

The Use of MathCAD Functions for Thermochemical Analysis of the CHON System in an Internal Combustion Engines Course

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Abstract

Data from “The Chemkin Thermodynamic Data Base” were used to generate MathCAD functions for the molar specific enthalpy, internal energy, entropy, specific heat at constant volume, and the specific heat at constant pressure for twelve chemical species of the carbon-hydrogen-oxygen-nitrogen (CHON) system. The MathCAD functions were made available for students in ME 448/548 Internal Combustion Engines to use in their homework and projects. The CHON functions were generated to ease the complication of using tabulated data for ideal gas properties and were used by the students to easily determine aspects of combustion such as the heat of combustion of a fuel, adiabatic flame temperature, equilibrium constant, and equilibrium compositions of reacting ideal-gas mixtures. The details and usage of the CHON-MathCAD functions are discussed, and specific examples of their application to problems in an internal combustion engines course are presented. The CHON functions for MathCAD are available for download at <http://www.eng.uab.edu/me/faculty/smcclain/me448/CHONdata.mcd>, and may be referenced by any other MathCAD worksheet.

Introduction

An introduction to combustion is an important component of a first course in internal combustion engines. The current manufacturers’ emphasis on lowering emissions requires that student engineers wanting a position in engine design and development understand the basics of combustion and equilibrium. Since combustion fundamentals may not be covered in their applied thermodynamics course, this material must be covered in an internal combustion (IC) engine fundamentals course.

The combustion material covered in an internal combustion engines course usually includes enthalpy of combustion, adiabatic flame temperature, and chemical equilibrium.^{1,2,3} Without using computer programs, working fundamental combustion problems requires the arduous use of tables. Undergraduates in an IC engines course often become frustrated using the tables, and fail to comprehend either the material or the

significance of the material. To help students understand the material and work more complicated combustion problems while relieving them of the tedious solution techniques, MathCAD functions were generated to calculate many important thermodynamic properties of the constituents most commonly associated with combustion in reciprocating engines.

Many computer codes are available for solving combustion problems. “The CSU Engine Web Pages” are excellent websites to assist students in an IC engines course.⁴ “The CSU Engine Web Pages” contains several applets that solve combustion problems; however, only the final answers are displayed. The thermodynamic functions were generated for MathCAD because the appearance of MathCAD worksheets is very similar to the mathematics used to describe the solutions. Using MathCAD, students not only see the solutions to complex engineering problems, but they also see the worksheet code that looks very similar to the theory and mathematics presented to solve the problem. The mathematical appearance of MathCAD reinforces the theory presented to the students.

Format of Function Worksheet

The data used to create the functions came from “The Chemkin Thermodynamic Data Base” as reported by Turns.⁵ Turns reports fourteen constants used to determine thermodynamic data for twelve species (CO, CO₂, H₂, H, OH, H₂O, N₂, N, NO, NO₂, O, O₂) of the carbon-hydrogen-oxygen-nitrogen (CHON) system as a function of temperature. The first seven constants for each species are used to determine thermodynamic properties in the temperature range of 300 K to 1000 K. The second seven constants for each species are valid between 1000 K and 5000 K. The property constant table was entered in the MathCAD worksheet, *CHONData.mcd*. The property constant table can be found in Appendix A.

Using the appropriate seven constants (a_1, a_2, \dots, a_7) for the temperature range, the specific heats, the enthalpy, the internal energy, the entropy, and the Gibbs free energy are calculated as functions of temperature. Using the appropriate constants, the function for the molar specific heat at constant pressure for each species was created using the formula

$$\bar{c}_p(T) = R_u (a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \quad (1)$$

The function for the molar specific heat at constant pressure is called from MathCAD as “cpm_{XX}(T)”, where the “m” was added as a reminder that the property is reported on a per-unit-mole basis, and the “XX” represents the chemical formula for the species. The function molar specific heat at constant volume, $\bar{c}_v(T)$, was created using

$$\bar{c}_v(T) = \bar{c}_p(T) - R_u \quad (2)$$

The function for $\bar{c}_v(T)$ is called from MathCAD as “cvm_{XX}(T)”. The function for the molar specific enthalpy, $\bar{h}^\circ(T)$, was created using the formula

$$\bar{h}^\circ(T) = R_u T \left(a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T} \right) \quad (3)$$

The function for $\bar{h}^\circ(T)$ is called from MathCAD as “hm_{XX}(T)”. The function for the molar specific internal energy, $\bar{u}(T)$, was created using

$$\bar{u}(T) = \bar{h}^\circ(T) - R_u T \quad (4)$$

The function for $\bar{u}(T)$ is called from MathCAD as “um_{XX}(T)”. The function for the molar specific entropy, $\bar{s}^\circ(T)$, was created using

$$\bar{s}^\circ(T) = R_u \left(a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \right) \quad (5)$$

The function for $\bar{s}^\circ(T)$ is called from MathCAD as “sm_{XX}(T)”. The function for the molar specific Gibbs free energy, $\bar{g}^\circ(T)$, was created using

$$\bar{g}^\circ(T) = \bar{h}^\circ(T) - T\bar{s}^\circ(T) \quad (6)$$

The function for $\bar{g}^\circ(T)$ is called from MathCAD as “μm_{XX}(T)”.

For all of the thermodynamic functions reported above, the temperature must be dimensionless but have the magnitude of Kelvin. While the temperature must go into the function dimensionless, the output of the function will have the appropriate units. For example, the molar specific enthalpy of O₂ at 3000 K would be found in MathCAD using the statement:

$$\text{hm}_{\text{O}_2}(3000) = 9.803 \times 10^7 \frac{\text{J}}{\text{kmol}}$$

Appendix A presents a page from *CHONdata.mcd* showing the generation and testing of the thermodynamic property functions for CO.

