

Module 1: Introduction and Thermochemistry

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Objectives, Scope, Required Reading, & Assignment Schedule

Objectives

By the end of this module, students should be able to:

- Define Premixed Flame
- Define Diffusion Flame
- Understand the concept of Equivalence Ratio
- Define what is meant by flammability limits
- Recall a basic understanding of Thermodynamics
- Calculate the Adiabatic Flame Temperatures for a given fuel for various equivalence ratios

Scope

- Introduction to the course
- Examine the nature of fire by exploring premixed and diffusion flames
- Review Thermodynamics
- Analysis of equivalence ratio and adiabatic flame temperature

Reading Assignments

- Turns: Chapter 1 and 2
- Drysdale: Chapter 1

Assignment Schedule

Five problems worth two points each are to be completed and submitted online. See the last page of this module for more details.

A discussion space for Exercises 1.3 and 1.5 has been set up within the Discussion Board Area of the course. Commenting on these exercises will count towards your class participation grade for the week. All other exercises in this model are for your benefit and do not count towards your grade.

Introduction

To give you an idea of what to expect from this course, let us start by examining the title of the course, **Advanced Fire Dynamics**, in more detail.

Advanced: This course builds on your prior knowledge in chemistry, physics, heat transfer, fluid mechanics and fire dynamics/combustion.

Fire: A self-sustaining chemical process that generates heat and light. It involves the oxidation of a fuel by an oxidizer, most often oxygen in the air.

Dynamics: The process of fire initiation, growth, and spread is a very dynamic process which depends on heat and mass transfer, thermodynamics, and chemical kinetics.

In this course we will first review the basic chemistry and physics necessary for understanding fire dynamics (Modules 1 and 2). Next we will develop an understanding of the nature and structure of premixed and diffusion flames (Modules 3 and 4). We will review the physics of heat transfer and turbulent fluid flow (Module 5). We will then use this knowledge to examine the nature of turbulent flames and to examine combustion of liquids and spray flames (Module 6). This will lead us into an analysis of fire plumes and of flame spread (Module 7). Finally, we will combine this understanding to examine the nature of compartment fires (Module 8). This will include developing quantitative methods for examining the growth and spread of compartment fires, including an understanding of the nature of flashover. Our analysis of compartment fires will include understanding temperature and flow fields as well as generation and spread of smoke and toxic gases, especially carbon monoxide (Module 9). Finally, we will examine the use of computer modeling for quantitative analysis of various field quantities including temperature, heat flux, smoke, and toxic gases (Module 10).

The Nature of Fire

Let us begin our journey by examining the basic nature of fire. From a combustion science perspective there are two types of flames that we regularly encounter, premixed flames and diffusion flames. While most destructive fires are diffusion flames, many processes in fire protection engineering involve premixed flames. These processes include ignition, self-heating, and explosions. Table M1-1 shows a comparison of the properties of premixed and diffusion flames.

Table M1-1: Comparison of Premixed and Diffusion Flame Characteristics

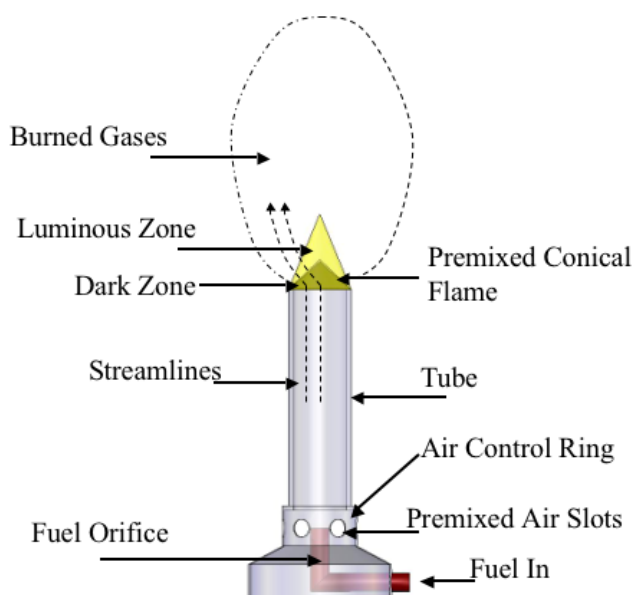
Premixed Flames	Diffusion Flames
<ul style="list-style-type: none"> Fuel and Oxidizer well mixed prior to flame 	<ul style="list-style-type: none"> Fuel and air separate prior to flame
<ul style="list-style-type: none"> Fuel burns at fixed mixture strength defined by equivalence ratio, ϕ $\phi < 1$ is lean, $\phi > 1$ is rich 	<ul style="list-style-type: none"> Fuel burns over a range of fuel/air mixtures
<ul style="list-style-type: none"> Flame temperature varies as a function of ϕ 	<ul style="list-style-type: none"> Over-ventilated flame temperatures near maximum for fuel/oxidizer

	combination
<ul style="list-style-type: none"> Has well defined flammability limits 	<ul style="list-style-type: none"> No defined flammability limits
<ul style="list-style-type: none"> Flame speed (burn rate) a function of ϕ 	<ul style="list-style-type: none"> Burn rate determined by supply rate of supply and mixing of fuel and air

