Cr, Cu, Fe and Ni species appear to be adequate; therefore, the results for these elements should be more readily acceptable.

**b. Comparison of CEA results with experimental values reported in literature**
In order to assess the validity of the results predicted by CEA program, two cases were chosen from the published literature. One of the reports[24] is an excellent review and comparison of data in open literature on flame spectroscopy and of relevance to us because it is a hydrocarbon in oxygen flame ($C_2H_2$ –$O_2$ flame diluted in He). It should be noted here that the objective of a majority of work reported in literature has been to artificially increase the free atom fractions in the flame by addition of K, Cs etc. as ionization suppressants. This practice reduces the number of cases available for valid comparison by a significant margin, because, only those cases where no foreign agent was added to the flame may be used. It is expected that in the example used, Helium does not participate in any of the flame reactions; therefore, β values for the elements remain unaffected and a fair comparison may be made between the calculated and experimentally determined values.

## Table-3 List of Species Included in the Free Energy Minimization Calculations

| # | Species | # | Species | # | Species | # | Species | # | Species | # | Species |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | e- | 57 | CH2OH | 113 | C4H8,1-butene | 169 | CaCO3(cr) | 225 | CuS(cr) | 281 | Mn(c) |
| 2 | Ag | 58 | CH2OH+ | 114 | C4H8,cis2-buten | 170 | CaCO3(L) | 226 | CuSO4(cr) | 282 | Mn(d) |
| 3 | Ag- | 59 | (CH3COOH)2 | 115 | C4H8,cyclo- | 171 | CaH | 227 | Fe | 283 | Mn(L) |
| 4 | Ag+ | 60 | (HCOOH)2 | 116 | C4H8,isobutene | 172 | CaH2(a) | 228 | Fe- | 284 | Ni |
| 5 | Ag(cr) | 61 | CH3CHO,ethanal | 117 | C4H8,tr2-butene | 173 | CaH2(b) | 229 | Fe+ | 285 | Ni- |
| 6 | Ag(L) | 62 | CH3CO,acetyl | 118 | C4H9,i-butyl | 174 | CaH2(L) | 230 | Fe(a) | 286 | Ni+ |
| 7 | AL | 63 | CH3COOH | 119 | C4H9,n-butyl | 175 | CaO(cr) | 231 | Fe(c) | 287 | Ni(cr) |
| 8 | AL2 | 64 | CH3O | 120 | C4H9,s-butyl | 176 | CaO(L) | 232 | Fe(CO)5 | 288 | Ni(L) |
| 9 | AL- | 65 | CH3O2CH3 | 121 | C4H9,t-butyl | 177 | CaOH | 233 | Fe(CO)5(L) | 289 | Ni3S2(a) |
| 10 | AL+ | 66 | CH3OCH3 | 122 | C5H10,1-pentene | 178 | CaOH+ | 234 | Fe(d) | 290 | Ni3S2(b) |
| 11 | ALO | 67 | CH3OH | 123 | C5H10,cyclo- | 179 | CaS | 235 | Fe(L) | 291 | Ni3S2(L) |
| 12 | AL(cr) | 68 | CH3OOH | 124 | C5H11,pentyl | 180 | CaS(cr) | 236 | Fe(OH)2 | 292 | Ni3S4(cr) |
| 13 | AL(L) | 69 | CH4 | 125 | C5H11,t-pentyl | 181 | CaS(L) | 237 | Fe(OH)2(cr) | 293 | NiO |
| 14 | AL(OH)2 | 70 | COOH | 126 | C5H12,i-pentane | 182 | CaSO4(I) | 238 | Fe(OH)3(cr) | 294 | NiS |
| 15 | AL(OH)3 | 71 | COS | 127 | C5H12,n-pentane | 183 | CaSO4(II) | 239 | Fe.947O(cr) | 295 | NiS(a) |
| 16 | AL(OH)3(a) | 72 | CS | 128 | C5H6,1,3cyclo- | 184 | CaSO4(L) | 240 | Fe.947O(L) | 296 | NiS(b) |
| 17 | AL2C2 | 73 | CS2 | 129 | C5H8,cyclo- | 185 | CH | 241 | Fe2(SO4)3(cr) | 297 | NiS(L) |
| 18 | AL2O | 74 | C2- | 130 | C6H10,cyclo- | 186 | CH+ | 242 | Fe2O3(cr) | 298 | NiS2(cr) |
| 19 | AL2O+ | 75 | C2H | 131 | C6H12,1-hexene | 187 | CO | 243 | Fe3O4(cr) | 299 | NiS2(L) |
| 20 | AL2O2 | 76 | C2H2,acetylene | 132 | C6H12,cyclo- | 188 | Co | 244 | Fe3O4(L) | 300 | O |
