

## **AC 2009-2477: THE CHEMICAL THERMODYNAMIC MODULE OF THE EXPERT SYSTEM FOR THERMODYNAMICS (“TEST”) WEB APPLICATION**

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# The Chemical Thermodynamic Module of The Expert System for Thermodynamics (“TEST”) Web Application

## Abstract

Hosted from [www.thermofluids.net](http://www.thermofluids.net), the TEST web portal is a freely accessible thermodynamics web-based software package for engineering education. It combines several modules – multi-media problems and examples, an online solution manual for educators, traditional thermodynamic charts and tables, fifteen chapters of animations to illustrate thermodynamic systems and fundamental concepts, and a suite of thermodynamic calculators called *daemons* for solving thermodynamic problems and pursuing *what-if* scenarios. Designed as ‘browsable’ Java applets, these daemons cover a wide range of topics - property evaluation of working substances, energy, entropy, and exergy analysis of generic open and closed systems, IC engines, gas and vapor power cycles, refrigeration, HVAC, combustion, chemical equilibrium, and gas dynamics.

In this paper, the chemistry module comprising of combustion and equilibrium analysis daemons for both open steady systems and unsteady processes is presented. The range of problems for which the combustion daemons can be used include balancing chemical reactions, evaluation of properties of reactants and products mixtures, energy and entropy analysis of premixed and non-premixed reactants, and calculation of adiabatic flame temperature for complete reaction. The equilibrium daemons build upon the combustion daemon, use very similar applet interface, and yet employ the powerful Gibbs function minimization algorithm to handle tens of species in the equilibrium products mixture. These simple-to-use daemons, comparable in their accuracy to established codes such as NASA CEA<sup>1</sup> and STANJAN<sup>2</sup>, are used to determine equilibrium constant, equilibrium composition, and equilibrium temperature of methane combustion as a function of equivalent ratio. This paper demonstrates how simple it is to calculate the equilibrium temperature and then pursue what-if studies by varying the fuel air ratio, fuel composition, or the number of species in the products mixture. Once a solution is achieved, what-if studies can be performed by changing the fuel, selecting different products species, varying the air fuel ratio, or any controllable property by simply changing the parameter and then pressing a single update button.

## Introduction

The advantages of web-based educational resources are obvious. Without any need for installation, students can access the latest version of software from any computer platform. Developers can update their software in real time and instructors can assign students exercises that require use of web-based software without having to rely on IT support personnel to make the software explicitly available on systems in university computer laboratories. Requiring only a standard web browser to operate, students can access these tools using devices other than laptops such as high-end mobile phones. Advances in Java programming, JavaScript, CSS, and

other browser technologies can enhance<sup>3</sup> the quality of education in a classroom. With the recent introduction of Web Service technology, data and software can be seamlessly integrated with any type of client application<sup>4</sup>. This can allow development of very powerful web applications that can exchange information with the server only when necessary, thereby giving the application a look and feel of a locally installed application while providing access to rich databases and calculation algorithms.

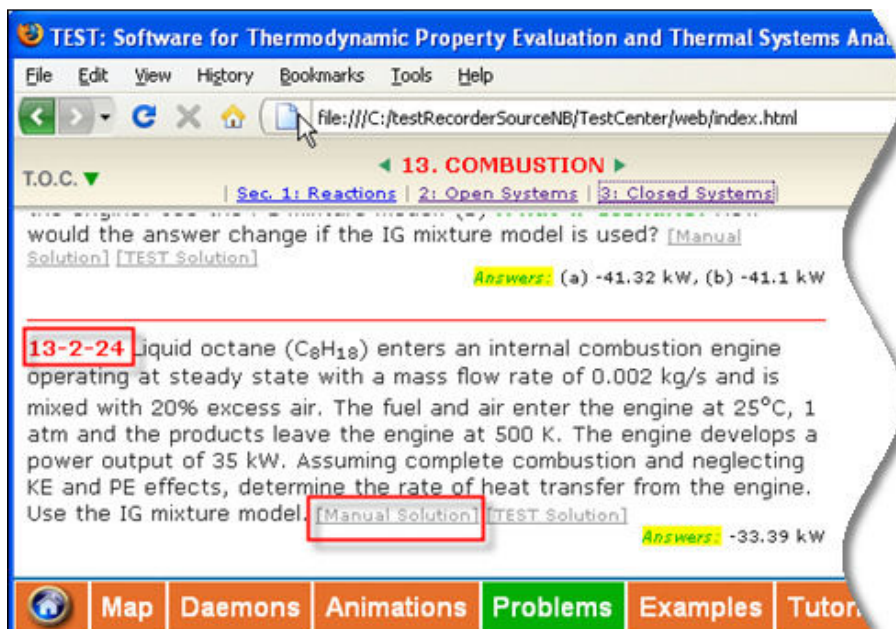
In the last couple of decades, a number of software applications for thermodynamic analysis have been developed. The ASME provides a comprehensive database for thermodynamics analysis<sup>5</sup>. However, EES<sup>6</sup> by F-Chart Software can be used to solve large sets of equations with built in functions for thermodynamic and transport properties of many substances. TPX<sup>7</sup> is an Excel plug-in where the core thermodynamic state can be evaluated by entering two independent properties. Thermoptim<sup>8</sup> is a Java based software for analyzing thermodynamic cycles and can be run over the web. A graphical menu driven installable program is GasCAD<sup>9</sup>. Another installable program is CyclePad<sup>10</sup>, which allows users to construct and analyze a wide variety of thermodynamic cycles. However, most of these software are not free to academic institutions and none of these resources, with the exception of EES, cover the diverse range of thermodynamic topics covered in a typical engineering thermodynamics textbook. Although EES can supply JANAF data, solution of chemical equilibrium using equilibrium constants becomes cumbersome for systems with more than a handful of species.

For solving complex combustion and equilibrium problems, educators frequently rely on STANJAN<sup>2</sup> or, in the case of advanced analysis in a graduate class room, NASA CEA<sup>1, 11</sup>, both written in FORTRAN. There are other applications such as *GasEQ*<sup>12</sup>, *REACT*<sup>13</sup>, *REACT!*<sup>14</sup>, SOLGASMIX<sup>15</sup>, FactSage<sup>16</sup> to name a few. Most of these applications must be locally installed on a PC and run only under the Windows operating system. Recently, Paolini and Bhattacharjee developed a platform independent equilibrium calculation tool<sup>17</sup> that uses NASA CEA thermochemical data. It incorporates gas and condensed species and can calculate equilibrium composition along with other state properties for systems with tens of species.