The chemical equilibrium functions as a function of temperature are also generated in the worksheet. For a general chemical reaction of the form



The standard state Gibbs function change is

$$\Delta G^\circ(T) = \left(e\bar{g}_E^\circ(T) + f\bar{g}_F^\circ(T) + \dots \right) - \left(a\bar{g}_A^\circ(T) + b\bar{g}_B^\circ(T) + \dots \right) \quad (8)$$

The equilibrium constant is then calculated from the standard state Gibbs function change using

$$K_p(T) = \exp\left(\frac{-\Delta G^\circ(T)}{R_u T}\right) \quad (9)$$

Equilibrium constant functions were generated for eight independent reactions of the CHON system. Those eight reactions are:


- I. $H_2 \Leftrightarrow 2H$
- II. $O_2 \Leftrightarrow 2O$
- III. $N_2 \Leftrightarrow 2N$
- IV. $H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$
- V. $2H_2O \Leftrightarrow H_2 + 2OH$
- VI. $N_2 + O_2 \Leftrightarrow 2NO$
- VII. $CO_2 \Leftrightarrow CO + \frac{1}{2}O_2$
- VIII. $CO_2 + H_2 \Leftrightarrow CO + H_2O$

The functions for the equilibrium constant are called using “Kp_{YY}(T)”, where “YY” represents the roman numeral listed for each reaction. For example, the equilibrium constant for $CO_2 + H_2 \Leftrightarrow CO + H_2O$ at 4500 K is found in MathCAD using the statement:

$$Kp_{VIII}(4500) = 8.932$$

Appendix A also presents the construction and validation of the equilibrium constant functions. The equilibrium constant functions were validated using data from the *JANAF Thermochemical Tables* as reported by Russell and Adebisi.⁶

All of the functions generated are in one file (*CHONdata.mcd*) and are available to the public for download at <http://www.eng.uab.edu/me/faculty/smcclain/me448/CHONdata.mcd>. (Note: If the web server is down or the file is unavailable, please email me at smcclain@uab.edu and request the file.) To use the functions in a new MathCAD worksheet, the information in *CHONdata.mcd* does not have to be copied into the new worksheet. The function worksheet may be referenced by using the <Insert, Reference> command, and identifying the *CHONdata.mcd* file. When this is done correctly, the statement

 Reference:C:\ICEEngines\CHONdata.mcd

will appear in the worksheet. All functions generated in *CHONdata.mcd* will then be available for use in the new worksheet.

Example Problems and Solutions

Three example problems are listed below, and the solutions are provided in the appendices. The example problems involve the calculation of an adiabatic flame temperature, the analysis of the compression of an exhaust/fresh-air mixture, and the calculation of equilibrium composition of a reacting mixture. The solutions to the example problems are not thoroughly discussed below, but the ways in which MathCAD and the CHON functions are used in the solution are discussed.

Adiabatic Flame Temperature

Problem Statement: A stoichiometric mixture of gasoline and air fill a 5 in³ insulated, rigid chamber at 25 °C and 1 atm. At some point, a spark plug ignites the mixture. What are the temperature and pressure of the products?

When applied to this example, the First Law of Thermodynamics states that the internal energy of the products must equal the internal energy of the reactants.

$$\sum_P N_i (\bar{h}_{f,i}^o + \bar{u}_i - \bar{u}_{i,ref}) = \sum_R N_i (\bar{h}_{f,i}^o + \bar{u}_i - \bar{u}_{i,ref}) \quad (10)$$

where $\bar{h}_{f,i}^o$ is the enthalpy of formation of each species. In terms of the enthalpy of combustion, $\Delta\bar{h}_c$:

$$\sum_P N_i (\bar{u}_i(T_P) - \bar{u}_{i,ref}) = \sum_R N_i (\bar{u}_i(T_R) - \bar{u}_{i,ref}) - N_{fuel} \Delta\bar{h}_c \quad (11)$$

The difficulty in solving equation (11) for the adiabatic flame temperature is that when solved using the tables, an iterative approach must be used. The temperature of the products must be assumed. The internal energy of the products must be evaluated based on the assumed temperature and compared to the internal energy of the reactants. Appendix B demonstrates how a Given-Find block in MathCAD is used with the CHON functions to quickly solve this problem.

Mixing and Compression of Products and Intake air

Problem Statement: Exhaust gases at 1000 °C and 100.0 kPa reside in the clearance volume of a piston/cylinder with a compression ratio of 10 and a displacement of 43.75 in³. Fresh air with a temperature of 100 °C and a pressure of 100.0 kPa is pulled into the cylinder. What is the temperature of the mixture in the cylinder after the intake process? If the mixture is compressed, what are the temperature and pressure of the mixture after compression? What is the work of compression? Assume that the exhaust is composed of the products of complete combustion of air and isoctane with no dissociation.

When applied to the mixing process of example, the First Law of Thermodynamics states that the total internal energy of the mixture must equal the sum of the internal energies for the exhaust and the fresh air.

$$\sum_{Mixture} N_i (\bar{u}_i(T_M) - \bar{u}_{i,ref}) = \sum_{Exhaust} N_i (\bar{u}_i(T_{Exhaust}) - \bar{u}_{i,ref}) + \sum_{Fresh} N_i (\bar{u}_i(T_{Fresh}) - \bar{u}_{i,ref}) \quad (12)$$

Like the adiabatic flame temperature example, this part of the example requires that an iterative process be used to determine the temperature of the mixture. A Given-Find block is again used to evaluate the temperature of the mixture.

To find the temperature after compression, the compression process must be assumed to be isentropic. For an isentropic process with no change in mixture composition,

$$S_2 - S_1 = 0 = \int_{T_1}^{T_2} \sum_{i=1}^k N_i c_{v,i} \frac{dT}{T} + \sum_{i=1}^k N_i \bar{R} \ln \frac{v_{2,i}}{v_{1,i}} \quad (13)$$

or

$$\int_{T_1}^{T_2} \sum_{i=1}^k N_i c_{v,i} \frac{dT}{T} = N \bar{R} \ln \frac{V_2}{V_1} \quad (14)$$

A Given-Find block is once again used to determine the answer to the second part of this example. The interesting feature of the Given-Find block in this example is that the term to be found, the temperature after compression, is a limit of integration. The computer code required to perform this operation in either FORTRAN or C++ is considerable, yet it is just three lines in MathCAD.