| 21 | AL2O2+ | 77 | C2H2,vinylidene | 133 | C6H13,n-hexyl | 189 | Co- | 245 | FeO | 301 | O- |
| 22 | AL2O3 | 78 | C2H3,vinyl | 134 | C6H14,n-hexane | 190 | Co+ | 246 | FeS(a) | 302 | O+ |
| 23 | AL2O3(a) | 79 | C2H4 | 135 | C6H2 | 191 | Co(a) | 247 | FeS(b) | 303 | O2 |
| 24 | AL2O3(L) | 80 | C2H4O,ethylen-o | 136 | C6H5,phenyl | 192 | Co(b) | 248 | FeS(c) | 304 | O2+ |
| 25 | AL2S | 81 | C2H5 | 137 | C6H5O,phenoxy | 193 | Co(L) | 249 | FeS(L) | 305 | OH |
| 26 | AL2S2 | 82 | C2H5OH | 138 | C6H5OH,phenol | 194 | CO+ | 250 | FeS2(cr) | 306 | OH+ |
| 27 | AL2S3(a) | 83 | C2H6 | 139 | C6H6 | 195 | CO2 | 251 | FeSO4(cr) | 307 | O(CH)2O |
| 28 | AL2S3(b) | 84 | C2O | 140 | C7H14,1-heptene | 196 | CO2+ | 252 | H2- | 308 | O2- |
| 29 | AL2S3(L) | 85 | C2S2 | 141 | C7H15,n-heptyl | 197 | Cr | 253 | H2O | 309 | O3 |
| 30 | AL4C3(cr) | 86 | C3H3,1-propynl | 142 | C7H16,2-methylh | 198 | Cr- | 254 | H2O(cr) | 310 | OH- |
| 31 | ALC | 87 | C3H3,2-propynl | 143 | C7H16,n-heptane | 199 | Cr+ | 255 | H2O(L) | 311 | OHCH2COOH |
| 32 | ALC2 | 88 | C3H4,allene | 144 | C7H7,benzyl | 200 | CrO | 256 | H2O2 | 312 | S |
| 33 | ALH | 89 | C3H4,cyclo- | 145 | C7H8 | 201 | Cr(cr) | 257 | H2S | 313 | S- |
| 34 | ALH2 | 90 | C3H4,propyne | 146 | C7H8O,cresol-mx | 202 | Cr(L) | 258 | H | 314 | S+ |
| 35 | ALH3 | 91 | C3H5,allyl | 147 | C8H10,ethylbenz | 203 | Cr2O3(I) | 259 | H- | 315 | S(a) |
| 36 | ALH3(a) | 92 | C3H6,cyclo- | 148 | C8H16,1-octene | 204 | Cr2O3(I') | 260 | H+ | 316 | S(b) |
| 37 | ALO- | 93 | C3H6,propylene | 149 | C8H17,n-octyl | 205 | Cr2O3(L) | 261 | H2 | 317 | S(L) |
| 38 | ALO+ | 94 | C3H6O,acetone | 150 | C8H18,isooctane | 206 | CrO2 | 262 | H2+ | 318 | S2 |
| 39 | ALO2 | 95 | C3H6O,propanal | 151 | C8H18,n-octane | 207 | CrO3 | 263 | H2O+ | 319 | S2- |
| 40 | ALO2- | 96 | C3H6O,propylox | 152 | C8H8,styrene | 208 | CrO3- | 264 | H3O+ | 320 | S2O |
| 41 | ALOH | 97 | C3H7,i-propyl | 153 | C9H19,n-nonyl | 209 | Cu | 265 | HCO+ | 321 | S3 |
| 42 | ALS | 98 | C3H7,n-propyl | 154 | C10H21,n-decyl | 210 | Cu- | 266 | H2SO4 | 322 | S4 |
| 43 | ALS2 | 99 | C3H8 | 155 | C10H8,naphthale | 211 | Cu+ | 267 | H2SO4(L) | 323 | S5 |
| 44 | C | 100 | C3H8O,1propanol | 156 | C12H10,biphenyl | 212 | Cu(cr) | 268 | HALO | 324 | S6 |
| 45 | C(gr) | 101 | C3H8O,2propanol | 157 | C12H9,o-bipheny | 213 | Cu(L) | 269 | HALO2 | 325 | S7 |
| 46 | C- | 102 | C3O2 | 158 | Ca | 214 | Cu(OH)2(cr) | 270 | HCCO | 326 | S8 |
| 47 | C+ | 103 | C3OS | 159 | Ca2 | 215 | Cu2 | 271 | HCHO,formaldehy | 327 | SH |
| 48 | C2 | 104 | C3S2 | 160 | Ca(a) | 216 | Cu2O(cr) | 272 | HCO | 328 | SH- |
| 49 | C2+ | 105 | C4H10,isobutane | 161 | Ca(b) | 217 | Cu2O(L) | 273 | HCOOH | 329 | SO |
| 50 | C3 | 106 | C4H10,n-butane | 162 | Ca(L) | 218 | Cu2S(a) | 274 | HO(CO)2OH | 330 | SO- |
| 51 | C4 | 107 | C4H2,butadiyne | 163 | Ca+ | 219 | Cu2S(b) | 275 | HO2 | 331 | SO2 |
| 52 | C5 | 108 | C4H4,1,3-cyclo- | 164 | CaO | 220 | Cu2S(c) | 276 | HO2- | 332 | SO2- |
| 53 | CH2 | 109 | C4H6,1butyne | 165 | CaO+ | 221 | Cu2S(L) | 277 | Mn | 333 | SO3 |
| 54 | CH3 | 110 | C4H6,2butyne | 166 | Ca(OH)2 | 222 | CuO | 278 | Mn+ | | |
| 55 | CH3C(CH3)2CH3 | 111 | C4H6,butadiene | 167 | Ca(OH)2(cr) | 223 | CuO(cr) | 279 | Mn(a) | | |
| 56 | CH2CO,ketene | 112 | C4H6,cyclo- | 168 | Ca(OH)2(L) | 224 | CuOH | 280 | Mn(b) | | |