The Expert System for Thermodynamics or (“TEST”), accessible from the portal [www.thermofluids.net](http://www.thermofluids.net), was launched<sup>18</sup> to make thermodynamic calculations completely web accessible and user friendly. Licensed freely to academic institutions, TEST is currently used in 135 universities around the world and even though registration is optional, more than 18,000 students, educators and professionals have signed up to use TEST. A visual manual for TEST has been published by Prentice Hall<sup>19</sup>. Some of the daemons have been reviewed and included in various public domain educational web sites such as the MERLOT project<sup>20</sup>. A comparison of various multimedia materials for statistical and thermal physics ranked TEST in the top category<sup>21</sup>. Other articles that refer to TEST can be found in the references<sup>22, 23, 24, 25, 21, 26, 27, 28</sup>.

In this article, the chemical module of TEST is presented with examples of practical problem solving. The module can be used for balancing a reaction, determining the equivalence ratio, evaluating adiabatic flame temperature, analyzing a combustion chamber for complete reactions, determining equilibrium composition, equilibrium flame temperature, and analyzing open and closed systems with equilibrium or complete chemistry. Through a few button clicks, the user friendly graphical user interface will produce equilibrium composition or temperature in a

combustion chamber as the equivalence ratio is varied over a wide range. Comparisons will be made with other established chemical analysis applications.



**Figure 1.** Chapters 13 and 14 of the Problems and Examples sections deal with combustion and chemical equilibrium.

## Combustion and Equilibrium Problems

TEST can be used as courseware for thermodynamics education and can complement leading thermodynamics textbooks<sup>29,30,31</sup>. While there are a few excellent online coursewares available<sup>32,33</sup>, TEST brings together pedagogic discussions, animations, examples and problem sets, and online solvers for the entire range of topics covered by engineering thermodynamics. All of TEST's resources are accessible from the task bar shown in Figure 1. The problems and examples link displays fifteen chapters. Chapter 13 deals with combustion and chapter 14 with phase and chemical equilibrium. Each problem is linked to a detailed manual solution and instructions for obtaining a TEST solution. While manual solutions to examples are accessible to all, only registered educators are allowed access to manual solutions in the *Problems* pages. Clicking on the solution link splits the screen into two frames with the solution displayed in the lower frame. Sometimes problem schematics, displayed in the right margin, are linked to animations, images, or tables and charts, which are also displayed in the lower frame. Each chapter is divided into several sections, such as the three sections – Reactions, Open Systems, Closed Systems - shown in Figure 1. Thus, problem 13-2-24 refers to the 24<sup>th</sup> problem in section 2 of chapter 13.

## Combustion Tables and Charts

The Map link on the task bar (see Figure 1) brings up a map of the daemons offered by TEST. Fifty charts and tables are linked from the *Tables & Charts* link shown in Figure 2. Several of those can be useful for a reaction analysis. Tables D.4 through D.15 are thermodynamic tables

for twelve combustion species in SI units and Tables D.4E through D.15E are the corresponding tables in English units (see Figure 3). Each table displays  $\bar{h}_{f,k}^\circ$  and  $\bar{M}_k$  for the species  $k$  in the header and lists properties  $\bar{h}_k(T)$ ,  $\bar{u}_k(T)$ , and  $\bar{s}_k^\circ(T)$  in increments of the independent variable temperature  $T$ . Tables G.1 and G.1E list  $\bar{M}_k$ ,  $\bar{h}_{f,k}^\circ$ ,  $\bar{g}_{f,k}^\circ$ , and  $\bar{s}_k^\circ(T)$  for twenty-nine species including several fuels in their condensed phase. Tables G.2 and G.2E list lower and higher heating values of

several fuels. Table G.3 lists equilibrium constants in  $\ln(K_p)$  form for several stoichiometric reactions as a function of temperature. The use of Cascading Style Sheets (CSS) makes these tables easily readable and the HTML format makes it easy to switch between tables or switch units.

### State Daemons

TEST is a web-based suite of applications for analyzing engineering thermodynamic systems. Java applets designed to solve a particular type of problem are called *daemons* in TEST. The state module<sup>34</sup>, for example, contains a number of daemons to evaluate system and flow states of various working substances. There are twenty-six customized daemons for evaluation of states of different working substances. These working substances include 50 common solids and liquids, 65 phase-change fluids, 60 gases, and several gas mixtures.

To illustrate how the state daemons can be used to look up thermodynamic properties, suppose we would like to evaluate specific enthalpy and specific entropy of carbon dioxide at 2525 K and 1 MPa. Interpolating  $\bar{h}_k(T)$  and  $\bar{s}_k^\circ(T)$  from Table D.6, we obtain

$$\begin{aligned} \bar{h}_k^{\text{IG}}(p, T) &= \bar{h}_k^{\text{IG}}(T) = \bar{h}_{f,k}^\circ + [\bar{h}_k(2000) - \bar{h}_k(298)]^{\text{IG}} \\ \Rightarrow \bar{h}_{\text{CO}_2}^{\text{IG}}(1 \text{ MPa}, 2525 \text{ K}) &= -393,522 + (123,465 - 0) = -270,057 \text{ kJ/kmol} \end{aligned} \quad (1)$$

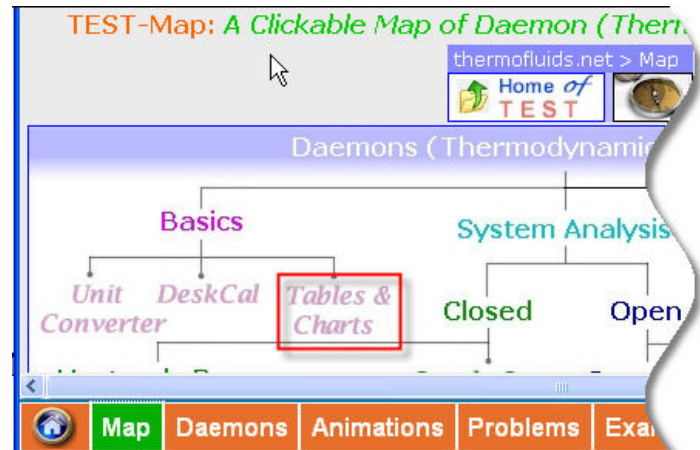


Figure 2. The Map link brings up a clickable map of different classes of TEST daemons.