Premixed Flames

As the term “premixed” flame implies, this flame involves complete mixing of the fuel and oxidizer prior to arrival at the flame zone. A common example of this type of flame is a Bunsen burner flame. A basic Bunsen burner is shown schematically in Figure M1-1.

Figure M1-1: Schematic of Bunsen Burner



In a Bunsen burner, natural gas enters through a control valve in the base of the burner. As the gas flows upward in the burner tube, air is inducted through slots near the base of the burner. The slots can be adjusted to control the amount of air inducted into the burner tube relative to the gas flow. This controls the strength of the fuel/air mixture, also known as the equivalence ratio. The mixture of fuel gas and air flows out the top of the burner tube where it is stabilized to create the familiar blue flame cone of a Bunsen burner.

As Table 1 shows, a premixed flame has several characteristics that distinguish it from a diffusion flame as will be discussed further below.

The premixing of the fuel and air prior to the flame zone creates a mixture strength that is characterized by an equivalence ratio designated by the Greek letter phi (ϕ). The equivalence ratio is defined as the ratio of the stoichiometric air/fuel ratio to the actual air/fuel ratio. That is

$$\phi = \frac{(\text{Air/Fuel})_{\text{Stoichiometric}}}{(\text{Air/Fuel})_{\text{Actual}}}$$

For hydrocarbon fuels, the stoichiometric air/fuel ratio, $(A/F)_{ST}$, is the ratio of the amount of air necessary to combust all of the fuel to carbon dioxide (CO_2) and water (H_2O) with no excess oxygen (O_2). For example, for methane (CH_4) as a fuel, the stoichiometric mixture is determined as shown in Table M1-2. It shows that 1 mole of CH_4 requires 2 moles of air (A mole of air consisting of 1 mole of O_2 plus 3.77 moles of N_2 , reflecting the fact that air is approximately 79% N_2 and 21% O_2). One of the O_2 is required to convert the carbon in methane to CO_2 , while the other O_2 is required to convert the 4 hydrogens to 2 waters. It should be noted that nitrogen in the air does not react and therefore gets carried along with the products of combustion, CO_2 and H_2O .

Table M1-2: Flame Stoichiometry—Methane/Air

$\text{CH}_4 + 2 (\text{O}_2 + 3.77 \text{ N}_2) \Rightarrow \text{CO}_2 + 2 \text{ H}_2\text{O} + 7.54 \text{ N}_2$
$(A/F)_{st} = 9.54 \text{ moles air/ 1 mole CH}_4$ <u>or</u> $(A/F)_{st} = 2 (32 \text{ gms O}_2) + 2 (3.77)(28 \text{ gms N}_2)/ 1 (16 \text{ gms CH}_4)$
$\phi = 1$ Stoichiometric mixture
$\phi < 1$ Fuel lean mixture (excess air)
$\phi > 1$ Fuel rich mixture (excess fuel)

From this stoichiometric equation, one can now determine the stoichiometric Air to Fuel ratio, $(A/F)_{ST}$. This property of the fuel/air mixture can be determined on either a molar basis or a mass basis. For methane,

$$(A/F)_{ST} = \begin{cases} 9.54 \text{ on a molar basis} \\ \text{or} \\ 17.2 \text{ on a mass basis} \end{cases}$$

For a given mixture of methane and air, the actual air-to-fuel ratio of the mixture can be compared to the stoichiometric air-to-fuel ratio in order to determine the equivalence ratio, ϕ . If the $(A/F)_{act}$ is a stoichiometric mixture, then $\phi = 1$. If $(A/F)_{act}$ is greater than $(A/F)_{ST}$ then $\phi < 1$ and if $(A/F)_{act}$ is less than $(A/F)_{ST}$ then $\phi > 1$.

For equivalence ratios less than 1.0, the mixture is said to be lean. This indicates a mixture with excess air. Similarly, for $\phi > 1$, the mixture is called a rich mixture indicating excess fuel.

