

Part 2.C: Introduction to Thermochemistry

[SB&VW-14.1-14.6]

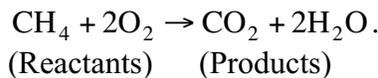
Until now, we have specified the heat given to the devices analyzed, and not concerned ourselves with how this heat might be produced. In this section, we examine the issue of how we obtain the heat needed for work production. For the most part, this is from converting chemical energy into heat, so the discussion will be on reacting mixtures of gas which are involved in chemical combustion processes.

The topic addressed is “thermochemistry”, which is the combining of thermodynamics with chemistry to predict such items as how much heat is released from a chemical reaction. This is the “Q” or “q” that we have used in the cycle analysis. The principal components of the approach are use of a chemical balance plus the steady flow energy equation (SFEE) which equates the sum of shaft work (from) and heat transfer (to) a control volume to the difference in control volume inlet and exit enthalpy fluxes.

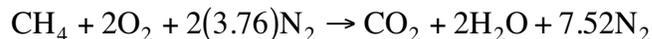
2.C.1 Fuels

There are a wide variety of fuels used for aerospace power and propulsion. A primary one is jet fuel (octane, essentially kerosene) which has the chemical formula C_8H_{18} . Other fuels we consider are hydrogen (H_2) and methane (CH_4).

The chemical process in which a fuel, for example methane, is burned consists of (on a very basic level—there are many intermediate reactions that need to be accounted for when computations of the combustion process are carried out):



The reactions we describe are carried out in air, which can be approximated as 21% O_2 and 79% N_2 . This composition is referred to as “theoretical air”. There are other components of air (for example Argon, which is roughly 1%), but the results given using the theoretical air approximation are more than adequate for our purposes. With this definition, for each mole of O_2 , 3.76 (79/21) moles of N_2 are involved:



Even if the nitrogen is not part of the combustion process, it leaves the combustion chamber at the same temperature as the other products, and this change in state (change in enthalpy) needs to be accounted for in the steady flow energy equation. At the high temperatures achieved in internal combustion engines (aircraft and automobile) reaction does occur between the nitrogen and oxygen, which gives rise to oxides of nitrogen, although we will not consider these reactions.

The condition at which the mixture of fuel and air is such that both completely participate in the reaction is called stoichiometric. In gas turbines, excess air is often used so that the

temperatures of the gas exiting the combustor is kept to within desired limits (see Figures A-8, A-9, A-11 in Part 1 for data on these limits.)

Muddy points

Why is there 3.76 N₂? (MP 2C.1)

What is the most effective way to solve for the number of moles in the reactions? (MP 2C.2)

2.C.2 Fuel-Air Ratio

The reaction for aeroengine fuel at stoichiometric conditions is:



On a molar basis, the ratio of fuel to air is $[1/(12.5+47.0)] = 1/59.5 = 0.0167$.

To find the ratio on a mass flow basis, which is the way in which the aeroengine industry discusses it, we need to “weight” the molar proportions by the molecular weight of the components. The fuel molecular weight is 114, the oxygen molecular weight is 32 and the nitrogen molecular weight is (approximately) 28. The fuel/air ratio on a mass flow basis is thus

$$\text{Fuel-air ratio} = \frac{1 \times 114}{12.5 \times 32 + 12.5 \times 3.76 \times 28} = 0.0664$$

If we used the actual constituents of air we would get 0.0667, a value about 0.5% different.

Muddy points

Do we always assume 100% complete combustion? How good an approximation is this? (MP 2C.3)

2.C.3 Enthalpy of formation

The systems we have worked with until now have been of fixed chemical composition. Because of this, we could use thermodynamic properties relative to an arbitrary base, since all comparisons could be made with respect to the chosen base. For example, the specific energy $u_f(0.01^\circ\text{C}) = 0.0$ for steam. If there are no changes in composition, and only changes in properties of given substances, this is adequate. If there are changes in composition, however, we need to have a reference state so there is consistency for different substances.

The convention used is that the reference state is a temperature of 25°C (298 K) and a pressure of 0.1 MPa. (These are roughly room conditions.) At these reference conditions, the enthalpy of the elements (oxygen, hydrogen, nitrogen, carbon, etc.) is taken as zero.

The results of a combustion process can be diagrammed as below. The reactants enter at standard conditions; the combustion (reaction) takes place in the volume indicated. Downstream of the reaction zone there is an appropriate amount of heat transfer with the surroundings so that the products leave at the standard conditions. For the reaction of carbon and oxygen to produce CO₂, the heat that has to be extracted is $Q_{CV} = -393,522 \text{ kJ/kmole}$; this is heat that comes out of the control volume.