Note: No subscripts or no phase for gaseous species; (cr): crystal; (a), (b), (c) (d), (l), (ll): different crystal structures, (L): liquid, (gr): graphite. For detailed explanation of the species, see ref. 14.

Free atom fraction is highly dependent upon experimental conditions and instrumentation. The common factors affecting the measured β are the flame chemistry, flame temperature and pressure, burner designs, nebulization efficiencies, observation height and entrainment of air in the flame which affects the fuel/oxidant ratio. Because of these reasons, investigators prefer to bypass these issues and prepare a calibration curve[25], or report β values relative to a reference element (e.g. Cu, Mg, Ag) that may be assumed to be completely atomized (β = 1) at the flame condition. The review article[24]

used in this report for comparison purposes, assumes that Cu is completely atomized in air-$C_2H_2$ flame.

**b1. $C_2H_2$-$O_2$-He system**
As mentioned before, the first case studied is the combustion of acetylene in oxygen diluted by helium. The calculated β values are reported in Table 4.

**Table-4  Reported vs. Calculated β Values, $C_2H_2$-$O_2$-He System**

| O/F ratio = 1.368 | | | |
|---|---|---|---|
|  | Calculated from CEA 2750 K | Reported[24] 2750 K | β Ratio calc./reported |
| Ca | .573 | .22 | 2.60 |
| Cr | .763 | .41 | 1.86 |
| Cu | .999 | .84 | 1.19 |
| Fe | .985 | .82 | 1.2 |
| O/F ratio = 1.758 | | | |
|  | Calculated from CEA 2750 K | Reported[24] 2750 K | Ratio calc./reported |
| Ca | .151 | .15 | 1.01 |
| Cr | .245 | .25 | .980 |
| Cu | .997 | 1.04 | .959 |
| Fe | .908 | .97 | .936 |

Excellent agreement is seen between the calculated and predicted β values except for Ca and Cr at O/F ratio of 1.368. Even for this case, the ratio is well within a factor of 3.0. It is reasonable to say that the β values predicted from CEA would be safe to extend to the $CH_4$ and RP-1 fuels for Ca, Cr, Cu and Fe.

**b2. $H_2$-$O_2$ System**
Tejwani et. al. reported an occasion[3] when the material loss from bearing balls on the low pressure oxidizer turbo pump shaft in the space shuttle main engine could be measured

**Table-5   Reported vs. Calculated β Values $H_2$-$O_2$ System**

| O/F ratio = 6.0, pressure 2.455 atm. | | | |
|---|---|---|---|
|  | Calculated from CEA 3097 K | Reported[3] 3097 K | β Ratio calc./reported |
| Cr | .098 | .056 | 1.75 |
| Cu | .985 | .77 | 1.28 |
| Fe | .752 | .49 | 1.53 |
| Mn | .993 | .57 | 1.74 |
| Ni | .983 | .91 | 1.08 |

after a flightworthiness test and β values could be estimated for some elements in the alloy. These values along with the values calculated from the CEA code are given in Table-5.

