Chemical Equilibrium Applied to Combustion

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## Chemical Equilibrium Concepts

The most common form that chemical reactions are presented as is one-way, complete chemical reactions, in which given product chemicals react completely and irreversibly to form a predefined set of products. For example, the standard, perfect combustion of nitrous oxide and ethane could be portrayed as follows:

For most applications, this way of modeling chemical reactions is perfectly valid. Generally speaking, the products shown in standard chemical reactions are indeed the most chemically stable products at standard temperatures and pressures. In the context of chemical equilibrium, these are known as the *major* product species. However, when working at high temperatures and pressures as seen in a rocket, *minor* combustion species can become relevant. In other words, an unknown amount of the product atoms will rearrange into some quantity of minor species. So, in reality, the formula of the chemical reaction would look something like this:

…

…And so on, for dozens more possible minor combustion products, where the letter coefficients (a), (b), (c), etcetera, represent a variable quantity of each product, such that the number of atoms of each element are conserved. When considering that depending on certain conditions like mixture ratio and pressure it’s possible to have no minor combustion products, and that the flame temperature is generally highest when no minor combustion products form, this temperature is the maximum adiabatic flame temperature. In practice, this means that when using the traditional constant-coefficient combustion reaction to predict the flame temperature within the combustion chamber would almost always yield a significantly higher flame temperature than will actually be produced.

The significance of variable chemical reactions necessitates a means of predicting which products a reaction will produce at a given initial temperature, pressure, and mixture ratio.

The second law of thermodynamics states that entropy will never decrease, or that for a given closed system, the entropy will always increase to a local maximum and achieve equilibrium there.

While entropy *can* be used to predict chemical reactions, a similar, more readily available property can be found in Gibbs Free Energy. The Gibbs Free Energy of a gas can be expressed as a function of the enthalpy, entropy, and temperature of the gas, as shown qualitatively in Equation 1. A more detailed explanation of Gibbs free energy can be found in Intro to Combustion [1].

(1)

For our purposes, as with perfect combustion in existing documentation regarding enthalpy, we will be considering total gibbs free energy. In other words, much like there is a certain kinematic enthalpy in the form of temperature and pressure in a gas *and* a certain chemical potential enthalpy, there is also a potential gibbs free energy in the form of the gibbs free energy of formation *and* gibbs free energy characterized by an ideal gas, where the total gibbs free energy is the sum of the two.

As far as predicting chemical equilibrium is concerned, Gibbs free energy is a chemical analogue to entropy. However, unlike entropy, total gibbs free energy will always *decrease*. In terms of a chemical reaction, if the change in Gibbs free energy of a reaction is negative, or , then the reaction will happen spontaneously. Similarly, if , or if the delta-G of the reaction is positive, the reaction happens in *reverse*. So, for a given chemical reaction, the system reaches equilibrium (i.e. effectively, no more chemical reactions occur), . For example, consider carbon dioxide decomposition below:

Much like enthalpy of a reaction, the change in Gibbs function of reaction for a given amount of decomposition here can be expressed as the difference in the sum of Gibbs energies of formation for each species. For standard pressure , the of reaction at a given temperature is simply as follows:

Where:

* is the number of moles of the species before reaction
* is the number of moles of the species after reaction
* is the standard Gibbs function of formation of species at temperature

While this is, again, perfectly fine for modeling chemical reactions at standard pressures, we are *not* operating at standard pressures. For example, in the carbon dioxide decomposition above, pressure has a significant effect on the chemical reaction, as increasing pressure tends to reduce the amount of carbon dioxide decomposition. The effect of non-standard pressures on the gibbs function of each of the product species must then be accounted for in some way.

## Finding Chemical Equilibrium Fractions

Looking again to Intro to Combustion, a means of adjusting for different pressures can be found. An equilibrium constant is described in general form below, as shown in equation 2.65 of Intro to Combustion [1].

(1)

Where:

* is the equilibrium constant at a given pressure
* are the stoichiometric coefficients of the reactant species
* are the stoichiometric coefficients of the product species
* is the *partial* pressure of the species , such that the partial pressure is the mole fraction of the substance at equilibrium times the mixture pressure

Also given in Intro to Combustion is the following equation at chemical equilibrium:

(2)

Where is the of a *complete*, one-way reaction at standard pressure and at temperature . For a fixed temperature, this could be solved analytically for and, using the conservation of atoms and mass, individual quantities could be backed out. However, numerically solving this is generally easier to apply to a variety of reactions, especially if each molar fraction can be defined as a function of the quantity of one species. So, for example, for equilibrium of carbon dioxide decomposition, the following equations can be derived from their general forms above:

(3)

(4)

(5)

(6)