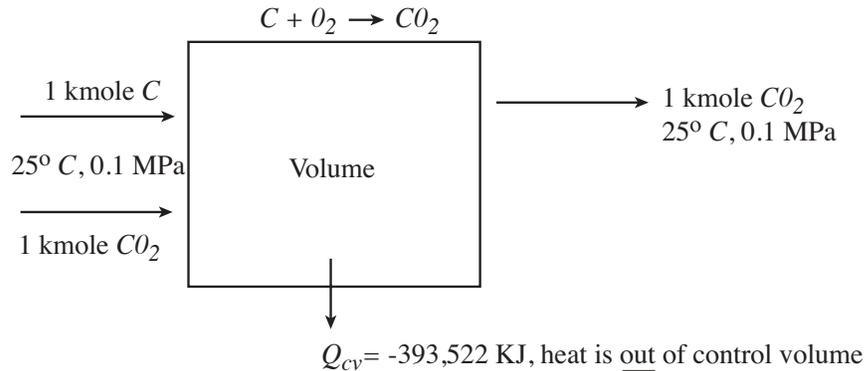


Figure C-1: Constant pressure combustion

There is no shaft work done in the control volume and the first law for the control volume (SFEE) reduces to:

mass flow of enthalpy in + rate of heat addition = mass flow of enthalpy out.

We can write this statement in the form

$$\sum_R \dot{m}_i h_i + \dot{Q}_{CV} = \sum_P \dot{m}_e h_e \quad (C.3.1)$$

In Eq. (C.3.1) the subscripts “R” and “P” on the summations refer to the reactants (R) and products (P) respectively. The subscripts on the mass flow rates and enthalpies refer to all of the components at inlet and at exit.

The relation in terms of mass flows can be written in molar form, which is often more convenient for reacting flow problems, by using the molecular weight, M_i , to define the molar mass flow rate, \dot{n}_i , and molar enthalpy, \bar{h}_i , for any individual i^{th} (or e^{th}) component as

$$\begin{aligned} \dot{n}_i &= \dot{m}_i / M_i ; \text{ mass flow rate in terms of kmoles/sec} \\ \bar{h}_i &= M_i h_i ; \text{ enthalpy per kmole} \end{aligned}$$

The SFEE is, in these terms,

$$\sum_R \dot{n}_i \bar{h}_i + \dot{Q}_{CV} = \sum_P \dot{n}_e \bar{h}_e \quad (C.3.2)$$

The statements that have been made do not necessarily need to be viewed in the context of flow processes. Suppose we have one unit of C and one unit of O_2 at the initial conditions and we carry out a constant pressure reaction at ambient pressure, P_{amb} . If so,

$$\begin{aligned}
 U_{final} - U_{initial} &= Q - W \\
 &= Q_{CV} - P_{amb}(V_{final} - V_{initial}),
 \end{aligned}$$

since $P_i = P_f = P_{amb}$. Combining terms,

$$U_{final} + P_{final}V_{final} - (U_{initial} + P_{initial}V_{initial}) = Q_{CV},$$

or,

$$H_{final} - H_{initial} = Q_{CV}.$$

In terms of the numbers of moles and the specific enthalpy this is

$$\sum_R n_i \bar{h}_i + Q_{CV} = \sum_P n_e \bar{h}_e \quad (\text{C.3.3})$$

The enthalpy of CO_2 , at 25°C and 0.1 MPa , with reference to a base where the enthalpy of the elements is zero, is called the enthalpy of formation and denoted by \bar{h}_f^o . Values of the heat of formation for a number of substances are given in Table A.9 in SB&VW.

The enthalpies of the reactants and products for the formation of CO_2 are:

$$\bar{h}_{\text{O}_2} = \bar{h}_{\text{C}} = 0$$

$$\text{For one kmole: } Q_{CV} = \sum_P n_e h_e = H_P = (h_f^o)_{\text{CO}_2} = -393,522 \text{ kJ/kmole.}$$

The enthalpy of CO_2 in any other state (T,P) is given by

$$\bar{h}_{T,P} = (h_f^o)_{298\text{K},0.1\text{MPa}} + (\Delta\bar{h})_{298\text{K},0.1\text{MPa} \rightarrow T,P}$$

These descriptions can be applied to any compound. For elements or compounds that exist in more than one state at the reference conditions (for example, carbon exists as diamond and as graphite), we also need to specify the state.