Substance	Formula	$\bar{M}$ kg/kmol	$\bar{h}_f^\circ$ kJ/kmol	$\bar{g}_f^\circ$ kJ/kmol	$\bar{s}^\circ$ kJ/kmol·K
Carbon	C(s)	12.001	0	0	5.74
Hydrogen	H2(g)	2.016	0	0	130.68
Nitrogen	N2(g)	28.012	0	0	191.61
Oxygen	O2(g)	32	0	0	205.04
Carbon monoxide	CO(g)	28.013	-110,530	-137,150	197.65

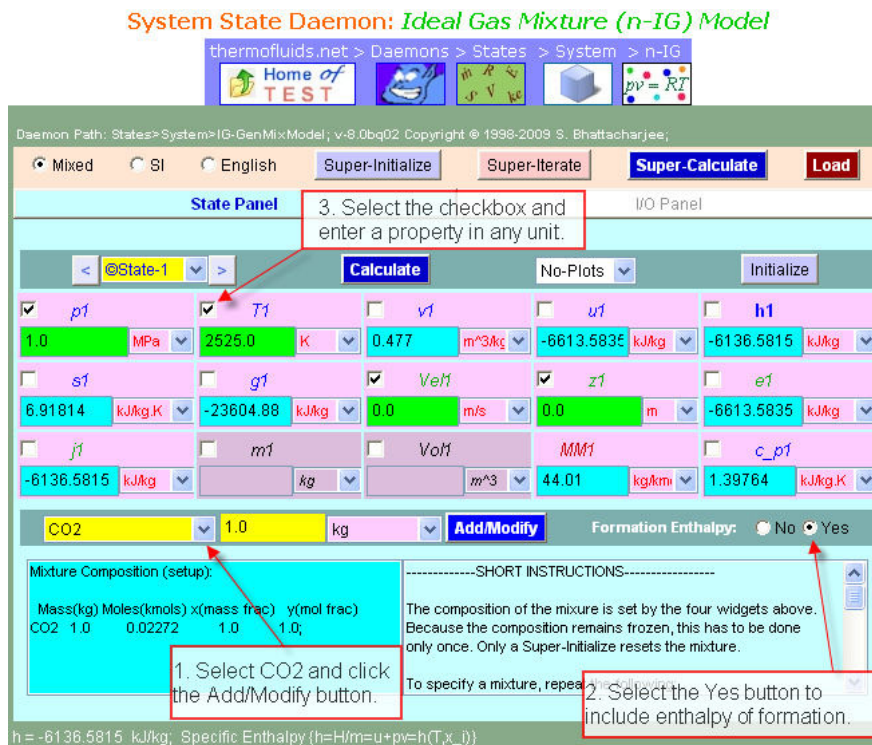
Figure 3. Traditional tables and charts for combustion and equilibrium analysis in both SI and English units are easily accessible.



$$\bar{s}_k^{IG}(p, T) = \bar{s}_k^0(T) - \bar{R} \ln \frac{p}{p_0}$$

$$\Rightarrow \bar{s}_{CO_2}^{IG}(1 \text{ MPa}, 2525 \text{ K}) = 323.417 - 8.314 \ln \frac{1000}{101} = 304.35 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \quad (2)$$

Although the ideal gas (IG) daemon can be used to evaluate a complete thermodynamic state of a gas, the enthalpy calculated does not include the enthalpy of formation which is displayed in the message panel instead. The n-IG mixture daemon, located at the *Daemons > States > System > n-IG Model page* and shown in **Figure 4**, is more suitable for evaluating properties of pure gases and their mixtures. Launch the daemon by selecting the n-IG (ideal gas mixture of *n* species) model in the system state page linked from the TEST map.



**Figure 4.** Properties of carbon dioxide evaluated at 1 MPa, 2525 K by the n-IG system state.

To evaluate a state, create an ideal gas mixture – in this case pure CO<sub>2</sub> – by adding 1 kg of CO<sub>2</sub>. Make sure the enthalpy of formation is included in the calculation by clicking the *Yes* radio button. Enter *p1* and *T1* in appropriate units. The expert system behind the daemon will not allow any further properties to be entered since two thermodynamic properties are sufficient for finding an equilibrium state. Press the *Enter* key or the *Calculate* button and the complete state is calculated and displayed. The green background signifies input and the cyan background indicates a computed property. The property symbols are also color coded – red for material properties such as the molar mass *MM*, blue for all thermodynamic properties, green for extrinsic properties, and black for system properties<sup>34</sup>.

While the ideal gas table displays only  $\bar{h}_k(T)$ ,  $\bar{u}_k(T)$ , and  $\bar{s}_k^0(T)$ , the state daemon produces the complete set of thermodynamic properties –  $v$ ,  $u$ ,  $h$ ,  $s$ ,  $g$ , and  $c_p$ . To obtain mole based values, switch to the I/O panel which serves as a calculator. Evaluate the expressions  $=MM1 * h1$  and  $=MM1 * s1$  to obtain  $-270,071$  kJ/kmol and  $304.46$  kJ/(kmol·K), respectively, which agree with the results of equation (1) and (2).

The daemon is superior to the table, not only by eliminating interpolation, but by producing the complete state. Moreover, any combination of independent properties can be entered to produce a state. Given entropy and pressure or specific volume, for instance, the manual procedure is not trivial to obtain the temperature. The daemon, on the other hand, can calculate the state instantly, even from unusual combinations such as  $c_p$  and  $g$ .

### Combustion Daemons

The combustion daemons are organized in the system tree (see the TEST map in **Figure 2**) under both open steady systems and closed process categories (see

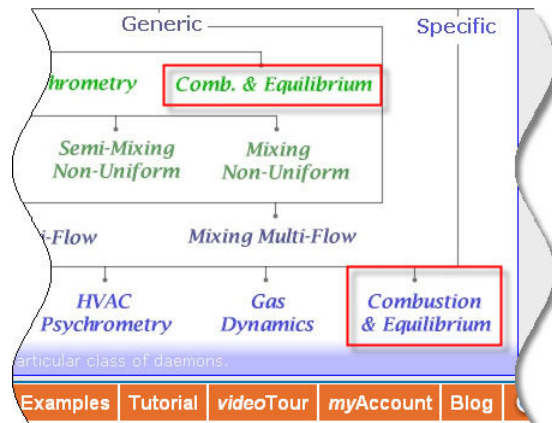
**Figure 5**). The open steady daemons are used for analyzing steady flow combustion chambers and reaction chambers, while the closed process daemons are meant for

analyzing a reacting process in a closed chamber. In each branch of the TEST Map, the combustion daemons are separated into two types – *non-premixed*, where fuel and oxidizer are initially separated, and *premixed*, where the fuel and oxidizer are mixed before ignition occurs. Finally, for each type of daemon, two material models – IG (ideal gas) and PG (perfect gas) models – can be selected.