It should be noted that in determining the equivalence ratio, one can use either a mass basis or a molar basis for calculating the air-to-fuel ratio, as long as the same basis is used for both the $(A/F)_{ST}$ and $(A/F)_{act}$ calculations.

For example, if 1 mole of methane is added to 4 moles of air, we can calculate the equivalence ratio of the mixture as follows:

The mixture is $1 \text{ CH}_4 + 4 (\text{O}_2 + 3.77\text{N}_2)$.

On a molar basis,

$$(A/F)_{act} = \frac{4 (4.77)}{1} = 19.08$$

therefore, the equivalence ratio is:

$$\phi = \frac{(A/F)_{Stoichiometric}}{(A/F)_{Actual}} = \frac{9.54}{19.08} = 0.50$$

On a mass basis:

$$(A/F)_{act} = \frac{4(32) + 4(3.77)(28) \text{ gms air}}{1 (16) \text{ gm fuel}} = \frac{550.24}{16} = 34.4$$

So:

$$\phi = \frac{(A/F)_{Stoichiometric}}{(A/F)_{Actual}} = \frac{17.2}{34.4} = 0.50$$

Thus, either way leads to a determination of $\phi=0.5$, indicating that this lean mixture has half the fuel of a stoichiometric mixture relative to the air.

At this point you may be thinking “OK, I can calculate this quantity, ϕ , the equivalence ratio, but so what?” We will see later that, ϕ , is a powerful quantity for understanding the behavior of premixed flames. It will help us to see similarities in premixed flames of different fuels in air. For example, as Table M1-1 summarizes, the flame temperature of most premixed flames vary similarly with equivalence ratio. Also, premixed flames have distinct flammability limits that can be characterized by ϕ . These flammability limits are rich and lean limits that define the range of premixed mixture strengths that can support a flame. We will see shortly that this property of flammability limits does not exist for diffusion flames. However, it does determine ignitability even for diffusion flames as we will see when we discuss ignition.

To summarize, a premixed flame is characterized by the fuel and oxidizer being well-mixed prior to entering the flame zone. The fuel burns at a fixed mixture defined by the equivalence ratio, ϕ . If ϕ is less than 1.0, the mixture is (fuel) lean and if ϕ is greater than 1.0 the mixture is (fuel) rich. Premixed flames can only exist within a limit range of equivalence ratios called the flammability limits. Finally, the flame temperature of a premixed flame varies as a function of the equivalence ratio, ϕ .

Diffusion Flames

Now let's turn our attention to diffusion flames. A common example of a diffusion flame is a candle. In a diffusion flame, the fuel and air are separated prior to combustion. That is, the fuel and air meet at the flames front. In a candle flame for example, the vaporized wax from the wick diffuses outward while the oxygen (and to a lesser extent the nitrogen) from the air diffuses inward. At the flame front, in a region where the fuel and oxygen are in near stoichiometric proportions, they react to produce the flame. Since the concentration of oxygen is higher in the rest of the room than near the flame front (because oxygen is being consumed at the flame front), the O_2 diffuses toward the flame from the rest of the room. Similarly, since the concentration of fuel vapor is much higher at the wick than in the rest of the room, the fuel vapor diffuses outward. Hence, such a flame is called a diffusion flame.

In a diffusion flame, the fuel and air burn over a range of mixture strengths around a stoichiometric mixture, unlike a premixed flame which burns at a single, well-defined mixture strength. As a result, the concept of flammability limits does not apply to a diffusion flame.

For example, a candle burning in a large room is no different than the same candle burning in a smaller room even though the overall fuel-to-air ratio is significantly higher in the smaller room. By contrast, if we release a fixed amount of natural gas in a small room such that when it is fully mixed the room has a stoichiometric mixture of natural gas and air, that mixture is readily burnable. But if we release and mix the same amount of natural gas in a room four times as large as the first room, that premixed mixture is outside the flammability limit for natural gas and will not support combustion.

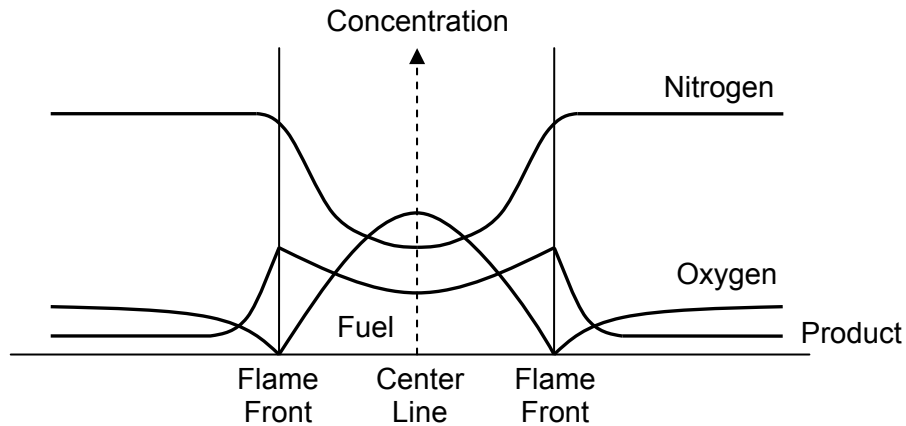
Thus, a diffusion flame differs from a premixed flame in that it does not have discrete flammability limits.