Given

$$\int_{\frac{T_1}{K}}^{\frac{T_2}{K}} \frac{N_{O_2} \cdot cv_{mO_2}(T) + N_{N_2} \cdot cv_{mN_2}(T) \dots + N_{H_2O} \cdot cv_{mH_2O}(T) + N_{CO_2} \cdot cv_{mCO_2}(T)}{T} dT = (N_{exh} + N_{fa}) \cdot R_u \cdot \ln(r_c)$$

$$T_2 := \text{Find}(T_2)$$

The final part of this solution is the application of the First Law of Thermodynamics to the compression process.

$$W_{comp} = -\sum_{i=1}^k N_i (\bar{u}_{2,i} - \bar{u}_{1,i}) \quad (15)$$

The complete solution to this example is found in Appendix C.

Chemical Equilibrium

Problem Statement: One mole of methane is burned in air with a pressure of 10 atm. If the products of combustion are CO₂, CO, H₂, H₂O, OH, O₂ and N₂, what is the equilibrium composition at 3000 K and with 95% theoretical air? How does the equilibrium composition vary if the percentage theoretical air varies from 90% to 110% at 3000 K? How does the equilibrium composition vary if the temperature varies from 2500 to 5000 K with 95% theoretical air?

The equations to solve for the equilibrium composition of this system are developed from the conservation of species and from the equilibrium equations. Each of the equilibrium equations has the form

$$K_p = \frac{N_E^e N_F^f \cdots \left(\frac{P}{N}\right)^{(e+f+\dots)-(a+b+\dots)}}{N_A^a N_b^B \cdots} \quad (16)$$

based on the general chemical reaction of equation (7). In equation (16), P is the total pressure in atmospheres, and N is the total moles of reacting and inert species. Since the problem states that the N₂ does not dissociate into N or form NO_x, there are six unknowns that must be found. Three linear equations come from the conservation of carbon, oxygen, and hydrogen. The other three equations are nonlinear and come from the equilibrium of reactions IV, V, and VII.

A Given-Find block is again used to solve the system of six nonlinear equations and six unknowns. The interesting aspect of this solution is that the Given-Find block was made to be a function of the temperature and the percentage theoretical air. This allowed the equilibrium composition to be easily plotted versus either temperature or percentage theoretical air. The complete solution to this example is found in Appendix D.

Discussion and Conclusions

The CHON functions were presented to the students through lectures on combustion fundamentals. At the end of the lectures, example problems using the CHON functions would be distributed in class and discussed. Homework sets would then be given. The students were given the electronic copy of *CHONdata.mcd* and were expected to expand on the class examples.

The techniques demonstrated in the three examples can be combined to perform a thermochemical analysis of engine cycles that is much more accurate than the pure substance analysis or perfect gas analysis taught in a junior level applied thermodynamics

course. For one of their final projects, the students were asked to find an engine with a considerable amount of information regarding specifications and performance and make predictions of maximum brake power and maximum brake torque. Students used other MathCAD worksheets to estimate engine parameters such as volumetric efficiency and engine heat transfer with the CHON functions to create highly detailed models of engine performance that in most cases were very close to the engine ratings.

The main purposes for constructing the CHON functions in MathCAD were to shorten the time required to teach combustion and to make solving complicated combustion problems easier for the students. The CHON functions were only used in the Fall 2003 semester, and after only one semester of using the CHON functions in MathCAD, it is difficult to tell if the functions shortened the time spent on combustion material. However, it was very obvious that the MathCAD functions eased the tediousness of solving thermochemical problems presented in an internal combustion engines course and allowed a deeper understanding of combustion-problem intricacies.

The student surveys for courses at the University of Alabama at Birmingham list the question, "What did you like most about the course?" Two of the responses for this question were:

"The MathCAD assignments were good and useful and was *<sic>* a great idea."

"Use of MathCAD in I. C. engine analysis and all other topics."

No discouraging comments were made regarding the MathCAD analysis homework problems or projects in the student surveys. During informal chats with the students, the ease of using the MathCAD worksheets was also readily apparent. While it is currently unclear if the CHON functions decreased the time required to cover combustion material, the students' performance on homework and projects and the student comments in the student surveys and in informal chats demonstrated that the CHON functions were highly successful in easing the instruction of combustion material in an internal combustion engines course.

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Appendix A: Format of the CHONData.mcd File

CHEMKIN property data were entered into the matrix A. This file can be referenced by any other MathCAD program. The functions created in this file can then be used throughout the new MathCAD program.