In this case, Tejwani divided the plume cross section into three layers – one central layer and two outside layers. Only the central layer containing the Mach diamond and fairly constant temperature of 3097 K is considered here for comparison.

Here the agreement is well within a factor of two. Considering the experimental error and many assumptions made in arriving at the final β values, this agreement is considered quite acceptable.

### c. Calculation of β values using CEA code
Based on the results of Tables 4 and 5 above, it can be said that β values generated from the CEA codes for Ca, Cr, Cu, Fe, Mn, and Ni are fairly reliable. The value for Ag at the high temperature and fuel rich conditions should be fairly close to one – even though the CEA data base on Ag is not extensive. It is expected that β for Al should also be reliable because the CEA data base on Al species is fairly complete. The current data base for Co is not extensive so β for Co results should be treated with caution.

Having thus generated some degree of confidence in the CEA data base and the free energy minimization method of determining free atom fractions, we now embark upon the prediction of β values for the nine elements under the chemical environment of direct interest to us.

### c1. CH₄-O₂ system

c1. $CH_4$-$O_2$ system

The range of O/F ratio of 2.0 – 2.5 is used in this report because some of the initial experiments with the pilot thruster at present are being conducted at these ratios. It is likely that in future this range may be increased to cover O/F ratios from 1.75 to 4.0. New β values can be generated then.

The data is also presented graphically in Figure-1. The graphs are provided to show the extreme non-linear nature of β as a function of temperature for many elements. The temperature scale is the same in all graphs; however, the ordinate varies to accommodate the range of β values for a particular element. The ordinate scale for an element is kept the same for $CH_4$-$O_2$ and RP-1-$O_2$ cases presented in the next section.

### c2. RP-1-O₂ with and without Sulfur

c2. RP-1-$O_2$ with and without Sulfur

RP-1 specifications allow for a maximum sulfur content of 30 ppm by mass. This case was run as a worse case scenario. It was observed that except for nickel, the calculated β values for all other metals did not change in the presence of sulfur. Even in the case of Ni, β values only at 1600 K were different - 1.000 without sulfur and 0.999 with sulfur. Co and Mn do not have compounds with S in the database; therefore, the effect of sulfur on their free atom fractions can not be stated conclusively. Apparently, the sulfur compounds of the remaining elements are not stable at the temperatures considered, thus they do not affect the free atom fractions.

**Table-6   Calculated β Values for CH$_4$-O$_2$ System**

| O/F ratio 2.0 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Temp K | 1600 | 2000 | 2400 | 2600 | 2800 | 3000 | 3100 |
| Ag | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.998 | 0.995 |
| Al | 0.000 | 0.000 | 0.001 | 0.003 | 0.007 | 0.016 | 0.023 |
| Ca | 0.000 | 0.002 | 0.023 | 0.053 | 0.099 | 0.149 | 0.160 |
| Co | 0.559 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Cr | 0.002 | 0.458 | 0.401 | 0.380 | 0.364 | 0.356 | 0.357 |
| Cu | 0.999 | 0.998 | 0.998 | 0.997 | 0.997 | 0.996 | 0.995 |
| Fe | 0.033 | 0.490 | 0.870 | 0.911 | 0.921 | 0.918 | 0.915 |
| Mn | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.998 |
| Ni | 0.628 | 0.999 | 0.998 | 0.998 | 0.996 | 0.995 | 0.994 |
| Pd | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | | | | | | |
| O/F ratio 2.25 | | | | | | | |
| Temp K | 1600 | 2000 | 2400 | 2600 | 2800 | 3000 | 3100 |
| Ag | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.998 | 0.995 |
| Al | 0.000 | 0.000 | 0.001 | 0.002 | 0.005 | 0.012 | 0.017 |
| Ca | 0.000 | 0.001 | 0.013 | 0.031 | 0.062 | 0.101 | 0.118 |
| Co | 0.559 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Cr | 0.001 | 0.312 | 0.269 | 0.254 | 0.244 | 0.243 | 0.249 |
| Cu | 0.998 | 0.998 | 0.997 | 0.996 | 0.995 | 0.994 | 0.993 |
| Fe | 0.019 | 0.347 | 0.793 | 0.860 | 0.880 | 0.880 | 0.879 |
| Mn | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.998 |
| Ni | 0.628 | 0.999 | 0.998 | 0.996 | 0.995 | 0.993 | 0.992 |
| Pd | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| | | | | | | | |
| O/F ratio 2.50 | | | | | | | |
| Temp K | 1600 | 2000 | 2400 | 2600 | 2800 | 3000 | 3100 |
| Ag | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.997 | 0.995 |
| Al | 0.000 | 0.000 | 0.000 | 0.001 | 0.004 | 0.009 | 0.013 |
| Ca | 0.000 | 0.001 | 0.008 | 0.019 | 0.039 | 0.069 | 0.086 |
| Co | 0.559 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Cr | 0.001 | 0.195 | 0.165 | 0.156 | 0.152 | 0.158 | 0.167 |
| Cu | 0.998 | 0.997 | 0.996 | 0.995 | 0.993 | 0.992 | 0.991 |
| Fe | 0.011 | 0.237 | 0.694 | 0.791 | 0.825 | 0.833 | 0.836 |
| Mn | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.998 |
| Ni | 0.628 | 0.999 | 0.996 | 0.994 | 0.992 | 0.990 | 0.989 |
| Pd | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