For a diffusion flame, the rate of burning (i.e. the size of the flame) is determined by the supply rate of the fuel and the air. Provided there is sufficient air, a diffusion flame will get larger as the fuel flow rate is increased. A simple example is a kerosene-fueled hurricane lamp. As the length of the wick is increased, the amount of fuel vaporized increases, and the flame length increases.

A candle flame is not a solid cone of flame. Rather, the flame cone is a conical-shaped sheet that separates the air side from the fuel side. The combustion reaction actually occurs in a narrow region where the fuel and air meet. This is sometimes referred to as The Flame Sheet.

Figure M1-2 shows a cross-section cut through a simple diffusion flame. Note that both the fuel and the oxygen concentration go to zero at the flame front. The fuel has its maximum concentration at the centerline, while the oxygen has its maximum in the free stream far from the flame front.

Figure M1-2: Cross Section of a Simple Diffusion Flame



One other important difference between diffusion flames and premixed flames, as shown in Table M1-1, needs mention. While the temperature of premixed flames varies depending on the equivalence ratio, ϕ , diffusion flame temperatures depend only on the fuel/oxidizer combination. Because of this fact, nearly all ordinary combustibles made up of hydrocarbons (including wood, textiles, synthetics, hydrocarbon liquids, etc.) have similar flame temperature when burned in air. Thus, as we will see shortly, a diffusion flame from a piece of wood burning has approximately the same flame temperature as a burning pool of gasoline.

To summarize:

- Diffusion flames result when the fuel and air are separated prior to the flame zone
- The fuel and air burn in a range of mixtures around stoichiometric
- The burn rate of a diffusion flame is controlled by the supply rate of fuel and air
- Diffusion flames (unlike premixed flames) have no flammability limits
- Finally, because diffusion flames burn near a stoichiometric mixture, their temperatures are usually near the maximum for the particular fuel-oxidizer mixture.

Review of Thermodynamics

In order to better understand the nature of flames we need to review some thermodynamics. Our specific goal is to be able to calculate flame temperatures for different fuel-oxidizer combinations and to understand the effects of chemical equilibrium on the products of combustion.

1st Law

As with most discussions of thermodynamics, we start with the 1st Law. The first Law of thermodynamics is a statement of conservation of energy. It states that any change in the internal energy (E) of a system must be equal to the heat produced by the system minus the work done by the system.

$$1^{\text{st}} \text{ Law} - \Delta E = Q - W$$

Q in positive
W out positive.

For flow system, we use enthalpy ($H = E + PV$) as a convenient energy variable since it combines energy with flow work –

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + P\Delta V + V\Delta P$$

At constant Pressure, P,

$$\Delta H = \Delta E + P\Delta V$$

$$\text{since } V\Delta P \rightarrow 0$$

But if the only work is flow work, i.e. $P\Delta V$ work, then

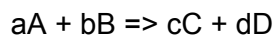
$$Q = \Delta E + W = \Delta E + P\Delta V = \Delta H$$

So, if no work other than flow work

$$\Delta H = Q.$$

Heats of Reaction

For a given reaction



The heat of reaction (i.e. the heat produced or absorbed by the reaction) is given by

$$\Delta H_{\text{RXN}} = cH_c + dH_d - aH_a - bH_b$$

ΔH_R is in units of joules/mole (J/mole) or kilojoules/mole (kJ/mole).

Since enthalpy is a function of temperature only i.e. $H = H(T)$

Then heats of reaction are only a function of temperature, i.e.

$$\Delta H_R = \Delta H_R(T \text{ only})$$

In order to facilitate calculation of ΔH_R 's we set an arbitrary baseline (or reference) enthalpy for all species since we are only interested in the change, ΔH .

Standard Enthalpy

In order to calculate the heat of reaction for a combustion reaction (i.e. the reaction of a particular fuel with a particular oxidizer), we need to establish a standard baseline for the enthalpies of all the reactant and products involved in a combustion reaction. These are known as “standard heats of formation” and are defined below.