$$A := \begin{pmatrix} 3.025078 \times 10^0 & 1.4426885 \times 10^{-3} & -5.630827 \times 10^{-7} & 1.0185813 \times 10^{-10} & -6.910951 \times 10^{-15} & -1.426835 \times 10^4 & 6.108217 \times 10^0 \\ 3.262451 \times 10^0 & 1.5119409 \times 10^{-3} & -3.881755 \times 10^{-6} & 5.581944 \times 10^{-9} & -2.474951 \times 10^{-12} & -1.4310539 \times 10^4 & 4.848897 \times 10^0 \\ 4.453623 \times 10^0 & 3.140168 \times 10^{-3} & -1.2784105 \times 10^{-6} & 2.393996 \times 10^{-10} & -1.6690333 \times 10^{-14} & -4.896696 \times 10^4 & -9.553959 \times 10^{-1} \\ 2.275724 \times 10^0 & 9.922072 \times 10^{-3} & -1.0409113 \times 10^{-5} & 6.866686 \times 10^{-9} & -2.11725 \times 10^{-12} & -4.837314 \times 10^4 & 1.0188488 \times 10^1 \\ 2.991423 \times 10^0 & 7.000644 \times 10^{-4} & -5.633828 \times 10^{-8} & -9.231575 \times 10^{-12} & 1.5827519 \times 10^{-15} & -8.35034 \times 10^2 & -1.3551101 \times 10^0 \\ 3.298124 \times 10^0 & 8.249441 \times 10^{-4} & -8.143015 \times 10^{-7} & -9.475434 \times 10^{-11} & 4.134872 \times 10^{-13} & -1.0125209 \times 10^3 & -3.294094 \times 10^0 \\ 2.5 \times 10^0 & 0 \times 10^0 & 0 \times 10^0 & 0 \times 10^0 & 0 \times 10^0 & 2.547162 \times 10^4 & -4.601176 \times 10^{-1} \\ 2.5 \times 10^0 & 0 \times 10^0 & 0 \times 10^0 & 0 \times 10^0 & 0 \times 10^0 & 2.547162 \times 10^4 & -4.601176 \times 10^{-1} \\ 2.88273 \times 10^0 & 1.0139743 \times 10^{-3} & -2.276877 \times 10^{-7} & 2.174683 \times 10^{-11} & -5.126305 \times 10^{-16} & 3.886888 \times 10^3 & 5.595712 \times 10^0 \\ 3.637266 \times 10^0 & 1.85091 \times 10^{-4} & -1.6761646 \times 10^{-6} & 2.387202 \times 10^{-9} & -8.431442 \times 10^{-13} & 3.606781 \times 10^3 & 1.3588605 \times 10^0 \\ 2.672145 \times 10^0 & 3.056293 \times 10^{-3} & -8.73026 \times 10^{-7} & 1.2009964 \times 10^{-10} & -6.391618 \times 10^{-15} & -2.989921 \times 10^4 & 6.862817 \times 10^0 \\ 3.386842 \times 10^0 & 3.474982 \times 10^{-3} & -6.354696 \times 10^{-6} & 6.968581 \times 10^{-9} & -2.506588 \times 10^{-12} & -3.020811 \times 10^4 & 2.590232 \times 10^0 \\ 2.92664 \times 10^0 & 1.4879768 \times 10^{-3} & -5.68476 \times 10^{-7} & 1.0097038 \times 10^{-10} & -6.753351 \times 10^{-15} & -9.227977 \times 10^2 & 5.980528 \times 10^0 \\ 3.298677 \times 10^0 & 1.4082404 \times 10^{-3} & -3.963222 \times 10^{-6} & 5.641515 \times 10^{-9} & -2.444854 \times 10^{-12} & -1.0208999 \times 10^3 & 3.950372 \times 10^0 \\ 2.450268 \times 10^0 & 1.0661458 \times 10^{-4} & -7.465337 \times 10^{-8} & 1.879652 \times 10^{-11} & -1.0259839 \times 10^{-15} & 5.611604 \times 10^4 & 4.448758 \times 10^0 \\ 2.503071 \times 10^0 & -2.180018 \times 10^{-5} & 5.420529 \times 10^{-8} & -5.64756 \times 10^{-11} & 2.099904 \times 10^{-14} & 5.60989 \times 10^4 & 4.167566 \times 10^0 \\ 3.245435 \times 10^0 & 1.2691383 \times 10^{-3} & -5.01589 \times 10^{-7} & 9.169283 \times 10^{-11} & -6.275419 \times 10^{-15} & 9.80084 \times 10^3 & 6.417293 \times 10^0 \\ 3.376541 \times 10^0 & 1.2530634 \times 10^{-3} & -3.30275 \times 10^{-6} & 5.21781 \times 10^{-9} & -2.446262 \times 10^{-12} & 9.817961 \times 10^3 & 5.82959 \times 10^0 \\ 4.682859 \times 10^0 & 2.462429 \times 10^{-3} & -1.0422585 \times 10^{-6} & 1.976902 \times 10^{-10} & -1.3917168 \times 10^{-14} & 2.261292 \times 10^3 & 9.885985 \times 10^{-1} \\ 2.6706 \times 10^0 & 7.8385 \times 10^{-3} & -8.063864 \times 10^{-6} & 6.161714 \times 10^{-9} & -2.32015 \times 10^{-12} & 2.89629 \times 10^3 & 1.1612071 \times 10^1 \\ 3.697578 \times 10^0 & 6.135197 \times 10^{-4} & -1.258842 \times 10^{-7} & 1.775281 \times 10^{-11} & -1.1364354 \times 10^{-15} & -1.2339301 \times 10^3 & 3.189165 \times 10^0 \\ 3.212936 \times 10^0 & 1.1274864 \times 10^{-3} & -5.75615 \times 10^{-7} & 1.3138773 \times 10^{-9} & -8.768554 \times 10^{-13} & -1.005249 \times 10^3 & 6.034737 \times 10^0 \\ 2.542059 \times 10^0 & -2.755061 \times 10^{-5} & -3.102803 \times 10^{-9} & 4.551067 \times 10^{-12} & -0.04368051 \times 10^{-14} & 2.92308 \times 10^4 & 4.920308 \times 10^0 \\ 2.946428 \times 10^0 & -1.6381665 \times 10^{-3} & 2.421031 \times 10^{-6} & -1.6028431 \times 10^{-9} & 3.890696 \times 10^{-13} & 2.914764 \times 10^4 & 2.963995 \times 10^0 \end{pmatrix}$$

$$\text{kmol} := 1000 \cdot \text{mol} \quad \text{kJ} := 1000 \cdot \text{J}$$

$$R_u := 8.314 \cdot \frac{\text{kJ}}{\text{kmol} \cdot \text{K}}$$

Example sheet of the properties functions is shown below.