# Figure-1  β Values for CH4-O2 System at Various Temperatures and O/F Ratios
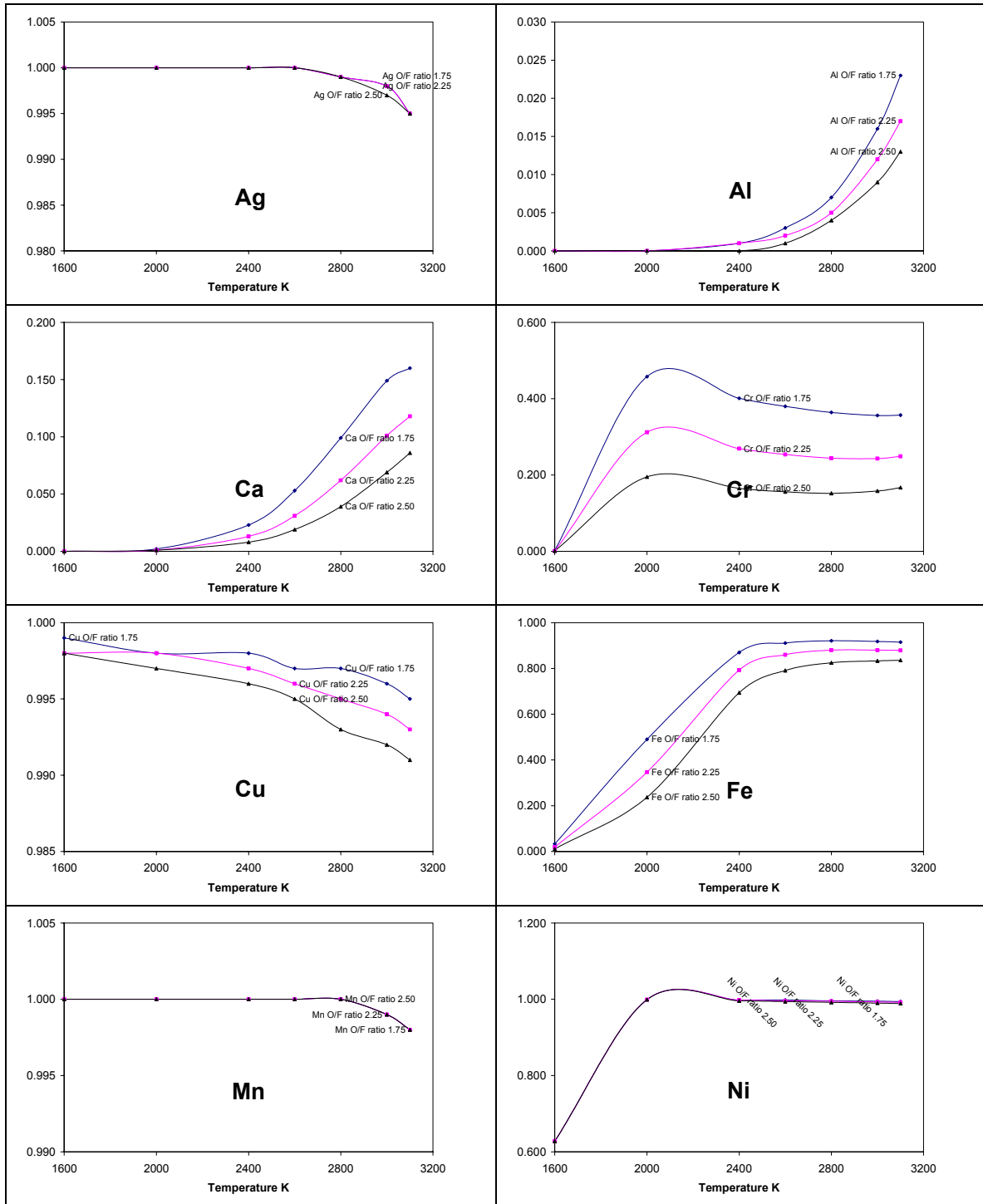
**Table- 7    Calculated β Values for RP-1-O₂ System**

