MathCAD Functions for Thermodynamic Analysis of Ideal Gases

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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 system. The functions for oxygen and nitrogen were then used to generate ideal gas functions for air, including functions for relative pressure and relative volume. The MathCAD functions were made available for students in ME 242 Thermodynamics II and in ME 448/548 Internal Combustion Engines. The ideal gas functions were generated to ease the complication of using tabulated data for ideal gas properties, to allow parametric studies of thermodynamic systems using ideal gases, and to enable the students to generate relative pressure and relative volume tables for substances other than air. The details and usage of the ideal gas MathCAD functions are discussed, and specific examples of their application to problems in thermodynamics and combustion are presented.

Keywords: MathCAD, thermodynamics, ideal gas, air, combustion

INTRODUCTION

Learning with a combination of a textbook and a software package is a contemporary engineering-thermodynamics pedagogy. Many software tools are available for evaluating thermodynamic properties of engineering fluids. Many of these software tools are proprietary packages sold by textbook publishers, such as "Interactive Thermodynamics: IT" [1]. In fact, finding a thermodynamics text that does not come with a software package is difficult. Some textbooks are now built around using a software or web-based internet package [2]. While many educational software packages are available for evaluating thermodynamic properties, evidence that shows that practicing engineers continue to use these software packages after entering the workforce is not readily available.

Many schools teach and require the use of a computational tool such as MathCAD or MatLab [3]. From conversations with former students of mine, many of them continue to use these computational tools after graduation. Developing extensions or toolkits for software that the students will use after graduation seems more appropriate than developing complete software packages that will only be used by students in an educational environment. Because of the need for thermochemical functions for one of the widely used computational tools, functions were generated to evaluate the thermodynamic properties of air and the thermochemical properties of twelve species of the CHON system in MathCAD.

This effort started in an ME 448/548 Internal Combustion Engines course. Since combustion is an important topic in a senior/graduate level internal combustion (IC) engines course, the initial intent was to take some of the effort and distraction away from working combustion problems and to allow the students to analyze more complicated combustion problems. The combustion material covered in an IC engines course usually includes enthalpy of combustion, adiabatic flame temperature, and chemical equilibrium [4,5,6]. Without using computer programs, working fundamental combustion problems requires the arduous use of tables. Undergraduates in an IC engines

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course often become frustrated using the tables and fail to comprehend either the material or the significance of the material.

The students in my ME 448/548 course received the MathCAD functions very well and performed very complicated engine analyses with the functions [7]. After the MathCAD functions were successfully used in ME 448/548, the utility of the functions for an undergraduate thermodynamics course was easily recognized. I subsequently introduced the ideal gas functions to students in my ME 242 Thermodynamics II course the next semester for analyzing ideal-gas air cycles such as Brayton, Otto, and Diesel Cycles.

MathCAD and MatLab are both powerful computational and analytical packages. Both analysis packages have strengths and weaknesses when compared to the other. MathCAD was chosen for this project because of its mathematical report appearance, because of its ability to perform calculations with units, and because of its wide use in the Department of Mechanical Engineering at the University of Alabama at Birmingham.

FUNCTION WORKSHEET FORMAT

The data used to create the functions came from "The Chemkin Thermodynamic Data Base" as reported by Turns [8]. Turns reports fourteen constants used to determine thermodynamic data for twelve species (CO, CO_2, H_2, H, OH, H_2O, N_2, N, NO, NO_2, O, O_2) 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, *GASData.mcd*. The property constant table can be found in Appendix A.