Note that there is a minus sign for the heat of formation. The heat transfer is *out* of the control volume and is thus negative by our convention. This means that $\bar{h}_{elements} > \bar{h}_{\text{CO}_2} = -393,522 \text{ kJ}$.

Muddy points

Is the enthalpy of formation equal to the heat transfer out of the combustion during the formation reaction? (MP 2C.4)

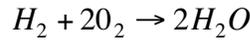
Are the enthalpies of H_2 and H (monoatomic hydrogen) both zero at 298K? (MP 2C.5)

2.C.4 First Law Analysis of Reacting Systems

The form of the first law for the control volume is (there is no shaft work):

$$\sum_R \dot{n}_i \bar{h}_i + \dot{Q}_{CV} = \sum_P \dot{n}_e \bar{h}_e.$$

This is given in terms of the moles of the different constituents, and it reduces to the more familiar form for a single fluid (say air) with no reactions occurring. We need to specify one parameter as the basis of the solution; 1 kmole of fuel, 1 kmole of air, 1 kmole total, etc. We use 1 kmole of fuel as the basic unit and examine the burning of hydrogen.



The reactants and the products are both taken to be at 0.1MPa and 25°C, so the inlet and exit P and T are specified. The control volume is the combustion chamber. There is no shaft work done and the SFEE is in the form of Equation (C.1.2). The enthalpy of the entering gas is zero for both the hydrogen and the oxygen (elements have enthalpies defined as zero at the reference state). If the exit products are in the gaseous state, the exit enthalpy is therefore related to the enthalpy of formation of the product by:

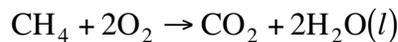
$$\begin{aligned} \dot{n}_{e_{H_2O}} \bar{h}_{e_{H_2O}} &= \dot{n}_{e_{H_2O}} (\bar{h}_f^o)_{H_2O(g)} \\ &= 2 \times (-241,827) \text{kJ} = -483,654 \text{kJ}; \text{ gaseous state at exit.} \end{aligned}$$

If the water is in a liquid state at the exit of the process:

$$\begin{aligned} \dot{n}_{e_{H_2O}} \bar{h}_{e_{H_2O}} &= \dot{n}_{e_{H_2O}} (\bar{h}_f^o)_{H_2O(l)} \\ &= 2 \times (-285,783) \text{kJ} = -571,676. \end{aligned}$$

There is more heat given up if the products emerge as liquid. The difference between the two values is the enthalpy needed to turn the liquid into gas at 25°C: $h_{fg} = 2442 \text{ kJ/kmole}$.

A more complex example is provided by the burning of methane (natural gas) in oxygen, producing .



The components in this reaction equation are three ideal gases (methane, oxygen, and CO_2) and liquid water. We again specify that the inlet and exit states are at the reference conditions so that:

$$\begin{aligned} \sum_R \dot{n}_i \bar{h}_i &= (\bar{h}_f^o)_{CH_4} = -74,873 \text{ kJ} \\ \sum_P \dot{n}_e \bar{h}_e &= (\bar{h}_f^o)_{CO_2} + 2(\bar{h}_f^o)_{H_2O(l)} \\ &= -393,522 + 2(-285,838) = -965,198 \text{ kJ} \\ Q_{CV} &= -965,198 \text{ kJ} - (-74,873) = -890,325 \text{ kJ.} \end{aligned}$$

Suppose the substances which comprise the reactants and the products are not at 25°C and 0.1MPa. If so, the expression that connects the reactants and products is;

$$Q_{CV} + \sum_R n_i \left(\bar{h}_f^o + \underbrace{\Delta \bar{h}}_{\substack{\text{Between} \\ T_i, P_i \text{ and reference} \\ \text{conditions}}} \right)_i = \sum_P n_e \left(\bar{h}_f^o + \underbrace{\Delta \bar{h}}_{\substack{\text{Between} \\ T_e, P_e \text{ and reference} \\ \text{conditions}}} \right)_e \quad (\text{C.4.1})$$

Equation (C.4.1) shows that we must compute the enthalpy difference $\Delta \bar{h}$ between the reference conditions and the given state if the inlet or exit conditions are not the reference pressure and temperature.

There are different levels of approximation for the computation: (a) assume the specific heat is constant over the range at some average value, (b) use the polynomial expressions (Table A.6) in the integral, and (c) use tabulated values. The first is the simplest and the crudest. Combustion processes often involve changes of a thousand degrees or more and, as Figure C-2 shows, the specific heat for some gases can change by a factor of two or more over this range, although the changes for air are more modest. This means that, depending on the accuracy desired, one may need to consider the temperature dependence of the specific heat in computing Δh .