O/F ratio 1.75

|    | 1600 | 2000 | 2400 | 2600 | 2800 | 3000 | 3100 |
|----|------|------|------|------|------|------|------|
| Ag | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.993 | 0.985 |
| Al | 0.000 | 0.000 | 0.001 | 0.004 | 0.009 | 0.019 | 0.028 |
| Ca | 0.000 | 0.003 | 0.033 | 0.071 | 0.114 | 0.129 | 0.117 |
| Co | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 |
| Cr | 0.017 | 0.499 | 0.429 | 0.403 | 0.383 | 0.371 | 0.368 |
| Cu | 0.999 | 0.999 | 0.998 | 0.998 | 0.997 | 0.996 | 0.995 |
| Fe | 0.056 | 0.602 | 0.903 | 0.928 | 0.930 | 0.924 | 0.920 |
| Mn | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.997 | 0.994 |
| Ni | 0.999 | 0.999 | 0.998 | 0.998 | 0.997 | 0.995 | 0.994 |
| Pd | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

O/F ratio 2.0

|    | 1600 | 2000 | 2400 | 2600 | 2800 | 3000 | 3100 |
|----|------|------|------|------|------|------|------|
| Ag | 1.000 | 1.000 | 1.000 | 1.000 | 0.998 | 0.992 | 0.984 |
| Al | 0.000 | 0.000 | 0.001 | 0.002 | 0.006 | 0.012 | 0.018 |
| Ca | 0.000 | 0.001 | 0.014 | 0.033 | 0.059 | 0.078 | 0.077 |
| Co | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 |
| Cr | 0.008 | 0.290 | 0.238 | 0.221 | 0.210 | 0.210 | 0.216 |
| Cu | 0.999 | 0.998 | 0.997 | 0.996 | 0.995 | 0.993 | 0.992 |
| Fe | 0.025 | 0.390 | 0.806 | 0.861 | 0.873 | 0.870 | 0.867 |
| Mn | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.997 | 0.993 |
| Ni | 0.999 | 0.999 | 0.997 | 0.996 | 0.994 | 0.992 | 0.990 |
| Pd | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

O/F ratio 2.25

|    | 1600 | 2000 | 2400 | 2600 | 2800 | 3000 | 3100 |
|----|------|------|------|------|------|------|------|
| Ag | 1.000 | 1.000 | 1.000 | 1.000 | 0.998 | 0.992 | 0.983 |
| Al | 0.000 | 0.000 | 0.000 | 0.001 | 0.004 | 0.009 | 0.013 |
| Ca | 0.000 | 0.001 | 0.007 | 0.017 | 0.033 | 0.049 | 0.053 |
| Co | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.999 |
| Cr | 0.004 | 0.146 | 0.115 | 0.106 | 0.103 | 0.111 | 0.121 |
| Cu | 0.998 | 0.997 | 0.995 | 0.994 | 0.992 | 0.990 | 0.988 |
| Fe | 0.013 | 0.239 | 0.675 | 0.765 | 0.792 | 0.799 | 0.803 |
| Mn | 1.000 | 1.000 | 1.000 | 1.000 | 0.999 | 0.996 | 0.993 |
| Ni | 0.998 | 0.998 | 0.995 | 0.993 | 0.990 | 0.986 | 0.985 |
| Pd | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |

The tabular data is presented in the graphical form in Figure 2. Once again, the non-linear nature of β is exemplified.