### Balancing Reactions

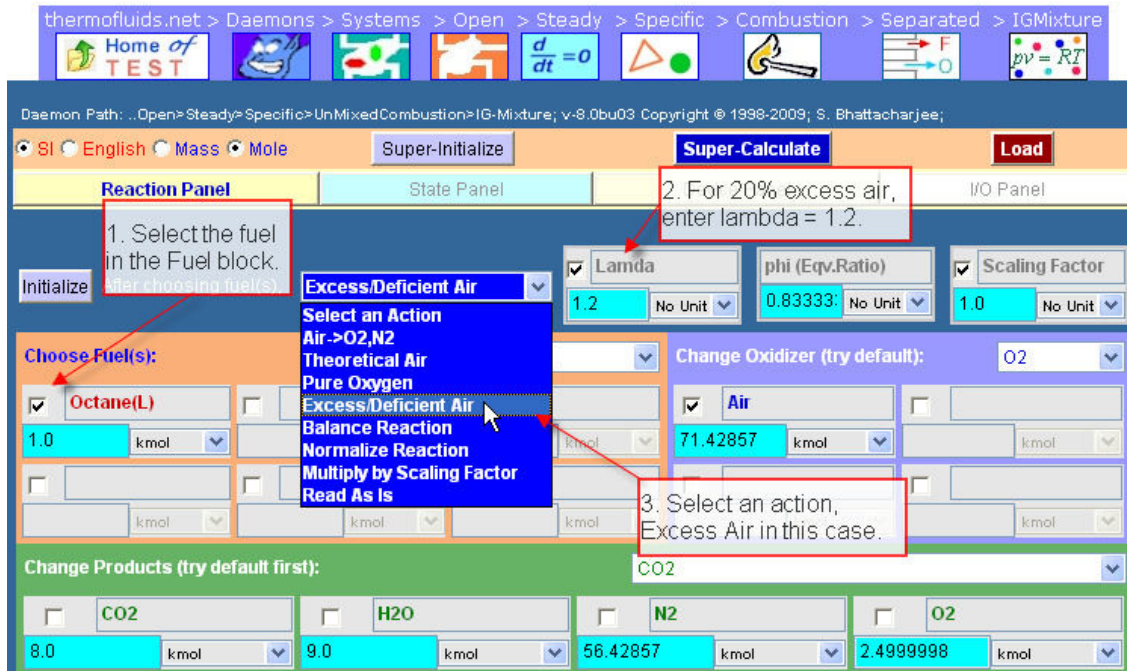
To illustrate how the combustion daemons work, let us analyze a combustion chamber operating in a steady state, described by problem 13-2-24 in **Figure 1**. Launch the non-premixed IG combustion daemon located in *Daemons > Systems > Open > Steady > Specific > Combustion > Non-Premixed > IG-Model* page. The daemon has four different panels – Reaction, State, Device, and I/O Panels – and the Reaction Panel is displayed by default as shown in

**Figure 6**. Select octane(L) in the fuel block. Standard reactions such as a theoretical reaction with air or pure oxygen can be instantly obtained by selecting the appropriate action from the action menu (see **Figure 6**). For 20% excess air, enter  $\lambda = 1.2$  and then select *Excess/Deficient Air* from the action menu. Products composition for complete combustion along with left over oxygen and nitrogen are displayed in the products block. The amount of air, 71.43 kmol per kmol of fuel, is the air-fuel ratio on a mole basis. Note that the equivalence ratio,  $\phi$ , is also reported next to  $\lambda$ . Air can be decomposed into a mixture of oxygen and nitrogen by selecting the *Air->O2, N2* from



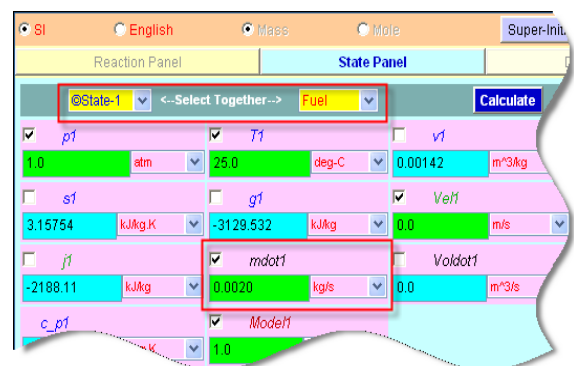
**Figure 5.** Different combustion daemons are used to analyze open steady systems and closed processes.

the action menu. Note that for a reaction with deficient air, the same procedure can be followed with  $\lambda < 1$ . To determine the air-fuel ratio on a mass basis, select the *mass* radio button that appears above the Reaction Panel tab and the molar amount of each species is converted to mass. Select *Normalize* from the action menu to express the reaction in terms of 1 kg of fuel. The amount of air, 18.11 kg, then represents the mass based air-fuel ratio. The theoretical air fuel ratio, likewise, can be obtained as 151 kg of air/kg of fuel or 59.52 kmol of air/kmol of fuel.



**Figure 6.** Reaction between liquid octane and 20% excess air is balanced using the three steps described in this image. The product composition for complete combustion is automatically selected.

Another common type of reaction encountered in combustion involves products analysis. Given a dry product analysis, a reaction can be balanced by selecting the fuel, oxidizer, and products species, and then entering the known amounts of products components until there are as many unknowns as atoms. For example, suppose a volumetric dry products analysis in the combustion of octane with air produces (see Problem 13-1-19) 10.02% CO<sub>2</sub>, 0.88% CO, 5.62% O<sub>2</sub>, and 83.48% N<sub>2</sub>. To solve this problem, select octane as the fuel, and enter CO<sub>2</sub>, CO, and O<sub>2</sub> amounts in kmol in the products block. This leaves the fuel, air, and nitrogen amounts as unknowns and three atom balance equations. Select *Balance Equation* from the action menu and then normalize to produce a molar air fuel ratio of 77.63. With the molar theoretical air fuel ratio already calculated as 59.52, the percent theoretical air used can be calculated as  $77.63/59.52 = 1.30$  or 130%.