$$hm_{CO}(T) := \begin{cases} h \leftarrow T \cdot K \cdot R_u \cdot \left(A_{1,0} + \frac{A_{1,1}}{2} \cdot T + \frac{A_{1,2}}{3} \cdot T^2 + \frac{A_{1,3}}{4} \cdot T^3 + \frac{A_{1,4}}{5} \cdot T^4 + \frac{A_{1,5}}{T} \right) & \text{if } T \leq 1000 \\ h \leftarrow T \cdot K \cdot R_u \cdot \left(A_{0,0} + \frac{A_{0,1}}{2} \cdot T + \frac{A_{0,2}}{3} \cdot T^2 + \frac{A_{0,3}}{4} \cdot T^3 + \frac{A_{0,4}}{5} \cdot T^4 + \frac{A_{0,5}}{T} \right) & \text{if } T > 1000 \\ h & \end{cases}$$

$$sm_{CO}(T) := \begin{cases} s \leftarrow R_u \cdot \left(A_{1,0} \cdot \ln(T) + A_{1,1} \cdot T + \frac{A_{1,2}}{2} \cdot T^2 + \frac{A_{1,3}}{3} \cdot T^3 + \frac{A_{1,4}}{4} \cdot T^4 + A_{1,6} \right) & \text{if } T \leq 1000 \\ s \leftarrow R_u \cdot \left(A_{0,0} \cdot \ln(T) + A_{0,1} \cdot T + \frac{A_{0,2}}{2} \cdot T^2 + \frac{A_{0,3}}{3} \cdot T^3 + \frac{A_{0,4}}{4} \cdot T^4 + A_{0,6} \right) & \text{if } T > 1000 \\ s & \end{cases}$$

$$um_{CO}(T) := hm_{CO}(T) - R_u \cdot T \cdot K \qquad um_{CO}(1000) = -97153580.253 \frac{J}{kmol}$$

$$hm_{CO}(5000) = 58404648.8 \frac{J}{kmol}$$

$$sm_{CO}(5000) = 292757.159 \frac{J}{kmol \cdot K}$$

$$cpm_{CO}(T) := \begin{cases} cp \leftarrow R_u \cdot \left(A_{1,0} + A_{1,1} \cdot T + A_{1,2} \cdot T^2 + A_{1,3} \cdot T^3 + A_{1,4} \cdot T^4 \right) & \text{if } T \leq 1000 \\ cp \leftarrow R_u \cdot \left(A_{0,0} + A_{0,1} \cdot T + A_{0,2} \cdot T^2 + A_{0,3} \cdot T^3 + A_{0,4} \cdot T^4 \right) & \text{if } T > 1000 \\ cp & \end{cases}$$

$$cvm_{CO}(T) := cpm_{CO}(T) - R_u$$

$$cpm_{CO}(298) = 29069.855 \frac{J}{kmol \cdot K}$$

$$cvm_{CO}(298) = 20.756 \frac{kg \cdot m^2}{s^2 \cdot K \cdot mol}$$

$$\frac{cpm_{CO}(298)}{cvm_{CO}(298)} = 1.401$$

$$\mu m_{CO}(T) := hm_{CO}(T) - T \cdot K \cdot sm_{CO}(T)$$

The generation and testing of the equilibrium constant functions is presented below.

$\ln K_{pI}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (2 \cdot \mu_{mH}(T) - \mu_{mH_2}(T))$	$\ln K_{pI}(1000) = -39.817$	$K_{pI}(T) := e^{\ln K_{pI}(T)}$
$\ln K_{pII}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (2 \cdot \mu_{mO}(T) - \mu_{mO_2}(T))$	$\ln K_{pII}(1000) = -45.168$	$K_{pII}(T) := e^{\ln K_{pII}(T)}$
$\ln K_{pIII}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (2 \cdot \mu_{mN}(T) - \mu_{mN_2}(T))$	$\ln K_{pIII}(1000) = -99.149$	$K_{pIII}(T) := e^{\ln K_{pIII}(T)}$
$\ln K_{pIV}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (\mu_{mH_2O}(T) - \mu_{mH_2}(T) - \frac{1}{2} \cdot \mu_{mO_2}(T))$	$\ln K_{pIV}(1000) = 23.171$	$K_{pIV}(T) := e^{\ln K_{pIV}(T)}$
$\ln K_{pV}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (\mu_{mH_2}(T) + 2 \cdot \mu_{mOH}(T) - 2 \cdot \mu_{mH_2O}(T))$	$\ln K_{pV}(1000) = -51.969$	$K_{pV}(T) := e^{\ln K_{pV}(T)}$
$\ln K_{pVI}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (2 \cdot \mu_{mNO}(T) - \mu_{mO_2}(T) - \mu_{mN_2}(T))$	$\ln K_{pVI}(1000) = -18.709$	$K_{pVI}(T) := e^{\ln K_{pVI}(T)}$
$\ln K_{pVII}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (\mu_{mCO_2}(T) - \mu_{mCO}(T) - \frac{1}{2} \cdot \mu_{mO_2}(T))$	$\ln K_{pVII}(1000) = 23.538$	$K_{pVII}(T) := e^{\ln K_{pVII}(T)}$
$\ln K_{pVIII}(T) := \frac{-1}{R_u \cdot T \cdot K} \cdot (\mu_{mCO}(T) + \mu_{mH_2O}(T) - \mu_{mCO_2}(T) - \mu_{mH_2}(T))$	$\ln K_{pVIII}(1000) = -0.367$	$K_{pVIII}(T) := e^{\ln K_{pVIII}(T)}$

Appendix B: Flame Temperature Calculation

Reference: C:\ICEngines\CHONdata.mcd

Problem Statement: A stoichiometric mixture of gasoline and air fill a 5 in³ insulated chamber at 25 C and 1 atm. At some point, a spark plug ignites the mixture. What are the temperature and pressure of the products?