Standard Heat of Formation, ΔH_f°

Heat evolved or absorbed on formation of one mole of a substance from its elements in their standard states @ 1 atm and 298 K.

E.G.

Element	std. state
Hydrogen	- H ₂ gas
Oxygen	- O ₂ gas
Nitrogen	- N ₂ gas
Carbon	- graphite solid
Mercury	- liquid

By definition –

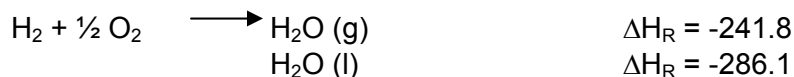
$$\Delta H_f (\text{std state elements}) = 0$$



How about O-atoms?



Water?



We define a reference enthalpy @ 298K and 1 atmosphere such that

$$H(T) = \Delta H_{f,298}^\circ + \int_{298}^T C_p dT$$

We can now use these standard enthalpies to determine "Standard Heats of Reaction." "Standard Heat of Reaction" are defined as the heat of reaction determined at 298K, 1 atm of pressure, i.e.

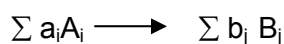
$$\Delta H_{R, 298}^0 = c H_{C, 298}^0 + d H_{D, 298}^0 - a H_{A, 298}^0 - b H_{B, 298}^0$$

or using our standard heats of formation this becomes

$$\Delta H_{R, 298}^0 = c \Delta H_{f, 298, C}^0 + d \Delta H_{f, 298, D}^0 - a \Delta H_{f, 298, A}^0 - b \Delta H_{f, 298, B}^0$$

ΔH_f^0 are tabulated (e.g. <http://webbook.nist.gov/chemistry/>)

The heat of reaction at a temperature, T, different from 298K, $\Delta H_{R, 0T}$ for the reaction



is given by

$$\Delta H_{R, T}^0 = \Delta H_{R, 298}^0 + \underbrace{\sum_j b_j \int_{298}^T C_{p,j} dT - \sum_i a_i \int_{298}^T C_{p,i} dT}_{\text{(these terms often } \ll \Delta H_{R, 298}^0)}$$

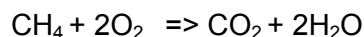
However, $C_p dT$ terms are frequently much less than $\Delta H_{R, 298}^0$, so frequently

$$\Delta H_{R, T}^0 \approx \Delta H_{R, 298}^0$$

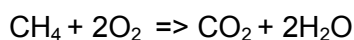
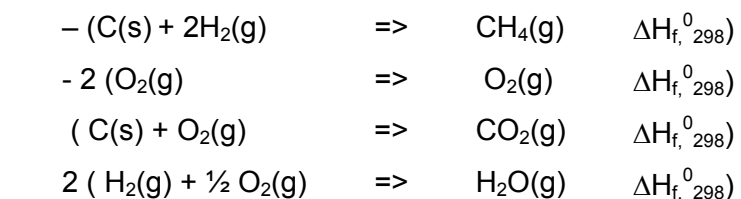
NOTE: JANAF gives $\Delta H_{f, T}$

$$\text{so, } \Delta H_{R, T}^0 = \sum b_j \Delta H_{f, T, 298, j}^0 - \sum a_i \Delta H_{f, T, 298, i}^0$$

Hess' Law of additive Heats of Formation allows us to sum any combination of ΔH_f to get ΔH_R , e.g. to get the heat of combustion, ΔH_R , (or heating value) of methane (CH_4) calculate the heat of reaction for the reaction:



add



Therefore,

$$\Delta H_{R, 298}^0 = - (\Delta H_{f, 298, \text{CH}_4}^0) - 2(\Delta H_{f, 298, \text{O}_2}^0) + (\Delta H_{f, 298, \text{CO}_2}^0) + 2(\Delta H_{f, 298, \text{H}_2\text{O(g)}}^0)$$

$$\Delta H_{R, 298}^0 = -(-74.873) - 2(0.0) + (-393.522) + 2(-241.826)$$

so

$$\Delta H_{R, 298}^0 = -802.301 \text{ kJ/mole CH}_4$$

NOTE: $\Delta H_R < 0$ exothermic
 $\Delta H_R > 0$ endothermic

Exercise 1.1:

Using <http://webbook.nist.gov/chemistry/>, calculate the heat of combustion for methane (CH₄), ethane (C₂H₆) and propane (C₃H₈). What, if any, conclusions can you draw about the heating value of hydrocarbon fuels on a per carbon atom basis?