Using the appropriate seven constants (a_1, a_2,..., 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

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

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

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

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

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

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

$$\bar{u}(T) = \bar{h}°(T) - R_u T \tag{4}$$

The function for $\bar{u}(T)$ is called from MathCAD as "um$_{XX}$(T)". The function for the molar specific entropy, $\bar{s}°(T)$, was created using

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

The function for $\bar{s}°(T)$ is called from MathCAD as "sm$_{XX}$(T)". The function for the molar specific Gibbs free energy, $\bar{g}°(T)$, was created using

$$\bar{g}°(T) = \bar{h}°(T) - T\bar{s}°(T) \tag{6}$$

The function for $\bar{g}°(T)$ 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 O_2 at 3000 K would be found in MathCAD using the statement:

$$\mathrm{hm}_{O2}(3000) = 9.803\times 10^{7}\,\frac{\mathrm{J}}{\mathrm{kmol}}$$

Chemical equilibrium functions are also generated in the worksheet. For a general chemical reaction of the form

$$aA + bB + \ldots \rightarrow eE + fF + \ldots \tag{7}$$

The standard state Gibbs function change is

$$\Delta G°(T) = \left(e\bar{g}_E^o(T) + f\bar{g}_F^o(T) + \ldots\right) - \left(a\bar{g}_A^o(T) + b\bar{g}_B^o(T) + \ldots\right) \tag{8}$$

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

$$K_P(T) = \exp\left(\frac{-\Delta G°(T)}{R_u T}\right) \tag{9}$$

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:

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

The equilibrium constant functions were validated using data from the *JANAF Thermochemical Tables* as reported by Russell and Adebiyi [9].

Along with the thermodynamic functions for the species of the CHON system, the thermodynamic functions for air were also generated. The specific internal energy, the specific enthalpy, and the specific entropy were generated using the equations

$$u_{air}(T) = \frac{y_{N_2}\bar{u}_{N_2}(T) + y_{O_2}\bar{u}_{O_2}(T)}{M_{air}} + u_{air,298K} \tag{10}$$

$$h_{air}(T) = \frac{y_{N_2}\bar{h}_{N_2}(T) + y_{O_2}\bar{h}_{O_2}(T)}{M_{air}} + h_{air,298K} \tag{11}$$

$$s^o_{air}(T) = \frac{y_{N_2}\bar{s}^o_{N_2}(T) + y_{O_2}\bar{s}^o_{O_2}(T)}{M_{air}} + s^o_{air,298K} \tag{12}$$

where y_{N_2} is the mole fraction of diatomic nitrogen (79%), and y_{O_2} is the mole fraction of diatomic oxygen. The reference values of the properties at 298 K were added so that the values reported by the functions equaled the values found in traditional ideal-gas air tables [10]. The functions were created on a gravimetric basis for the same reason. Along with the functions for internal energy, enthalpy, and entropy, functions were also created for the relative pressure and relative volume. The formulas used to create the relative pressure and relative volume functions are

$$P_{r,air} = \frac{\exp\left[\frac{s^o_{air}(T)}{R_{air}}\right]}{C} \tag{13}$$

$$v_{r,air}(T) = \frac{CR_{air}T}{\exp\left[\frac{s^o_{air}(T)}{R_{air}}\right]} \tag{14}$$

where R_{air} is the gas constant for air and C is a constant used to force the function for the relative pressure report the value found at 298 K in the traditional ideal-gas air tables [10]. The ideal-gas air functions are called in MathCAD using the statements "$u_{air}(T)$", "$h_{air}(T)$", "$s_{air}(T)$", "$pr_{air}(T)$", and "$vr_{air}(T)$".

The inverse functions, which find temperature from the other air properties, are also available in the worksheet. These function are called using the MathCAD statements "$T\_u_{air}(u)$", "$T\_h_{air}(h)$", "$T\_s_{air}(s)$", "$T\_pr_{air}(pr)$", or "$T\_vr_{air}(vr)$". The internal energy, enthalpy, and entropy must be entered in the function with the correct units. Functions that provide internal energy and enthalpy as functions of relative pressure or relative volume are also available; these functions are called using the statements "$u\_pr_{air}(pr)$", "$u\_vr_{air}(vr)$", "$h\_pr_{air}(pr)$", or "$h\_vr_{air}(vr)$". The relative pressure and relative volume are dimensionless.