Solution: The important input parameters such as the temperature of the reactants, the reference temperature and the volume of the chamber are entered below.

$$T_R := 298\text{ K} \quad P_R := 101325\text{ Pa} \quad \text{Vol} := 5 \cdot \text{in}^3 \quad \text{Vol} = 8.194 \times 10^{-5} \text{ m}^3$$

$$T_{\text{ref}} := 298\text{ K} \quad M_R := 28.97 \frac{\text{kg}}{\text{kmol}} \quad M_{\text{fuel}} := 111 \frac{\text{kg}}{\text{kmol}}$$

The heat of combustion of gasoline and the stoichiometric air to fuel ratio (gravimetric) is entered below.

$$\Delta h_c := -48.2 \cdot 10^6 \frac{\text{J}}{\text{kg}} \quad \Delta h_{m_c} := \Delta h_c \cdot M_{\text{fuel}} \quad \Delta h_{m_c} = -5.3502 \times 10^6 \frac{\text{kJ}}{\text{kmol}}$$

$$\text{AoF} := 14.6$$

The mass of air in the chamber is found using ideal gas law. The mass of fuel is found using the air to fuel ratio.

$$m_{\text{air}} := \frac{P_R \cdot \text{Vol}}{\frac{R_u}{M_R} \cdot T_R} \quad m_{\text{air}} = 9.708 \times 10^{-5} \text{ kg} \quad m_{\text{fuel}} := \frac{m_{\text{air}}}{\text{AoF}} \quad m_{\text{fuel}} = 6.649 \times 10^{-6} \text{ kg}$$

The total mass of reactants is the sum of the mass of fuel and the mass of air.

$$m_R := m_{\text{air}} + m_{\text{fuel}} \quad m_R = 1.037 \times 10^{-4} \text{ kg}$$

The reaction equation is: $\text{C}_8\text{H}_{15} + 11.75(\text{O}_2 + 3.76\text{N}_2) = 8\text{CO}_2 + 7.5\text{H}_2\text{O} + 44.18\text{N}_2$

Thus, for the combustion of one mole of fuel, the moles of each product are entered below.

$$N_{\text{CO}_2} := 8 \cdot \text{kmol} \quad N_{\text{H}_2\text{O}} := 7.5 \cdot \text{kmol} \quad N_{\text{N}_2} := 44.18 \text{ kmol} \quad N_{\text{fuel}} := 1 \cdot \text{kmol}$$

The first law as applied to the adiabatic reaction is:

$$\sum_{i=1}^{k_P} N_i (u_{m_i}(T_P) - u_{m_i}(T_{\text{ref}})) = \sum_{i=1}^{k_R} N_i (u_{m_i}(T_R) - u_{m_i}(T_{\text{ref}})) - N_{\text{fuel}} \cdot \Delta h_{m_c}$$

The temperature of the reactants equals the reference temperature so the First Law becomes

$$\sum_{i=1}^{k_P} N_i \cdot u_{m_i}(T_P) = \sum_{i=1}^{k_P} N_i \cdot u_{m_i}(T_{\text{ref}}) - N_{\text{fuel}} \cdot \Delta h_{m_c} = U_P$$

The internal energy of the reactants is then evaluated as:

$$U_P := N_{\text{CO}_2} \cdot u_{\text{CO}_2}(298) + N_{\text{H}_2\text{O}} \cdot u_{\text{H}_2\text{O}}(298) + N_{\text{N}_2} \cdot u_{\text{N}_2}(298) - N_{\text{fuel}} \cdot \Delta h_{\text{m}_c}$$

$$U_P = 2.402 \times 10^8 \text{ J}$$

A Given-Find block can now be used to find the combustion temperature. An initial guess must be made.

$$T_P := 2500 \text{ K}$$

Given

$$U_P = N_{\text{CO}_2} \cdot u_{\text{CO}_2}\left(\frac{T_P}{\text{K}}\right) + N_{\text{H}_2\text{O}} \cdot u_{\text{H}_2\text{O}}\left(\frac{T_P}{\text{K}}\right) + N_{\text{N}_2} \cdot u_{\text{N}_2}\left(\frac{T_P}{\text{K}}\right)$$

$$T_P := \text{Find}(T_P) \quad \boxed{T_P = 3204.6 \text{ K}}$$

To find the pressure we must use the ideal gas law and the knowledge that the mass of the products must equal the mass of reactants.

$$m_P := m_R \quad m_P = 1.037 \times 10^{-4} \text{ kg}$$

To use the ideal gas law, the average molecular weight of the products must be found.

$$M_{\text{CO}_2} := 44.011 \frac{\text{kg}}{\text{kmol}} \quad M_{\text{H}_2\text{O}} := 18.0152 \frac{\text{kg}}{\text{kmol}} \quad M_{\text{N}_2} := 28.0134 \frac{\text{kg}}{\text{kmol}}$$

$$M_P := \frac{1}{N_{\text{CO}_2} + N_{\text{H}_2\text{O}} + N_{\text{N}_2}} \cdot (N_{\text{CO}_2} \cdot M_{\text{CO}_2} + N_{\text{H}_2\text{O}} \cdot M_{\text{H}_2\text{O}} + N_{\text{N}_2} \cdot M_{\text{N}_2})$$

$$M_P = 28.901 \frac{\text{kg}}{\text{kmol}}$$

Applying the Ideal Gas Law:

$$P_P := m_P \cdot \frac{R_u \cdot T_P}{M_P \cdot \text{Vol}} \quad \boxed{P_P = 1.167 \times 10^6 \text{ Pa}}$$

Thus, the temperature and pressure in the container after combustion are 3204.6 K and 11.67 MPa, respectively.

Appendix C: Isentropic Compression and Expansion Calculation

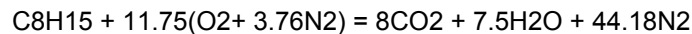
☞ Reference: C:\ICEngines\CHONdata.mcd

Problem Statement: Exhaust gases at 1000 C and 100.0 kPa reside in the clearance volume of a piston/cylinder with a compression ratio of 10 and a displacement of 43.75 in³. Fresh air with a temperature of 100 C and a pressure of 100.0 kPa is pulled into the cylinder. What is the temperature of the mixture in the cylinder after the intake process? If the mixture is compressed, what are the temperature and pressure of the mixture after compression? What is the work of compression? Assume that the exhaust is composed of the products of complete combustion of air and isooctane with no dissociation.