The *heat of reaction* for a stoichiometric mixture of a hydrocarbon fuel in air reacting to CO₂ and H₂O is also referred to as the *heat of combustion* of that fuel or alternatively at the *heating value* of the fuel.

Exercise 1.2:

The heating values of various fuels can be quoted on a “higher heating value” or “lower heating value” basis. Given the difference in the heat of formation of liquid versus gaseous water shown above, can you surmise the difference in these two terms? (Hint: remember that the larger the negative value of the heat of reaction, the greater the energy that is released by the reaction).

Adiabatic Flame Temperature

Now we are ready to determine the flame temperature for various fuel-oxidizer combinations. A benchmark temperature for any combustion system is the “Adiabatic Flame Temperature”. This temperature is defined as the temperature that is achieved by allowing a fuel to react with an oxidizer and approach equilibrium by means of an isobaric and adiabatic process.

The adiabatic flame temperature is the highest temperature a system can achieve at constant Pressure. (but not a const. V). This temperature is achieved by a combustion system at constant pressure when there are no heat losses from the system. In other words, all of the heat from the combustion reaction is used to heat up the products of combustion.

Next, we want to learn how to calculate this benchmark temperature for a combustion system. If a fuel and oxidizer react at some initial temperature, T_1 , the heat of reaction is given for the i reactants and j products by

$$\Delta H = \sum_i n_i \left[\left(H_{T_1}^0 - H_{298}^0 \right) - \left(H_{T_0}^0 - H_{298}^0 \right) \right] + (\Delta H_f^0)_{298}$$

$\nearrow 0 \text{ if } T_0 = 298$

$$-\sum_j n_j \left[\left(H_{T_2}^0 - H_{298}^0 \right) - \left(H_{T_0}^0 - H_{298}^0 \right) \right] + (\Delta H_f^0)_{298,j}$$

where the n_i are the moles of the various i reactants and the n_j are the moles of the various products.

To determine the adiabatic flame temperature, by definition $\Delta H = 0$, $p = \text{const}$

$$\sum_i n_i [H_{T_1}^0 - H_{298}^0 + (\Delta H_f^0)_{298,i}] = \sum_j n_j [H_{T_2}^0 - H_{298}^0 + (\Delta H_f^0)_{298,j}]$$

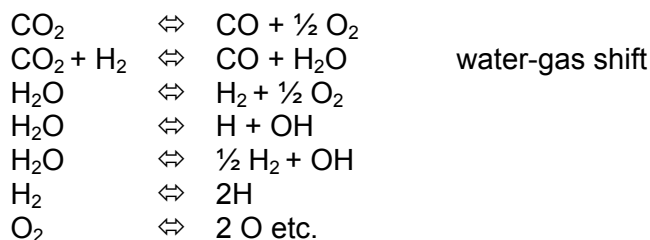
So

The value of T_2 that makes this equation true is the adiabatic flame temperature by definition.

Below $\sim 1200\text{K}$, products for most hydrocarbon fuels in air are CO_2 , H_2O , N_2 , O_2 . However, for most combustion systems we must consider other reactions and products, e.g.

CO , H , OH , O , NO , NO_2 etc.

Through reactions like



For each reaction there is an equilibrium (defined by an equilibrium constant, K) so the n_i 's and n_j 's above are also unknown's for adiabatic flame temperature, so we must iterate because K 's are $f(T)$.

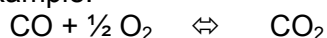
To summarize, the adiabatic flame temperature for a given fuel-oxidizer combination is determined by finding the final state temperature (i.e. the adiabatic flame temperature) for which the sum of the enthalpies of the reactants equal the sum of the enthalpies of the products. However, since the distribution of the products can be dependant on temperature as well, in order to determine the adiabatic flame temperature, we must guess a final (adiabatic) temperature, calculate the distribution of products of combustion through chemical equilibrium, determine the enthalpy of this set of products and compare it with the enthalpy of the reactants. We keep iterating until we find the temperature for which $H_{\text{reactants}} = H_{\text{products}}$ with all the products in equilibrium.

We will now look at how we calculate the equilibrium among the various combustion products such as CO , CO_2 , H_2O , O , H , OH , etc.

Calculation of Equilibrium Concentrations

Let us look at a simple example of how we can calculate the equilibrium concentration of products since this is integral to calculating the adiabatic flame temperature of a fuel-air mixture. Take the example of carbon monoxide in equilibrium with carbon dioxide. This is a very important reaction in fires since it helps determine the amount of CO that is generated in a given fire situation.

Example:



Find equilibrium concentrations for a mixture of 2 moles CO and 1.5 moles O₂ at 1600K @ 1 atm. (You should also determine the equivalence ratio, ϕ , of this mixture. Although it is not necessary to know ϕ in order to solve the equilibrium problem).