All of the functions generated are in one file (*GASdata.mcd*) and are available to the public for download at *http://www.eng.uab.edu/me/faculty/smcclain/me242/GASdata.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 *GASdata.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 *GASdata.mcd* file. When this is done correctly, a statement similar to

➔ Reference:C:\ThermoII\GASdata.mcd

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

EXAMPLE PROBLEMS AND SOLUTIONS

Three example problems are discussed below. The example problems involve the analysis of an ideal-gas Brayton cycle, an analysis of the variation of thermal efficiency of Otto cycles versus compression ratio, 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 ideal gas functions are used in the solution are discussed.

Brayton Cycle Analysis

> Problem Statement: A simple Brayton cycle using air as the working fluid has a pressure ratio of 12. The minimum and maximum temperatures are 300 K and 1200 K. Assuming an isentropic efficiency of 85% for the compressor and 92% for the turbine, determine (a) the air temperature at the turbine exit, (b) the net work output, and (c) the thermal efficiency. Figure 1 presents a schematic for the cycle and the cycle T-s diagram.

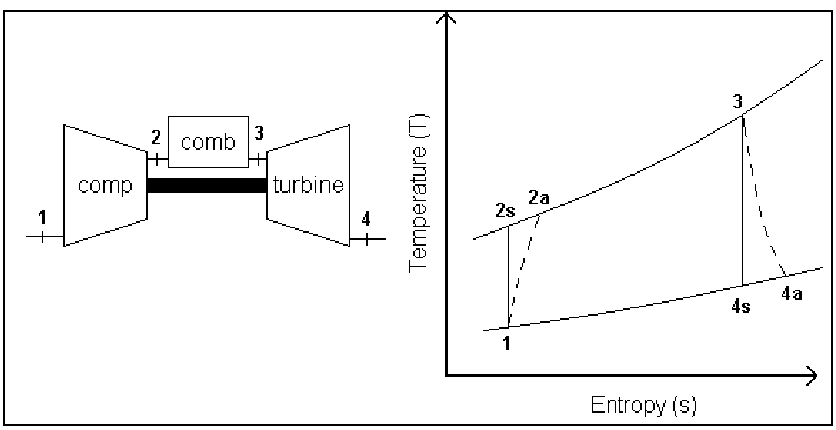

Figure 1. Brayton Cycle Schematic and T-s Diagram

The Brayton cycle analysis is an excellent example to demonstrate the use ideal gas functions for air. For an ideal gas analysis, the actual properties of the air exiting the compressor, indicated at state 2a, must be found by first evaluating the properties of air that exits an isentropic compressor with the same pressure ratio. The isentropic compressor exit properties, indicated at state 2s in Figure 1, are determined using a relative pressure analysis. The relative pressure at state 2s equals the product of the relative pressure at state 1 and the pressure ratio between states 1 and 2a. Once the relative pressure at state 2s is known, the relevant properties at states 2s and 2a may be found using either ideal-gas air tables from a thermodynamics text or the MathCAD functions. The properties of the air exiting the turbine are also found using the assigned properties at state 3 entering the turbine and the ratio of the relative pressures between states 3 and 4s. The detailed solution to the Brayton cycle analysis using the ideal-gas air functions for MathCAD is presented in Appendix 1. At each state in the Brayton cycle, at least one of the ideal gas properties of air, such as temperature, relative pressure, or enthalpy, is evaluated using the functions included in the GASdata.mcd file.

Otto Cycle Variation Analysis

> Problem Statement: Air at 300 K and 1 atmosphere enters a piston and cylinder device that completes an ideal Otto cycle using isooctane as a fuel at the stoichiometric air-to-fuel ratio. How does the cycle efficiency vary as the compression ratio of the cycle varies from 3 to 12 if the intake air and combustion products are perfect gases with the properties of air at room temperature? How does the cycle efficiency vary if the intake air and combustion products are ideal gases with the properties of air? How does the cycle efficiency vary if the combustion products are evaluated as the gas mixture that would result from the complete, stoichiometric combustion of isooctane in air?