*Figure C-2 available from:
Sonntag, Bognakke and Van Wylen, Fundamentals of Thermodynamics, 6th Ed., John Wiley & Sons. Figure 5.11 p.137.*

Figure C-2: Specific heat as a function of temperature [from SB&VW]

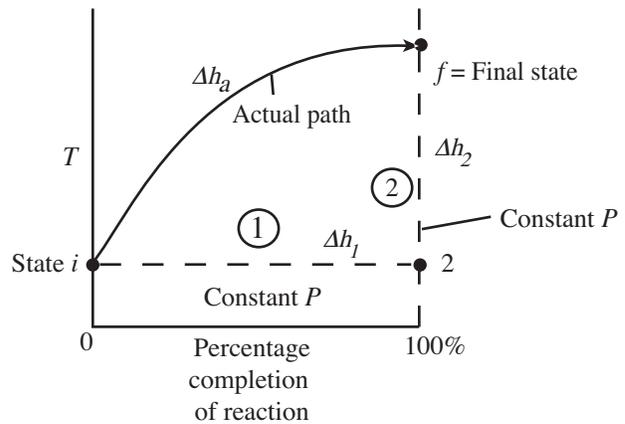
Muddy points

When doing cycle analysis, do we have to consider combustion products and their effect on specific heat ratio (γ is not 1.4)? (MP 2C.6)

2.C.5 Adiabatic Flame Temperature

For a combustion process that takes place adiabatically with no shaft work, the temperature of the products is referred to as the adiabatic flame temperature. This is the maximum temperature that can be achieved for given reactants. Heat transfer, incomplete combustion, and dissociation, all result in lower temperature. The maximum adiabatic flame temperature for a given fuel and oxidizer combination occurs with a stoichiometric mixture (correct proportions such that all fuel and all oxidizer are consumed). The amount of excess air can be tailored as part of the design to control the adiabatic flame temperature. The considerable distance between present temperatures in a gas turbine engine and the maximum adiabatic flame temperature at stoichiometric conditions is shown in Figure A-11 of Part 1, based on a compressor exit temperature of 1200°F (922 K).

An initial view of the concept of adiabatic flame temperature is provided by examining two reacting gases, at a given pressure, and asking what the end temperature is. The process is shown schematically at the right, where temperature is plotted versus the percentage completion of the reaction. The initial state is i and the final state is f , with the final state at a higher temperature than the initial state. The solid line in the figure shows a representation of the “actual” process. To see how we would arrive at the final state the dashed lines break the state change



Schematic of adiabatic flame temperature

into two parts. Process (1) is reaction at constant T and P . To carry out such a process, we would need to extract heat. Suppose the total amount of heat extracted per unit mass is q_1 . The relation between the enthalpy changes in Process (1) is

$$h_2 - h_i = -q_1 = \left(h_f^o \right)_{\text{unit mass}}$$

where q_1 is the “heat of reaction”.

For Process (2), we put this amount back into the products to raise their temperature to the final level. For this process, $h_f - h_2 = q_1$, or, if we can approximate the specific heat as constant (using some appropriate average value) $c_{p,av.} (T_f - T_2) = q_1$. For the overall process there is no work done and no heat exchanged so that the difference in enthalpy between initial and final states is zero:

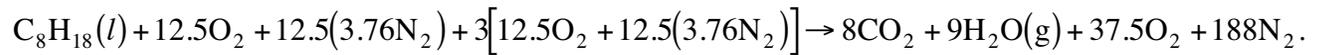
$$\Delta h_1 + \Delta h_2 = \Delta h_{\text{adiabatic}} = 0.$$

The temperature change during this second process is therefore given by (approximately)

$$(T_f - T_2) = \frac{q_1}{c_{p_{av.}}} = \frac{\left| \left(\bar{h}_f^o \right)_{unit\ mass} \right|}{c_{p_{av.}}} \quad (C.5.1)$$

The value of the adiabatic flame temperature given in Equation (C.5.1) is for 100% completion of the reaction. In reality, as the temperature increases, the tendency is for the degree of reaction to be less than 100%. For example, for the combustion of hydrogen and oxygen, at high temperatures the combustion product (water) dissociates back into the simpler elemental reactants. The degree of reaction is thus itself a function of temperature that needs to be computed. We used this idea in discussing the stoichiometric ramjet, when we said that the maximum temperature was independent of flight Mach number and hence of inlet stagnation temperature. It is also to be emphasized that the idea of a constant (average) specific heat, $c_{p_{av.}}$, is for illustration and not inherently part of the definition of adiabatic flame temperature.