We can use the information on <http://webbook.nist.gov/chemistry/> to find the log Kp for each of the species. Since these log Kp are also thermodynamic properties and a function of T only we can add them like we add heats of formation. So

@ 1600K

$$\begin{aligned}\log K_p(\text{CO}) &= 8.234 \\ \log K_p(\text{O}_2) &= 0 \\ \log K_p(\text{CO}_2) &= 12.940\end{aligned}$$

so

$$\begin{aligned}\log K_p(\text{RXN}) &= \log K_p(\text{CO}_2) - \log K_p(\text{O}_2) - \log K_p(\text{CO}) \\ &= 12.940 - 0.0 - 8.234 = 4.706\end{aligned}$$

$$K_p = 5 \times 10^4$$

$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{O}_2}^{1/2} P_{\text{CO}}} = \left(\frac{\left(\frac{NRT}{V} \right)}{\left(\frac{NRT}{V} \right)^{1/2}} \right)_{\text{O}_2} \left(\frac{\left(\frac{NRT}{V} \right)}{\left(\frac{NRT}{V} \right)} \right)_{\text{CO}} = \frac{N_{\text{CO}_2}}{N_{\text{O}_2}^{1/2} N_{\text{CO}}} \left(\frac{V}{RT} \right)^{1/2}$$

Using atom balances

C atom

$$N_{\text{CO}} + N_{\text{CO}_2} = 2$$

O atom

$$N_{\text{O}_2} + \frac{1}{2} N_{\text{CO}} + N_{\text{CO}_2} = 2.5$$

$$N_{\text{O}_2} + N_{\text{CO}} + N_{\text{CO}_2} = N_{\text{T}}$$

$$P_{\text{CO}_2} = \frac{N_{\text{CO}_2}}{N_{\text{T}}} P_{\text{T}}$$

$$P_{\text{CO}} = \frac{N_{\text{CO}}}{N_{\text{T}}} P_{\text{T}}$$

$$P_{O_2} = \frac{N_{O_2}}{N_T} P_T$$

So

$$K_p = \frac{\frac{N_{CO_2}}{N_T} P_T}{\left(\frac{N_{O_2}}{N_T} P_T\right)^{1/2} \left(\frac{N_{CO}}{N_T} P_T\right)} = \frac{N_{CO_2}}{N_{O_2}^{1/2} N_{CO}} \left(\frac{N_T}{P_T}\right)^{1/2}$$

Thus, we get 4 equations, 4 unknowns which can be solved simultaneously to determine the equilibrium distribution among CO, CO₂ and O₂.

Although 4 equations and 4 unknowns are manageable for hand calculations, as the number of species goes up, so do the number of equations. Thus, for more complicated cases, we can use a chemical thermodynamics computer program (e.g. GASEQ, download at <http://www.arcl02.dsl.pipex.com/> and look in the course resources section for some brief tutorials) to calculate the adiabatic flame temperature while properly accounting for the simultaneous equilibria. To calculate equilibrium concentrations for a given starting mixture, you need only determine the products that you wish to consider in the equilibrium (this will usually include the reactants to account for incomplete reactions). Once the initial mixture and the products are specified, then one need only specify the T and P for which the equilibrium calculation is desired. In fact, you can specify only the relative amounts of atoms making up the mixture and the desired equilibrium products in order to get a solution, since the mixture equilibrium is independent of the starting point.

At this point, download the GASEQ program with the above link, as you will need it to calculate adiabatic flame temperatures and equilibrium concentrations as we move forward.

Discussion Exercise 1.3

Using GASEQ, calculate the CO-CO₂ equilibrium for the case above (i.e. at 1600K) and for several other equivalence ratios. You can exchange your values with your fellow students until you have a reasonable graph of the concentrations of CO and CO₂ from a Φ of 0.5 to a Φ of 3.0. Plot the results. What does this tell you about CO formation in different fire conditions?

Post your findings/opinions in the '**M1-CO Formation**' topic in the Discussion area.

Flame Temperature Calculations

Now, let us take a look at calculating some adiabatic flame temperatures. To calculate the adiabatic flame temperature with one of these programs, one first must pick the reactants and their relative concentrations as well as a starting temperature (e.g. room temperature, 300K) and pressure (e.g. 1 atm). The enthalpy, H , of the reactant mixture is first calculated to determine the enthalpy of the system. Next, products of the combustion reaction are chosen (usually including the reactants to account for incomplete reaction) and the program is run at the same pressure and enthalpy as was determined for the reactant mixture. The program will iterate on temperature until it finds a product mixture for which $H_{\text{reactants}} = H_{\text{products}}$. This temperature, by definition, is the adiabatic flame temperature for the reactant mixture. In addition, the calculation will also provide the equilibrium product concentrations.