(7)

Where:

* is the standard gibbs free energy of formation of species
* is the molar fraction within the total gas of species
* is the gas pressure
* is the partial pressure of species
* is standard pressure of 1 atm
* T is the temperature
* is the universal gas constant

For a fixed temperature , or an isothermal reaction, this equation can be combined with the conservation of carbon and oxygen atoms to analytically yield a resulting fraction of each gas species. For the purposes of combustion, however, the reaction is *not* isothermal, but *adiabatic*. This means that, corresponding with the differing enthalpies of formation of the equilibrium products, the flame temperature is affected by carbon dioxide decomposition. Specifically, since carbon dioxide decomposition is endothermic, as more and more carbon monoxide is produced in the reaction, the flame temperature decreases in temperature. The solution, then, must be found numerically. Referencing Equation 6, Equation 6 can be rearranged to…

(8)

In this case, if we wanted to find only the quantity of carbon dioxide decomposition (as carbon dioxide decomposition is one of the most significant post-combustion chemical reactions) without accounting for other reactions, then the variable combustion reaction below can be employed:

Which, for partial pressure yields, in the case of species …

(9)

So, for example, for carbon monoxide, the partial pressure is…

(10)

(11)

By using the variable carbon-oxide chemical formula above to calculate the flame temperature as outlined in flame temperature documentation [A] as a function of or , then the value of the left hand side of Equation 8 can be calculated as a function of . Since the right hand side is zero, then, for a set of discretely calculated left-hand-side values for a set of values between 0 and 2, then the value which produces the value closest to zero is approximately the equilibrium , and since the rest of the formula is either constant or defined in terms of , the rest of the equilibrium reaction formula can be backed out from there. Using the equilibrium , the equilibrium flame temperature after carbon dioxide decomposition can be calculated using adiabatic methods [A].

## Other Reactions to Consider

While accounting for carbon monoxide decomposition already yields a far more accurate prediction of flame temperature than using the traditional combustion formula with only major combustion product species, but there are yet more reactions which might also be accounted for in order to further enhance the accuracy of exhaust models, such as [1] [2]:

Water-Gas Shift

Ethylene-Hydrogen Decomposition

Acetylene-Hydrogen Decomposition

Diatomic Dissociation

…as well as other minor reactions as listed throughout Intro to Combustion [1]. The reactions listed above are listed in order of significance, i.e. the water-gas shift reaction is far more noticeable than acetylene-hydrogen pyrolysis, which is several orders of magnitude more noticeable than the dissociation of diatomic gasses.

## Limitations of Analytically Modeling Chemical Equilibrium

The methods listed above have been shown to yield predictions of combustion product conditions with some degree of accuracy. For example, temperature is shown to roughly match more in-depth models and experimental values, with similar degrees of accuracy for specific heat ratio, and somewhat lesser accuracy for predicted specific gas constant (due to the sheer number of lightweight unaccounted for product species). Even greater accuracy can be achieved when the predicted properties are compared to discrete experimental data and correction factors are applied (e.g. if experimental data measures only 95% of the predicted , so multiply by 0.95 for future uses). However, the sheer number of possible combustion products, numbering in the dozens, quickly become impractical to account for with this method. While the effects of this inaccuracy has relatively little effect on predicted combustion temperature, its effects on specific heat ratio and specific gas constant. These inaccuracies can then cascade through calculations to produce even larger inaccuracies in subsequent calculations relative to rocket modeling, such as thrust or Isp.

Due to the dozens of possible reactions secondary and dozens more possible combustion products, for most applications in rocketry, software purpose-made for chemical equilibrium analysis (often referred to as CEA) is employed. These softwares are often able to predict the results of a combustion reaction, namely the gas properties, with much higher fidelity than any analytical method.

## Chemical Equilibrium Software and Cantera

Many high-accuracy chemical equilibrium softwares are employed throughout the aerospace industry when designing and modeling rocket engines. One such notable example is CEQUEL, which is widely used for specifically bipropellant rocket combustion applications. NASA’s Glenn Research Center also has a publicly available CEA which is a bit more unwieldy but no less accurate. RPA and RPA-C are also frequently cited as having good CEA capabilities. However, for the purposes of this project software which can be called or wrapped into MATLAB *and* does not require paid licensing (as this is a student project) is desirable. RPA-C requires licensing (save for a free trial), as does CEQUEL. The GRC’s software is completely open source and freely available, but would be somewhat difficult to wrap into MATLAB.