**Figure-2   β Values for RP-1-O2 System at Various Temperatures and O/F Ratios**
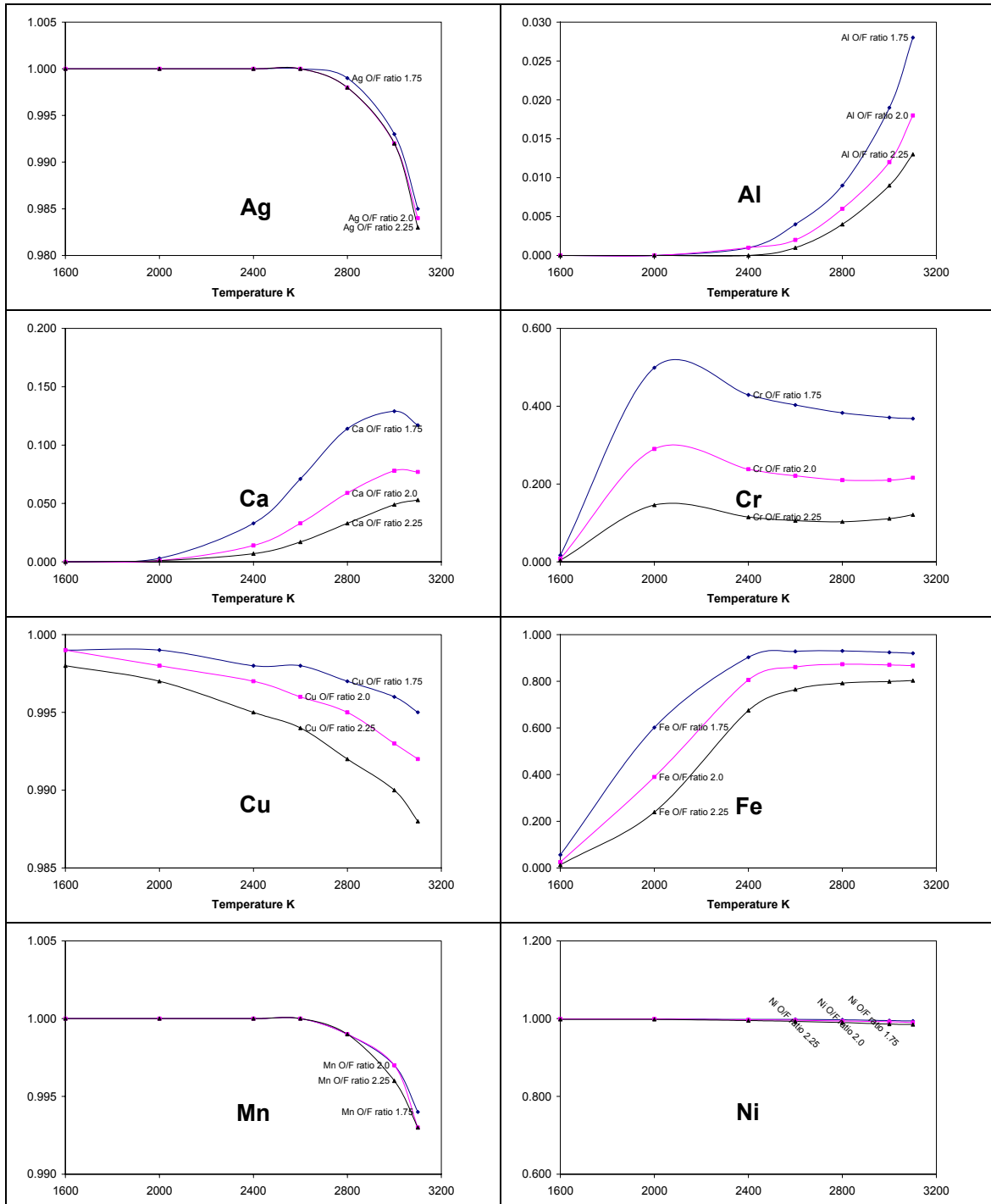
**d. β values for Pd**

As a trial case, β values were calculated with eight elements without Ag in the database. No difference in β values was seen for these elements compared to the case that included Ag. Apparently, C, H and O species are abundant enough in the mixture so that presence or absence of these elements in part per million quantities does not affect the result. Similarly, it is reasonable to assume that the absence of Pd from the CEA data base will not affect the β value for the nine elements documented in this report.

**Table-8  First Ionization Potential and Bond Energies (eV) of the Ten Elements**

| At. No. | | I.P. | M-O | M-H | M-S | M-M |
|---|---|---|---|---|---|---|
| 13 | Al | 5.986 | 5.31 | 2.95 | 3.88 | 1.93 |
| 20 | Ca | 6.113 | 4.81 | 1.74 | 3.25 | 0.16 |
| 24 | Cr | 6.766 | 4.43 | 2.9 | 4.14 | 1.61 |
| 25 | Mn | 7.435 | 4.17 | 2.4* | 3.12 | 0.44 |
| 47 | Ag | 7.576 | 2.21 | 2.34 | 2.25* | 1.68 |
| 28 | Ni | 7.635 | 4.06 | 3 | 3.73 | 2.71 |
| 29 | Cu | 7.726 | 3.55 | 2.9 | 2.95 | 2.09 |
| 27 | Co | 7.86 | 3.81 | 2.34* | 3.55 | 1.73 |
| 26 | Fe | 7.87 | 4.24 | 1.86* | 3.34* | 1.04 |
| 46 | Pd | 8.34 | 2.0 | 2.43* | | 0.00 |