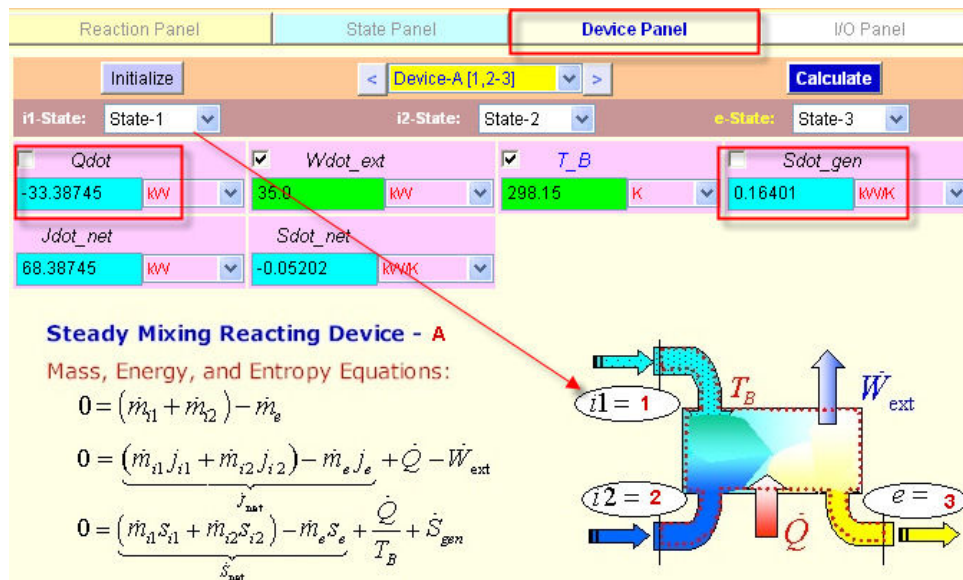


**Figure 7.** Evaluate three states for fuel, oxidizer, and products.



## Analysis of Steady-State Reactors

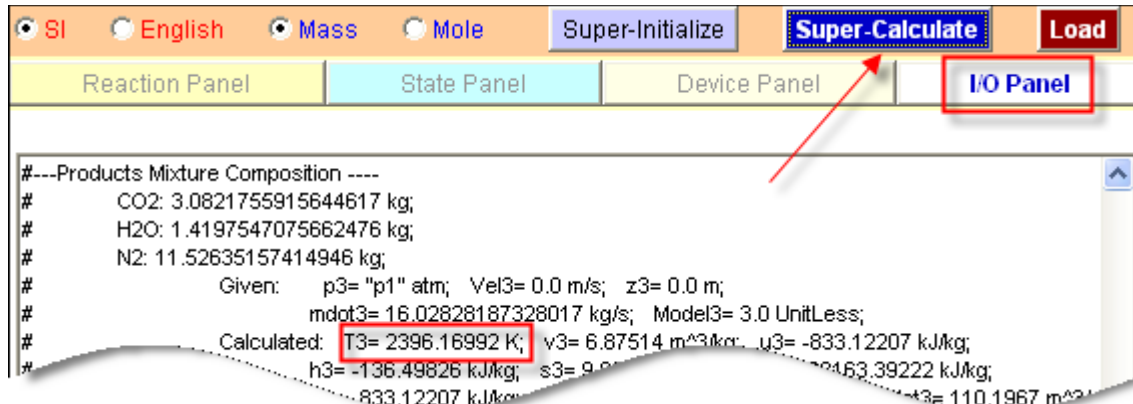
The State Panel picks up the composition of fuel, oxidizer, and products from the Reaction Panel. Returning to the combustion of liquid octane with air (see **Figure 1**), we can express the reaction in terms of 1 kg of fuel. Using a scaling factor of 0.002 and selecting *Multiply by Scaling Factor* from the action menu, the reaction is expressed in terms of 0.002 kg of octane. In the State Panel, evaluate *state-1* for fuel, *state-2* for oxidizer, and *state-3* for products. A state number must be associated with fuel, oxidizer, and products mixtures. Enter the known pressure and temperature at each state and the states are evaluated with the mass flow rates obtained from the Reaction Panel. The Device Panel shows an image of the combustion chamber with the mass, energy, and entropy equations simplified for an open steady system. After selecting *state-1* (fuel) as the *i1* (inlet-1) state, *state-2* (oxidizer) as the *i2* (inlet-2) state, and *state-3* (products) as the *e* (exit) state, observe in Figure 8 how the image of the system adjusts as the port states are loaded. Enter the known amount of external work and press the *Calculate* button to solve the mass, energy, and entropy equations. Because the states are already completely known, the heat transfer and entropy generation rates are calculated and displayed. The negative amount, -33.38 kW, indicates that heat is being rejected by the engine at this rate.



**Figure 8.** The device panel of the open steady non-premixed combustion daemon showing the solution to Problem 13-2-24 in Figure 1.

To determine the adiabatic flame temperature, set  $T_3$  as an unknown in *state-3*, and enter  $Q_{dot}$  and  $W_{dot\_ext}$  as zero in the Device Panel. The *Super-Calculate* button can be used to update all solutions and  $T_3$  is calculated and posted as *state-3*. A detailed output is also generated by the *Super-Calculate* operation. For a parametric study – say, how the adiabatic flame temperature changes with the equivalence ratio – change  $\lambda$ , select *Excess/Deficient Air* from the action menu, and then click *Super-Calculate*. For theoretical combustion ( $\lambda = 1$ ), the detailed output is shown in **Figure 9** with the adiabatic flame temperature for a complete theoretical reaction

calculated as 2396 K. The fuel can also be used as a parameter. To do so, de-select octane in the fuel block and select methane. From the action menu, select *Theoretical Air* to produce the balanced complete reaction. Now, press the *Super-Calculate* button to produce a T3 of 2329 K as the adiabatic flame temperature.



**Figure 9.** Adiabatic flame temperature for theoretical combustion of liquid octane obtained from the open-steady non-premixed combustion daemon.

Evaluation of heating values of a fuel can be accomplished by configuring a theoretical reaction and specifying standard atmospheric conditions for fuel, oxidizer, and products. The heating value is simply the heat transfer calculated in the device panel for 1 kg of fuel. For example, for methane, configuring a theoretical reaction on the basis of 1 kg of fuel, the heat transfer can be calculated as 50,024 kW, that is, the heating value is 50,024 kJ/kg since the daemon interprets the fuel mass as the mass flowing into the chamber every second. This must be the lower heating value since the water in the products is assumed to be in the vapor phase. To obtain the higher heating value, simply de-select H2O in the products block and replace it with H2O(L), as shown in **Figure 10**. Balance the reaction by selecting *Balance Reaction* and then press the *Super-Calculate* button. The higher heating value in the device panel is then shown as 55,511 kJ/kg. These values can be verified from the tabulated values of higher and lower heating values of different fuels in Table G.1.



**Figure 10.** To obtain a higher heating value, de-select H2O and select H2O(L) from the products menu. Select *Balance Reaction* from the action menu and then press *Super-Calculate* to update all results.