For the perfect-gas (constant specific heats) Otto-cycle analysis, the thermal efficiency is only a function of the compression ratio.

$$\eta_{PG} = 1 - r_c^{1-k} \tag{15}$$

For the ideal gas Otto-cycle analysis treating the combustion products as air, the cycle must be analyzed using the relative volumes. The air-standard, ideal-gas Otto cycle analysis is easily performed using the MathCAD functions. For the Otto-cycle analysis based on the complete, stoichiometric combustion products of isooctane in air, new thermodynamic functions were constructed for the specific internal energy, entropy, and relative volume for a gas mixture that is 12.5% CO_2, 14% H_2O, and 73.5% N_2 by volume. While a complete and detailed solution to the problem cannot be presented here because of the article length limitation, Figure 2 presents the efficiency of the Otto cycle based on the perfect gas air standard analysis, η_{PG}, the ideal gas air standard analysis, η_{IG}, and the ideal gas analysis considering stoichiometric combustion, η_{IGC}. (Please email me at smcclain@uab.edu to request the detailed MathCAD solution.)

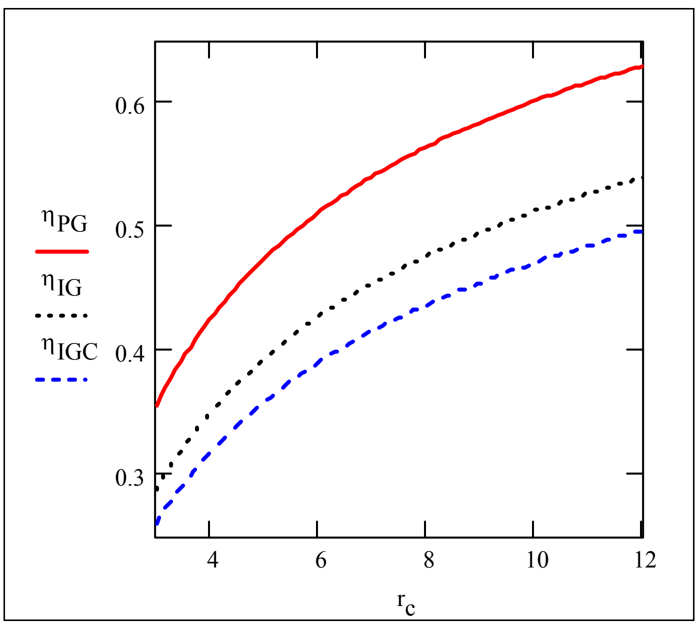

Figure 2. Thermal Efficiency of a Three Different Otto Cycles Versus the Compression Ratio

Chemical Equilibrium

Problem Statement: One mole of methane is burned in air with a pressure of 10 atm. If the products of combustion are CO_2, CO, H_2, H_2O, OH, O_2 and N_2, how does the equilibrium composition vary if the temperature varies from 2500 K 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

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

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 N_2 does not dissociate into N or form NO_x, there are six unknowns that must be determined. 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 in MathCAD is 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. Figure 3 presents the results of the MathCAD analysis and shows how the composition of each species varies as the temperature of the products varies from 2500 K to 5000 K. The detailed solution of the combustion equilibrium problem is presented in McClain [7].