Values are taken from Lange's Handbook[31], except those marked with asterisk are from CRC Handbook[32]

A β = 1 is suggested for Pd at the temperature range under consideration. First ionization potential (I.P.) and bond energies for M-O, M-OH, and M-H bonds are given in Table 8. It can be seen that Pd possess the highest first ionization potential of all of the ten elements under consideration, while at the same time, Pd-O, Pd-H and Pd-OH bond energies are lowest of all M-O, M-H and M-OH bonds. Pd does not exist as a dimer (Pd$_2$). These facts indicate that the most likely stable specie at high temperatures would be Pd in its free atomic form (β = 1).

**Table-9   Estimates of Standard Heats of Formation of Pd Species**

| | MW | H$^{o}_{f}$ kcal/mole |
|---|---|---|
| Pd (cr) | 106.42 | 0 |
| Pd gas(30) | 106.42 | 377 |
| Pd+ | 106.41945 | 804.687 |
| Pd$_2$H | 213.84794 | 468.92 |
| PdH$_2$ | 108.436 | 468.92 |
| PdO | 122.4194 | 192.971 |

Therefore, it is recommended that a β value of one be used for Pd, until such time that full thermodynamic data become available on compounds of Pd. A few useful

references[27 - 30] that contain information on Pd species relevant to the hydrocarbon environment under consideration are included in the list of reference.

If one were to neglect the entropy contribution, the heats of formation at 298.15 K for the following Pd species Pd(cr), Pd, Pd+, $Pd_2H$, $PdH_2$ and PdO can be calculated from the bond energies reported in Table 8. These values are given in Table 9. These data may also be added to the CEA data base to provide a first order approximation of species distribution and an estimate of $\beta$, even though the temperature dependence data (coefficients $a_1$ - $a_7$, $b_1$, $b_2$ in equations 2 -4) on these species is not available.

**e. Addendum needed to CEA Data Base**
The following data on Co and Pd should be added to either the original CEA database or to the data base used by an individual:

1. Thermodynamic data on CoO (cr), $Co_3O_4$ (cr), and $CoSO_4$ (cr) as functions of temperature are available in the JANAF Tables. The nine thermodynamic constants used in equations 2, 3 and 4 will have to derived from this data before it can be inputted into the data base. Dr. Russell Claus[33] at the Glenn Research Center has agreed to generate these coefficients. $\beta$ values for Co may be updated once these species have been inserted in the CEA data base. Several other compounds of Co of interest to us ($CoS_2$, $Co_3S_4$, $Co_9S_8$) are reported in the literature[30]. However, no useful thermodynamic data is available on these compounds.

2. Add NiH and $Ni_2O_3$ to the data base.

3. Add Pd species Pd (cr), Pd, Pd+, $Pd_2H$, $PdH_2$ and PdO to the data base.

4. Compounds of Ag of interest to us, such as AgOH, $Ag_2O$, $Ag_2O_2$, $Ag_2O_3$, $Ag_3O_4$, $Ag_3O$, $Ag_2S$ reported in literature[30] should also be added to the data base. It is suspected that many of these compounds may not be thermally stable at the high temperatures of interest to us, because the bond energies of Ag-O and Ag-S are the lowest in the nine elements, and thus may not affect $\beta$ for Ag.

The CEA data base in its current form does not allow addition of a new element such as Pd and species based on it.

**Conclusion**
Reasonable conformity is seen between the $\beta$ values reported in the literature and those calculated from the CEA program. $\beta$ for six elements (Al, Ca, Cr, Cu, Fe and Ni) out of the ten elements may be used until actual experimental data become available. $\beta = 1$ for Pd is suggested based on the bond energy considerations. The calculated $\beta$ values for the remaining three elements (Ag, Co and Mn) are suspected to be on the high side and may not be used with high degree of confidence.

Results from pilot tests with RP-1 on the CR-101 thruster can be used to establish the base line for the trace amounts of these elements in RP-1 fuel. The thruster does not have any moving parts, therefore, it can also be used for plume seeding experiments with these elements to generate $\beta$ values and compare them with those predicted from the CEA code.

The CEA data base should be extended with appropriate oxides, hydrides, hydroxide and sulfur containing species of Pd, Ag, Co and Mn as relevant thermodynamic data become available.

**Acknowledgements**

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