
2 Combustion in Gas-phase Processes

2.1 Equilibrium

2.1.1 Adiabatic Flame Temperature

2.1.1.1 Project Description

This user tutorial presents the use of a gas-phase equilibrium calculation to determine the adiabatic flame temperature for the hydrogen/air system. The adiabatic flame temperature is a measure of the maximum temperature that could be reached by combusting a particular gas mixture under a specific set of conditions. In a real system which includes heat losses, chemical kinetic and/or mass transport limitations, the flame temperature is likely to be lower than the adiabatic flame temperature.

2.1.1.2 Project Setup

The project file is called ***equilibrium__gas.ckprj***. The data files used for this sample are located in the ***samples41\equilibrium\gas directory***. This reactor diagram consists of a single equilibrium reactor.

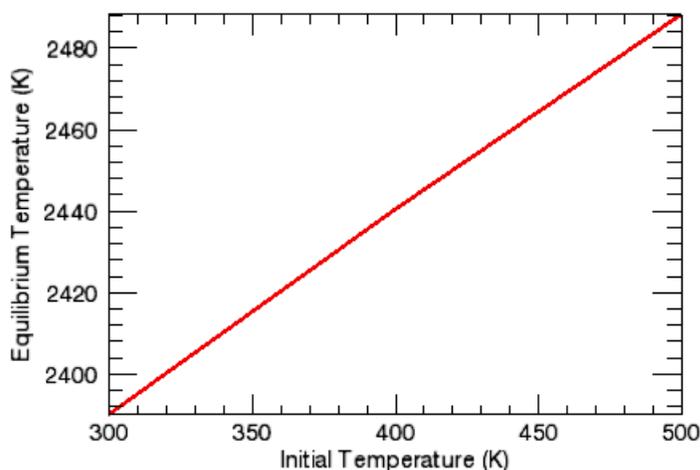
The equilibrium calculation only needs a list of species with their thermodynamic data. There is no need for a reaction list. For this sample problem, the chemistry input file includes only 3 elements: H, O and N; and 9 species: H₂, H, O₂, O, OH, HO₂, H₂O, N₂, and H₂O₂. It is important to include all likely radical species as well as stable species in the product list so as to obtain an accurate flame temperature prediction. For equilibrium calculations generally, it is better to include many unimportant species than to leave out species that may turn out to be important.

Setting up this problem first involves the C1 Equilibrium panel. The problem type (constant pressure and enthalpy), initial temperature (300 K) and pressure (1 atm) are entered on the Reactor Physical Properties tab. An estimated solution temperature of 2000 K is used to help ensure that the solution obtained is for an ignited gas rather than the unburned state. The presence of an estimated solution temperature is often unnecessary for equilibrium simulations but required when a trivial secondary solution may exist. The starting composition is entered on the Reactant sub-tab of the Species-specific Data tab. The reactant mixture defines the initial state, which provides the initial moles of chemical elements and the initial energy of the system. The Continuations panel is used to specify two additional simulations with increasing initial temperatures.

2.1.1.3 Project Results

Figure 2-1 shows the equilibrium temperatures from these simulations, which represent the adiabatic flame temperatures for a hydrogen/air mixture with a H/O ratio of 2.0. The temperatures are on the order of ~2400 K, and thus clearly correspond to the combusted gas. As expected, these adiabatic flame temperatures increase with increasing initial gas temperature.

Figure 2-1 Adiabatic Flame Temperatures—Hydrogen/Air Mixture



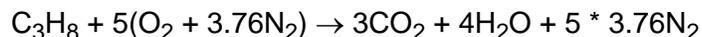
2.2 Using Equivalence Ratio

Many properties of combustion processes strongly depend on the stoichiometry of the combustion mixture. The parameter used most frequently to describe the stoichiometry of the mixture is the equivalence ratio, ϕ . CHEMKIN gives the user an option of describing the initial mixture composition by either listing all of the reactant species and their respective mole or mass fractions, or identifying fuel, oxidizer and complete-combustion (stoichiometric) product species, the mole fraction of any

additional species (such as an inert like Ar or N₂) and the equivalence ratio. Examples of the use of the equivalence ratio can be found in [Section 2.3.1](#), Steady-state Gas-phase Combustion, and [Section 2.3.6](#), Parameter Study: Varying Equivalence Ratio of Propane/Air Flame.