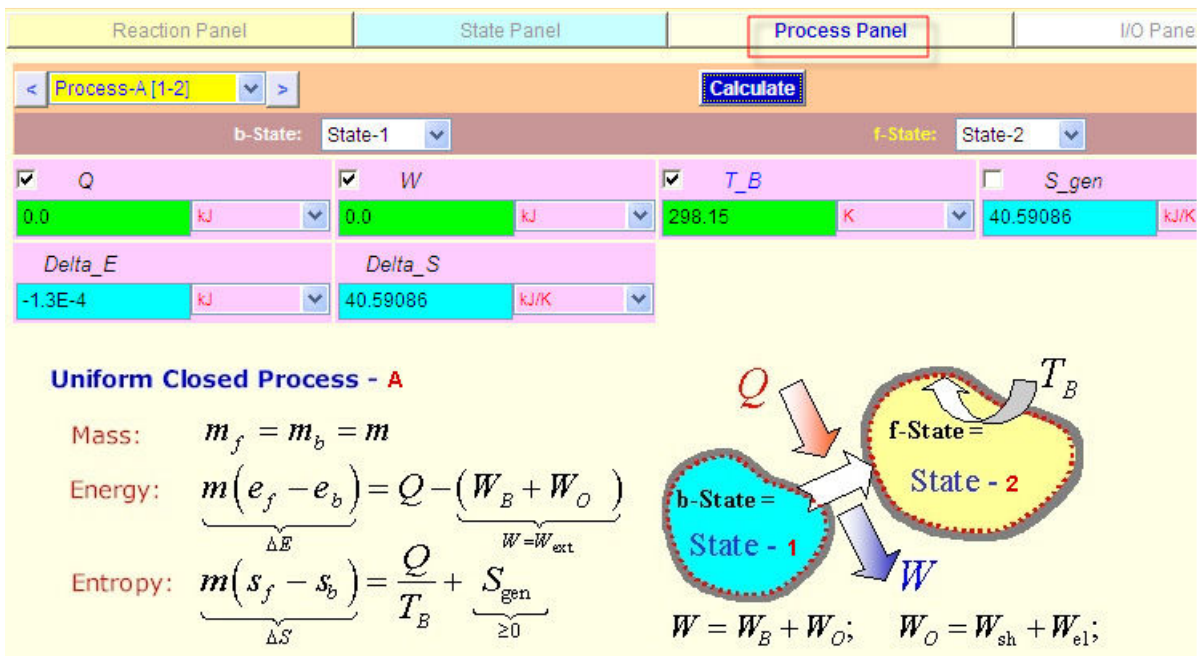
The approximate value of the fuel chemical exergy can also be obtained by simply evaluating the expression for reversible work in the IO Panel as

$$= \dot{m}_1 * g_1 + \dot{m}_2 * g_2 - \dot{m}_3 * g_3$$

The above expression evaluates to 50,869 kJ/kg for methane, an approximation because the contribution of mixing to the exergy is ignored in this result.

So far, we have used the non-premixed open-steady IG daemon in the previous examples. The corresponding PG daemon differs only in one aspect – it assumes constant specific heat values for each component. Analysis with the PG daemons may not be accurate, especially at high temperatures, but may serve a useful purpose in establishing the importance of variable specific heat and for verification of manual solutions. For example, the adiabatic flame temperature of methane calculated with the PG model is 2792 K as opposed to 2329 K from the IG daemon.

The premixed daemons work almost the same way as the non-premixed daemons. The difference comes from the fact that the Reaction Panel now has only two blocks – one for reactants and one



**Figure 11.** The Process Panel set up for calculating the adiabatic temperature in a closed chamber.

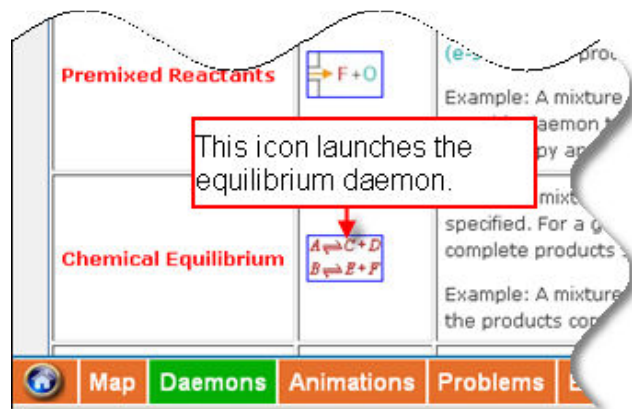
for products. Therefore the State Panel and the Device Panel are also modified to reflect a single inlet and a single exit for the premixed reactor. Balancing a reaction requires selecting the reactants and products and entering amounts of  $(n - a)$  components, where  $n$  is the total number of species that appear in the reaction and  $a$  is the number of atoms. For the theoretical combustion of methane, the reaction can be balanced by entering 1 kg of methane and 17.201 kg of air as reactants, selecting the products of complete combustion, and then selecting *Balance Reaction* from the action menu. In the State Panel, evaluate the reactants and products states. The heating value, 55,511 kJ/kg, calculated in the Device Panel is identical to the one determined by the non-premixed daemon. However, the reversible work (i.e.  $m \cdot g_1 - m \cdot g_2$ ) calculated in the I/O Panel as 50757 kJ/kg is slightly lower because the fuel in the reactants now has a lower partial pressure than in the non-premixed case.

The entropy generation rate in the reactor is calculated as part of the device variables and reported in the Device Panel (see **Figure 8**). The boundary temperature  $T_B$  in the Device Panel

refers to the temperature of any external thermal energy reservoir with which the heat interaction occurs. In most situations, it can be left at the default value of 298 K, the temperature of standard surroundings.

## Analysis of Closed Combustion Processes

TEST offers separate combustion and equilibrium daemons for analyzing unsteady combustion processes executed in a closed system. The fuel and oxidizer can be premixed in a closed chamber or separated into two sub-chambers in the beginning of the process. As an example, consider the combustion of 1 kg of liquid octane with a theoretical amount of air, 15.096 kg, obtained from any non-premixed daemon. The reactants are kept at 1 atm, 25°C in a rigid chamber and ignited. To analyze the resulting process, launch the premixed closed-process IG combustion daemon located in the *Daemons > Systems > UnsteadyProcess > Specific > Combustion > Premixed > IG Model* page. Configure the reaction in the Reaction Panel for theoretical combustion of octane. Evaluate the reactants state with  $p_1 = 1$  atm,  $T_1 = 298$  K, and partially evaluate the products state with  $Vol_2 = Vol_1$  (for a constant-volume process). In the Process Panel, load *state-1* as the beginning state (b-state) and *state-2* as the final state (f-state), and enter  $Q = W = 0$ . Click *Calculate* and then *Super-Calculate* to obtain the final state. The final pressure and temperature are found in *state-2* as 1065 kPa and 2911 K, respectively. In processes where a boundary work transfer is involved, work must be evaluated manually (or using an expression such as  $'=p_1 * (Vol_2 - Vol_1)'$ ) and entered in the Process Panel.