One consideration in making these calculations is what products of combustion to consider as part of the final equilibrium mixture. Dissociation of species can have a significant impact on flame temperatures especially at temperatures over 2000K at 1 atm.

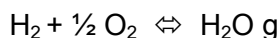
When to consider dissociation of products for $T_2 > 2200\text{K}$ $P = 1$ atm.

At higher T 's, dissociation reactions such as



are important because they absorb some of the heat of reaction and reduce the flame temperature.

For example, consider



$$\Delta H_{R,298} = \Delta H_{f,298} = -241.9 \text{ kJ/mole}$$

$$T_{\text{adiabatic}} \Rightarrow -\Delta H_{f,298} = \int_{298}^T C_{p,\text{H}_2\text{O}} \Delta T$$

$$C_p/R = 2.717 + 2.945T - 0.8022T^2 + 0.1023T^3 - 0.004847T^4$$

$$R = 8.316 \text{ J/mole}^\circ\text{K}$$

So

$$-(-241.9 \text{ J/mole}) = 8.316 \text{ J} \int_{298}^T 2.717 + 2.945T - 0.8022T^2 + 0.1023T^3 - 0.004847T^4$$

Integrating and solving for T_{ad} gives

$$T_{\text{ad}} = 5000\text{K}$$

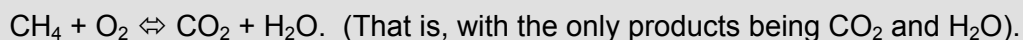
However, if dissociation is considered (i.e. H, O, and OH as products) the adiabatic flame temperature is only

$$T_{\text{ad}} = 3188$$

Clearly, under these conditions, dissociation can have a substantial impact on the flame temperature.

Exercise 1.4:

1) Use GASEQ to calculate the adiabatic flame temperature for a stoichiometric mixture of methane and oxygen assuming the reaction:



2) Repeat the calculation but allow for CO as a product.

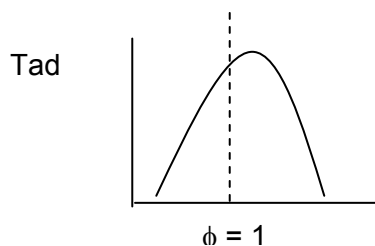
3) Repeat the calculation again but allow for CO, O, OH, H and H₂ as products.

Finally, let us examine the effect of equivalence ratio on adiabatic flame temperature, T_{ad} . For the case of a hydrogen-oxygen flame, I have calculated the following adiabatic flame temperatures as a function of equivalence ratio assuming H, OH and O as dissociation products (you might want to calculate them yourself for comparison).

Example: $\phi \text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \phi \text{H}_2\text{O} \text{ etc.}$

$\phi = 0.5$	$T_{ad} = 2914$
0.6	2981
0.7	3027
0.8	3056
0.9	3072
1.0	3079
1.1	3077
1.2	3067
1.3	3052
1.4	3030
1.5	3004
2.0	2830

Qualitatively, the plot of T_{ad} versus ϕ looks like:



Discussion Exercise 1.5:

It has often been said during fire investigations that a “hot” fire is indicative of the use of an accelerant such as gasoline. To examine the accuracy of this statement, let us look at the adiabatic flame temperature for some representative components in wood and in gasoline. Using GASEQ, calculate the adiabatic flame temperature for formaldehyde (CH_2O) and methanol (CH_3OH) (two products of wood pyrolysis) and compare them with the flame temperatures for hexane (C_6H_{14}) and heptane (C_7H_{16}) (two common components of gasoline). Discuss your findings with your fellow students. What do you conclude about the statement that “hot” fires are indicative of use of an accelerant?

Instructions:

A topic **M1-Hot Fires** has been set up in the discussions space for this exercise. Post your findings/opinions there.

Module 1 Assignment

In completing this assignment, you should show all work. The approach that you use is the essential part of developing a solution, where obtaining the correct answer in these assignments is only of modest importance.

Formats for submitting assignments

Problems that are due on the same date can be completed in one document and submitted as one electronic file. You may complete your assignment in the following formats: word processed (.doc, .rtf, etc.) or scanned (.pdf). See the instructions at the bottom of this page for procedures on submitting the assignment.

Due Dates: See course Calendar

Total Points: 10

All problems can be found in the m1_problems.doc in the assignment for module 1.