2.2.1 Example: Propane in Air

Stoichiometric equation for propane in air combustion:



Here, the equivalence ratio, ϕ , is defined as the ratio of the actual fuel/oxidizer ratio to the fuel/oxidizer ratio in the stoichiometric equation, as follows:

$$\phi = \frac{X_{\text{C}_3\text{H}_8}/X_{\text{O}_2}}{(X_{\text{C}_3\text{H}_8}/X_{\text{O}_2})_{\text{stoich}}} = 5(X_{\text{C}_3\text{H}_8}/X_{\text{O}_2})$$

CHEMKIN is able to interpret all of the input formats as illustrated in [Tables 2-1](#) to [2-4](#):

Table 2-1 Reactant Mole Fractions Sum to 1.0

| | <i>Name</i> | <i>Mole Fraction</i> |
|-----------------|-------------------------------|----------------------|
| Reactant | C ₃ H ₈ | 0.04 |
| Reactant | O ₂ | 0.202 |
| Reactant | N ₂ | 0.758 |

Table 2-2 Relative Moles Normalized So Mole Fractions Sum to 1.0

| | <i>Name</i> | <i>Mole Fraction</i> |
|-----------------|-------------------------------|----------------------|
| Reactant | C ₃ H ₈ | 0.2 |
| Reactant | O ₂ | 1 |
| Reactant | N ₂ | 3.76 |

Note that in [Table 2-2](#), the relative moles given will be normalized such that the total mole fractions sum to 1.0. However, it is often more convenient to enter relative moles, as described in [Tables 2-3](#) and [2-4](#).

Table 2-3 N₂ as Added Diluent

| <i>Equivalence ratio = 1</i> | | |
|------------------------------------|-------------------------------|----------------------|
| | <i>Name</i> | <i>Mole Fraction</i> |
| Fuel | C ₃ H ₈ | 1.0 |
| Oxidizer | O ₂ | 1.0 |
| Added Species | N ₂ | 0.758 |
| Complete-combustion Product | H ₂ O | |
| Complete-combustion Product | CO ₂ | |

Table 2-4 N₂ as Component of Oxidizer

| <i>Equivalence ratio = 1</i> | | |
|------------------------------------|-------------------------------|----------------------|
| | <i>Name</i> | <i>Mole Fraction</i> |
| Fuel | C ₃ H ₈ | 1.0 |
| Oxidizer | O ₂ | 1.0 |
| Oxidizer | N ₂ | 3.76 |
| Complete-combustion Product | H ₂ O | |
| Complete-combustion Product | CO ₂ | |
| Complete-combustion Product | N ₂ | |

Note that in the second case ([Tables 2-3](#) and [2-4](#)), N₂ can be considered as either an added diluent ([Table 2-3](#)), or a component of the oxidizer, i.e., air ([Table 2-4](#)). If it is considered part of the oxidizer then it must be included in the complete-combustion products list. Also, the oxidizer composition can be given in relative moles or in mole fractions that sum to one (relative moles will subsequently be normalized to sum to 1.0). If using the equivalence ratio input format ([Tables 2-3](#) and [2-4](#)), the mole fraction of fuel is relative to the total number of moles of fuel and the mole fraction of oxidizer is relative to the total number of moles of oxidizer, they will equal to unity unless more than one species is given for each field of fuel and/or oxidizer. However, the “added species” mole fractions are relative to the total number of moles of the reactants, thus the total mole fraction of added species should not sum up to unity.

In general, the equivalence ratio is a good parameter for quantification of mixture stoichiometry for combustion of hydrocarbon fuels (composed only of hydrogen and carbon atoms) in air or in oxygen. However, one has to be careful when applying ϕ to describe fuel stoichiometry for oxygenates (oxygen is chemically bound to the fuel molecule) as well as other non-traditional fuels and oxidizers. Because the definition of the equivalence ratio does not properly account for the oxygen that might be chemically bound in the fuel, it might not be a useful parameter for some fuels.¹

When trying to determine the Complete-combustion or Stoichiometric Products for such fuels, one must remember that a species can be a saturated Stoichiometric Product if and only if the valence orbitals of all of its constituent atoms are filled. That is, if the oxidation numbers of all of the atoms in a given product species sum up to zero.

2.2.2 Example: Stoichiometric Products

Table 2-5 Determining Stoichiometric Products

| <i>Element</i> | <i>Oxidation number</i> |
|----------------|-------------------------|
| C | +4 |
| H | +1 |
| O | -2 |
| N | 0 |
| Ar | 0 |

The oxidation numbers of the atoms in CO_2 sum up to $(+4) + 2 * (-2) = 0$ and in H_2O they sum up to $(-2) + 2 * (+1) = 0$ as well, thus CO_2 and H_2O are Stoichiometric Products. However, oxidation numbers of the atoms in O_2 do not sum up to zero $(-2 + -2 = -4)$, thus O_2 can not be entered as a Stoichiometric Product.^{2,3}

1. C. J. Mueller, M. P. B. Musculus, L. M. Pickett, W. J. Pitz, C. K. Westbrook. "The Oxygen Ratio: A Fuel-Independent Measure of Mixture Stoichiometry", *30th International Symposium on Combustion* (2004).
2. D. W. Oxtoby, H. P. Gillis, and N. H. Nachtrieb, *Principles of Modern Chemistry*, Thompson Learning, Inc. (2002).
3. S. S. Zumdahl, *Chemistry*. D.C. Heath and Company, Lexington, Massachusetts (1989).