**Figure 12.** The equilibrium daemons for analyzing open-steady closed-process reactors can be found in the same pages as the corresponding combustion daemons.

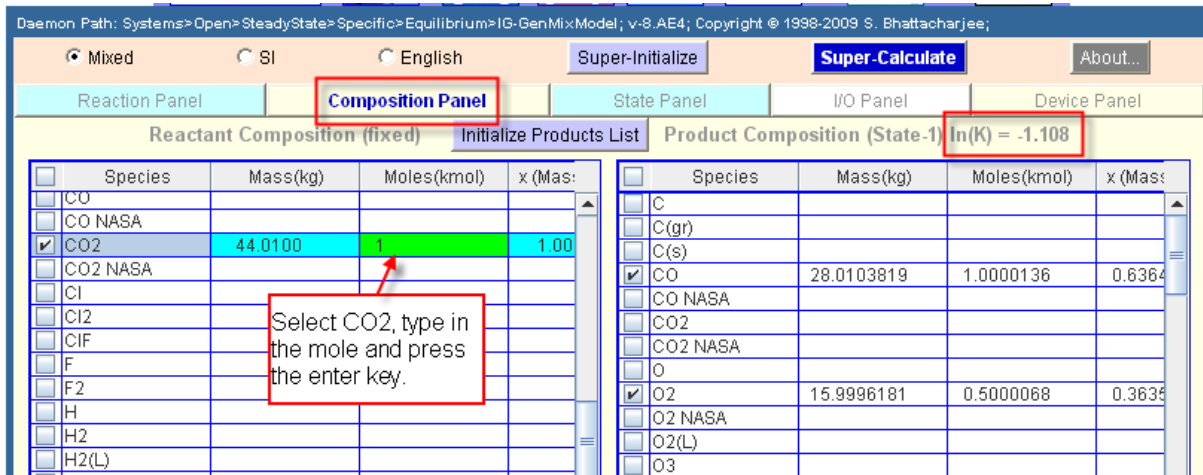
## Chemical Equilibrium Analysis

TEST offers several daemons for chemical equilibrium analysis, which can be used for evaluation of equilibrium constants, determination of equilibrium composition, and energy and entropy analysis of open steady systems and closed processes.

There are two approaches for evaluating the equilibrium composition of a mixture at a given temperature and pressure. The entropy maximum principle for an isolated system at equilibrium can be shown to reduce to the minimization of the system's Gibbs function if the temperature and pressure remain constant. Assuming the mixture to consist of  $n$  given species, the mixture's Gibbs function can be expressed as a function of  $n$  unknown mole fractions subject to an atom balance constraint. The traditional numerical practice used for solving optimization problems<sup>35,36</sup> of this type is the method of Lagrange multipliers using an iterative Newton-Raphson technique for solving the resulting set of nonlinear equations. Both NASA CEA<sup>1</sup> and STANJAN<sup>2</sup> employ the method of element potentials. Both of these codes are written in FORTRAN and cannot be easily incorporated into other codes. The second approach, used mostly for calculating a manual

solution, uses equilibrium constants that relate mole fractions of products and reactants derived from the Gibbs function minimization principle. A number of simultaneous stoichiometric equations are selected and their equilibrium constants are obtained from a table such as Table G.3 at a given temperature. By selecting as many reactions as the number of unknowns,  $n - a$  (where  $a$  is the number of different atoms), a set of simultaneous algebraic non-linear equations can be constructed. For systems with few species (say, the dissociation of oxygen at high temperature), a manual solution of these equations can be obtained which results in the composition of the equilibrium mixture.

Paolini and Bhattacharjee<sup>17</sup> modified the CEA algorithm and developed an object-oriented Java code for solving for an equilibrium distribution using the method of element potentials. Front-end Java applets with easy-to-use graphical user interfaces were developed to run this equilibrium code through a web browser. These applets are enhanced and integrated with the chemical module of TEST in this work.



**Figure 13.** Determination of the equilibrium constant for the dissociation reaction  $\text{CO}_2 \rightleftharpoons \text{CO} + 0.5\text{O}_2$  at 3000 K.

The open-steady equilibrium daemon, located in *Daemons> Systems> Open> Steady> Specific> Combustion> Chemical Equilibrium* page, and the closed-process equilibrium daemon, located in *Daemons> Systems> Closed> Process> Specific> Combustion> Chemical Equilibrium* page, have the same look and feel as the corresponding non-premixed combustion daemon with the addition of a new panel called the Composition Panel. To illustrate the use of the equilibrium daemons, suppose we are to evaluate the equilibrium constant,  $\ln(K_p)$ , of the stoichiometric reaction  $\text{CO}_2 \rightleftharpoons \text{CO} + 0.5\text{O}_2$  at 3000 K, which is listed in Table G.3 as -1.111. As depicted in **Figure 13**, launch the open-steady equilibrium daemon and switch to the Composition Panel. To configure the stoichiometric reaction, select CO<sub>2</sub>, change its molar amount to 1 kmol, and press the *Enter* key to register the input. Notice that the products table on the right gets populated by all atomically feasible species. Select CO and O<sub>2</sub> in products table, leaving their amounts unknown. In the State Panel, enter  $p_1 = 100$  kPa,  $T_1 = 3000$  K, select the *Products* radio button, and press the *Calculate* button. The stoichiometric reaction is balanced and the log of the



equilibrium constant  $\ln(K_p)$  is reported in the Composition and I/O Panel as -1.108. If this is the only possible reaction, the equilibrium products will contain all three species.

To determine the equilibrium composition of 1 kmol of CO<sub>2</sub> at 100 kPa and 3000 K, select as many probable species – CO, O<sub>2</sub>, CO<sub>2</sub>, CO, O<sub>2</sub>, O, and C(graphite), for example, in the products table. Since the State Panel is already configured, use the *Super-Calculate* button to update all results. The equilibrium composition is displayed in the Composition and I/O Panel as shown in **Figure 13**. Once the reactants (in this case 1 kmol of CO<sub>2</sub>) are configured, it becomes easy to perform *what-if* studies. For example, to learn how an increase in pressure would affect the amount of CO, change p1 to 1 MPa and click *Super-Calculate*. The amount of CO decreases from 0.454 kmol to 0.245 kmol, as Le Chatelier's Principle would dictate for the dissociation of CO<sub>2</sub>.

The combination of the Reaction Panel along with the equilibrium solver creates a powerful tool for equilibrium energy and entropy analysis. In the next example, adiabatic flame temperature is calculated using different models – complete reaction with PG model, complete reaction with IG model, and equilibrium calculations with eight different species in the products.