An example computation of adiabatic flame temperature is furnished by the combustion of liquid octane at 25°C with 400% theoretical air. The reaction is



For an adiabatic process

$$\sum_R n_i (\bar{h}_f^o + \Delta\bar{h})_i = \sum_P n_e (\bar{h}_f^o + \Delta\bar{h})_e \quad (C.5.2)$$

At adiabatic flame temperature

We can again think of the general process in steps:

- Bring reactants to 25°C [the term $(\Delta\bar{h})_i$] from the initial temperature, using whatever heat transfer, q_a , is needed. In this example we do not need step (i) because we are already at the reference temperature.
- Reaction at 25°C - [the term $(\bar{h}_f^o)_{reactants \rightarrow products}$]. There will be some heat transfer in this step, q_b , out of the combustor.
- Put back heat $q_a + q_b$ into the products of combustion. The resulting temperature is the adiabatic flame temperature.

In the present case Equation (C.1.6) is, explicitly:

$$\bar{h}_f^o_{C_8H_{18}}(l) = 8\bar{h}_f^o_{CO_2} + 9\bar{h}_f^o_{H_2O} + \left\{ \Delta\bar{h}_{CO_2} + 9\Delta\bar{h}_{H_2O} + 37.5\Delta\bar{h}_{O_2} + 188\Delta\bar{h}_{N_2} \right\}$$

We can examine the terms in the SFEE separately, starting with the heat of formation terms,

$$\bar{h}_f^o : 8\bar{h}_f^o_{CO_2} + 9\bar{h}_f^o_{H_2O} - \bar{h}_f^o_{C_8H_{18}}(l) = 8(-393,522) + 9(-241,827) - (-249,952)$$

$$= -5.075 \times 10^6 \text{ kJ/kmole.}$$

The exit state at the adiabatic flame temperature is specified by:

$$\sum_P n_e \Delta \bar{h}_e = 5.075 \times 10^6 \text{ kJ/kmole}$$

We find the adiabatic flame temperature in three ways, approximate solution using an average value of c_p , a more accurate one using the tabulated evolution of c_p with temperature and a more precise solution using the tabulated values for gas enthalpy in Table A.8 of SB&VW.

a) Approximate solution using “average” values of specific heat:

From Figure C-2 we can use the values at 500K as representative. These are:

Gas	c_p (kJ/kmole)
CO ₂	45
H ₂ O	35
O ₂	30
N ₂	30.

Using $\Delta \bar{h} = \bar{c}_{p,ave} \Delta T$,

$$\sum_P n_e \Delta \bar{h}_e = \Delta T \left\{ 8(c_p)_{\text{CO}_2} + 9(c_p)_{\text{H}_2\text{O}} + 37.5(c_p)_{\text{O}_2} + 188(c_p)_{\text{N}_2} \right\}$$

where $\Delta T = T_{final} - 25^\circ \text{C} = T_{final} - 298 \text{ K}$

$$\sum_P n_e \Delta \bar{h}_e = 7440 \Delta T \text{ kJ}$$

$$\Delta T = 682 \Rightarrow T_{final} = 980 \text{ K.}$$

b) Solution for adiabatic flame temperature using evolutions of specific heats with temperature

Tables give the following evolutions of specific heats with temperature:

Gas	Evolution of c_p/\bar{R} with T (kJ/kmol)
CO ₂	$2.401 + 8.735 \cdot 10^{-3} \times T - 6.607 \cdot 10^{-6} \times T^2 + 2.002 \cdot 10^{-9} \times T^3$
H ₂ O	$4.070 - 1.108 \cdot 10^{-3} \times T + 4.152 \cdot 10^{-6} \times T^2 - 2.964 \cdot 10^{-9} \times T^3 + 0.807 \cdot 10^{-12} \times T^4$
O ₂	$3.626 - 1.878 \cdot 10^{-3} \times T + 7.055 \cdot 10^{-6} \times T^2 - 6.764 \cdot 10^{-9} \times T^3 + 2.156 \cdot 10^{-12} \times T^4$
N ₂	$3.675 - 1.208 \cdot 10^{-3} \times T + 2.324 \cdot 10^{-6} \times T^2 - 0.632 \cdot 10^{-9} \times T^3 - 0.226 \cdot 10^{-12} \times T^4$