One software which *does* fulfill the requirements of this project is Cantera. Cantera is an open-source python-based software which offers a MATLAB wrapper with quite easy installation (see document [B]). The software supports chemical equilibrium analysis oriented towards combustion of hydrocarbons in air, or reactions which contain nitrogen, oxygen, carbon, and hydrogen atoms - which, conveniently, are the exact elements found in our own combustion reaction, as well as most other rocket propellant reactions (bar those with halogen oxidizers).

## Applying Cantera CEA

Applying Cantera to predict combustion conditions is relatively simple, once familiar with the basics. The first step is understanding the GRI 3.0 class which comes stock with Cantera. The GRI 3.0 class represents a gas, and contains as object properties most of the thermochemical properties of any mixture of gasses. The GRI 3.0 class is intended for use in predicting hydrocarbon-air combustion, or reactions which contain the same elements, carbon, hydrogen, oxygen, and nitrogen. Initializing a gas as a GRI 3.0 mixture in MATLAB is done simply as demonstrated below:

*gasName = GRI30;*

Where:

* *gasName* is the variable name assigned to the gas object
* *GRI30* is the object class of GRI 3.0

The next step is to set the initial conditions of the gas *before* combustion, which can be determined using the principles shown in the chamber conditions documentation[A]. This can be done using the following commands:

*set(gasName, ‘T’, T0, ‘P’, pc, ‘X’, mixString);*

Or…

*set(gasName, ‘T’, T0, ‘P’, pc, ‘MassFractions’, mixString);*

Where *mixString* is the initial composition of the injected gas mixture of the format:

*mixString = [‘C2H6:1, N2O:’, r\_molar]*

Or…

*mixString = [‘C2H6:1, N2O:’, r\_mass]*

…respectively.

Where:

* *gasName* is the variable name of the gas object
* *‘T’* specifies that the next input argument is the gas temperature
* *T0* is the initial temperature of the propellants at injection in K
* *‘P’* specifies that the next input argument is the gas pressure
* *pc* is the reaction pressure, or chamber pressure, in Pa
* *‘X’* specifies that the next argument is a string list of the *molar* components of the gas
* *‘MassFractions’* specifies that the next argument is a string list of the *mass* components of the gas
* *mixString* is a string list of the components of the gas by moles or by mass, depending on the argument specified above.

It is important to note that Cantera prefers single quotes for string input arguments, such as *‘T’* instead of *“T”*. Using double quotes such as *“T”* can cause errors in some cases, and should be avoided.

Following the setting of initial conditions of the reactant gas, Cantera can perform chemical equilibrium analysis of combustion with a simple one-line command:

*equilibrate(gasName, ‘HP’);*

The argument *‘HP’* specifies that the reaction occurs at constant enthalpy (i.e. no heat is added throughout the reaction other than that released by the reaction itself), and occurs at fixed pressure. For other applications *‘TP’* can be used for fixed temperature and pressure, or *‘TV’* for fixed temperature and volume. These will likely not be used for the purposes of rocket combustion, however, and *‘HP’* is for the most part the only relevant condition.

Following the *equilibrate()* command, the object gas is “combusted” and the object now contains the properties corresponding to the product gas, including temperature, specific heats, and mean molecular weight (which is especially important for the calculation of the specific gas constant[A]). These can be called using in-built Cantera functions, which usually are called by the property name, such as:

*Tc = temperature(gasName);*

*cp = cp\_mass(gasName);*

*cv = cv\_mass(gasName);*

*M = meanMolecularWeight(gasName);*

*Mu = viscosity(gasName);*

…and so on. A full list of methods for the GRI30 class can be found by entering in the command prompt:

*methods Solution -full*

…noting that *Solution* is case-sensitive. A full display of all gas properties, including chemical composition, can be displayed in the command prompt for debugging purposes by simply entering the gas object name *gasName* into the command prompt.

Programming-wise, this method is very simple to learn and employ and is equally easy to integrate into the numerical methods employed in other areas of the engine model. Cantera can be used to incorporate fairly accurate temperature, and more importantly, specific heat ratio and gas constant of the working fluid into any numerical model of this project’s rocket engine.

## References and Sources

[1] [Introduction to Combustion](https://drive.google.com/file/d/1V93_c_ekuT-lM256LfNEVRspmNPMu8Vh/view?usp=sharing)

[2] [NIST WebBook, Ethane](https://webbook.nist.gov/cgi/cbook.cgi?ID=C74840&Mask=8)

## Related Documentation

[A] [Flame Temperature Calculation](https://docs.google.com/document/d/1d_NiXlDQG8T_QP-7L1u7jTly_aJhEoFRetvkPETi3QE/edit?usp=sharing)

[B] [Cantera Quick Reference](https://docs.google.com/document/d/1qyf48IUYjvoWwlnIdurIilh9O9bYv-0zfA_flUvgOP8/edit?usp=sharing)