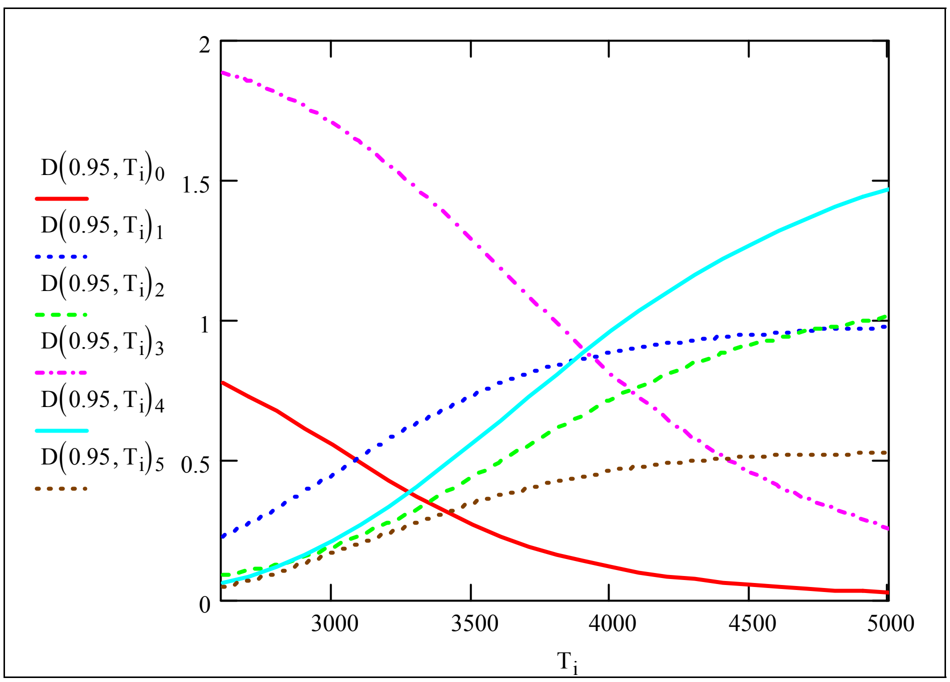

Figure 3. Equilibrium Composition of Selected Methane Combustion Products

DISCUSSION AND CONCLUSIONS

The MathCAD functions were provided to students in ME 242 Thermodynamics I and in ME 448/548 Internal Combustion Engines. The functions were introduced with a brief review of MathCAD and then with examples worked in class using a laptop and computer projector system. The students were required to use the functions in selected homework problems and on their projects. The projects in ME 448/548 required significant MathCAD programming [7].

The main purposes for constructing the air and CHON functions in MathCAD were to develop ideal gas thermodynamics tools for a modern computational software system, to shorten the time required to teach combustion in ME 448/548, and to make solving complicated ideal-gas thermodynamics and combustion problems easier for the students. The CHON functions were used in the Fall 2003 semester in ME 448/548 and in the Spring 2004 semester in ME 242. After only one semester of using the MathCAD functions in ME 448/548, 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 students in ME 242 used the air functions to perform complicated Brayton, Otto, and Diesel cycle analyses that would have been impractical to solve using tabulated information.

Student response to the MathCAD functions was overwhelmingly positive. Once the students are comfortable using MathCAD, there is very little time required to learn to use the air and CHON functions. Learning MathCAD took several students in ME 242, who had never had a programming language, a little longer than expected, but I received many positive responses from the students once they became comfortable with MathCAD's syntax. The positive student comments focused on the ability of MathCAD to easily handle calculations with units and the ability to perform the complicated ideal gas analyses for air without interpolating using the air tables.

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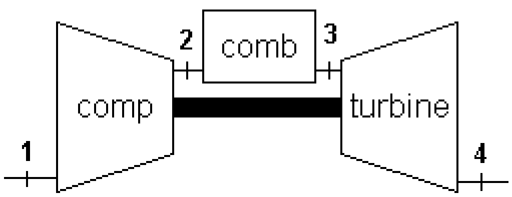
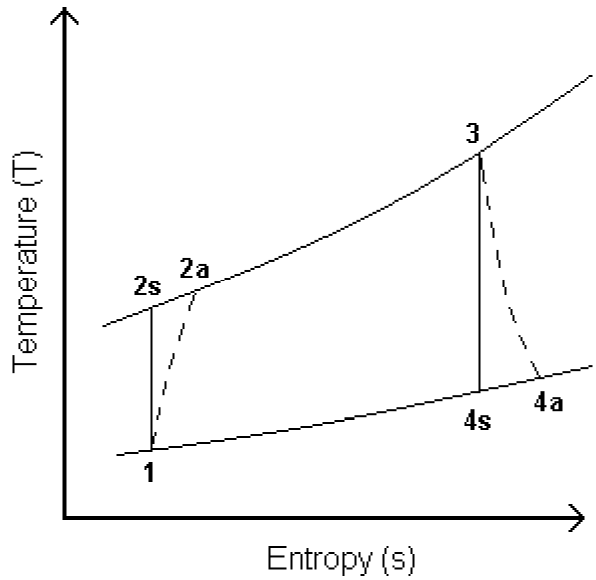
Appendix A – Example Brayton Cycle Problem

Reference:C:\ThermoII\GASdata.mcd

Problem Statement: A simple Brayton cycle using air as the working fluid has a pressure ratio of 12. The minimum and maximum temperatures are 300 K and 1200 K. Assuming an isentropic efficiency of 85% for the compressor and 92% for the turbine, determine (a) the air temperature at the turbine exit, (b) the net work output, and (c) the thermal efficiency.