Solution: The important engine parameters are entered below.

$$V_d := 43.75 \text{ in}^3 \quad r_c := 10 \quad V_c := \frac{V_d}{r_c - 1} \quad V_c = 4.861 \text{ in}^3 \quad V_c = 79.659 \text{ cm}^3$$
$$P_{\text{exh}} := 100 \cdot 10^3 \cdot \text{Pa} \quad T_{\text{exh}} := 1273 \cdot \text{K} \quad P_{\text{fa}} := P_{\text{exh}} \quad T_{\text{fa}} := 373 \cdot \text{K}$$

The reaction equation for complete combustion of isooctane with air is



The mole fraction for each product species is

$$y_{\text{CO}_2} := \frac{8}{59.68} \quad y_{\text{H}_2\text{O}} := \frac{7.5}{59.68} \quad y_{\text{N}_2} := \frac{44.18}{59.68}$$

The total number of moles in the clearance volume is found using the Ideal Gas Law.

$$N_{\text{exh}} := \frac{P_{\text{exh}} \cdot V_c}{R_u \cdot T_{\text{exh}}} \quad N_{\text{exh}} = 7.527 \times 10^{-7} \text{ kmol}$$

The moles of each species of the exhaust is determined below.

$$N_{\text{CO}_2} := y_{\text{CO}_2} \cdot N_{\text{exh}} \quad N_{\text{H}_2\text{O}} := y_{\text{H}_2\text{O}} \cdot N_{\text{exh}} \quad N_{\text{N}_2\text{exh}} := y_{\text{N}_2} \cdot N_{\text{exh}}$$
$$N_{\text{CO}_2} = 1.009 \times 10^{-4} \text{ mol} \quad N_{\text{H}_2\text{O}} = 9.459 \times 10^{-5} \text{ mol} \quad N_{\text{N}_2\text{exh}} = 5.572 \times 10^{-4} \text{ mol}$$

The total number of moles of fresh air entering the cylinder is

$$N_{\text{fa}} := \frac{P_{\text{fa}} \cdot V_d}{R_u \cdot T_{\text{fa}}} \quad N_{\text{fa}} = 2.312 \times 10^{-5} \text{ kmol}$$

Assuming an air analysis of 79% N₂ and 21% O₂ yields the moles of N₂ and O₂ entering the cylinder.

$$N_{\text{N}_2\text{fa}} := 0.79 \cdot N_{\text{fa}} \quad N_{\text{N}_2\text{fa}} = 0.018 \text{ mol} \quad N_{\text{O}_2} := 0.21 \cdot N_{\text{fa}} \quad N_{\text{O}_2} = 4.855 \times 10^{-3} \text{ mol}$$

The total number of moles of N₂ after mixing is

$$N_{\text{N}_2\text{t}} := N_{\text{N}_2\text{exh}} + N_{\text{N}_2\text{fa}}$$

The First Law, as written below, is used to determine the temperature of the mixture.

$$\sum_{\text{mixture}} N_i \cdot u_{m_i} = \sum_{\text{exhaust}} N_i \cdot u_{m_i} + \sum_{\text{freshair}} N_i \cdot u_{m_i}$$

An iterative procedure is required to determine the mixed temperature. In Mathcad, a Given-Find block is used. The initial guess of 400 K is used.

$$T_1 := 400 \cdot \text{K}$$

Given

$$\begin{aligned} N_{\text{CO}_2} \cdot u_{\text{CO}_2} \left(\frac{T_1}{\text{K}} \right) + N_{\text{H}_2\text{O}} \cdot u_{\text{H}_2\text{O}} \left(\frac{T_1}{\text{K}} \right) \dots &= N_{\text{CO}_2} \cdot u_{\text{CO}_2} \left(\frac{T_{\text{exh}}}{\text{K}} \right) + N_{\text{H}_2\text{O}} \cdot u_{\text{H}_2\text{O}} \left(\frac{T_{\text{exh}}}{\text{K}} \right) \dots \\ + N_{\text{N}_2\text{t}} \cdot u_{\text{N}_2} \left(\frac{T_1}{\text{K}} \right) \dots &+ N_{\text{N}_2\text{exh}} \cdot u_{\text{N}_2} \left(\frac{T_{\text{exh}}}{\text{K}} \right) + N_{\text{N}_2\text{fa}} \cdot u_{\text{N}_2} \left(\frac{T_{\text{fa}}}{\text{K}} \right) \dots \\ + N_{\text{O}_2} \cdot u_{\text{O}_2} \left(\frac{T_1}{\text{K}} \right) &+ N_{\text{O}_2} \cdot u_{\text{O}_2} \left(\frac{T_{\text{fa}}}{\text{K}} \right) \end{aligned}$$

$$T_1 := \text{Find}(T_1) \quad \boxed{T_1 = 408.809 \text{K}}$$

The pressure after mixing is found from the ideal gas equation.

$$P_1 := \frac{(N_{\text{CO}_2} + N_{\text{H}_2\text{O}} + N_{\text{O}_2} + N_{\text{N}_2\text{t}}) \cdot R_u \cdot T_1}{V_c \cdot r_c} \quad P_1 = 1.019 \times 10^5 \text{ Pa}$$

The expression below is used to determine the temperature following the isentropic compression of the ideal gas mixture.

$$\int_{T_1}^{T_2} \frac{\sum_{i=1}^k (N_i \cdot c_{v_i})}{T} dT = N \cdot R_u \cdot \ln \left(\frac{V_2}{V_1} \right)$$

The isentropic compression expression must also be solved using a Given-Find block. An initial guess of 700 K is used for the temperature following compression.