Using $\Delta h = \int_{298 \text{ K}}^{T_f \text{ in K}} c_p(T) \cdot dT$ and the same equation as above, we obtain:

$$T_f = 899 \text{ K}$$

c) Solution for adiabatic flame temperature using tabulated values for gas enthalpy:

	$\Delta \bar{h}_{\text{CO}_2}$	$\Delta \bar{h}_{\text{H}_2\text{O}}$	$\Delta \bar{h}_{\text{O}_2}$	$\Delta \bar{h}_{\text{N}_2}$
$T = 900 \text{ K}$	28,041	21,924	19,246	18,221 kJ/kmole
$T = 1000 \text{ K}$	33,405	25,978	22,707	21,460 kJ/kmole

Plugging in the numbers shows the answer is between these two conditions. Linearly interpolating gives a value of $T_{final} = 962 \text{ K}$.

Muddy points

Does "adiabatic flame temperature" assume 100% combustion? (MP 2C.7)

What part of the computation for adiabatic flame temperature involves iteration? (MP 2C.8)

Muddiest points on part 2C

2C.1 Why is there 3.76 N₂?

This is to represent the components other than oxygen that are in air. From SB&VW, page 525, “The assumption that air is 21% oxygen and 79% nitrogen by volume leads to the conclusion that for each mole of oxygen, $79/21 = 3.76$ moles of nitrogen are involved.”

2C.2 What is the most effective way to solve for the number of moles in the reactions?

What we are doing is basically counting atoms on both sides of the reactants → products statement. See Section 14.2 of SB&VW for a description of the combustion process and for going from ratios in terms of moles to ratios in terms of mass.

2C.3 Do we always assume 100% complete combustion? How good an approximation is this?

In the problems we do, we will only consider 100% combustion. It is a good approximation for the range of problems that we address.

2C.4 Is the enthalpy of formation equal to the heat transfer out of the combustion during the formation reaction?

As defined, the enthalpy of formation relates to a process in which the initial and final states are at the same temperature. If there is combustion in between, heat will have to be removed for this condition to occur. The enthalpy of formation is equal to the negative of the magnitude of the heat outflow. If we consider the combustion as occurring in a control volume, then per kmole $\bar{h}_f^{o\Box} = -Q_{cv\Box}$ where $Q_{cv\Box}$ is the heat transfer out of the control volume per kmole. This is not in accord with our convention, and if you please feel free to transform it back into the notation we have used before. (I find that if I do this there are too many minus signs to keep track of easily.)

2C.5 Are the enthalpies of H₂ and H (monoatomic hydrogen) both zero at 298K?

The enthalpies of the elements are taken as zero at 298 and 0.1 MPa. In some cases there are more than one form of the element. In that case the form chosen to have the value of zero is that which is chemically stable at the reference state. The other forms then have an enthalpy which is consistent with the reaction that produces this form of the element. For hydrogen H₂ has zero enthalpy at the reference conditions and H has an enthalpy of 217,999 kJ/kmole (see Table A.8 in SB&VW), consistent with the idea that energy has to be supplied to break the molecule apart.

2C.6 When doing a cycle analysis, do we have to consider combustion products and their effect on specific heat ratio (γ is not 1.4)?

The specific heat ratio does depend on combustion products but the effect is not large because the fuel air ratio is small. For example, for conditions of fuel air ratio $\phi = 0.034$, the specific heat ratio at room temperature is about 1.38. A larger variation encountered in practice is with temperature; for a temperature of 1750K the specific heat ratio of pure air is 1.3.

2C.7 Does "adiabatic flame temperature" assume 100% combustion?

Yes. This is the maximum temperature that could be produced. Incomplete combustion will lower the temperature, as will heat transfer out of the combustion region.

2C.8 What part of the computation for adiabatic flame temperature involves iteration?

If the specific heat is not a simple analytic function of temperature (i.e., suppose it is known only in tabular form), we cannot get a closed form solution for the adiabatic flame temperature. We can, however, readily solve the enthalpy balance (SFEE) numerically (this is where the iteration comes in) to find at what temperature the products have to come out to have the same enthalpy (including the enthalpy of formation) as the reactants. We did not do this calculation yet, but we will do it to show what the iteration is all about.

Remember that the assumption of constant specific heat is just that, an assumption. While this is an excellent assumption for many practical problems, if the precision of the answer needed is very high, or if the range of temperatures is large (see Figure 5.11 in SB&VW), then we cannot assume constant specific heat.