Sketches:





Solution: The solution begins by entering known quantities:

$T_1 := 300 \cdot K \qquad T_3 := 1200 \cdot K \qquad r_p := 12 \qquad \eta_c := 85\% \qquad \eta_t := 92\%$

The enthalpies and relative pressures at each state are determined.

State 1: $h_1 := h_{air}\left(\frac{T_1}{K}\right) \qquad h_1 = 300.19\frac{kJ}{kg} \qquad pr_1 := pr_{air}\left(\frac{T_1}{K}\right) \qquad pr_1 = 1.386$

State 2: the relative pressure at state 2s is found from the pressure ratio and the relative pressure at state 1.

$pr_{2s} := pr_1 \cdot r_p \qquad pr_{2s} = 16.632 \qquad T_{2s} := T\_pr_{air}(pr_{2s}) \cdot K \qquad T_{2s} = 601.84K$

$h_{2s} := h_{air}\left(\frac{T_{2s}}{K}\right) \qquad h_{2s} = 610.17\frac{kJ}{kg}$

The actual state 2 properties are found from the definition of isentropic compressor efficiency:

$h_{2a} := h_1 + \frac{h_{2s} - h_1}{\eta_c} \qquad h_{2a} = 664.872\frac{kJ}{kg} \qquad T_{2a} := T\_h_{air}(h_{2a}) \cdot K \qquad T_{2a} = 653.515K$

State 3: $h_3 := h_{air}\left(\frac{T_3}{K}\right)$ $\quad h_3 = 1280.89\frac{kJ}{kg}$ $\quad pr_3 := pr_{air}\left(\frac{T_3}{K}\right)$ $\quad pr_3 = 242.177$

State 4: The relative pressure at state 4s is found from the pressure ratio and the relative pressure at state 3.

$$pr_{4s} := \frac{pr_3}{r_p} \qquad pr_{4s} = 20.181 \qquad T_{4s} := T\_pr_{air}(pr_{4s})\cdot K \qquad T_{4s} = 634.311K$$

$$h_{4s} := h_{air}\left(\frac{T_{4s}}{K}\right) \qquad h_{4s} = 644.474\frac{kJ}{kg}$$

The actual state 4 is found from the definition of isentropic turbine efficiency:

$$h_{4a} := h_3 - \eta_t\cdot(h_3 - h_{4s}) \qquad h_{4a} = 695.39\frac{kJ}{kg}$$

The actual temperature at state 4 is found using the actual enthalpy at state 4.

$$T_{4a} := T\_h_{air}(h_{4a})\cdot K \qquad \boxed{T_{4a} = 682.097K}$$

The specific net work output is the sum of the turbine work and the compressor work. Neglecting kinetic and potential energy changes across both devices, the specific work for each device is just the change in specific enthalpy across each device.

$$w_{net} := (h_3 - h_{4a}) + (h_1 - h_{2a}) \qquad \boxed{w_{net} = 220.822\frac{kJ}{kg}}$$

The specific heat input is the change in specific enthalpy across the boiler.

$$q_{in} := h_3 - h_{2a} \qquad q_{in} = 616.02\frac{kJ}{kg}$$

The First Law efficiency is then the specific net work over the specific heat input.

$$\eta_1 := \frac{w_{net}}{q_{in}} \qquad \boxed{\eta_1 = 35.847\%}$$

An ideal-gas Brayton cycle with a pressure ratio of 12, a compressor efficiency of 85%, a turbine efficiency of 92%, an entrance air temperature of 300 K, and a maximum cycle temperature of 1200 K will produce a specific net work of 220.8 kJ/kg of air and an efficiency of 35.85%.

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