$$T_2 := 700 \cdot \text{K}$$

Given

$$\int_{\frac{T_1}{\text{K}}}^{\frac{T_2}{\text{K}}} \frac{N_{\text{O}_2} \cdot c_{v\text{mO}_2}(T) + N_{\text{N}_2\text{t}} \cdot c_{v\text{mN}_2}(T) \dots + N_{\text{H}_2\text{O}} \cdot c_{v\text{mH}_2\text{O}}(T) + N_{\text{CO}_2} \cdot c_{v\text{mCO}_2}(T)}{T} dT = (N_{\text{exh}} + N_{\text{fa}}) \cdot R_u \cdot \ln(r_c)$$

$$T_2 := \text{Find}(T_2)$$

$$T_2 = 953.194\text{K}$$

The pressure after compression is found using the Ideal Gas Law.

$$\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2} \quad \text{or} \quad P_2 := P_1 \cdot \frac{T_2}{T_1} \cdot r_c \quad P_2 = 2.375 \times 10^6 \text{ Pa}$$

The First Law is again applied to determine the work required to compress the mixture.

$$W_{\text{comp}} := N_{\text{O}_2} \left(\text{um}_{\text{O}_2} \left(\frac{T_1}{\text{K}} \right) - \text{um}_{\text{O}_2} \left(\frac{T_2}{\text{K}} \right) \right) + N_{\text{N}_2} \left(\text{um}_{\text{N}_2} \left(\frac{T_1}{\text{K}} \right) - \text{um}_{\text{N}_2} \left(\frac{T_2}{\text{K}} \right) \right) \dots \\ + N_{\text{H}_2\text{O}} \left(\text{um}_{\text{H}_2\text{O}} \left(\frac{T_1}{\text{K}} \right) - \text{um}_{\text{H}_2\text{O}} \left(\frac{T_2}{\text{K}} \right) \right) + N_{\text{CO}_2} \left(\text{um}_{\text{CO}_2} \left(\frac{T_1}{\text{K}} \right) - \text{um}_{\text{CO}_2} \left(\frac{T_2}{\text{K}} \right) \right)$$

$$W_{\text{comp}} = -297.402\text{J}$$

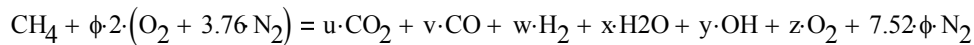
The negative sign implies that work is done on the gas mixture.

Appendix D: Equilibrium Composition Calculation

☞ Reference: C:\ICEngines\CHONdata.mcd

Problem Statement: One mole of methane is burned in air with a pressure of 10 atm. If the products of combustion are CO₂, CO, H₂, H₂O, OH, O₂ and N₂, what is the equilibrium composition at 3000 K and with 95% theoretical air? How does the equilibrium composition vary if the percentage theoretical air varies from 90% to 110% at 3000 K? How does the equilibrium composition vary if the temperature varies from 2500 to 5000 K with 95% theoretical air?

Solution: For the combustion of methane where it is assumed that all methane is consumed and that the nitrogen does not dissociate, the general reaction equation is:



where ϕ is the percentage theoretical air. Since the nitrogen does not dissociate, there are six unknowns in the reaction equation. Three equations come from the conservation of species of C, H, and O. The remaining three equations must come from equilibrium equations for the independent reactions. The remaining independent reactions are



A Given-Find block is setup to solve the set of 6 equations and 6 unknowns. The initial guesses are crucial. Without good initial guesses, even MathCAD has trouble solving the equations. The initial guesses are:

$$u := .5 \quad v := 0.5 \quad w := 0.15 \quad x := 1.6 \quad y := 0.5 \quad z := 0.1$$

Given

$$\text{C balance:} \quad 1 = u + v$$

$$\text{H balance:} \quad 4 = 2 \cdot w + 2 \cdot x + y$$

$$\text{O balance:} \quad 4 \cdot \phi = 2 \cdot u + v + x + y + 2 \cdot z$$

$$\text{Equilibrium equation for Reaction IV:} \quad K_{pIV}(T) = \frac{x}{w \cdot z^{0.5}} \left(\frac{10}{u + v + w + x + y + z + 7.52 \phi} \right)^{-0.5}$$

$$\text{Equilibrium equation for Reaction V:} \quad K_{pV}(T) = \frac{w \cdot y^2}{x^2} \left(\frac{10}{u + v + w + x + y + z + 7.52 \phi} \right)^1$$

$$\text{Equilibrium equation for Reaction VII:} \quad K_{pVII}(T) = \frac{u}{v \cdot z^{0.5}} \left(\frac{10}{u + v + w + x + y + z + 7.52 \phi} \right)^{-0.5}$$

$$D(\phi, T) := \text{Find}(u, v, w, x, y, z)$$

The Given-Find block was constructed as a function of the percentage theoretical air and the temperature. To find the equilibrium composition at 3000 K with 95% theoretical air:

$$D(0.95, 3000) = \begin{pmatrix} 0.5507 \\ 0.4493 \\ 0.1914 \\ 1.7026 \\ 0.2121 \\ 0.1673 \end{pmatrix}$$

Thus if 1 mole of methane is burned in air at 3000 K with 95% theoretical air, the equilibrium composition will consist of 0.5507 mol of CO₂, 0.4493 mol of CO, 0.1914 mol of H₂, 1.7026 mol of H₂O, 0.2121 mol of OH, and 0.1673 mol of O₂.

To show the variation in equilibrium composition as functions of the theoretical air and temperature, a counting variable, i , is defined. Percentage theoretical air and temperature vectors are then constructed using the counting variable.

$$i := 0..30 \quad \phi_i := 0.9 + \frac{0.2 \cdot i}{30} \quad T_i := 2000 + \frac{i}{10} \cdot 1000$$

The equilibrium compositions are then easily plotted as a function of the percentage theoretical air or as a function of temperature.