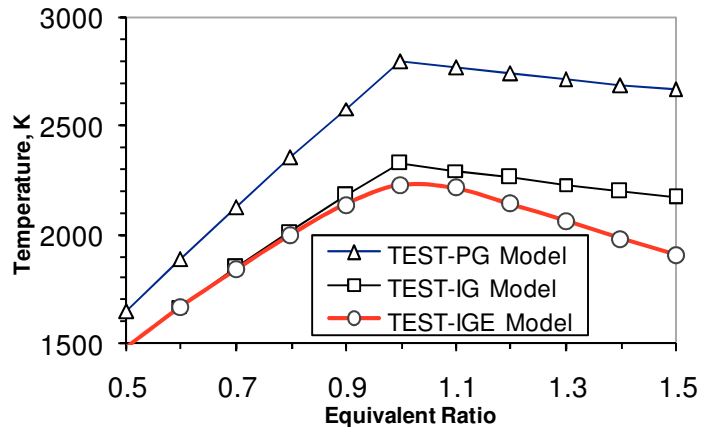
### **Example: Equilibrium Flame Temperature**

Suppose methane and air enters an adiabatic combustion chamber at 1 atm and 298 K. Do a parametric study of how the adiabatic flame temperature  $T_{af}$  depends on the equivalence ratio  $\phi$ . Vary  $\phi$  over the range 0.5 through 1.5. Use TEST daemons with (a) the PG mixture model (complete combustion), (b) IG mixture model (complete combustion), and (c) IGE mixture model (equilibrium combustion) with the following eight components in the products: CO<sub>2</sub>, CO, H<sub>2</sub>O, OH, O<sub>2</sub>, N<sub>2</sub>, NO, NO<sub>2</sub>. To solve this example problem using TEST, launch the open-steady non-premixed PG combustion daemon. On a separate tab, open the corresponding IG combustion daemon, and on a third browser tab, launch the open-steady equilibrium daemon.

In the Reaction Panel of each daemon, select methane in the fuel block, enter a value of  $\lambda = 1$  (inverse of the equivalence ratio) for a theoretical mixture, and select *Excess/Deficient Air* from the action menu. The balanced reaction is displayed. For the combustion daemons, the procedure has been already outlined. In the State Panel, evaluate state-1 and state-2 as the fuel and oxidizer states from the known pressure and temperature. Evaluate state-3 for the products, partially, by entering a value for p1 only. In the Device Panel, import the fuel, oxidizer, and products states, enter  $\dot{Q} = \dot{W}_{ext} = 0$ , and then click *Super-Calculate*. The adiabatic flame temperature for the theoretical reaction is given in state-3 as T3.

In the equilibrium daemon, the procedure is similar. In the Composition Panel, the reactants amounts are already imported from the reaction panel. Select the eight products species. In the State Panel, evaluate the reactants state, state-1, for the given pressure (1 atm) and temperature (298 K). For the products state, state-2, select the *Products* radio button and enter the pressure ( $=p1$ ). In the Device Panel, load the inlet and exit states, and enter  $\dot{Q} = \dot{W}_{ext} = 0$ . Click *Super-Calculate* and the equilibrium products composition, as well as the complete products state, state-2, is calculated and displayed. The temperature at state-2 is the adiabatic equilibrium flame temperature.

After compiling the three adiabatic temperatures in a spread sheet, to obtain the adiabatic temperatures at a different equivalence ratio, change  $\lambda$  to a new value in the reaction panel of each daemon and press the *Super-Calculate* button. Results compiled in this manner are plotted in **Figure 14**. As expected, the PG model over predicts the flame temperature due to the assumption of constant specific heat. Results from the equilibrium composition have been compared with NASA CEA with remarkable agreement. The IG model produces excellent agreement with equilibrium calculations for ultra-lean combustion. However, as the equivalence ratio increases, the discrepancy between the two models quickly increases as can be seen in **Figure 14**. The mole or mass fraction of any species can be similarly plotted.



**Figure 14.** Adiabatic flame temperature for methane and air combustion as a function of equivalence ratio. Prediction from the equilibrium computation (IGE model) is the most accurate.

### Use of TEST in the Classroom

Obviously, any software tool such as TEST cannot replace the traditional paper and pencil solution in the classroom. However, because of its intuitive graphical user interface, students can use TEST to verify different steps of a manual solution in seconds without having to write a full-blown program. An instructor can perform on-your-face calculations in the classroom to numerically back up a theoretical prediction. More importantly, given the simplicity of what-if studies, selected homework problems can be made more challenging and students can be asked to explore parametric effects on a solution such as the one shown in Fig. 15. Students of the graduate combustion class (ME 653, Fall 2008) used both STANJAN and TEST for emissions calculations. Out of the 10 students who took a blind survey, seven strongly agreed (5 in a scale of 1-5) and three agreed (4 in the same scale) that simplicity of the user interface made TEST a better choice than STANJAN for calculations of equilibrium composition. Without this simple-to-use tool, the theories that were taught could not have been applied to complex real world problems. Certainly, there are other software that can be used for this purpose, but most of them are not free for academic institutions, require installation, involve different degrees of programming, and generally has significant learning curves. TEST, on the other hand, can be accessed from any modern classroom and it offers a complete courseware package - traditional charts and tables, concept animations, online problems and examples, and the suite of calculators called daemons – allowing an instructor to decide to what degree to use its resources. While at SDSU, TEST is used only for homework verification and projects, some universities have reported use of TEST in the classroom, laboratories, and even during quizzes and examinations.

### Conclusion

TEST is a collection of thermodynamic databases, software, and courseware, accessible from [www.thermofluids.net](http://www.thermofluids.net). TEST is freely accessible from any academic institution and is currently

used in more than 100 institutions around the world. The thermodynamic calculators in TEST, called *daemons*, have been developed using an object-oriented paradigm in Java so that code can be reused. All TEST daemons have been thoroughly tested under different versions of IE, Firefox, and Safari running on Windows, MacOS, and Linux platforms. The only browser plug-in required to run TEST daemons is version 4 (or greater) of the Java Platform. The chemical module of TEST can be used to access thermodynamic data, two chapters of problems and examples on combustion and chemical equilibrium, and several daemons for the analysis of open and closed reacting systems. The combustion daemons can be used for balancing a reaction and carrying out energy and entropy analysis of a combustion chamber for a given reaction. The equilibrium daemons, which build upon the combustion daemon, preserve the simplicity of the combustion daemon and yet extend their usefulness by calculating the equilibrium composition of the products as part of the analysis. The capabilities of these equilibrium daemons are comparable to established applications such as NASA CEA<sup>37, 1,11</sup> and STANJAN<sup>2</sup>.

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